Hg/HgO electrode and hydrogen evolution potentials in aqueous sodium hydroxide

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Abstract

The Hg/HgO electrode is usually utilized as a reference electrode in alkaline solution such as for development of an alkaline hydrogen electrode. The reference electrode provides a suitable reference point but is available from few commercial vendors and suffers from inadequate documentation on potential in varying electrolytes. A new numerical method uses activity, activity coefficients, and a few correlated empirical equations to determine the potential values in both dilute and concentrated sodium hydroxide solutions at temperatures of 0–90 °C and at concentrations of 0.100–12.8 mol $kg_{H_2O}^{-1}$. The computed potentials of the Hg/HgO electrodes versus a normal hydrogen electrode (NHE) at 25 °C and 1 atm are 0.1634 V for 0.100m, 0.1077 V for 1.00m, and 0.0976 V for 1.45m NaOH solutions. The Hg/HgO reduction potential further changes to −0.0751 V versus NHE and hydrogen evolution potential changes to −0.9916 V versus NHE in a solution of 30.0 wt.% NaOH at 80 °C. The calculated values are compared with the measured data at 25 and 75 °C. The experimental data agree well with the numerical values computed from the theoretical and empirical equations.
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1. Introduction

For energy and cost reduction in the production of hydrogen fuel by alkaline water electrolysis, Wendt et al. [1] developed a unit consisting of a cathode, anode, and diaphragm as a substitute for the conventionally used perforated sheet electrodes and the harmful asbestos diaphragms. In North America, over $1.8 billion of electricity is spent annually on the production of chlorine and caustic via the electrolysis of brine. This tremendous monetary expense has resulted in an ongoing interest in developing activated cathodes with low overpotential. Even small reductions (less than 10 mV) in overpotential are associated with millions of dollars in annual savings nationwide [2]. The successful development and comparison of activated cathodes require that a properly calibrated and compatible reference electrode be available to measure overpotential. Balej [3] derived a few equations

for determining the oxygen and hydrogen overvoltage by using mercury oxide and reversible hydrogen reference electrode in concentrated alkaline hydroxide solutions. Based on the hydroxide anion, the Hg/HgO electrode proves highly suitable for use in sodium hydroxide electrolyte; however, few commercial vendors exist so the electrode must often be prepared in-house. Furthermore, information on the potential of the Hg/HgO half-reaction is either incomplete or inadequately documented for real applications.

A mercury oxide reference electrode is also ideal for alkaline battery research, process monitoring in strong alkali or fluoride streams, and electro-analysis in alkaline solution or fluoride solution [4]. The reference electrode needs to be charged or discharged within an electrolyte in a reproducible fashion. This process is often required to be practically reversible. The standard electrode potential of the mercury/mercury oxide half-cell is well accepted as +0.098 V versus the standard hydrogen electrode in alkaline solution. The most important aspect of the half-cell reaction for a reference electrode is considered to be reversibility. The half-cell reaction at an electrode is either an oxidation or a reduction depending on the system of interest. An ideal reference electrode is reproducible, non-polarizable,

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and passes no current. Passing zero current through the reference electrode is impossible; however, the Butler–Volmer equation shows that an electrode with a high exchange current density (i.e., a smaller overpotential) best approximates the non-polarizable state [5]. The normal hydrogen electrode (NHE, also called the standard hydrogen electrode, i.e., SHE) in a H_2, Pt|HCl system is used as the arbitrary standard. This consists of hydrogen at unit activity (i.e., solution in equilibrium with hydrogen gas at 1 atm) in equilibrium with hydrogen ions of unit activity in solution (1.19 M HCl solution). The equilibrium potential is detected with a platinum electrode that is coated with platinum black (finely divided platinum) to enlarge the effective surface area, because platinum has a very high exchange current density towards the hydrogen evolution reaction [6]. The Hg/HgO electrode potential at a certain temperature during an experimental test is simply unaddressed in most previous publications, or the semi-empirical equations are quite complicated. The community usually has hard time to find useful documents for different applications. The main problem is obtaining the activities of hydroxide ion, hydrogen, and water, especially because much less activity and activity coefficient data are available in concentrated aqueous sodium hydroxide. In consideration of reactant/product activities and temperature variations of the standard state potential in both dilute and concentrated solutions, this work has been undertaken to determine individual potentials of both the Hg/HgO and alkaline hydrogen half-reactions at temperatures of 0–90 °C and in sodium caustic concentrations of 0.100–12.8m. The potentials of the reference electrodes are also discussed at different working conditions.

