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MERCURY(II) OXIDE AND SILVER(I) OXIDE ELECTRODES IN AQUEOUS SOLUTIONS

(Technical Report)

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Abstract - The standard aqueous potentials of the mercury(II) oxide electrode and of the silver(I) oxide electrode covering the temperature range from 283 to 318 K have been critically analysed (with special attention to the standard states implied) and redetermined: as a result, recommended values are tabulated for both the respective «acid» and «basic» standard potentials. From these potentials, accurate values for the standard solubility products of the corresponding hydroxides, $Hg(OH)_2$ and $AgOH$, have been also derived. The usefulness and applications of the mercury(II) oxide electrode, as well as the limited applicability of the silver(I) oxide electrode, are described.

1. INTRODUCTION

The Sb_2O_3 electrode, so popular in connection with pH-metric and titrimetric applications, and its congeners As_2O_3, Bi_2O_3, WO_2, MbO_2, and TeO_2 electrodes were reviewed critically in Ives and Janz's well-known book on reference electrodes (ref. 1) and, therefore, they need no further discussion here.

Another important oxide electrode, the mercury(II) oxide (HgO) electrode, together with the related silver(I) oxide (Ag_2O) electrode, has been re-examined recently (ref. 2), with redetermination of the relevant standard potentials and of the thermodynamic solubility product of the corresponding hydroxides: these results are the experimental basis of the present document.

After the pioneer study by Brønsted (ref. 3) the reliability of the HgO electrode (refs. 4-6) was confirmed by the Japanese group (refs. 7-11) and, later, by Every and Banks (ref. 12), Case and Bignold (ref. 13), Johansson et al. (ref. 14) and Corti and Fernàndez-Prini (ref. 15). However, significant discrepancies existed between the standard aqueous potentials reported, and this prompted the redetermination by Longhi et al. (ref. 2), who analysed in detail the possible causes of such discrepancies, e.g. electrode design, cell assemblage, electrolyte concentration, liquid junction potentials, mixed potentials due to traces of oxygen or other oxidising species in solution, electrode poisoning by certain diffusable species, and found that all the above causes made the measured potentials and the standard potentials decrease. The redetermined standard potentials, in turn, allowed redetermination of the thermodynamic solubility product for the corresponding aqueous $Hg(OH)_2$ and $AgOH$ hydroxides, with results in good agreement with those obtained by other methods, which provides a confirmation of reliability.

2. THE STANDARD POTENTIALS OF THE MERCURY(II) OXIDE ELECTRODE AT VARIOUS TEMPERATURES

Redetermining the standard potential of the HgO electrode means redetermining the standard electromotive force (e.m.f.) $E°$ of the following reversible cell:

$$Pt \mid H_2 \text{ (1 bar)} \mid NaOH(aq) \mid HgO \mid Hg \qquad \text{(cell I)}$$

the e.m.f. of which is expressed by:

$$E = E° - (k/2) \log a_{H_2O} \qquad (1)$$

where $k = (\ln 10)RT/F$. E is found to be independent of the electrolyte concentration (at molalities lower than ~0.5 mol kg^{-1}) except for minimal differences attributable to varying water activity, a_{H_2O}. Knowledge of a_{H_2O} is evidently essential for determining $E°$ from the measured E values, and appropriate a_{H_2O} values are available (ref. 16). The relevant $E°$ values have been obtained as average values of the function ψ:

$$E° = (\Sigma \psi)/n = (1/n) \Sigma \{E + (k/2) \log a_{H_2O}\} \qquad (2)$$

where n is the number of data at each temperature of experiment.

