

Redetermination of the standard potential of the mercuric oxide electrode at temperatures between 283 and 363 K and the solubility product constant of mercuric hydroxide

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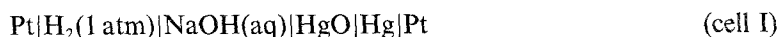
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From e.m.f. measurements of the reversible cell H_2 (1 bar)|NaOH(aq)|HgO|Hg at temperatures between 283 and 363 K, the standard potential of the mercuric oxide electrode has been redetermined; its new observed value at 298.15 K is 0.92699 V (acid scale) or 0.09900 V (basic scale). New values of the related Gibbs energies, enthalpies and entropies for the cell reaction and mercuric oxide, HgO, have been calculated therefrom. From literature data for the cell Hg|HgO|NaOH(aq)|Ag₂O|Ag the standard potential of the silver oxide electrode at 298.15 K has also been redetermined as 1.1713 V (acid scale) or 0.3433 V (basic scale). In parallel, the solubility product constants at 298.15 K for Hg(OH)₂ and for AgOH have been redetermined as 3.13×10^{-26} and 1.959×10^{-8} , respectively. Applications of the mercuric oxide electrode are discussed.

1. Introduction

The present knowledge of the standard potential of the mercuric oxide electrode in aqueous solution, $E^\circ_{\text{Hg}/\text{HgO}/\text{OH}^-}$, together with the relevant temperature coefficient, $dE^\circ_{\text{Hg}/\text{HgO}/\text{OH}^-}/dT$, still relies on the work carried out over 60 years ago by Fried [1] who extended the earlier, pioneering measurements by Brønsted [2]. Both authors measured the e.m.f. of the cell



at NaOH concentrations of 1 to 10 mol dm⁻³ (unusually high for E° determinations) and covering an overall range of temperatures (273 to 333 K), allowing the temperature coefficient dE°/dT to be determined; however, the range 333 to 363 K, which is important for electrochemical measurements in alkaline processes of industrial interest, was left uncovered.

The good behaviour of the mercuric oxide electrode [3, 4] was confirmed in approximately the same period by measurements at 298 K by Japanese workers [5-9] and, recently, by measurements of Every and Banks [10], Case and Bignold [11] and Johansson *et al.* [12] at temperatures up to 523 K not, however, leading to reassessment of E° and dE°/dT .

This situation prompted the present work of redetermination over the temperature range 283 to 363 K for the sake of completion and systematization.

2. Experimental details

The solutions were made up by weight from reagent grade chemicals and triply distilled water and were appropriately deaerated before use. The hydrogen electrodes were constructed from platinum sheets of approximately 6 cm², 0.3 mm thick, spot-welded to 1 mm platinum wire sealed in glass

tubing. Before electrode operation, each platinum sheet was preliminarily cathodized in dilute sulphuric acid at 4 mA cm^{-2} for 15 min, thoroughly washed in distilled water, then platinized following the directions of Bates [13, 14], again washed repeatedly in distilled water and subsequently conditioned for 1 h out of air contact in a solution identical to the cell solution. The hydrogen gas (99.999% pure) was bubbled through Friedrich's presaturators filled with the same cell solution, before entering its half-cell compartment. Reagent grade, finely ground, red mercuric oxide was thoroughly extracted with water, dried and placed on top of a redistilled mercury pool in contact with a platinum wire sealed in the glass bulb, and conditioned for 1 h with the appropriate NaOH solution before electrode operation in the cell. For the e.m.f. measurements a Type K-5 Leeds & Northrup potentiometer was used, having a built-in electronic millivoltmeter as a null-point detector; the high input impedance of the latter ($> 10^{14} \Omega$) enabled the e.m.f. measurements to be carried out while keeping the stopcock separating the hydrogen electrode half-cell from the mercuric oxide half cell closed to prevent any undesired interdiffusion between electrode compartments. All e.m.f. readings were corrected to 1 bar (10^5 Pa) pressure of hydrogen. The temperature of the cell was controlled to $\pm 0.02 \text{ K}$ by means of an air thermostat described previously [15].

3. Results and discussion

The e.m.f. of cell I is expressed by

$$E = E^\circ - (k/2) \log a_{\text{H}_2\text{O}} \quad (1)$$

where $k = (\ln 10)RT/F$, and turns out to be independent of the electrolyte concentration (at molalities lower than $\approx 0.5 \text{ mol kg}^{-1}$) except for minimal differences attributable to varying H_2O activity, $a_{\text{H}_2\text{O}}$. As shown by Equation 1, the standard e.m.f., E° , of cell I can be determined from the measured E values provided that the corresponding values of the water activity are known. These were taken by interpolation from work by MacMullin [16]. The E values are quoted in Table 1 at various temperatures and NaOH molalities in the range 0.1 to 0.5 mol kg^{-1} , and the relevant E° values have been obtained as average values of the function ψ :

$$E^\circ = \sum \psi/n = \sum [E + (k/2) \log a_{\text{H}_2\text{O}}]/n, \quad (2)$$

where n represents the number of data at each experimental temperature.