2. Experimental details

For the measurement of hydrogen evolution electrode potential in aqueous sodium hydroxide, the Hg/HgO reference electrode was constructed with three steps. First, a couple of plastic tubes (1.8 cm internal diameter, 2.0 cm of tube body, and 6.0 cm in total length) with two narrowing small holes on each side were well matched for sealing. The hole on the bottom of one tube was sealed with a small plug of polyolefin fabric (Freudenberg, FS 2227). Then the container was filled to approximately 20% capacity with a mixture of mercury (Fisher Scientific, ACS certified) and mercury oxide powder (Fisher Scientific, ACS certified). Later, a platinum wire was inserted into the mixture through the top-tube hole and connected to the outside circuit. The internal element was also filled with polyolefin fabric (Freudenberg, FS 2227) for holding the mercury and mercury oxide mixture.

Two platinum-foil electrodes (each 0.5 cm^2) connected with platinum wires were placed in a laboratory plastic container (3.0 cm in diameter and 8.5 cm in height). The reference electrode was filled with sodium hydroxide solution and put into the solution with the bottom hole close to the cathode surface for further testing. The alkaline solution was made from sodium hydroxide pellets (Fisher Scientific, ACS certified, 98.1%). The container for testing was separated from the atmosphere and placed in a temperature-controlled water jacket. Following a stabilization period of more than 12 h, the hydrogen evolution

potential of the platinum cathode was then measured against the Hg/HgO reference electrode in a NaOH solution. An E3611 dc power supply (Hewlett-Packard) provided dc current for water electrolysis. A TRUE RMS 111 digital multimeter (Fluke Corporation) was applied for the potential measurement. The applied current was less than 1 mA cm^{-2}, and data were recorded after the hydrogen bubbles stably and slowly generated from the platinum surface. The pressure of the hydrogen bubbles at the platinum cathode surface is assumed to be the same as the atmosphere pressure at room temperature. The above steps were repeated after changing of the solutions. The liquid in the internal tube of the reference electrode was also replaced by the new alkaline solution.

3. Numerical analysis of electrode potentials in solutions of sodium hydroxide
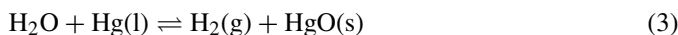
3.1. Nernst equation of electrode potentials

The half-cell standard reduction potential for the Hg/HgO reference electrode in alkaline electrolyte agrees with the value of $E^\circ_{HgO,Hg} = 0.098$ V versus NHE. The electrode potential[1] for the corresponding Nernst equation is expressed as:

$$E_{HgO,Hg} = E^\circ_{HgO,Hg} - \frac{RT}{2F} \ln \frac{(\alpha_{OH^-})^2}{\alpha_{H_2O}} \tag{1}$$

The half-cell reduction potential for alkaline hydrogen evolution is expressed as the value of $E^\circ_{H_2O,H_2} = -0.828$ V versus NHE. The corresponding Nernst equation is given by:

$$E_{H_2O,H_2} = E^\circ_{H_2O,H_2} - \frac{RT}{2F} \ln \frac{(\alpha_{OH^-})^2(\alpha_{H_2})}{\alpha^2_{H_2O}} \tag{2}$$

The standard potential of hydrogen evolution versus the mercury reference electrode is normally written as $E^\circ_{H_2,HgO} = -0.926$ V versus NHE. The above three values of the standard potentials are generally reported in most reference literature [7–10]. The overall electrolytic reaction of H_2 evolution in alkaline electrolyte can be conveniently obtained by the reaction of

$$H_2O + Hg(l) \rightleftharpoons H_2(g) + HgO(s) \tag{3}$$

The hydrogen evolution potential versus the Hg/HgO electrode, similar to a combined cell, is described by the Nernst equation at a temperature of T

$$E_{H_2,HgO} = E^\circ_{H_2,HgO} - \frac{RT}{2F} \ln \frac{\alpha_{H_2}}{\alpha_{H_2O}} \tag{4}$$

The presence of activity terms in Eqs. (1), (2) and (4) is a universal problem with solving the Nernst equation. The necessary data are seldom available and, as a result, data approximations are typically employed. Typical approximations include:

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[1] The symbol of the electrode potential in the half-cell reaction uses an order from reactant to product at the subscript. The subscript of the working electrode potential versus a reference electrode utilizes only products which are in order from the product of the working electrode to the product of the reference electrode in this work.

(1) assuming an activity coefficient of unity for the solute(s), solvent(s), or both constituents, (2) setting the activity of a single gaseous species equal to the total system pressure, and (3) using only the second term of the Nernst equation (4) to describe temperature dependencies. The first approximation is especially common with water and dilute solute. Approximation #2 is common with low temperature systems. The working electrode potential as a function of temperature is simply unaddressed in most available publications. Further discussion in this document examines the appropriateness of these assumptions for the current system of interest.

