

XC.—*A Standard Electrode with Alkaline
Electrolyte: Hg | HgO Alkali.*

By FREDERICK GEORGE DONNAN and ARTHUR JOHN ALLMAND.

IN a recently published investigation (*Zeitsch. Elektrochem.*, 1910, 16, 254) of the electromotive behaviour of the oxides of mercury in alkaline electrolytes, one of us was able to show that the two mercuric oxides, yellow and red, are identical—a view the correctness of which had been challenged—and that all discrepancies previously observed in their electromotive behaviour could be ascribed to the use of samples containing particles of different degrees of fineness of division. At the same time, the close agreement between the results given by different specimens of oxide justified the continuance of the work, using more refined methods of measurement, in the hope that well-defined alkaline normal electrodes would result. An account of this work is here presented, and it will be seen that the expectations have been justified.

Plan of Work.—It was decided to carry out measurements on two distinct samples of oxide. As electrolytes were chosen *N*-sodium hydroxide and *N*-potassium hydroxide, which had previously (*loc. cit.*) given unexpectedly varying potential values, and *N*/10-sodium hydroxide. The corresponding auxiliary electrodes were *N*- and *N*/10-calomel electrodes. 0° and 25° were selected as working temperatures.

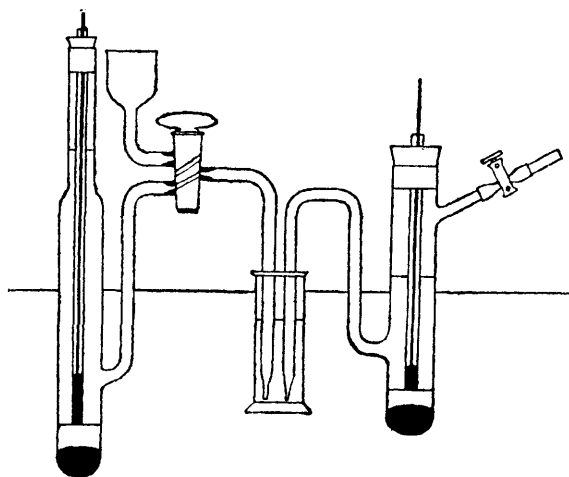
Materials, Apparatus, and Methods of Measurement.—The two samples of mercuric oxide used were prepared by the action of heat in one case on mercuric nitrate, and in the other on mercurous nitrate. As previously found, if either of these salts be fused in a porcelain basin and the heating be gently continued, with constant stirring and occasional cooling and gentle powdering, until no further traces of nitrogen oxides are given off, the resulting products, which are of a light reddish-brown colour, only contain a very small proportion of particles of small size, and quickly give constant electromotive systems.

The alkaline solutions were free from carbonate and prepared from clean metal. The *N*/10-sodium hydroxide was prepared by dilution of the *N*-sodium hydroxide. In all cases, of course, the solutions were carefully checked against standard acid before use.

The thermostat used at 25° allowed of a regulation of $\pm 0.04^\circ$. For the measurements at 0°, an arrangement of two rectangular boxes, one inside the other, was employed. The inner vessel was made of tinned iron, and the outer one of wood, well coated externally with layers of felt. The interspace was packed with cotton wool. This outer vessel was considerably higher than the inner, and even when the latter was supported inside on corks and cotton wool, there was space for a thick layer of cotton wool between the tops of the electrodes and the lid of the outer box. The inner vessel was packed full with a mixture of finely ground ice and water, and could be kept below 0.5° for several days, the exact time depending, of course, on the external temperature and the proportion of ice present.

The type of electrode vessel used, one described by Wilsmore (*Zeitsch. Elektrochem.*, 1904, **10**, 685), is shown in the figure. Mercury was poured in to the depth of 1—2 cm., and on this was placed a layer of the oxide. The vessel was then filled with the electrolyte up to the shoulder, and the rubber stopper and tube making connexion with the mercury firmly inserted. The displaced alkali flowed out through the tap, which was at once closed. The rubber stopper and glass rubber junctions were then waxed over, and the connecting tube washed free from alkali by means of the water placed in the cup. The half element was then placed in the