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.* $m_{\text{H}^+} = 1$ (say, $a_{\text{H}^+} = 1$), this is congruent with the Stockholm Convention of IUPAC [17–19] for the aqueous scale of electrode potentials. Therefore, one should write

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

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

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

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

where $E^\circ(\text{H}_2\text{O} + e = \frac{1}{2}\text{H}_2 + \text{OH}^-) = E^\circ(\text{H}^+ + e = \frac{1}{2}\text{H}_2) + k \log K_w$ is the standard potential of the hydrogen electrode in 'basic' solution, and $E^\circ(\text{HgO} + 2e + \text{H}_2\text{O} = \text{Hg} + 2\text{OH}^-)$,

henceforth abbreviated to $E_{\text{Hg}/\text{HgO}/\text{OH}^-}^\circ$, is the corresponding 'basic' standard potential of the mercuric oxide electrode, whereby

$$E_{\text{Hg}/\text{HgO}/\text{OH}^-}^\circ = E_{\text{Hg}/\text{HgO}/\text{H}^+}^\circ + k \log K_w \quad (5)$$

For the K_w values required by Equation 5, accurate data are available in the literature [20, 21]. Both $E_{\text{Hg}/\text{HgO}/\text{H}^+}^\circ$ and $E_{\text{Hg}/\text{HgO}/\text{OH}^-}^\circ$ are reported in Table 2, reference being made to the new standard-state pressure of 1 bar (10^5 Pa) which was recently recommended by IUPAC [22–24]. However, since all determinations of standard electrode potentials prior to 1985 were instead referred to the old standard-state pressure of 1 atm (101 325 Pa), Table 2 also quotes the parallel values, obtained as $E_{1 \text{ atm}}^\circ = E_{1 \text{ bar}}^\circ + (k/2) \log (101\,325/100\,000)$, to facilitate comparison with earlier literature data. From the results in Table 2 it is evident that the present values of $E^\circ \equiv E_{\text{Hg}/\text{HgO}/\text{H}^+}^\circ$ are higher than the earlier values (duly converted from international volts to absolute volts) by 1.5 mV or more. In this connection, it is important to consider the following points.

(a) Hydrogen gas bubbling into the hydrogen electrode compartment of the cell might, if containing oxygen or other oxidizing species, produce a mixed potential causing the actual potential of the hydrogen electrode to increase and, consequently, the measured E values of the cell (and the E° values derived therefrom) to decrease.

(b) If hydrogen can diffuse in solution reaching the mercuric oxide electrode compartment, another mixed potential might arise, lowering the actual potential of the mercuric oxide electrode and thus, again, decreasing E and E° of the cell.

Table 1. Values of the e.m.f. of cell I, corrected to 1 bar (10^5 Pa) standard-state pressure of hydrogen, at various temperatures and molalities of sodium hydroxide, with corresponding values of water activity [16] required by Equation 2

T (K)	m_{NaOH} (mol kg^{-1})	E (mV)	$a_{\text{H}_2\text{O}}$
283.15	0.1	931.23	0.9846
	0.2	931.71	0.9834
	0.3	931.61	0.9813
	0.5	931.77	0.9777
298.15	0.3	927.19	0.9821
	0.5	927.31	0.9776
313.15	0.2	922.95	0.9850
	0.4	922.57	0.9807
333.15	0.1	918.66	0.9888
	0.2	918.80	0.9865
	0.3	918.77	0.9839
	0.4	918.88	0.9817
	0.5	918.90	0.9792
348.15	0.2	914.18	0.9874
	0.3	914.29	0.9850
	0.4	914.37	0.9824
	0.5	914.40	0.9798
363.15	0.1	909.90	0.9909
	0.2	910.20	0.9884
	0.3	909.59	0.9858
	0.4	910.25	0.9832
	0.5	910.61	0.9805

Table 2. Values of the standard 'acid' potential (coincident with the standard e.m.f. of cell I) and of the standard 'basic' potential of the mercuric oxide electrode at various temperatures, with ultimate reference to 1 bar (10^5 Pa) standard-state pressure of hydrogen, as obtained from the averaging function (Equation 2) (with corresponding mean absolute deviations) or from the multilinear regression Equations 7 to 11 (with corresponding estimated standard errors), respectively. Parallel values referred to 1 atm (101.325 Pa) are also quoted to facilitate comparison with earlier data in the literature