In terms of the standard potentials of the constituent electrodes, E° can be interpreted in two ways:

(i) If reference is made to the standard state of *hyp.* $m_{H^+} = 1$ (namely, $a_{H^+} = 1$), this is in agreement with the Stockholm convention of IUPAC (refs. 17-19) for the aqueous scale of standard electrode potentials. Therefore one should write:

$$E^\circ = E^\circ(\text{HgO} + 2\text{H}^+ + 2\text{e} = \text{Hg} + \text{H}_2\text{O}) - E^\circ(\text{H}^+ + \text{e} = \tfrac{1}{2}\text{H}_2) \tag{3}$$

where the standard potential of the hydrogen electrode, $E^\circ(\text{H}^+ + \text{e} = \tfrac{1}{2}\text{H}_2)$, is taken as zero at all temperatures, and $E^\circ = E^\circ(\text{HgO} + 2\text{H}^+ + 2\text{e} = \text{Hg} + \text{H}_2\text{O})$, here abbreviated to $E^\circ_{\text{Hg|HgO|H}^+}$, is the standard potential of the HgO electrode in *acid* solution and coincides numerically with the standard e.m.f. E° of cell (I).

(ii) If reference is made to the standard state of *hyp.* $m_{OH^-} = 1$ (namely, $a_{OH^-} = 1$, to which corresponds $a_{H^+} = K_W$, where K_W is the ionic activity product constant of water), one should instead write:

$$E^\circ = E^\circ(\text{HgO} + 2\text{e} + \text{H}_2\text{O} = \text{Hg} + 2\text{OH}^-) - E^\circ(\text{H}_2\text{O} + \text{e} = \tfrac{1}{2}\text{H}_2 + \text{OH}^-) \tag{4}$$

where $E^\circ(\text{H}_2\text{O} + \text{e} = \tfrac{1}{2}\text{H}_2 + \text{OH}^-) = E^\circ(\text{H}^+ + \text{e} = \tfrac{1}{2}\text{H}_2) + k\log K_W$ is the standard potential of the hydrogen electrode in *basic* solution, and $E^\circ(\text{HgO} + 2\text{e} + \text{H}_2\text{O} = \text{Hg} + 2\text{OH}^-)$, here abbreviated to $E^\circ_{\text{Hg|HgO|OH}^-}$, is the corresponding *basic* standard potential of the HgO electrode, whereby

$$E^\circ_{\text{Hg|HgO|OH}^-} = E^\circ_{\text{Hg|HgO|H}^+} + k \log K_W \tag{5}$$

For K_W, accurate data are available in the literature (refs. 20,21). Both $E^\circ_{\text{Hg|HgO|H}^+}$ and $E^\circ_{\text{Hg|HgO|OH}^-}$ are quoted in Table 1, columns A, reference being made to the new standard-state pressure of 1 bar (10^5 Pa) for the scale-defining hydrogen electrode, as was recently recommended by IUPAC (refs. 22-24). All determinations of standard electrode potentials prior to 1985 were, however, referred to the old standard-state pressure of 1 atm (101325 Pa); therefore, Table 1 also quotes the parallel values, obtained as $E^\circ_{1\ \text{atm}} = E^\circ_{1\ \text{bar}} + \log(101325/100000)$, in columns B, to facilitate comparison with earlier data. The same one-stage multilinear regression method recently applied to E° values of the hydrogen/silver chloride cell in aqueous organic solvent mixtures (ref. 25) has been applied to check the internal consistency of the present E° values (and related thermodynamic functions), with the results likewise quoted in Table 1, columns C.

TABLE 1

Values of the standard *acid* potential $E^\circ_{\text{Hg|HgO|H}^+}$ and of the standard *basic* potential

$E^\circ_{\text{Hg|HgO|OH}^-}$ **of the HgO electrode in aqueous solution at various temperatures T, with ultimate reference to 1 bar (10^5 Pa) standard-state pressure of H_2 , columns A, as obtained from eq. (2), with mean absolute deviations. [Corresponding values referred to 1 atm (101325 Pa) arre quoted (column B) to facilitate comparison with earlier datat in the literature]. Parallel values from the multilinear regression analysis (ref. 25) with standard errors, are quoted in columns C.**

