XLIII.—*The Normal Oxidation–Reduction Potential of Mercury.*

By SYDNEY RAYMOND CARTER and ROBERT ROBINSON.

THE normal oxidation potential of mercury has hitherto only been obtained by indirect methods, since most of the mercuric or mercurous salts suffer from one or more of the disadvantages of low solubility, small degree of ionisation, and a tendency towards the formation of complex salts and ions.

An examination of the mercurous and mercuric perchlorates shows that these salts are practically free from the above objections, and as they can be prepared in a state of purity they are suitable for a direct determination of this potential

Preparation of Perchlorates.

Mercuric perchlorate was prepared according to Chikashigé (J., 1895, **67**, 1013): a slight excess of red mercuric oxide was ground up with $2N$-perchloric acid and, after filtration through asbestos, the solution was concentrated at 40—50° under reduced pressure until crystals separated. Evaporation under reduced pressure appeared to inhibit the formation of basic perchlorates. The crystals were recrystallised from water by a similar evaporation and then dissolved in water, giving a solution in which $[Hg(ClO_4)_2] = 0{\cdot}0922N$, the mercury being determined by precipitation with hydrogen sulphide. In preparing the solution of mercuric perchlorate for the second series of determinations, the salt was not isolated, the heated and filtered solution being diluted suitably.

Mercurous perchlorate was prepared (Linhart, *J. Amer. Chem. Soc.*, 1916, **38**, 2358) by treating perchloric acid with a slight excess of mercurous oxide, in contact with mercury. After standing for some time, the solution was filtered and allowed to remain in contact with mercury for several days. By precipitation with potassium chloride, it was found that $[Hg_2(ClO_4)_2] = 0{\cdot}080N$. The solution also contained a small amount of mercuric perchlorate equal to $0{\cdot}0148N$. In preparing the solution of mercurous perchlorate for the second series of experiments, mercuric perchlorate was reduced with mercury; reduction was not complete, the resulting solution containing a mixture of mercurous and mercuric perchlorates.

To check the purity of the solution of mercurous perchlorate, it was diluted to a strength of $0{\cdot}1N\text{-}\frac{1}{2}Hg_2(ClO_4)_2$, and the following cell constructed:

$$Hg|0{\cdot}1N\text{-}\tfrac{1}{2}Hg_2(ClO_4)_2|0{\cdot}1N\text{-}KNO_3|N\text{-}KCl|N\text{-}KCl,Hg_2Cl_2|Hg.$$

It was found to have a potential of 0·4720 and 0·4718 volt on two successive days. For a similar cell, Ley and Heimbucher (*Z. Elektrochem.*, 1904, **10**, 301) found the potential 0·4719 volt.

Construction of Cells.

The oxidation element consisted of about 100 c.c. of a solution prepared by mixing the above two solutions in the requisite proportions. Three electrodes of bright, unplatinised platinum foil were used, about 1 sq. cm. in area. The complete cell was:

$$Pt|Hg(ClO_4)_2,\ Hg_2(ClO_4)_2\underset{a}{|}0{\cdot}1N\text{-}KNO_3\underset{b}{|}N\text{-}KCl|N\text{-}KCl,Hg_2Cl_2|Hg.$$

The connecting syphon tubes at *a* and *b* were filled with the solution of the oxidation element and with N-KCl, respectively. The three electrodes gave perfect agreement between themselves, and the potential was constant over several days. The cells could be reproduced with a variation of about 0·3 millivolt. After measuring the potential, the cell solution was analysed, mercurous mercury being estimated as calomel, whilst the mercuric mercury in the filtrate was determined as sulphide. All measurements were made at 18°; potentials were referred to the absolute scale and were given a positive sign if the current flowed through the cell from the normal calomel electrode.

The diffusion potentials at *a* and *b* have been shown by Ley and Heimbucher (*loc. cit.*) to be of a small order (less than 1 milllivolt), and have been neglected in this investigation.

Deduction of the Normal Oxidation Potential.

The behaviour of the system is determined by the equation:

$$E = E_0 + 0{\cdot}029 \log [\mathrm{Hg}^{\bullet\bullet}]^2/[\mathrm{Hg}_2^{\bullet\bullet}] \quad . \quad . \quad . \quad . \quad (1)$$

E_0 being the normal oxidation potential and E the potential of the half-element corresponding to the given mercurous- and mercuric-ion concentrations. Now if α_1 and α_2 are the degrees of dissociation of the mercuric and mercurous perchlorates, respectively, then

$$E = E_0 + 0{\cdot}029 \log \alpha_1{}^2[\mathrm{Hg(ClO_4)_2}]^2/\alpha_2[\mathrm{Hg_2(ClO_4)_2}] \quad . \quad . \quad (2)$$

which may be written:

$$E = E_0 + 0{\cdot}029 \log [\mathrm{Hg(ClO_4)_2}]^2/[\mathrm{Hg_2(ClO_4)_2}] + 0{\cdot}029 \log \alpha_1{}^2/\alpha_2 \quad (3).$$

The last term introduces a small correction, due to the incomplete dissociation of the perchlorates. Hence, if the potential of the half-element is known, and also the concentrations of the mercurous and mercuric perchlorates, then, by substitution in equation (3), E_0, the normal oxidation potential, may be calculated.