Standard potential (mV)	283.15 K	298.15 K	313.15 K	333.15 K	348.15 K	363.15 K
$E_{\text{Hg}^0/\text{HgO}/\text{H}^+}^0$, Equation 2	931.36 \pm 0.16	926.99 \pm 0.03	922.53 \pm 0.22	918.57 \pm 0.04	914.06 \pm 0.04	909.88 \pm 0.25
$E_{\text{Hg}^0/\text{HgO}/\text{H}^+}^0$, referred to 1 atm	931.52	927.16	922.71	918.76	914.26	910.09
$E_{\text{Hg}^0/\text{HgO}/\text{H}^+}^0$, multilinear regression	931.20 \pm 0.18	927.30 \pm 0.14	923.37 \pm 0.16	918.08 \pm 0.15	914.07 \pm 0.13	910.04 \pm 0.20
pK_w^a	14.535	13.996	13.535	13.017	12.70	12.42
$E_{\text{Hg}^0/\text{HgO}/\text{OH}^-}$, Equation 2	114.73 \pm 0.16	99.00 \pm 0.03	81.52 \pm 0.22	58.09 \pm 0.04	36.74 \pm 0.04	14.91 \pm 0.25
$E_{\text{Hg}^0/\text{HgO}/\text{OH}^-}$, referred to 1 atm	114.89	99.17	81.70	58.28	36.94	15.12
$E_{\text{Hg}^0/\text{HgO}/\text{OH}^-}$, multilinear regression	114.57 \pm 0.21	99.34 \pm 0.16	82.44 \pm 0.18	57.45 \pm 0.17	36.95 \pm 0.15	15.02 \pm 0.24

^a pK_w values are required by the conversion Equation 5, and are here taken from [20] at $T \leq 333.15$ K, and from [21] at $T \geq 348.15$ K.

(c) HgO solubilization in concentrated NaOH solutions (possible case of earlier works [1, 2]) might cause poisoning [11] of the hydrogen electrode upon reaching it by solute diffusion and, though leaving the ionic strength of the NaOH solution substantially unchanged (so that the relevant activity coefficients also remain constant), it would cause the NaOH molality, m , to decrease to m' , which would make the potential of the mercuric oxide electrode increase by $\Delta E = (k/2) \log(m/m')$. At the same time, however, it would create a liquid junction potential, E_j , between the two half-cells, equal to $(t_{\text{Na}^+} - t_{\text{OH}^-})k \log(m/m')$, where $t_{\text{Na}^+} \approx 0.2$ and $t_{\text{OH}^-} \approx 0.8$. This potential is greater than, and opposite in sign to, ΔE , so that the total contribution $E_j + \Delta E \approx -0.1k \log(m/m')$ would again make E and E° decrease.

The experimental conditions in the present work have been such as to best ensure freedom from the effects of all of the above features, which cumulatively tend to give lower E and E° values. In particular, points (b) and (c) make it mandatory to operate during all the experiment stages (equilibration plus e.m.f. measurement) with the two half-cells separated by a closed stopcock, a technique that is now commonly made possible by use of the high-impedance electrometric null-point detector. This latter instrument was, however, not yet available at the time of the earlier E° determinations reported in the literature [1–9]. Therefore, the present E° results are basically more reliable and are to be preferred.

The one-stage multilinear regression method recently applied to E° values of the hydrogen–silver chloride cell in acetonitrile–water solvent mixtures [25] lends itself well to the critical analysis of the results and for the determination of the standard thermodynamic functions ΔG° , ΔH° and ΔS° (together with the relevant estimated standard errors) for the cell reaction:



which are related to the standard e.m.f. E° of cell. This method is based on Clarke and Glew's treatment [26] of the temperature dependence of the standard molar Gibbs energy change, ΔG_T° , which for the present case implies assuming that:

$$2FE_T^\circ/T = -\Delta G_T^\circ/T = -\Delta G_\theta^\circ/\theta + z(\Delta H_\theta^\circ/\theta)/(1+z) + \Delta C_{p,\theta}^\circ[\ln(1+z) - z/(1+z)] \\ + (\theta/2)(d\Delta C_p^\circ/dT)_\theta[z + z/(1+z) - 21 \ln(1+z)] \quad (7)$$

where ΔC_p° is the heat capacity change at constant pressure for the cell reaction 6, and $z = (T - \theta)/\theta$ where $\theta = 298.15$ K is a reference temperature. Defining:

$$d_0 = E_\theta^\circ/\theta \quad (8a)$$

$$d_1 = \Delta H_\theta^\circ/(2\theta F) \quad (8b)$$

$$d_2 = \Delta C_{p,\theta}^\circ/2F \quad (8c)$$

$$d_3 = (\theta/4F)(d\Delta C_p^\circ/dT)_\theta \quad (8d)$$

$$v_1 = z/(1+z) \quad (8e)$$

$$v_2 = \ln(1+z) - z/(1+z) \quad (8f)$$

$$v_3 = z + z/(1+z) - 21 \ln(1+z) \quad (8g)$$

the standard e.m.f. of the cell I is represented by

$$E_T^\circ = T(d_0 + d_1 v_1 + d_2 v_2 + d_3 v_3) \quad (9)$$

and:

$$\Delta G_\theta^\circ = -2F\theta d_0, \quad \delta(\Delta G_\theta^\circ) = 2F\theta \delta(d_0) \quad (10a)$$

$$\Delta H_\theta^\circ = 2F\theta d_1, \quad \delta(\Delta H_\theta^\circ) = 2F\theta \delta(d_1) \quad (10b)$$

$$\Delta C_{p,\theta}^\circ = 2F d_2, \quad \delta(\Delta C_{p,\theta}^\circ) = 2F \delta(d_2) \quad (10c)$$

Table 3. Standard thermodynamic functions for reaction 6 and for mercuric oxide, HgO, at 298.15 K

H ₂ + HgO = H ₂ O + Hg	ΔG° (kJ mol ⁻¹) = -178.940 ± 0.026	ΔH° (kJ mol ⁻¹) = -193.96 ± 0.44	ΔS° (JK ⁻¹ mol ⁻¹) = -50.203 ± 0.056
HgO	G_{HgO}° (kJ mol ⁻¹) = -58.238 ± 0.026	H_{HgO}° (kJ mol ⁻¹) = -91.87 ± 0.44	S_{HgO}° (JK ⁻¹ mol ⁻¹) = +65.559 ± 0.063

$$(d\Delta C_p^\circ/dT)_\theta = 4Fd_3/\theta, \quad \delta(d\Delta C_p^\circ/dT)_\theta = 4F\delta(d_3)/\theta \quad (10d)$$

where δ denotes the standard error [27] of estimate. The estimate of d_3 was not significantly different from zero and therefore the corresponding terms in d_3 were dropped from Equations 8, 9 and 10, thus reducing the number of independent variables to two. This implies the assumption that ΔC_p° be independent of temperature in the present range, which is an acceptable assumption.

Finally, since $\Delta G_\theta^\circ = \Delta H_\theta^\circ - T\Delta S_\theta^\circ$, the standard molar entropy change of reaction 6 at the reference temperature, θ , is

$$\Delta S_\theta^\circ = \Delta H_\theta^\circ/\theta - \Delta G_\theta^\circ/\theta = 2F(d_0 + d_1) \quad (11)$$

The values of these standard thermodynamic functions, together with their standard errors, were computed using the MULTIREG program [25] and are quoted in Table 3 (the parent values of E° are to be seen in Table 2). The temperature coefficients of the standard 'acid' and 'basic' electrode potentials at $T = \theta = 298.15$ K come from Equation 11 as

$$(dE_{\text{Hg}/\text{HgO}/\text{H}^+}^\circ/dT)_\theta = \Delta S_\theta^\circ/2F = d_0 + d_1 = -0.26099 \pm 0.00029 \text{ mV K}^{-1} \quad (12)$$

and

$$(dE_{\text{Hg}/\text{HgO}/\text{OH}^-}^\circ/dT)_\theta = -1.07162 \pm 0.00034 \text{ mV K}^{-1} \quad (13)$$

respectively.

For the sake of easy interpolation, the standard potential results based on Equation 2 and quoted in Table 2 can be reproduced by the following least-squares polynomials in temperature:

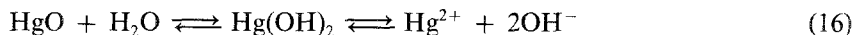
$$E_{\text{Hg}/\text{HgO}/\text{H}^+}^\circ = 992.74 - 0.180807T - 0.000129576T^2 \quad (14)$$

$$E_{\text{Hg}/\text{HgO}/\text{OH}^-}^\circ = 109.27 + 1.00420T - 0.00348053T^2 \quad (15)$$

The values of E° (mV) calculated at each value of T (K) through equations 14 and 15 are affected by estimated standard errors not greater than ± 0.20 and ± 0.23 mV, respectively. The relevant temperature coefficients calculated from the first derivative of Equations 14 and 15 at $T = \theta = 298.15$ K are -0.25807 and -1.07124 mV K⁻¹, respectively, in excellent agreement with those calculated through the multilinear regression scheme (Equations 12 and 13).