	$E^\circ_{\text{Hg|HgO|H}^+}$ /mV			$E^\circ_{\text{Hg|HgO|OH}^-}$ /mV		
T/K	A	B*	C	A	B*	C
283.15	931.4±0.2	*931.5*	931.20±0.18	114.7±0.2	*114.9*	114.57±0.21
298.15	926.99±0.03	*927.16*	927.30±0.14	99.00±0.03	*99.17*	99.34±0.16
313.15	922.5±0.2	*922.7*	923.37±0.16	81.5±0.2	*81.7*	82.44±0.18
333.15	918.57±0.04	*918.76*	918.08±0.15	58.09±0.04	*58.28*	57.45±0.17
348.15	914.06±0.04	*914.26*	914.07±0.13	36.74±0.04	*36.94*	36.95±0.15
363.15	909.9±0.1	*910.1*	910.04±0.20	14.9±0.1	*15.1*	15.02±0.24

* The uncertainty figures are the same as those in columns A.

For interpolation purposes, the standard potentials quoted in columns A of Table 1 can be reproduced by the following least-squares polynomials in temperature T :

$$E^\circ_{Hg|HgO|H^+} / \text{mV} = 992.74 - 0.18081 \ (T/\text{K}) - 0.00012958 \ (T/\text{K})^2 \tag{6}$$

$$E^\circ_{Hg|HgO|OH^-} / \text{mV} = 109.27 - 1.0042 \ (T/\text{K}) - 0.0034805 \ (T/\text{K})^2 \tag{7}$$

with estimated standard errors not greater than ±0.20 and ±0.23 mV, respectively. The temperature coefficients calculated from the first derivative of equations (6) and (7) at $T = 298.15$ K are $dE^\circ_{Hg|HgO|H^+} / dT = -0.2581$ mV K^{-1} and $dE^\circ_{Hg|HgO|OH^-} / dT = -1.0712$ mV K^{-1} , in excellent agreement with the values calculated through the multilinear regression scheme: -0.2610 and -1.0716 mV K^{-1}, respectively.

In terms of the standard solubility product, K°_{sol} , of the aqueous mercury(II) hydroxide, Hg(OH)$_2$, referring to the equilibrium:

$$HgO + H_2O = Hg(OH)_2 = Hg^{2+} + 2 \ OH^- \tag{8}$$

one can write:

$$E^\circ_{Hg|HgO|OH^-} = E^\circ_{Hg^{2+}|Hg} + (k/2) \log \ (K^\circ_{sol})_{Hg(OH)_2} \tag{9}$$

where $E^\circ_{Hg^{2+}|Hg}$ is an abbreviation for $E^\circ(Hg^{2+} + 2e = Hg)$, the standard potential of the mercury/mercury(II) ion electrode. Only at 298.15 K is a critical $E^\circ_{Hg^{2+}|Hg}$ value available: 0.8537 ± 0.0005 V (refs. 26-28), here duly referred to 1 bar pressure. Introducing this value into equation (9) together with $E^\circ_{Hg|HgO|OH^-} = 0.09934 \pm 0.00016$ V from Table 1, one finds $(K^\circ_{sol})_{Hg(OH)_2} = (3.13 \pm 0.12) \times 10^{-24}$, in good agreement with the earlier value, 2.8×10^{-24} , obtained by independent methods (refs. 26,28,29).

3. APPLICATIONS OF MERCURY(II) OXIDE ELECTRODES

The HgO electrode has been proposed as a reference electrode, especially in strongly alkaline solutions at moderately high temperatures, for studies in the areas of electrochemistry, corrosion, and fuel cells and storage cells (refs. 12.13.30.31). The fixed-potential electrode role, with a half-cell configuration of the type:

Pt | Hg | HgO | saturated Ba(OH)$_2$, or saturated Ca(OH)$_2$ | (cell II)
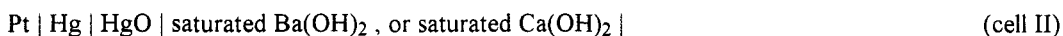
was proposed (refs. 32.33), but an obvious, appropriate use of the HgO electrode would be in a pH-metric role (refs. 1,12,39), namely, as an OH$^-$ sensor (pOH) in high-temperature, strongly alkaline solutions (*e.g.* 1-10 *m* NaOH) where the classical glass electrode or the Sb$_2$O$_3$ electrode (or even the Bi$_2$O$_3$ electrode reinvestigated quite recently (ref. 34)) would incur serious problems. The measuring cell configuration would be of the type:

Hg | Hg$_2$Cl$_2$ | satd. KCl ‖ satd. CsCl ‖ NaOH, (pOH)$_X$ | HgO | Hg   (cell III)

where the double bars indicate minimized liquid junction potentials, and the insertion of the second salt bridge (saturated CsCl) is essential because the popular built-in, saturated-KCl bridge of the familiar calomel electrode, though reasonably equitransferent, would have a concentration (4.804 mol kg^{-1} at 298 K) insufficient to minimize the liquid junction potentials (E_J) at the junctions where NaOH concentrations were of several mol kg^{-1} . The saturated CsCl bridge, which is much more closely equitransferent than the KCl bridge (ref. 35), is 11.3 mol kg^{-1} at 298 K, 13.0 mol kg^{-1} at 323 K, and 15.5 mol kg^{-1} at 363 K, so that it can minimize values of E_J even at junctions with alkaline solutions of molalities lower by some

units than that of saturated CsCl. The e.m.f. equation for the determination of pOH = –log(a_{OH^-}) = – log($m_{OH^-}\gamma_{OH^-}$), where γ_{OH^-} is the single OH⁻ ion activity coefficient, would be:

$$E_{III} = E^\circ_{Hg|HgO|OH^-} - k \log(m_{OH^-}\gamma_{OH^-}) + (k/2) \log a_{H_2O} - E_{Hg|Hg_2Cl_2|sat.CsCl} + E_J \qquad (10)$$

which shows that if E_J can be assumed as abated (zeroed), and the required values of water activity are known independently, good estimates of γ_{OH^-} could be obtained.

4. STANDARD POTENTIALS OF THE SILVER(I) OXIDE ELECTRODE

The redetermined $E^\circ_{Hg|HgO|OH^-}$ values discussed above warrant redetermination of the corresponding values $E^\circ_{Ag|Ag_2O|OH^-}$ of the Ag₂O electrode. In fact, Hamer and Craig (ref. 30) measured the e.m.f. of the cell:

Hg | HgO | NaOH (aq) | Ag₂O | Ag   (cell IV)

at irregular temperature intervals within the range from 273 to 363 K. The results for E_{IV} (which coincides with the *standard* e.m.f. E°_{IV} of the cell) can be reproduced to within ±0.5 mV by the following equation:

$$E^\circ_{IV} / mV = 305.50 - 0.2063 \, (T/K) \qquad (11)$$

Therefrom, since

$$E^\circ_{IV} = E^\circ_{Ag|Ag_2O|OH^-} - E^\circ_{Hg|HgO|OH^-} , \qquad (12)$$

taking the relevant $E^\circ_{Hg|HgO|OH^-}$ values from Table 1, column C, one obtains those of the standard *basic* potential of the Ag₂O electrode, $E^\circ_{Ag|Ag_2O|OH^-}$, to be found in Table 2 together with the values of the corresponding *acid* potential, $E^\circ_{Ag|Ag_2O|H^+}$.

TABLE 2

Values of the standard *acid* potential $E^\circ_{Ag|Ag_2O|H^+}$ and of the standard *basic* potential $E^\circ_{Ag|Ag_2O|OH^-}$ of the Ag₂O electrode (standard errors: ±0.5 mV) in aqueous solution at various temperatures T; standard-state pressure: 1 bar (10^5 Pa). The parallel values referred to 1 atm standard-state pressure can be obtained from the foregoing by adding 0.2 mV throughout. Corresponding values of the standard solubility product K°_{sol} of AgOH (standard errors: ±0.008) are quoted as pK°_{sol} for convenience.

