

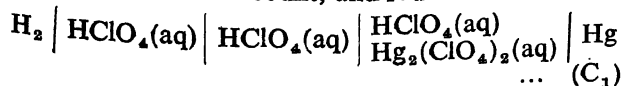
Standard Electrode Potential of Mercury-Mercurous Electrode at a Number of Temperatures

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From the study of the cell ; Pt Q.H. (sat.) $\text{HClO}_4(c_1) | \text{HClO}_4(c_1) | \text{HClO}_4(c_1) | \text{Hg}_2(\text{ClO}_4)_2(c_2) | \text{Hg}$, the standard electrode potential of mercury-mercurous electrode has been determined from 5° to 35° at 5° intervals. Over this range of temperatures the results can be expressed by the equation, $E_t = 0.80252 - 2.51 \times 10^{-4}t - 1.0668 \times 10^{-6}t^2$. ΔH° , ΔG° and ΔS° of the reaction $\text{Hg}_2^{2+} + \text{H}_2 = 2\text{Hg} + 2\text{H}^+$ have also been calculated.

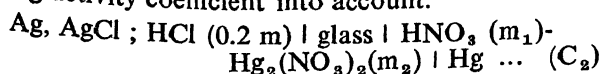
THE standard electrode potential of mercury-mercurous was first determined by Linhart¹ by using the cell (C₁) at 25°, without taking the activity coefficient into account, and found as 0.7926v.



Lewis and Randall² revised the value of Linhart to 0.7986 int. volt by taking activity coefficient into account. By plotting the original data of Linhart in a $\mu^{\frac{1}{2}}$ diagram, Bray and Hershey³ adopted the value of $E_{\text{Hg}^\circ, \text{Hg}_2^{2+}}$ equal to 0.7975 ± 0.0010 int. volt.

El Wakkad and Slem⁴ found the value of $E_{\text{Hg}^\circ, \text{Hg}_2^{2+}}$ by taking activity coefficient into account, to be 0.7988 ab. volt in presence of air and 0.7971 ab. volt in absence of air.

Bonner and Unietis⁵ found the $E_{\text{Hg}^\circ, \text{Hg}_2^{2+}}$ value as 0.7961 ab. volt at 25° using the cell (C₂) after taking activity coefficient into account.



The discrepancies in the values of $E_{\text{Hg}^\circ, \text{Hg}_2^{2+}}$ observed by various workers may be due to two factors viz, (i) the liquid junction potential and (ii) incorrect value of activity coefficient.

In the present work, Linhart's cell (C₁) with certain modifications was used. For the elimination of liquid junction potential a modification of Owen's⁶ procedure was adopted.

Materials and Methods :

Double distilled deoxygenated water was used throughout the experiments. Perchloric acid (AR, 60%) was used and diluted according to requirements. Mercurous perchlorate was prepared by vigorously shaking a mixture of HgO (prepared as recommended by Vogel⁷), deoxygenated double distilled water, excess of (i) mercury and (ii) perchloric acid in absence of air and light. To confirm the completion of the reaction, a few drops of liquid

were withdrawn, diluted with deoxygenated double distilled water and treated with excess NaCl and filtered. No Hg²⁺ ion was left in the solution as the filtrate did not give the black colouration with H₂S.

Mercurous perchlorate was estimated by titrating against KBr (AR) as well as NaCl (AR) using bromophenol blue as indicator^{7,8}. There was negligible difference in the results. The amount of free HClO₄ in the solution was estimated by taking a known volume of the solution into a measuring flask and adding a slight excess of NaCl (AR). The mercurous ions in the solution were precipitated as mercurous chloride. The solution in the measuring flask (precipitate not removed) was made upto the mark by adding double distilled water. (A correction in the volume of the solution was made for the volume of insoluble Hg₂Cl₂). The Hg₂Cl₂ settled at the bottom and a portion of the supernatant was titrated against borax using methyl red as indicator.

The cell solutions were prepared in molarity at the experimental temperature from the stock solution of HClO₄, and a mixture of HClO₄ and Hg₂(ClO₄)₂ in deoxygenated double distilled water. The quinhydrone electrode was prepared as described earlier⁹. Temperature control was within +0.05°. All the cells were studied in duplicate. The difference in the duplicates was less than 0.1 mV. The e.m.f. of the cells was measured in ab. volts at hourly interval for at least 3 hr by a Tinsley Vernier potentiometer using a Bajaj mirror galvanometer, type M.G.8. The values of E (ab. volts) given in Tables 1 to 7 represents the mean of the duplicate cells.