From the above values of ΔG_θ° , ΔH_θ° and ΔS_θ° for reaction 6, the standard Gibbs energy, enthalpy and entropy of HgO at 298.15 K have been calculated (see Table 3), the necessary data for the species H₂, H₂O and Hg being taken from the NBS compilation [28]. In view of the new and more accurate parent value of E° obtained in the present work, the value $G_{\text{HgO}}^\circ = -58.238 \pm 0.026$ kJ mol⁻¹ determined here is preferred to the earlier value ($G_{\text{HgO}}^\circ = -58.555$ kJ mol⁻¹) adopted by Hepler and Olofsson in their key review of 1975 [29]. Since the optimum physical condition of applicability of this multilinear regression method is that the temperature range of the experiment symmetrically spans the reference temperature θ ($= 298.15$ K), whereas the present one (283.15 to 363.15 K) does not, the values of H_{HgO}° and S_{HgO}° quoted in Table 3, which depend on the first derivative of E in T , are probably not to be preferred to the calorimetric ones ($H_{\text{HgO}}^\circ = -90.83$ kJ mol⁻¹ and $S_{\text{HgO}}^\circ = +70.29$ J K⁻¹ mol⁻¹, respectively [29]).

In terms of the solubility product constant, K_{sp} , of the aqueous mercuric hydroxide, $\text{Hg}(\text{OH})_2$, referring to the equilibrium

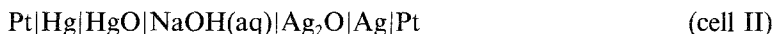


one can write

$$E_{\text{Hg}/\text{HgO}/\text{OH}^-}^\circ = E_{\text{Hg}^{2+}/\text{Hg}}^\circ + (k/2) \log K_{sp} \quad (17)$$

where $E_{\text{Hg}^{2+}/\text{Hg}}^\circ$ is an abbreviation for $E^\circ(\text{Hg}^{2+} + 2e = \text{Hg})$, the standard potential of the mercury–mercuric ion electrode. Only at 298.15 K is the $E_{\text{Hg}^{2+}/\text{Hg}}^\circ$ datum available from the critical revision by Vanderzee and Swanson [29–31]: $E_{\text{Hg}^{2+}/\text{Hg}}^\circ = 0.8537 \pm 0.0005 \text{ V}$ (referred to 1 bar standard-state pressure). Introducing this value into Equation 17 in conjunction with $E_{\text{Hg}/\text{HgO}/\text{OH}^-}^\circ = 0.09934 \pm 0.00016 \text{ V}$ from Table 2, it turns out that $K_{sp} = (3.13 \pm 0.12) \times 10^{-26}$. This compares with earlier values: 2.8×10^{-26} quoted in [31] and [29, 32], and 0.53×10^{-26} quoted in [33, 34].

The availability of the new $E_{\text{Hg}/\text{HgO}/\text{OH}^-}^\circ$ value warrants redetermination of the corresponding $E_{\text{Ag}/\text{Ag}_2\text{O}/\text{OH}^-}^\circ$ of the silver oxide electrode. In fact, Hamer and Craig [35] found that the standard e.m.f. (E_{II}°) of the cell:



was $E_{\text{II}}^\circ = 0.2440 \pm 0.0005 \text{ V}$ at 298.15 K. Now, since

$$E_{\text{II}}^\circ = E_{\text{Ag}/\text{Ag}_2\text{O}/\text{OH}^-}^\circ - E_{\text{Hg}/\text{HgO}/\text{OH}^-}^\circ \quad (18)$$

again taking $E_{\text{Hg}/\text{HgO}/\text{OH}^-}^\circ = 0.09934 \pm 0.00016 \text{ V}$ from Table 2, one obtains $E_{\text{Ag}/\text{Ag}_2\text{O}/\text{OH}^-}^\circ = 0.3433 \pm 0.0005 \text{ V}$, which is the standard ‘basic’ potential of the silver oxide electrode; the corresponding ‘acid’ value is $E_{\text{Ag}/\text{Ag}_2\text{O}/\text{H}^+}^\circ = 1.1713 \pm 0.0005 \text{ V}$. Moreover, for the solubility product constant of silver hydroxide we have

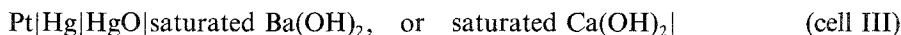
$$E_{\text{Ag}/\text{Ag}_2\text{O}/\text{OH}^-}^\circ = E_{\text{Ag}^+/\text{Ag}}^\circ + k \log K_{sp} \quad (19)$$

Taking $E_{\text{Ag}^+/\text{Ag}}^\circ = 0.7993 \pm 0.0001 \text{ V}$ (referred to 1 bar standard-state pressure) for the standard potential of the silver–silver ion electrode [36], we obtain $K_{sp} = (1.959 \pm 0.036) \times 10^{-8}$, to be compared with 1.96×10^{-8} quoted by Ives [37] and 2.0×10^{-8} quoted by Zhutaeva and Shumilova [36].