thermostat, and remained there until all measurements with it had been made. The calomel electrode vessels were of the ordinary type (see figure). Several electrodes of each kind were made up at different times. The authors can confirm the observation made by Lewis and Sargent (*J. Amer. Chem. Soc.*, 1909, **31**, 362) on the differences between the potential values obtained when, on the one hand, the mercurous chloride depolariser has been only shaken with the potassium chloride solution, and, on the other, previously ground up into a paste with mercury and the solution, and subsequently shaken (*Physiko-Chemische Messungen*, 3rd edition, p. 443). The former electrodes, which were nearly always 0.2 m.v. more negative than the latter, undoubtedly give the more correct potential value, and were used in all the measurements of



the calomel-mercuric oxide combination. *N*-Calomel electrodes prepared in this way almost invariably agreed to within 0.2 m.v., and generally within 0.1 m.v. With *N*/10-electrodes, the variations were slightly greater. In all cases, before readings were taken, the auxiliary electrodes were compared with one another, and were only used if they agreed to within 0.1 m.v. in the case of *N*-electrodes, and 0.2 m.v. in the case of *N*/10-electrodes.

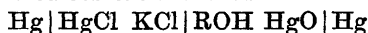
The normal cadmium element used was of the type recommended by Smith, and had been standardised in the National Physical Laboratory. Its *E.M.F.* was taken as $1.0184 - 0.0004 (t^\circ - 20)$ (see *Phil. Trans.*, 1907, A, **207**, 393).

The potentiometer was a Clark-Fisher instrument, which had been previously calibrated at the National Physical Laboratory. One mm. on its slide wire corresponded with 0.0001 volt.

The manner of carrying out a series of measurements was as follows. A stoppered bottle was filled with the same carbonate-free standard alkali as that in the mercuric oxide electrode, and was hung in the thermostat. Whilst this was being heated or cooled to the thermostat temperature, the potentials of the various calomel electrodes which had been placed in the thermostat about an hour before were compared. This was done in the ordinary way, the two opposed electrodes being measured in series with the normal cadmium element. The connecting vessel (see figure) consisted of a small glass cylinder almost entirely immersed in the thermostat. It was filled, of course, with potassium chloride of the same strength as that in the calomel electrodes, a bottle containing such a solution being continually kept in the thermostat. From the results of this comparison, two electrodes were selected for the actual measurements, and fixed ready for use. One of the mercuric oxide electrodes was then taken, and its empty vertical connecting tube filled with alkali from the bottle previously placed in the thermostat. With the end of the connecting tube in the alkali bottle, the tap was turned for an instant so as to put the electrode vessel itself in connexion with the side-tube, and thus equalise any slight pressure difference between the inside of the electrode vessel and the atmosphere. The tap was then closed, the outside of the connecting tube wiped, and the electrode vessel replaced in the thermostat, but this time with the side-tube dipping down into the cylinder containing the potassium chloride solution. Electrical connexions were made. After waiting a few minutes for all temperatures to adjust themselves, the tap was opened, and measurements were commenced. The combinations calomel i, mercuric oxide, and calomel ii, mercuric oxide, were each measured in series with, and in series against, the standard cell. Each mercuric oxide electrode was thus measured four times. By working in this way, any fluctuations in the single potential of the mercuric oxide electrode due to its being easily polarised by current passing through would be detected. As a matter of fact, no evidence of any such polarisation was found. The mean was taken of the four almost identical values for the *E.M.F.* of the combination $\text{Hg}|\text{HgCl}|\text{KCl}|\text{alkali}|\text{HgO}|\text{Hg}$, and it is this mean value which appears in the subsequent tables of experimental results. When the readings with an electrode were completed, the tap was closed, the side-tube carefully washed out, and the vessel placed back in its old position in the thermostat.

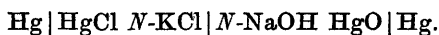
Results.

The figures obtained for the *E.M.F.*'s of the combinations



are given in volts in the following tables. Current always flows in the cell from the mercuric oxide to the calomel. The method of preparation of the oxide is indicated in each case. Sample (17) of table V is also sample (17) of the previous paper on mercuric oxides (*loc. cit.*), and was prepared by shaking up *yellow* mercuric oxide obtained from Kahlbaum with 10 per cent. sodium hydroxide at room temperature for seven weeks.

TABLE I.