3.2. Potentials of Hg/HgO electrode and hydrogen evolution at a standard state

The standard state potential (E°) is a function of temperature whereby this functionality is expressed with a Taylor series expansion as follows:

$$E^\circ(T) = E^\circ + \frac{dE^\circ}{dT}(T - 298) + \frac{1}{2}\frac{d^2E^\circ}{dT^2}(T - 298)^2 \quad (5)$$

For computing the standard electromotive force of a cell, Salvi and de Bethune [11] derived the above equation including the first and second order derivatives, entitled the "first" and "second isothermal temperature coefficients", respectively. Values are obtainable through manipulation of tabulated thermodynamic data. For the current study of the Hg/HgO, H_2/H_2O electrode potentials, the appropriate values in volts versus NHE [11] are further simplified as a function of temperature:

$$E^\circ_{HgO,Hg}(T) = 0.0980 - 1.120 \times 10^{-3}(T - 298)$$
$$- 3.388 \times 10^{-6}(T - 298)^2 \quad (6)$$

$$E^\circ_{H_2O,H_2}(T) = -0.82806 - 0.8342 \times 10^{-3}(T - 298)$$
$$- 3.636 \times 10^{-6}(T - 298)^2 \quad (7)$$

Expressions (6) and (7) show standard state potentials as a function of temperature for the individual half-cell reactions. Standard state potentials can be obtained at different temperatures, and then the real electrode potentials can be determined by using Eqs. (1) and (2) including the activities. From the results of the potential calculation, temperature effects are significant as the Hg/HgO potential varies more than 113 mV for a change of 90 °C. A temperature shift of 10 °C changes the alkaline hydrogen potential by approximately 13 mV.

3.3. Hydrogen, water, and sodium hydroxide activities

From 0 to 90 °C at a pressure of 1 atm, hydrogen is assumed to be an ideal gas. For an ideal gas in solution, the activity is the ratio of the fugacity in solution to the fugacity in the standard state. The fugacity of an ideal gas in solution is simply the partial pressure of the gas; thus, the activity value of hydrogen gas is
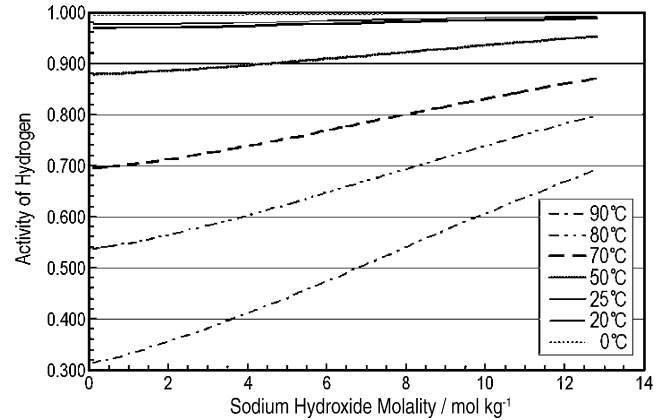

Fig. 1. Computed activity of hydrogen in aqueous NaOH as a function of temperature and molal concentration using Eqs. (8)–(10).

equal to its partial pressure due to $p^\circ_{H_2} = 1$ atm.

$$\alpha_{H_2} = \frac{p_{H_2}}{p^\circ_{H_2}} \quad (8)$$

The partial pressure of hydrogen is simply the difference of the total system pressure and the vapor pressure of water, which is expressed as:

$$p_{H_2} = P - p_{H_2O} \quad (9)$$

At conditions of 0–25m NaOH and 0–300 °C, the vapor pressure (in atm) of water over solutions of sodium hydroxide is obtained from Balej's work [12]:

$$\log p_{H_2O} = -0.010986m - 1.461 \times 10^{-3}m^2 + 2.03528E^{-5}m^3$$
$$+ (1 - 1.3414 \times 10^{-3}m + 7.07241 \times 10^{-4}m^2$$
$$- 9.5362 \times 10^{-6}m^3) \times \left(35.4462 - \frac{3343.93}{T}\right.$$
$$\left. - 10.9\log T + 0.004165T\right) \times 0.987 \quad (10)$$

Using Eqs. (8)–(10) and the related assumptions, hydrogen activity (Fig. 1) is calculated and obtained when the total system pressure is ca. 1.013×10^5 Pa (760 mmHg). At 80 °C and 30.0 wt.% (10.71m) NaOH, activity of hydrogen is equal to a value of 0.755. Hydrogen activity is a weak function of temperature below ca. 40 °C. Above 40 °C, the strong correlation can be attributed to the rapidly increasing vapor pressure of water in the system. For the 80 °C isotherm specifically, the activity value increases by 48.8% within the observed concentration range from 0.100 to 12.8m NaOH. The activity of hydrogen can be viewed as unity ($\alpha_{H_2} \geq 0.970$) at a temperature of no more than 25 °C.