T/K	$E^\circ_{Ag|Ag_2O|H^+}$/mV	$E^\circ_{Ag|Ag_2O|OH^-}$/mV	$(pK^\circ_{sol})_{AgOH}$
283.15	1178.3	361.7	8.044
288.15	1176.0	355.7	7.922
293.15	1173.6	349.6	7.809
298.15	1171.3	343.3	7.702
303.15	1169.0	336.9	7.598
308.15	1166.7	330.3	7.502
313.15	1164.4	323.4	7.411
318.15	1162.0	316.4	7.327

For interpolation purposes the standard potentials in Table 2 can be reproduced accurately (in practice, with all significant figures) by the following equations in T:

$$E^\circ_{Ag|Ag_2O|H^+} / mV = 1309.82 - 0.4645\ (T/K) \tag{13}$$

$$E^\circ_{Ag|Ag_2O|OH^-} / mV = 410.60 + 0.82506\ (T/K) - 0.003524\ (T/K)^2 \tag{14}$$

The corresponding temperature coefficients at 298.15 K, $dE^\circ_{Ag|Ag_2O|H^+} / dT = -0.4645$ mV K^{-1} and $dE^\circ_{Ag|Ag_2O|OH^-} / dT = -1.2763$ mV K^{-1}, respectively, together with the temperature coefficient of the standard e.m.f. E°_{IV}, i.e. $dE^\circ_{IV} / dT = -0.2063$ mV K^{-1}, are correlated with $S^\circ_{Ag_2O} = 119.2$ J mol^{-1} K^{-1}, in good agreement with the calorimetric datum $S^\circ_{Ag_2O} = 121.3$ J mol^{-1} K^{-1} (ref. 36).

Finally, for the standard solubility product of silver(I) hydroxide we have:

$$E^\circ_{Ag|Ag_2O|OH^-} = E^\circ_{Ag^+|Ag} + k\ \log(K^\circ_{sol})_{AgOH} \tag{15}$$

Therefore, taking for the standard potential of the silver/silver ion electrode, $E^\circ_{Ag^+|Ag}$, the values expressed by Harned and Owen's (ref. 37) equation:

$$E^\circ_{Ag^+|Ag} / mV = 798.9 - 0.988\ (T/K - 298.15) - 0.0007\ (T/K - 298.15)^2 \tag{16}$$

together with the $E^\circ_{Ag|Ag_2O|OH^-}$ values in Table 2 (cf. equation (14)), one obtains the K°_{sol} values given as pK°_{sol} in Table 2, which can be reproduced to ±0.001 by the following equation in T:

$$(pK^\circ_{sol})_{AgOH} = -7.4659 + 3192.7\ (T/K)^{-1} + 0.01495\ (T/K) \tag{17}$$

As can be seen, the value at 298.15 K, $(K^\circ_{sol})_{AgOH} = 1.988 \times 10^{-8}$, is in excellent agreement with the earlier, independently determined value, 1.96×10^{-8} (ref. 38).

5. CONCLUSIONS

While there is no doubt about the usefulness and applicability of the HgO electrode in the areas mentioned above, some caution is necessary when using the Ag_2O electrode. In fact, within the practical range of temperatures, the standard solubility product of AgOH predicts that the Ag_2O electrode cannot be used as a OH^- sensor at OH^- molalities lower than $\approx10^{-4}$ mol kg^{-1} because, below this level, the electrode material itself would contribute appreciably to the total OH^- molality. This detection limit might be more favourable in nonaqueous or aqueous-organic solvents, analogously to what was verified e.g. with that of the Hg_2SO_4 electrode for the SO_4^{2-} ion (ref. 40). Accumulation of the relevant data is awaited.

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