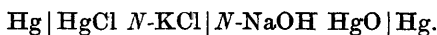


Temperature 25°.

Electrodes set up		May 28.	May 29.	June 1.	June 6.	June 11.
May 26.						
From	1	0.1540	0.1542	0.1541	0.1540	0.1540
mercurous	2	0.1542	0.1544	0.1546	0.1542	0.1544
nitrate.	3	0.1538	0.1541	0.1540	0.1540	0.1540
From	4	0.1539	0.1541	0.1540	0.1540	0.1541
mercuric	5	0.1540	0.1541	0.1540	0.1540	0.1541
nitrate.	6	0.1541	0.1542	0.1542	0.1542	0.1543

Mean value 0.1541 \pm 0.00002.

TABLE II.

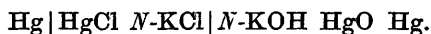


Temperature 0°.

	July 1.	July 6.
3	0.1348	0.1348
4	0.1353	0.1353
5	0.1348	0.1349
6	0.1348	0.1349

Mean value 0.1349 \pm 0.00008.

TABLE III.

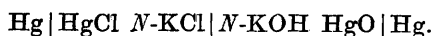


Temperature 25°.

Electrodes set up		June 22.	June 24.	June 29.	July 4.
June 20.					
From mercurous	7	0.1618	0.1620	0.1621	0.1620
nitrate.	8	0.1620	0.1621	0.1621	0.1621
From mercuric	9	0.1620	0.1617	0.1618	Broken
nitrate.	10	0.1619	0.1619	0.1621	0.1620

Mean value 0.1620 \pm 0.00004.

TABLE IV.

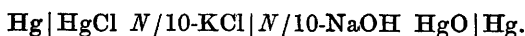


Temperature 0°.

	July 8.	July 12.
7.....	0.1431	0.1429
8.....	0.1435	0.1434
10.....	0.1432	0.1436

Mean value 0.1433 ± 0.00011 .

TABLE V.

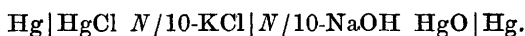


Temperature 25°.

Electrodes set up.				
July 14.		July 16.	July 19.	July 25.
From	11.....	0.1499*	0.1518	0.1514
mercurous	12.....	0.1487*	0.1505*	0.1506*
nitrate.	13.....	0.1493*	0.1500*	0.1515
From	14.....	0.1523	0.1516	0.1517
mercuric	15.....	0.1518	0.1519	0.1522
nitrate.	16.....	0.1509*	0.1518	0.1518
Yellow	17.....	0.1496*	0.1490*	0.1515
mercuric				
oxide.				

Mean value 0.1518 ± 0.00008 .

TABLE VI.



Temperature 0°.

	July 26.
11.....	0.1326
13.....	0.1324
14.....	0.1328
16.....	0.1326

Mean value 0.1326 ± 0.00008 .

In the calculation of the mean values and mean errors, the following readings are not taken into account:

Table I.—Those of May 28, as equilibrium had probably not completely set in.

Table III.—Those of June 22, for the same reason.

Table V.—All the readings marked with an asterisk, where equilibrium had clearly not been reached.

It is obvious from the above figures that the mercuric oxide electrode can be very exactly defined. This is particularly clear from the results at 25°. The readings at 0° were not carried out with such exact care, as the temperature-coefficient of the electrode, to ascertain which those particular measurements were undertaken,

is not appreciably affected by a small error in the *E.M.F.* determinations. It is satisfactory that the electrode made up with yellow mercuric oxide (17) gives essentially the same behaviour as those made up with the red oxide, only requiring a rather longer time to settle down. This, of course, is a confirmation of conclusions previously arrived at. The results obtained for the different combinations, and the temperature-coefficients of *E.M.F.* calculated for the same, are collected in table VII.

TABLE VII.