A simple equation for calculating the activity of water in aqueous solutions of sodium hydroxide is taken from the previous paper [12].

$$\log \alpha_{H_2O} = -0.01332m + 0.002542m^2 - 3.06 \times 10^{-5}m^3$$
$$+ \frac{(1.5827m - 1.5669m^2 + 0.021296m^3)}{T} \quad (11)$$

Table 1
Water activities in NaOH solutions

NaOH molality (m)	Water activity	
	25 °C	80 °C
0.11	0.9979	0.9977
0.50	0.9893	0.9888
1.00	0.9757	0.9757
1.45	0.9605	0.9605
2.00	0.9407	0.9440
3.00	0.8967	0.9062
5.10	0.7834	0.8120
8.78	0.5597	0.6256
10.71	0.4497	0.5300

Table 2
Activities and activity coefficients of NaOH solutions

T (°C)	α_{OH^-}	γ_{NaOH}	
	$m = 1.45$	$m = 5.00$	$m = 10.71$
0	0.9566	1.1025	5.0282
10	0.9786	1.1063	4.6935
15	0.9863	1.1043	4.5089
20	0.9918	1.0996	4.3152
25	0.9950	1.0923	4.1142
30	0.9960	1.0824	3.9077
40	0.9909	1.0553	3.4853
50	0.9767	1.0190	3.0619
60	0.9539	0.9746	2.6493
70	0.9230	0.9232	2.2579
80	0.8848	0.8661	1.8953

The expression shows that the activity coefficient of sodium hydroxide is a function of both temperature and molal concentration. For the abscissa, molality is chosen due to molarity's undesirable temperature dependence. In dilute solution, the value of α_{H_2O} behaves as expected and assumes a value near unity; however, significant change ($\alpha_{H_2O} \approx 0.940$) occurs at concentrations as low as 2.00m NaOH (Table 1). At concentrations greater than 5.10m ($\alpha_{H_2O} = 0.783$ at 25 °C), the isotherms diverge and the system shows strong temperature dependence. The value of α_{H_2O} equals to 0.530 at a temperature of 80 °C and 30 wt.% (10.71m) NaOH, a condition which is quite close to the chlor-alkali electrolytic process. As a whole, the activity of water can be approximated as unity ($\alpha_{H_2O} \geq 0.960$) in a dilute solution of no more than 1.45m NaOH.

The activity of a solvated species, such as OH^-, can be calculated either directly or indirectly through the activity coefficient.

$$\alpha_{OH^-} = \gamma_{OH^-} m_{OH^-} \quad (12)$$

Calculation of individual ionic activity coefficients is not possible; therefore, a mean ionic activity coefficient is defined and used to calculate the hydroxide activity.

$$\gamma_{NaOH} = \sqrt{\gamma_{Na^+} \gamma_{OH^-}} \quad (13)$$

$$\alpha_{OH^-} \approx \gamma_{NaOH} m_{NaOH} \quad (14)$$

For this analysis, the activity coefficient values (γ_{NaOH}) are taken from the previous publication [13] as a complex series of equations applying to conditions of 0–70 °C and 0–18m. The value expression for γ_{NaOH} is given by:

$$\log \gamma_{NaOH} = -\frac{u\sqrt{m}}{1 + \sqrt{2m}} + Bm + Cm^2 + Dm^3 + Em^4 \quad (15)$$

where

$$B = 0.006519 + 0.0015995 t_p - 0.000018327 t_p^2 \quad (15a)$$

$$C = 0.013713 - 0.00050071 t_p + 0.0000056385 t_p^2 \quad (15b)$$

$$D = 0.0005994 + 0.000050215 t_p - 0.00000064754 t_p^2 \quad (15c)$$

$$E = -0.00000596 - 0.0000018056 t_p + 0.000000024073 t_p^2 \quad (15d)$$

$$u = 8.000 \times 10^{-6} t_p^2 + 0.0005 t_p + 0.4874 \quad (15e)$$

where m is the concentration in molality (mol $kg_{H_2O}^{-1}$), t_p the solution temperature (°C), and u is the universal constant of the limiting law at various temperatures. For this analysis, these equations are extrapolated to 90 °C to evaluate the electrode potentials. Some of the calculated activity data are listed in Table 2 according to the above analysis and related empirical equations. At concentrations greater than 6.00m, the isotherms diverge, and γ_{NaOH} as a function of temperature becomes significant. Only at a concentration of 5.00m does the activity coefficient approximate unity ($\gamma_{NaOH} \approx 1.0$ from 0 to 60 °C). For very dilute solutions (0.100–0.500m), the activity coefficient changes from approximately 0.800–0.700; significantly different from unity. The specific interest to chlor-alkali membrane reactors is the activity coefficient at 80 °C and 30 wt.% (10.71m) NaOH. At this point, the value of NaOH activity is calculated as $\gamma_{NaOH} = 1.895$. An interesting observation, discussed later in detail, is that the activity of hydroxide ion equals to unity in 1.45m NaOH solution at room temperature from 10 to 40 °C. From the above analysis, activities of hydrogen, water, and hydroxide ion were then determined using the above Eqs. (8)–(14), and the electrode potentials were then calculated using Nernst equation.