TABLE 1
Temperature 5°

$c_1 \times 10^3$	10.0249	20.0635	40.065	60.200	80.234
$c_2 \times 10^4$	E	E	E	E	E
9.952	0.11171	0.09427	0.07675	0.06624	0.05856
20.076	0.12010	0.10257	0.08521	0.07450	0.06690
30.028	0.12479	0.10732	0.08977	0.07941	0.07186
40.150	0.12816	0.11076	0.09334	0.08275	0.07545
50.103	0.13077	0.11346	0.09601	0.08536	0.07790
$q_0 -$	0.08702	0.08689	0.08704	0.08712	0.08688

TABLE 2

		Temperature 10°			
$c_1 \times 10^3$	10.055	20.149	40.198	60.348	80.465
$c_2 \times 10^4$	E	E	E	E	E
9.980	0.11475	0.09693	0.07902	0.06828	0.06099
20.131	0.12285	0.10524	0.08725	0.07670	0.06926
30.111	0.12763	0.11016	0.09206	0.08169	0.07420
40.263	0.13123	0.11339	0.09560	0.08481	0.07765
50.243	0.13389	0.11613	0.09806	0.08760	0.08024
q_0	0.08953	0.08961	0.08966	0.08971	0.08986

TABLE 3

		Temperature 15°				
$c_1 \times 10^3$	10.005	$c_1 \times 10^3$	19.902	39.992	60.019	79.981
$c_2 \times 10^4$	E	$c_2 \times 10^4$	E	E	E	E
9.990	0.11784	9.990	0.09979	0.08155	0.07074	0.06301
20.000	0.12634	20.054	0.10805	0.08996	0.07925	0.07156
25.160	0.12914	29.970	0.11328	0.09493	0.08423	0.07667
30.044	0.13132	39.960	0.11695	0.09844	0.08784	0.08026
39.960	0.13511	50.024	0.11948	0.10134	0.09068	0.08313
q_0	0.09193	q_0	0.09203	0.09216	0.09225	0.09230

TABLE 4

		Temperature 20°			
$c_1 \times 10^3$	10.042	20.063	40.127	60.190	80.354
$c_2 \times 10^4$	E	E	E	E	E
10.106	0.12038	0.10235	0.08324	0.07232	0.06413
20.043	0.12904	0.11071	0.09217	0.08082	0.07303
30.151	0.13396	0.11556	0.09717	0.08580	0.07821
40.087	0.13748	0.11901	0.10043	0.08952	0.08180
50.195	0.14032	0.12211	0.10328	0.09250	0.08475
q_0	0.09428	0.09436	0.09430	0.09417	0.09406

TABLE 5

		Temperature 25°			
$c_1 \times 10^3$	9.998	20.005	39.948	60.022	80.000
$c_2 \times 10^4$	E	E	E	E	E
9.923	0.12317	0.10467	0.08563	0.07423	0.06632
20.017	0.13240	0.11359	0.09471	0.08337	0.07535
29.940	0.13732	0.11845	0.09969	0.08862	0.08030
40.035	0.14105	0.12216	0.10363	0.09227	0.08430
49.958	0.14382	0.12504	0.10624	0.09494	0.08705
q_0	0.09675	0.09691	0.09685	0.09686	0.09698

TABLE 6

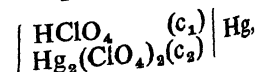
		Temperature 30°			
$c_1 \times 10^3$	10.016	20.012	40.024	60.036	80.148
$c_2 \times 10^4$	E	E	E	E	E
10.082	0.12591	0.10712	0.08773	0.07594	0.06776
19.992	0.13467	0.11604	0.09671	0.08508	0.07701
30.074	0.13998	0.12113	0.10224	0.09031	0.08223
39.985	0.14379	0.12477	0.10573	0.09401	0.08603
50.066	0.14662	0.12791	0.10854	0.09718	0.08926
q_0	0.09879	0.09904	0.09897	0.09869	0.09869

TABLE 7

		Temperature 35°			
$c_1 \times 10^3$	9.998	20.035	39.970	60.005	80.010
$c_2 \times 10^4$	E	E	E	E	E
9.923	0.12858	0.10950	0.09003	0.07821	0.07053
20.017	0.13769	0.11869	0.09930	0.08750	0.07957
29.940	0.14290	0.12417	0.10459	0.09281	0.08490
40.034	0.14683	0.12787	0.10840	0.09643	0.08872
49.958	0.14948	0.13066	0.11130	0.09929	0.09165
q_0	0.10131	0.10160	0.10173	0.10175	0.10211

Results and Discussion

The e.m.f. (Stockholm convention) of the cell,
 $\text{Pt} \mid \text{Q.H. (sat.) HClO}_4(c_1) \mid \text{HClO}_4(c_1)$



is given by

$$E = E^0 + \frac{RT}{2F} \ln \frac{a_{\text{H}^+}^{2+}}{(a_{\text{H}^+})^2} + \text{l.j.p.} \quad \dots (1)$$

Applying the expression $-\log f_i = \frac{AZ_i^2 \sqrt{\mu}}{1 + \sqrt{\mu}} - B_i \mu$,
 for the activity coefficient of ions, we get
 equation (2),

$$E - \frac{2.30259RT}{2F} [\log c_2 - 2 \log c_1 + \frac{2A\sqrt{\mu_1}}{1 + \sqrt{\mu_1}} - \frac{4A\sqrt{\mu_2}}{1 + \sqrt{\mu_2}}] = E_{0,1,1}^0 + \frac{2.30259RT}{2F} [B_2 \mu_2 - B_1 \mu_1] + \text{l.j.p.} \quad \dots (2)$$

HClO_4 and $\text{Hg}_2(\text{ClO}_4)_2$ being completely ionized and A being known¹⁰, the L.H.S. in equation (2) was calculated.