Element.	<i>E.M.F.</i> at 0° in volts.	<i>E.M.F.</i> at 25° in volts.	Temperature- coefficient. volt degree
<i>N</i> -Calomel <i>N</i> -KOH HgO Hg } <i>N</i> -Calomel <i>N</i> -NaOH HgO Hg }	0.1433 ± 0.00011 0.1349 ± 0.00008	0.1620 ± 0.00004 0.1541 ± 0.00002	+ 0.00075 + 0.00077
<i>N</i> /10-Calomel <i>N</i> /10- NaOH HgO Hg }	0.1326 ± 0.00008	0.1518 ± 0.00008	+ 0.00077

It will be noticed that the temperature-coefficients are identical with *N*/10-sodium hydroxide and *N*-sodium hydroxide as electrolytes, and that the value with *N*-potassium hydroxide is only very slightly less.

The calculated errors in table VII are probable errors of the mean value; but if the electrode is to be recommended as a standard, it is also of importance to know the probable error to be expected in the setting up of any single electrode according to the above instructions. These probable errors have been calculated from the results at 25°. For electrodes with *N*-alkali electrolyte they hold good for readings made three days after setting up; with *N*/10-alkali electrodes the readings are taken eleven days after setting up. The electrode vessels are supposed to have been kept all the time at 25°:

Hg HgO <i>N</i> -NaOH	± 0.00015 volt.
Hg HgO <i>N</i> -KOH	± 0.00019 "
Hg HgO <i>N</i> /10-NaOH	± 0.00057 "

If we omit the value given by electrode (12) in table V, the mean error of setting up becomes, in the last case, ± 0.00032 volt. This last set of calculations assumes, of course, that fluctuations in the *E.M.F.*'s of the above elements are entirely due to the mercuric oxide half-element, the calomel electrode remaining constant.

From the above results we must now calculate the single potential differences and temperature-coefficients of the mercuric oxide electrodes.

Taking the potential of the *N*-calomel electrode at 18° as +0.283 volt, we will make use of Sauer's value (*Zeitsch. physikal. Chem.*, 1904, **47**, 146) for the potential of the *N*/10-calomel electrode at 18° (+0.335 volt) and Richards' values (*Zeitsch. physikal. Chem.*, 1897, **24**, 39) for the temperature-coefficients of the two electrodes (+0.00061 $\frac{\text{volt}}{\text{degree}}$ for the *N*-calomel and +0.00079 $\frac{\text{volt}}{\text{degree}}$ for the *N*/10-calomel).

Then we have:

<i>N</i> -Calomel electrode at 25°	+0.2873 volt.
<i>N</i> -" " " 0°	+0.2720 "
<i>N</i> /10-Calomel electrode at 25°	+0.3405 "
<i>N</i> /10-" " " 0°	+0.3208 "

The next step is the evaluation of the potential differences at the junction of the different electrolytes, and here we encounter the difficulty common to all calculations of this type—uncertainty as to how far the real values coincide with the calculated values. In very dilute solutions there is no reason to suppose discrepancies to occur, but in stronger solutions, where the degrees of dissociation are not so well known and may be unequal, and where, also, the ionic mobilities may be different from those at infinite dilution, it is very possible that errors may arise. For use in the Planck formula, the ionic mobilities of Na⁺, K⁺, Cl⁻, and OH⁻ were calculated for 0° and 25°, using the values for 18° and the temperature-coefficients given by Kohlrausch and von Steinwehr (*Sitzungsber. K. Akad. Wiss. Berlin*, 1902, 570, 581). The values obtained are:

	l_0	l_{25}
Na ⁺	24.5	51.0
K ⁺	39.4	74.5
Cl ⁻	40.0	74.3
OH ⁻	117.6	195.9

Introducing them into the Planck equations, we obtain for the liquid potential difference:

	0°.	25°.
$\left. \begin{array}{l} N\text{-NaOH} - N\text{-KCl} \\ N/10\text{-NaOH} - N/10\text{-KCl} \end{array} \right\}$	0.0209 volt	0.0197 volt
$N\text{-KOH} - N\text{-KCl}$	0.0160 "	0.0153 "

In the last case, we can also calculate on the lines indicated by Lewis and Sargent (*J. Amer. Chem. Soc.*, 1909, **31**, 363). They have pointed out that when one ion is common to the two electrolytes, the Planck equation becomes $E = \frac{RT}{F} \ln \frac{\lambda_0^1}{\lambda_0^2}$, where λ_0^1 and λ_0^2 represent the molecular conductivities of the solutions concerned at infinite dilution. As, however, the Planck equation rests on the assumption that the ionic mobilities do not vary with the concentration, and as this assumption is not always well founded,

it would be better to substitute for $\frac{\lambda_0^1}{\lambda_0^2}$, $\frac{\lambda_1}{\lambda_2}$, that is, the ratio of the conductivities of the actual solutions dealt with. In which case, the ionic mobilities entering into the calculation are those actually involved in the measurement. They have experimentally tested this method of calculation, using 0.1 and 0.2 *N*-solutions, and have obtained very good agreement. But whether the equation can be advantageously applied to more concentrated solutions, is yet doubtful.