3.4. Data analysis of Hg/HgO electrode potential

The numerical values of α_{OH^-} from Eqs. (12)–(15), α_{H_2} from Eqs. (8)–(10), and the other aforementioned parameters were compiled into a Microsoft Excel spreadsheet for calculation of electrode potentials (Table 3). The potentials of the Hg/HgO electrode and the alkaline hydrogen electrode were calculated in the context of Eqs. (1) and (2) at conditions of 0–90 °C and 0.100–12.8m NaOH, respectively. Fig. 2 illustrates the half-cell potential of the Hg/HgO reference electrode relative to the NHE at varying temperatures and concentrations in consideration of the activities of water and sodium hydroxide. The electrode potentials decrease with increasing solute concentration. Within the studied range from 0.100 to 12.8m NaOH, the electrode

Table 3
Hg/HgO potentials vs. NHE at 25 °C

NaOH molality (m)	Activity coefficient, γ_{NaOH}	H_2 activity, α_{H_2}	Water activity, α_{H_2O}	Potential, $E_{HgO,Hg}$ (V)
0.001	0.9655	0.9690	1.0000	0.2763
0.10	0.7820	0.9691	0.9981	0.1634
0.10 (23 °C)	(0.7825)	(0.9726)	(0.9981)	(0.1652) 0.165 [15]
0.30	0.7163	0.9692	0.9939	0.1374
1.00	0.6774	0.9698	0.9757	0.1077
	0.678 [14]			0.108 [10]
1.45 (5.48 wt.%)	0.6862	0.9703	0.9605	0.0976
5.00	1.092	0.9756	0.7892	0.0514
8.78 (26 wt.%)	2.570	0.9826	0.5597	0.0105
10.71 (30 wt.%)	4.114[a]	0.9859	0.4497	−0.0095

[a] Activity coefficient, $\gamma_{NaOH} = 1.895$ at 80 °C.

potential changes by ca. 200 mV at a defined temperature. Ives [9] noticed that the calculated potential of the Hg/HgO electrode versus hydrogen electrode in base ($E^{\circ}_{Hg,H_2O} = 0.926$ V) for the cell Pt, H_2(1 atm)/H_2O|NaOH(aq)|HgO(s)/Hg(l) at 25 °C is independent of NaOH concentration between 0.001 and 0.300m NaOH. This does not mean that the Hg/HgO reference electrode potential is independent of the hydroxide ionic concentration [10]. Where the solute's activity coefficient (γ_{NaOH}) equals 1.895 at 80 °C and 30 wt.% (10.71m NaOH) concentration, the Hg/HgO electrode potential is −0.0751 V versus NHE from Eq. (1). For the measurement of positive potentials in the alkaline battery formation process, the Hg/HgO electrode potential in 26 wt.% NaOH (8.78m, $\gamma_{NaOH} = 2.57$) is close to −0.0105 V versus NHE at 25 °C. For measurement of the battery negative potentials, the mercury oxide reference electrode undergoes reduction producing a potential of +0.0105 V versus NHE. The real potential values for normal electrode processes are then easily determined using the Hg/HgO reference electrode. Near a concentration of 1.45m (5.48 wt.% NaOH, 1.456 M), the potential of the Hg/HgO electrode is approximately its standard state potential of 0.098 V at a temperature of 25 °C. Similarly as shown in Table 3, the electrode potential (0.1077 V) is calculated using Eq. (1) at 1.00m (~1.00 M) NaOH, $\alpha_{H_2} = 0.970$, $\alpha_{H_2O} = 0.976$, and $\gamma_{NaOH} = 0.677$ at 25 °C. The calculated value

of γ_{NaOH} is reasonably close to the data ($\gamma_{NaOH} = 0.678$) listed in the 57th edition *Handbook of Chemistry and Physics* [14]. This result is well matched with Rodgers's [10] calculated data of 0.108 V. As a whole, the actual potential of the Hg/HgO reference electrode in the half-cell, NaOH(aq)|HgO(s)/Hg(l), depends on the ionic activity of OH^- as shown in Eq. (1), even at room temperature ($T = 25$ °C) and a low solute concentration ($\alpha_{H_2O} \approx 1.00$).