At any temperature, the e.m.f. values of five different series of cells were measured. Every series had five sets of cells. In every series c_1 was fixed and c_2 was varied. For the same concentration of HClO_4 , as c_2 decreases the difference between μ_2 and μ_1 also decreases.

The values of L.H.S. of equation (2) for the same series, when plotted against c_2 , gives a straight line (Fig. 1).

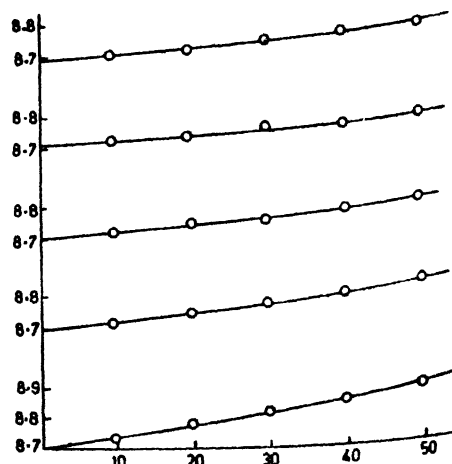


Fig. 1. Plot of $q \times 10^3$ vs $c_2 \times 10^4$.
 (Temp. 5°; $q = E_{0,1,1}^0 + \frac{2.30259RT}{2F} [B_2 \mu_2 - B_1 \mu_1] + \text{l.j.p.}$)

When $c_2 = 0$, $\mu_1 = \mu_2 = c_1$ and $\text{l.j.p.} = 0$, so that the values of L.H.S., corresponding to $c_2 = 0$, in the plots (denoted by q_0) is represented by

$$q_0 = E_{0,1,1}^0 + \frac{2.30259RT}{2F} (B_2 - B_1) \mu_1 \quad \dots (3)$$

Taking all the five series at any temperature, L.H.S. of equation (3), (denoted by q_0), is plotted

against μ_1 , a straight line is obtained (Fig. 2).

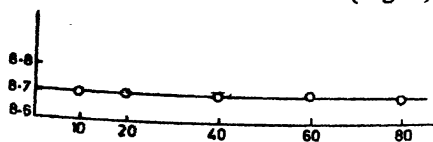


Fig. 2. Plot of $q_0 \times 10^3$ vs $\mu_1 \times 10^3$.
(Temp. 5° ; $q_0 = E_{\text{cell}}^\circ + \frac{2.30259 RT}{RF} [B_2 - B_1] \mu_1$)

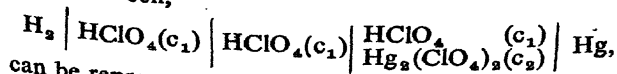
By extrapolation to $\mu = 0$, E_{cell}° (Stockholm convention) were found out on molarity scale as 0.08707, 0.08949, 0.09191, 0.09439, 0.09679, 0.09898 and 0.10130 at 5, 10, 15, 20, 25, 30 and 35° , respectively.

The conversion of E_{cell}° on molarity scale to E_m° on molality scale in these cells are governed by the equation, $E_m^\circ = E_{\text{cell}}^\circ - \frac{RT}{2F} \ln \rho$, where ρ = density

of water. E_{cell}° is known from literature¹¹. Hence $E_{\text{Hg}_2\text{Hg}_2^{2+}}^\circ$ were found out to be 0.80143, 0.80028, 0.79909, 0.79784, 0.79653, 0.79518 and 0.79377 ab.volt at 5, 10, 15, 20, 25, 30 and 35° , respectively.

For check and confirmation at one temperature (25°), the cell $\text{H}_2 | \text{HClO}_4(c_1) | \text{HClO}_4(c_2) | \text{Hg}_2(\text{ClO}_4)_2(c_2) | \text{Hg}$ was studied and almost the same value, 0.79663 ab.volt, of $E_{\text{Hg}_2\text{Hg}_2^{2+}}^\circ$ was obtained.

Thermodynamic functions: The standard potential of the cell,



can be represented by equation (4).

$$E_t = 0.80252 - 2.51 \times 10^{-4}t - 1.0668 \times 10^{-6}t^2 \dots (4)$$

With the help of equation (4) and other thermodynamic relations, the values of ΔG° , ΔS° and ΔH° at 5 to 35° at 5° interval for the cell reaction, $\text{Hg}_2^{2+} + \text{H}_2 = 2\text{Hg} + 2\text{H}^+$ were calculated and are given in Table 8.

TABLE 8

Temp. ($^\circ\text{C}$)	$-\Delta G^\circ$ (cal.)	$-\Delta S^\circ$ cal. degree $^{-1}$ mole $^{-1}$	$-\Delta H^\circ$ (cal.)
5	36962	12.08	40323
10	36906	12.54	40458
15	36850	13.05	40612
20	36796	13.56	40771
25	36738	14.02	40919
30	36670	14.53	41075
35	36607	15.04	41241

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