Correction for Incomplete Dissociation of the Perchlorates.—In order to obtain α_1 and α_2, the degrees of dissociation of the mercury perchlorates, we have assumed that these salts are dissociated to the same extent as barium perchlorate. This is based on a consideration of the conductivity-dilution curves and hydrolysis data for barium, mercurous, and mercuric perchlorates, which have been determined by Ley and Heimbucher (Diss., Würzburg, 1904). A solution used in these cells (with the exception of cell No. 3) may be considered as being made by the admixture in suitable proportions of two separate solutions, one of mercurous and the other of mercuric perchlorate, the concentration of each being equal to the total salt concentration in the cell; such solutions will be "isoionic" with one another, *i.e.*, the extent of dissociation of the original solutions will not be affected on mixing. Hence by taking the degree of dissociation of barium perchlorate for the total salt concentration, since $\alpha_1 = \alpha_2$, we can determine $0{\cdot}029 \log \alpha_1^2/\alpha_2$ for each cell solution.

Moreover, Ley and Heimbucher have shown that mercurous perchlorate is hydrolysed to the extent of 3—4% in these solutions; and we have shown that mercuric perchlorate is hydrolysed to a similar extent (3%) in 0·05*N* solution. Hence the correction to be applied is $0{\cdot}029 \log (0{\cdot}97\alpha_1)^2/(0{\cdot}97\alpha_2)$ or $0{\cdot}029 \log (0{\cdot}97\alpha_1)$. Now in the solutions that we have studied, $\alpha_1 = 0{\cdot}73$, hence the correction is — 0·0044 volt. It will be seen that the effects of hydrolysis of the perchlorates are of a small order and almost negligible.

Results.

Table I summarises the measurements of nine cells. The observed *E.M.F.*, E_c, of the whole cell is given in col. 7. From this value, the normal oxidation potential E_0 (col. 8) is deduced by substituting the logarithmic correction term (col. 6) in equation (2) and adding the potential of the calomel electrode, 0·560 volt.

TABLE I.

$m = [Hg(ClO_4)_2]$, $n = [Hg_2(ClO_4)_2]$.

Cell No.	m.	n.	m/n.	m^2/n.	$0{\cdot}029 \log m^2/n$.	E_c.	E_0.
1	0·0493	0·0431	1·144	0·0564	−0·0407	0·5885	1·1892
2	0·0493	0·0431	1·144	0·0564	−0·0407	0·5882	1·1889
3	0·0049	0·00417	1·175	0·00576	−0·0694	0·5569	1·1863
4	0·0236	0·0670	0·352	0·00831	−0·0647	0·5634	1·1890
5	0·0160	0·0770	0·208	0·00333	−0·0763	0·5540	1·1903
6	0·0121	0·0722	0·168	0·00203	−0·0825	0·5489	1·1914
7	0·0199	0·0707	0·282	0·00561	−0·0697	0·5607	1·1904
8	0·0560	0·0539	1·039	0·05818	−0·0404	0·5902	1·1906
9	0·0581	0·0609	0·954	0·05543	−0·0409	0·5907	1·1916

The results may be divided into two series, since the later cells (Nos. 7, 8, and 9) were made up from slightly different solutions, as previously indicated (see "Preparation of Perchlorates").

Cell No. 3 was a much more dilute solution, having been prepared by ten-fold dilution of Cell No. 1. In this case, hydrolysis of the mercuric perchlorate is considerable (about 15%), and is probably sufficient to account for the low value of E_0.

The mean *E.M.F.* of these cells (with the exception of Cell No. 3) is 1·1902 volt, with an average error of ± 0·0008 volt.

The Effect of Perchloric Acid on the Potential.—To determine this, four cells were constructed, by mixing 50 c.c. of a solution in which $[Hg(ClO_4)_2] = 0{\cdot}0687N$ and $[Hg_2(ClO_4)_2] = 0{\cdot}0396N$, with the calculated quantity of 2*N*-perchloric acid and sufficient water to make the total volume up to 100 c.c. The following potentials were observed :

TABLE II.