3.5. Hydrogen evolution potential in alkaline solution

Using Eq. (2), the cathodic reduction potentials for the alkaline water reaction is calculated and illustrated in Fig. 3 at varying temperatures and concentrations of sodium hydroxide. Similar to Fig. 2, the potential varies by more than 200 mV across the studied range from 0.100 to 12.8m NaOH. The standard potential of −0.8286 V versus NHE occurs at a solute concentration of 1.45m NaOH and at a temperature of 25 °C where the reactant and product activities are approximately unity ($\alpha_{H_2} = 0.970$, $\alpha_{H_2O} = 0.961$, and $\alpha_{OH^-} \approx 0.686 \times 1.45 = 0.995$; Tables 3 and 4). When the water reduction reaction is computed against the Hg/HgO reference electrode in an oxidation process ($E^{\circ}_{Hg,HgO} = -0.0976$ V versus NHE), the hydrogen evolution potential in the alkaline
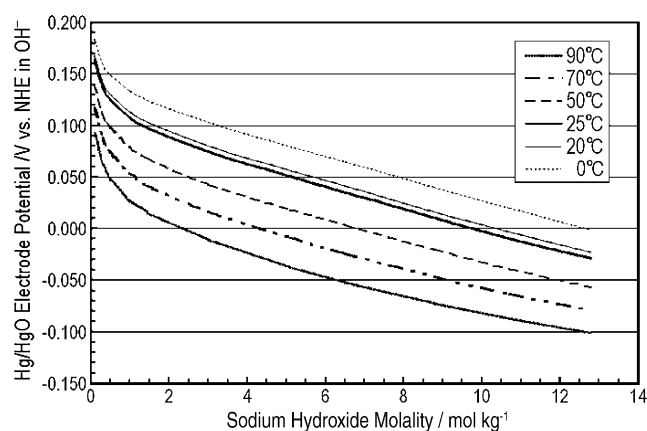

Fig. 2. Calculations for half-cell potential of the Hg/HgO reference electrode versus NHE based on an exact analysis of the relevant Nernst equation using Eqs. (1), (6), (11) and (12).
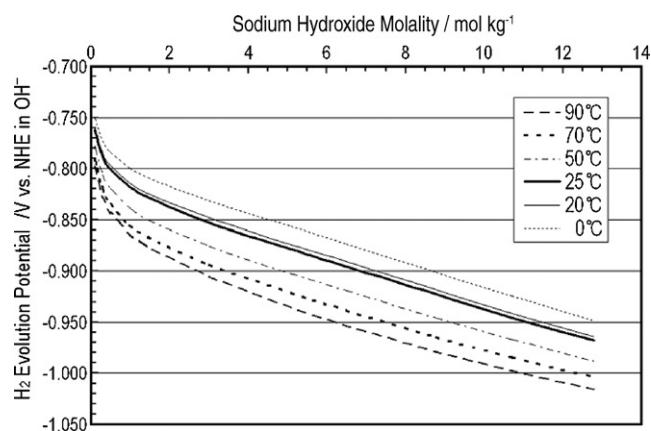

Fig. 3. Calculations for half-cell potential of alkaline hydrogen evolution versus NHE based on an exact analysis of the relevant Nernst equation using Eqs. (2), (7), (8), (11) and (12).

Table 4
Parameters and potentials vs. NHE at two temperatures

NaOH molality (m)	OH$^-$ activity, α_{OH^-}	H$_2$ activity, α_{H_2}	Potential E_{H_2O,H_2} (V)	Hydrogen-evolution potential, $E_{H_2,HgO}$[a] (V)
$T = 25\,°C$				
0.001	9.655×10^{-4}	0.9690	−0.6494	−0.9257
0.11	8.537×10^{-2}	0.9691	−0.7645	−0.9257
0.50	0.3461	0.9694	−0.8007	−0.9258
1.00	0.6774	0.9698	−0.8183	−0.9260
1.45	0.9950	0.9703	−0.8286	−0.9262
≤1.50		∼0.970		−0.926
$T \approx 23\,°C$				
5.10	5.677	0.9757	−0.8786	−0.9289
8.78	22.57	0.9826	−0.9228	−0.9333
10.71	44.06	0.9859	−0.9456	−0.9361
$T = 80\,°C$				
10.71	20.30	0.7552	−0.9916	−0.9165

[a] Hydrogen-evolution potentials are $E_{H_2,HgO}$ vs. Hg/HgO.

water reaction simply becomes: $E^\circ_{H_2,HgO} = E^\circ_{red+ox} = -0.8286$ V $+ (-0.09761\,V) = -0.9262$ V. This means that the same result using Eq. (4) is obtained as ($E^\circ_{H_2,HgO} = 0.9262$ V) considering only the activities of H$_2$ and water. Similarly at a solute concentration of approximately 0.100m ($\cong 0.100$ M) and a temperature of 25 °C, the potential of hydrogen evolution versus the Hg/HgO electrode becomes: $E^\circ_{H_2,HgO} = -0.9257$ V ($E^\circ_{HgO,Hg} = 0.1634$ V versus NHE, $E^\circ_{H_2O,H_2} = -0.7623$ V versus NHE). The value of $E^\circ_{HgO,Hg} = 0.1634$ V is quite close to the potential value of $E^\circ_{HgO,Hg} = 0.165$ V in 0.100 M NaOH solution [15]. The interesting thing as shown in Table 3, is that the value of $E^\circ_{HgO,Hg} = 0.165$ V in the above publication is identical to the calculated potential ($E^\circ_{HgO,Hg} = 0.1652$ V versus NHE, $E^\circ_{H_2O,H_2} = -0.7611$ V versus NHE, and $E^\circ_{H_2,HgO} = -0.9263$ V) in 0.100m NaOH at a temperature of 23 °C, which is close to the actual room temperature where most experimental data are obtained. The above results reveal that the hydrogen evolution potential versus the mercury reference electrode in a solute concentration of no more than 1.50m NaOH at room temperature can be viewed as a constant $E^\circ_{H_2,HgO} = -0.9260$ V, because water activity ($\alpha_{H_2O} \geq 0.960$) and hydrogen activity ($\alpha_{H_2} = 0.970$) are close to the unit value; hence, the potentials of two electrode couples (H$_2$O/H$_2$, Hg/HgO) are further simplified as a function of ionic activity of OH$^-$ at $C_{OH^-} \leq 1.50$ m and $T \leq 298$ K:

$$E_{HgO,Hg} \approx E^\circ_{HgO,Hg} - \frac{RT}{F} \ln \alpha_{OH^-} \quad (1a)$$

$$E_{H_2O,H_2} \approx E^\circ_{H_2O,H_2} - \frac{RT}{F} \ln \alpha_{OH^-} \quad (2a)$$

The hydrogen evolution potential versus the mercury electrode in sodium hydroxide solution is further simplified as a function of the standard potentials. Using Eqs. (1a), (2a), (6) and (7), the hydrogen evolution potential is obtained as:

$$E_{H_2,HgO} = E_{H_2O,H_2} + E_{Hg,HgO} = E^\circ_{H_2O,H_2}(T) - E^\circ_{HgO,Hg}(T) \quad (16)$$

which can be applied to approximately compute the hydrogen evolution potential at $C_{OH^-} \leq 1.50$m and $T \leq 298$ K. At 80 °C and 30 wt.% concentration (10.71m NaOH, $\alpha_{H_2} = 0.755$, $\alpha_{H_2O} = 0.530$, and $\gamma_{NaOH} = 1.895$), the alkaline water reaction has a theoretical reduction potential of −0.9916 V versus NHE (Table 4). The hydrogen evolution potential for the alkaline water reaction reduces by 20.7 mV due to the contribution of hydrogen and water activities (Eq. (4)) at 80 °C in 30.0 wt.% NaOH solution, than that at 25 °C in the same NaOH solution. When measured against the Hg/HgO reference electrode and using Eqs. (1) and (2), the potential of the alkaline water reaction simply becomes: −0.9916 V + 0.0751 V = −0.9165 V; or using Eq. (4), the hydrogen evolution potential versus the Hg/HgO electrode is obtained the same as −0.9165 V. Fig. 4 shows the hydrogen evolution potentials versus the Hg/HgO electrode in the combined Hg/HgO|NaOH|H$_2$O/H$_2$ cell as functions of varying temperatures and concentrations of sodium hydroxide. Data in this figure are calculated based on the Hg/HgO reference undergoing oxidation and the alkaline water reaction undergoing reduction. The electrode potentials from Eqs. (1) and (2) in comparison with values calculated from Eq. (4) in the combined cell show no
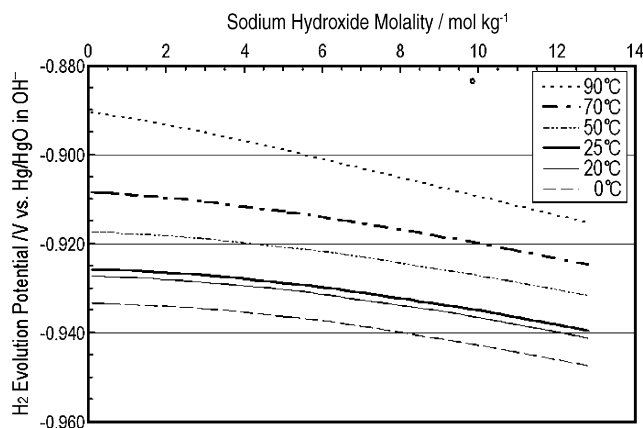

Fig. 4. Computed potential of alkaline hydrogen evolution vs. the Hg/HgO electrode based on an exact Nernstian analysis. This combined cell potential uses Eqs. (4), (6), (7), (8) and (11).

difference in this work. The potential of both the Hg/HgO and alkaline hydrogen half-reaction decreases over 200 mV in a concentration range of 0.100–12.8m NaOH (0.400–33.9 wt.%) and in a temperature range of 0–90 °C. This shift is directly associated with strong dependencies of the relevant Nernst equation on both temperature and activity. For studies involving activated cathodes with an overpotential in hydrogen evolution, it is clear that calculation of the overpotential using various standard reference potentials is inappropriate. The potential data values of the Hg/HgO electrode from the above analysis are compared with those few values best available from manufacturers and/or publications as listed in the above table. Koslow Scientific [4] and CH Instruments [18] supply mercury oxide electrodes with varying electrolytes and concentrations; however, data sheets for the electrodes list only the standard state potential of 0.098 V. The accurate measurements of electrode potentials of the half-cell reactions are also beneficial for identifying the real electrochemical reaction in the actual electrolysis and understanding the battery charge/discharge formation processes.