For the purpose of the present calculation, the molecular conductivities of *N*-potassium hydroxide and *N*-potassium chloride at 18° are taken as 182.5 and 98.3 respectively. Using as temperature-coefficients of conductivity, 0.0187 for potassium hydroxide and 0.0195 for potassium chloride, we obtain:

	λ for 0°.	λ for 25°.
<i>N</i> -KOH	121.1	206.4
<i>N</i> -KCl	63.8	111.7

and these figures give for the potential difference *N*-KOH—*N*-KCl:

0°.	25°.
0.0151 volt	0.0158 volt

The values differ by 0.5—0.9 m.v. from those obtained by the Planck formula. Which are the more correct, is not easy to say. According to the Planck formula, the P.D. is greater at 0° than at 25°; according to the Lewis-Sargent formula, the reverse is correct, which seems more probable. On the other hand, the latter authors themselves have both calculated and measured the potential difference at 25° between 0.1*N*-potassium hydroxide and 0.1*N*-potassium chloride and between 0.2*N*-potassium hydroxide and 0.2*N*-potassium chloride. They find 0.0165 and 0.0169 volt respectively, values which increase with the concentration, whilst the above figure for a much stronger solution is considerably lower.

Table VIII contains the values for the single potentials of the electrodes at 0° and 25°, and also their temperature-coefficients. In the case of the Hg|HgO *N*-KOH electrode, the calculation has been made, using both the Planck and the Lewis-Sargent formulæ.

TABLE VIII.

Electrode.	Potential at 0°.	Potential at 25°.	Temperature-coefficient. voltage/degree
Hg HgO <i>N</i> -KOH (Lewis and Sargent)	+0.1136 volt	+0.1095 volt	−0.00016
Hg HgO <i>N</i> -KOH (Planck)	0.1127 „	0.1100 „	−0.00011
Hg HgO <i>N</i> -NaOH	0.1162 „	0.1135 „	−0.00011
Hg HgO <i>N</i> /10-NaOH...	0.1673 „	0.1690 „	+0.00007

Several conclusions can be drawn from this table. As the tem-

perature-coefficients of the electrodes $\text{Hg}|\text{HgO } N\text{-NaOH}$ and $\text{Hg}|\text{HgO } N/10\text{-NaOH}$ are of opposite sign, whilst, on the other hand, the two combinations $\text{Hg}|\text{HgCl KCl}|\text{NaOH HgO}|\text{Hg}$ have identical temperature-coefficients, it would at first appear that some error had entered the intermediate calculation, or that faulty data had been used. This, however, is not so. The difference between the temperature-coefficients of the N - and $0.1N$ -calomel electrodes is exactly balanced by the difference between the temperature-coefficients of the N - and $0.1N$ -mercuric oxide electrodes; and, in both cases, these differences can be shown to have the calculated theoretical value. In the first case, the total energy change at the electrode is made up of the heat of ionisation of chlorine, minus the heat of formation of mercurous chloride, and is the same at both dilutions. If we take the temperature-coefficient of the $0.1N$ -electrode as $+0.00079$, we can at once put (per gram-equivalent):

$$U = 0.335 - 291.0.00079.$$

(Volt-faraday
at 18°)

If x is the temperature-coefficient of the N -electrode,

$$U = 0.283 - 291.x.$$

Hence :

$$0.052 = 291 (0.00079 - x)$$

$$x = +0.00061.$$

This is exactly the value found by Richards, and is confirmatory evidence in favour of his value, and against the higher figures obtained by other observers. Quite similarly, the calculated difference between the temperature-coefficients of the N - and $0.1N$ -mercuric oxide electrodes is $0.000186 \frac{\text{volt}}{\text{degree}}$, and the found value, $0.000176 \frac{\text{volt}}{\text{degree}}$