Cell No.	10.	11.	12.	13.
$[HClO_4]$	1*N*	0·5*N*	0·1*N*	Nil.
E.M.F. (obs.)	0·5390	0·5443	0·5728	0·5915

The addition of free perchloric acid to the solution decreases the extent of dissociation of both the perchlorates of mercury, the decrease in the case of the mercuric salt being the predominating factor, because the square of this concentration and only the first power of the mercurous salt concentration enters into equation (2). Thus the observed *E.M.F.* is diminished by addition of perchloric acid. Quantitatively the effect may be expressed thus: substituting the values $[Hg^{\cdot\cdot}] = K_1[Hg(ClO_4)_2]/[ClO_4']^2$ and $[Hg_2^{\cdot\cdot}] = K_2[Hg_2(ClO_4)_2]/[ClO_4']^2$ equation (1) becomes

$$E = E_0 + 0{\cdot}029 \log K_1^2[Hg(ClO_4)_2]^2/K_2[Hg_2(ClO_4)_2][ClO'_4]^2.$$

Since $[Hg(ClO_4)_2]$ and $[Hg_2(ClO_4)_2]$ are constant in the four cells of Table II, these quantities, together with K_1, K_2, and E_0, have been incorporated in a fresh symbol E'_0, and, therefore,

$$E = E'_0 - 0{\cdot}058 \log [ClO_4'].$$

Assuming complete dissociation of both the mercury salts and of the perchloric acid, and taking *E.M.F.* (obs.) = 0·5915 (Cell 13) as a starting point for *E.M.F.* (calc.), the following values of the potentials are calculated:

TABLE III.

Cell No.	10.	11.	12.	13.
$[ClO_4']$	1·11	0·61	0·21	0·11
E.M.F. (obs.)	0·5390	0·5443	0·5728	0·5915
E.M.F. (calc.)	0·5333	0·5483	0·5753	(0·5915)

It is evident that the variation of the potential with perchloric acid concentration can be accounted for satisfactorily, and it is therefore probable that complex-ion formation between the free acid and the salts is either absent or negligible.

It was necessary to show that the potentials measured in this investigation were not due to the perchlorate radical. Experiments were therefore carried out with a platinum-foil electrode dipping into solutions of *N*-perchloric acid and 0·1*N*-potassium perchlorate, respectively. The potentials obtained were ill-defined and in no way resembled those registered in the case of the mercury salts.

Comparison with Previous Data on the Normal Oxidation Potential.

The present investigation gives a value of $E_0 = + 1{\cdot}190$ volts on the absolute scale, or ${}_0E_h = + 0{\cdot}913$ volt on the hydrogen scale.

The value given in Abegg's " Handbuch der Anorganischen Chemie," [1905, II, (2), 561] is ${}_0E_h = 0{\cdot}87$, obtained by calculation from the normal electrode potential $\mathrm{Hg}\text{—}\mathrm{Hg}_2^{\cdot\cdot}$, ${}_0E_h = 0{\cdot}75$ volt, and the equilibrium relations in the system $\mathrm{Hg}\text{—}\mathrm{Hg}_2^{\cdot\cdot}\text{—}\mathrm{Hg}^{\cdot\cdot}$, in which the ratio $[\mathrm{Hg}^{\cdot\cdot}]/[\mathrm{Hg}_2^{\cdot\cdot}] = 235$. This value, 0·87 volt, is probably low, since later determinations of the potential $\mathrm{Hg}\text{—}\mathrm{Hg}_2^{\cdot\cdot}$ (${}_0E_h = 0{\cdot}75$) give a somewhat higher figure; thus Lewis and Randall ("Thermodynamics," 1923, 419) give ${}_0E_h = 0{\cdot}7986$, based on Linhart's measurements, and Abegg, Auerbach, and Luther (" Messungen elektromotorischer Kräfte galvanischer Ketten," 1915, 46) give ${}_0E_h = 0{\cdot}80$. The latter authors have given a value of the normal oxidation potential $2\mathrm{Hg}^{\cdot\cdot}\text{—}\mathrm{Hg}_2^{\cdot\cdot}$, ${}_0E_h = 0{\cdot}92$, which is in good agreement with our experimental results.

Conclusions.

Mercurous and mercuric perchlorates have been prepared and found to be suitable for electrochemical measurements, as their solutions are capable of registering steady potentials with platinum electrodes.

The normal oxidation potential of the process $2\mathrm{Hg}^{\cdot\cdot}\text{—}\mathrm{Hg}_2^{\cdot\cdot}$ is $+\ 1{\cdot}190$ volts.

The effect of free perchloric acid on the potential has been investigated.

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UNIVERSITY OF BIRMINGHAM,
EDGBASTON.

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