For all the calculations throughout this paper, the following values of fundamental constants have been used: $F = 96484.56 \text{ J V}^{-1} \text{ mol}^{-1}$ and $R = 8.31441 \text{ J K}^{-1} \text{ mol}^{-1}$.

4. Remarks on applications of mercuric oxide electrodes

The mercuric oxide electrode has been proposed as a reference electrode, especially in high-temperature concentrated alkali solutions, for studies in the domains of electrochemistry, corrosion and fuel cells and storage cells [10, 11, 35, 38]. The fixed-potential electrode role, with a half-cell configuration of the type



was also proposed [39, 40]. However, a natural and most appropriate use of the HgO electrode would be in a pH-metric role, 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 antimony electrode would meet and cause serious problems. The measuring cell configuration would be of the type



where double bars denote minimized liquid junction potentials, and the insertion of the second salt

Table 4. Single OH⁻ ion activity coefficients evaluated from e.m.f. measurements on cell IV at 298.15, 333.15 and 363.15 K with CsCl bridges of molality 11, 13 and 15 mol kg⁻¹ respectively, for comparison with the parallel mean molal activity coefficients of sodium hydroxide from the literature [42, 43], together with the potentials of the mercuric oxide electrode as a reference electrode in concentrated solutions of aqueous sodium hydroxide at various molalities. Ancillary values of water activity required by Equation 22 are also quoted for convenience

m_{NaOH} (mol kg ⁻¹)	298.15 K					333.15 K					363.15 K				
	γ_{OH^-}	$\gamma_{\pm \text{NaOH}}$	$a_{\text{H}_2\text{O}}$	$E_{\text{Hg/HgO/OH}^-}$ (mV)	γ_{OH^-}	$\gamma_{\pm \text{NaOH}}$	$a_{\text{H}_2\text{O}}$	$E_{\text{Hg/HgO/OH}^-}$ (mV)	γ_{OH^-}	$\gamma_{\pm \text{NaOH}}$	$a_{\text{H}_2\text{O}}$	$E_{\text{Hg/HgO/OH}^-}$ (mV)	γ_{OH^-}	$a_{\text{H}_2\text{O}}$	$E_{\text{Hg/HgO/OH}^-}$ (mV)
0.1	0.795	0.766	0.9863	164.2	0.801	0.765	0.9888	129.8	0.827	0.9909	0.9909	92.9			
0.2	0.766	0.727	0.9843	147.3	0.762	0.719	0.9865	111.3	0.784	0.9884	0.9884	72.8			
0.3	0.757	0.707	0.9821	137.2	0.746	0.695	0.9839	100.2	0.766	0.9858	0.9858	60.8			
0.5	0.762	0.693	0.9776	123.8	0.740	0.669	0.9792	85.7	0.758	0.9805	0.9805	45.1			
1	0.815	0.679	0.9647	104.1	0.774	0.650	0.9655	64.3	0.791	0.9662	0.9662	21.8			
2	0.947	0.700	0.9322	82.0	0.898	0.677	0.9333	39.6	0.911	0.9341	0.9341	-4.8			
3	1.065	0.774	0.8922	68.0	1.038	0.742	0.8952	23.3	1.040	0.8977	0.8977	-22.3			
4	1.172	0.890	0.8458	57.5	1.176	0.839	0.8522	10.7	1.157	0.8577	0.8577	-35.3			
5	1.299	1.060	0.7941	48.3	1.309	0.971	0.8053	0.4	1.261	0.8148	0.8148	-45.8			
6	1.502	1.280	0.7385	39.0	1.440	1.143	0.7552	-8.5	1.358	0.7696	0.7696	-54.7			
7	-	-	-	-	1.578	1.363	0.7031	-16.6	1.457	0.7229	0.7229	-62.7			
8	-	-	-	-	1.738	1.634	0.6498	-24.3	1.578	0.6752	0.6752	-70.5			
9	-	-	-	-	-	-	-	-	1.744	0.6274	0.6274	-78.4			
10	-	-	-	-	-	-	-	-	1.989	0.5800	0.5800	-87.1			