In addition to this, we notice, in the same table, that, if the Planck formula be used to express the liquid potential difference $N\text{-KOH} - N\text{-KCl}$, the values for the temperature-coefficients of the electrodes $\text{Hg}|\text{HgO } N\text{-KOH}$ and $\text{Hg}|\text{HgO } N\text{-NaOH}$ are identical. The calculated difference is only $0.00001 \frac{\text{volt}}{\text{degree}}$. If, on the other hand, the Lewis-Sargent be used, another value is obtained for the temperature-coefficient of the electrode $\text{Hg}|\text{HgO } N\text{-KOH}$, one differing considerably from that of $\text{Hg}|\text{HgO } N\text{-NaOH}$. This good agreement between the values of the temperature-coefficients of the different electrodes justifies our assuming that the Planck formula expresses the liquid potential difference in the present cases with considerable accuracy.

Using the values of the H_2 -electrode potential in N -sodium hydroxide obtained in the previous paper, namely:

$$-0.814 \text{ volt at } 0^\circ$$

$$-0.809 \text{ volt at } 25^\circ,$$

we can calculate the $E.M.F.$'s of the element $Hg|HgO \text{ } N\text{-NaOH}|H_2$ at different temperatures.

We obtain:

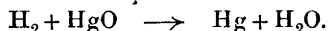
$$\text{at } 0^\circ \text{ } 0.9302 \text{ volt}$$

$$18^\circ \text{ } 0.9243 \text{ ,,}$$

$$25^\circ \text{ } 0.9225 \text{ ,,}$$

from which the temperature-coefficient of the cell works out at $-0.00031 \frac{\text{volt}}{\text{degree}}$. We can now calculate the heat of reaction at

18° corresponding with the equation:



We have:

$$U = A - T \frac{dA}{dT}.$$

$$A = 2 \times 96540 \times 0.9243 \text{ joules.}$$

$$-T \cdot \frac{dA}{dT} = 2 \times 96540 \times 291 \times 0.00031 \text{ joules.}$$

And

$$U = \frac{2 \times 96540}{4.19} [0.9243 + (291 \cdot 0.00031)] \text{ calories.}$$

$$= 46750 \text{ calories.}$$

The thermochemical value is 46,700 calories.

Summary of Results.

(i) Combinations of the type $Hg|Hg_2Cl_2 \text{ } KCl|ROH \text{ } HgO|Hg$ are measured at 25° and 0° . The mean error varies between ± 0.00002 volt and ± 0.00011 volt.

(ii) Assuming the correctness of the Planck liquid potential formula, the following values for single potentials hold good (N -cal. at $18^\circ = +0.283$ volt):

$$Hg|HgO \text{ } N\text{-KOH} = +0.1100 - 0.00011 (t - 25^\circ)$$

$$Hg|HgO \text{ } N\text{-NaOH} = +0.1135 - 0.00011 (t - 25^\circ)$$

$$Hg|HgO \text{ } N/10\text{-NaOH} = +0.1690 + 0.00007 (t - 25^\circ).$$

The mean errors will be the same as in the corresponding combinations with calomel electrodes.

(iii) The average error of setting up is, after some days, as follows:

$$Hg|HgO \text{ } N\text{-KOH} \quad \pm 0.00019 \text{ volt}$$

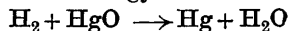
$$Hg|HgO \text{ } N\text{-NaOH} \quad \pm 0.00015 \text{ ,,}$$

$$Hg|HgO \text{ } N/10\text{-NaOH} \pm 0.00057 \text{ ,,}$$

(iv) The difference between the temperature-coefficients of the *N*- and 0.1*N*-electrodes is in close accordance with the calculated value.

(v) It follows that a standard alkaline electrode has, for the first time, been closely and accurately defined.

(vi) The change in total energy at 18° of the reaction



is calculated from electrochemical data, and shows excellent agreement with the thermochemical value.

The expenses of this work were defrayed by a grant from the Research Fund Committee of the Chemical Society, for which the authors wish to express their thanks.

MUSPRATT LABORATORY OF PHYSICAL AND ELECTROCHEMISTRY,
UNIVERSITY OF LIVERPOOL.