bridge (saturated CsCl) is essential because the routine built-in, saturated KCl bridge of the familiar calomel electrode, though equitransferent, would have a concentration ($\approx 4.6 \text{ mol kg}^{-1}$ at 298 K) insufficient to minimize the liquid junction potential at the junctions where NaOH concentrations range several mol kg^{-1} . The saturated CsCl bridge, also equitransferent [41], is at about 11 mol kg^{-1} at 298 K, 13 mol kg^{-1} at 333 K and 15 mol kg^{-1} at 363 K; that is to say, it can minimize values of E_J even at junctions with alkaline solutions of molalities lower by some units than that of saturated CsCl, such as those reported at Table 4. The functional expression for determining $\text{pOH} = -\log a_{\text{OH}^-} = -\log (m_{\text{OH}^-} \gamma_{\text{OH}^-})$, where γ_{OH^-} is the single OH^- ion activity coefficient, would be

$$E_{\text{IV}} = E_{\text{Hg}/\text{HgO}/\text{OH}^-}^{\circ} - k \log (m_{\text{OH}^-} \gamma_{\text{OH}^-}) + (k/2) \log a_{\text{H}_2\text{O}} - E_{\text{Hg}/\text{Hg}_2\text{Cl}_2/\text{sat. KCl}} + E_J \quad (20)$$

which shows that if E_J can be assumed as eliminated (zeroed) and the relevant values of the water activity are independently known, good estimates of γ_{OH^-} could be made. Table 4 shows γ_{OH^-} values for concentrated aqueous NaOH solutions, based on measurements of the e.m.f. E_{IV} [41] as well as literature values for $E_{\text{Hg}/\text{Hg}_2\text{Cl}_2/\text{sat. KCl}}$ [46] and use of Equation 20. Assuming an uncertainty of up to $\pm 1 \text{ mV}$ due to possible inaccurate zeroing of E_J by the CsCl salt bridge, this would amount to a $\pm 4\%$ maximum uncertainty in the γ_{OH^-} values. The latter can, at $m \geq 0.1 \text{ mol kg}^{-1}$, be described by an equation of the type

$$\log \gamma_{\text{OH}^-} = -Am^{1/2}/(1 + \alpha_0 Bm^{1/2}) - \log (1 + 0.036m) + C + C_1m + C_2m^2 + C_3m^3 \quad (21)$$

where A and B are the classical Debye-Hückel constants and, with an ion-size parameter $\alpha_0 = 0.324 \text{ nm}$ [42], the least-squares constants take the following values: $C = 0.003 178, 0.017 529$ and $0.038 964$; $C_1 = 0.200 621, 0.162 184$ and $0.168 142 \text{ kg mol}^{-1}$; $C_2 = -0.032 741 5, -0.014 994 7$ and $-0.017 702 6 \text{ kg}^2 \text{ mol}^{-2}$; $C_3 = 0.002 685 83, 0.000 730 32$ and $0.000 892 82 \text{ kg}^3 \text{ mol}^{-3}$, at 298.15, 333.15 and 363.15 K, respectively. Comparing these γ_{OH^-} values with the values of the *mean* molal activity coefficients, $\gamma_{\pm \text{NaOH}}$, of sodium hydroxide available in the literature [42, 43], it is evident that, as a function of m_{NaOH} , γ_{OH^-} runs systematically higher than $\gamma_{\pm \text{NaOH}}$. This feature is quite analogous to that recently observed for γ_{F^-} versus $\gamma_{\pm \text{NaF}}$ as well as $\gamma_{\text{SO}_4^{2-}}$ versus $\gamma_{\pm \text{Na}_2\text{SO}_4}$ by a totally independent method [44, 45]. Finally, Table 4 reports the calculated values of the 'basic' potential of the mercuric oxide electrode:

$$E_{\text{Hg}/\text{HgO}/\text{OH}^-} = E_{\text{Hg}/\text{HgO}/\text{OH}^-}^{\circ} - k \log (m_{\text{OH}^-} \gamma_{\text{OH}^-}) + (k/2) \log a_{\text{H}_2\text{O}} \quad (22)$$

for use as a reference electrode [46] in the range of high concentrations of aqueous sodium hydroxide.

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References

- [1] F. Fried, *Z. physik. Chem.* **123** (1926) 406.
- [2] J. N. Brönsted, *ibid.* **65** (1909) 84, 744.
- [3] F. G. Donnan and A. J. Allmand, *J. Chem. Soc.* **99** (1911) 845.
- [4] Ming Chow, *J. Amer. Chem. Soc.* **42** (1920) 488.
- [5] S. Mujamoto, *Sci. Papers Inst. Phys. Chem. Res. (Tokyo)* **1** (1922) 31.
- [6] F. Ishikawa and G. Kimura, *Sexaginti, Y. Osaka, Chem. Inst. Dept. Sci. Tokyo Imp. Univ.* **255** (1927).
- [7] F. L. E. Shibata and F. Murata, *J. Chem. Soc. (Japan)* **52** (1931) 399.
- [8] F. L. E. Shibata, Y. Kobayashi and S. Furukawa, *ibid.* **52** (1931) 404.
- [9] Y. Kobayashi and H. L. Wang, *J. Sci. Hiroshima Univ.* **5A** (1934) 71.
- [10] R. L. Every and W. F. Banks, *Corrosion* **23** (1967) 151.
- [11] B. Case and G. J. Bignold, *J. Appl. Electrochem.* **1** (1971) 141.

- [12] K. Johansson, K. Johnsson and D. Lewis, *Chem. Scr.* **6** (1974) 10.
- [13] R. G. Bates, 'Determination of pH – Theory and Practice', 2nd edn, Wiley, New York (1973) pp. 290–2.
- [14] D. J. G. Ives and G. J. Janz, 'Reference Electrodes – Theory and Practice', Academic Press, New York (1961) p. 107.
- [15] T. Mussini and A. Pagella, *J. Chem. Eng. Data* **16** (1971) 49.
- [16] R. B. MacMullin, *J. Electrochem. Soc.* **116** (1969) 416.
- [17] J. A. Christiansen and M. Pourbaix, 'Comptes Rendus des Conférences de l'Union Internationale de Chimie Pure et Appliquée, 17^e Conférence', Stockholm (1953) p. 83.
- [18] Reference [14], pp. 12, 13, 26–32.
- [19] Reference [13], pp. 4, 12–14.
- [20] H. S. Harned and B. B. Owen, 'The Physical Chemistry of Electrolytic Solutions', 3rd edn, Reinhold, New York (1958) p. 638.
- [21] J. R. Fisher and H. L. Barnes, *J. Phys. Chem.* **76** (1972) 90.
- [22] J. D. Cox, *Pure Appl. Chem.* **54** (1982) 1239.
- [23] R. D. Freeman, *J. Chem. Educ.* **62** (1985) 681.
- [24] S. Angus, *Chem. Intern.* **7** (1985) 17.
- [25] P. Longhi, T. Mussini, F. Penotti and S. Rondinini, *J. Chem. Thermodyn.* **17** (1985) 355.
- [26] E. C. Clarke and D. N. Glew, *Trans. Faraday Soc.* **62** (1966) 539.
- [27] O. L. Davies and P. L. Goldsmith, 'Statistical Methods in Research and Production', Longman, London (1976), pp. 237–75. Also, IUPAC Report, *J. Chem. Thermodyn.* **13** (1981) 603.
- [28] D. D. Wagman, W. H. E. Evans, V. B. Parker, I. Halow, S. M. Bailey and R. H. Schumm, 'Selected Values of Chemical Thermodynamic Properties': NBS Technical Note 270-3 (1968) pp. 12, 13 and NBS Technical Note 270-4 (1969) p. 1, Washington DC.
- [29] L. G. Hepler and G. Olofsson, *Chem. Rev.* **75**(1975) 585.
- [30] C. E. Vanderzee and J. A. Swanson, *J. Chem. Thermodyn.* **6** (1974) 827.
- [31] J. Balej, 'Standard Potentials in Aqueous Solution' (edited by A. J. Bard, R. Parsons and J. Jordan), Marcel Dekker, New York (1985) p. 281.
- [32] W. Feitknecht and P. S. Schindler, *Pure Appl. Chem.* **6** (1963) 130.
- [33] A. B. Garrett and W. W. Howell, *J. Amer. Chem. Soc.* **61** (1939) 1730.
- [34] A. B. Garrett and A. E. Hirschler, *ibid.* **60** (1938) 299.
- [35] W. J. Hamer and D. N. Craig, *J. Electrochem. Soc.* **104** (1957) 206.
- [36] G. V. Zhutavaeva and N. A. Shumilova, Reference [31], pp. 294–311.
- [37] D. J. Ives, Reference [14], p. 334.
- [38] G. W. D. Briggs, E. Jones and W. F. K. Wynne-Jones, *Trans. Faraday Soc.* **51** (1955) 1433.
- [39] G. J. Samuelson and D. J. Brown, *J. Electrochem. Soc.* **104** (1957) 206.
- [40] Reference [14], p. 336.
- [41] R. Orsenigo, 'Doctorate Thesis', University of Milan (1986).
- [42] H. S. Harned and B. B. Owen, 'The Physical Chemistry of Electrolytic Solutions', 3rd edn, Reinhold, New York (1958) pp. 498–500, 513, 729, 735.
- [43] G. Akerlöf and G. Kegeles, *J. Amer. Chem. Soc.* **62** (1940) 620.
- [44] A. Daggetti and S. Trasatti, *Can. J. Chem.* **59** (1981) 1925.
- [45] A. Uzzo, A. Daggetti and S. Trasatti, *Electrochim. Acta* **28** (1983) 1539.
- [46] Reference [14], p. 161.