Both the Hg/HgO and alkaline hydrogen evolution reactions are well-behaved in the sense that potential shifts are consistent with changes in temperature and/or concentration; however, the half-cells clearly show an unstable potential. Even minor experimental fluctuations in electrolyte concentration and/or temperature warrant a review of the data in Figs. 2 and 3. Based on the data of Fig. 3, the alkaline hydrogen half-cell can now be used as a suitable reference electrode. Because the electrode is thin (simply a platinum black foil suspended in the hydrogen gas field), it offers the possibility for use in commercial, near zero-gap cells. Such in situ monitoring of individual half-cell overpotential may provide improved control and/or the capability for monitoring a commercial cathode's remaining service life.

The calculated potentials of hydrogen evolution versus Hg/HgO electrode are illustrated in Fig. 5 in comparison with the measured potentials and best available values in previous publi-
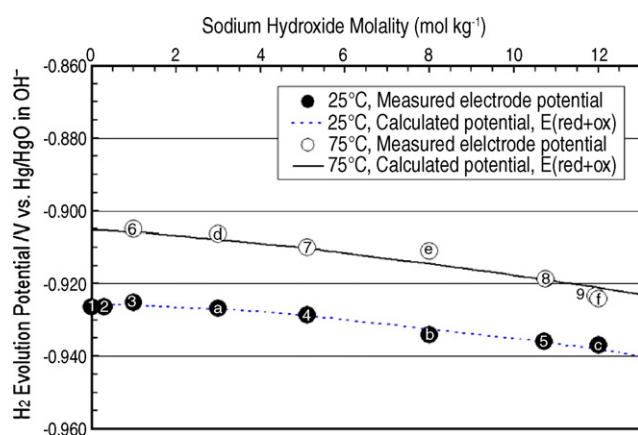

Fig. 5. Computed data and tested potential results of alkaline hydrogen evolution vs. the Hg/HgO reference electrode based on an exact Nernstian analysis. Calculated values of one solid and one dotted lines from the Nernst Eqs. (1) and (2). Measured data (filled circles and open circles) from no. 1–2 [16], no. 3, 4, 6–9 [3], and No. 5 [17], and circles of a–f from the experimental data of this work.

cations. They match well in a solution of less than 12.8m NaOH at temperatures of 25 and 75 °C. Furthermore, the hydrogen evolution potential is obtained as −0.9060 V at 75 °C in 0.100m NaOH solution when both calculated and measured data are extrapolated towards the y-axis. This is reasonable in comparison with the calculated value of −0.9053 V at 75 °C in 0.100m NaOH solution using Eqs. (1) and (2). At both temperatures as shown in Fig. 5, the computed potentials (Eqs. (1) and (2)) agree well with the experimental data (filled circles #1–5 and (a–c) at 25 °C, open circles #6–9 and (d–f) at 75 °C) even in a concentrated NaOH solution of no more than 12.8m. The error between the experimental and Nernst numerical values increases in more than 12.8m NaOH solution due to the limitation of several empirical equations used in the calculation. The electrode and solution theories most establish in dilute solution at room temperature with various assumptions; thus, the electrode behaviors may depart from the theoretical calculation in more concentrated solution at high temperature conditions, although various corrections and empirical equations with modified theoretical consideration are applied to the numerical calculation. Extensive work is necessary for accurate determination of activities of water, hydrogen, and hydroxide ions as well as OH^- activity coefficient in order to obtain a better matched potential result in concentrated NaOH solution, especially when $C_{OH^-} \geq 12.8m$ and $T \geq 353$ K. Overall, the determination of hydrogen production potential using the mercury/mercury oxide as a reference electrode illustrates the necessity of precisely analyzing the Nernst equation including the activities of the real reductants or oxidants when overpotential is a key variable of interest.

4. Summary

This work has been undertaken to determine individual potentials of both the Hg/HgO and alkaline hydrogen half-reactions at temperatures of 0–90 °C and in caustic concentrations of 0.100–12.8m. This study calculates potentials free of common approximations in the Nernst equation where significant errors in overpotential usually occur due approximations to ignoring variations of the standard state potential and reactant/product activities. Because this work describes individual half-cells, data is made available to correct previous studies and to provide a reasonable explanation for common errors of the Hg/HgO reference electrode. The numerical potential values of hydrogen evolution versus the Hg/HgO electrode are in good agreement with the literature data in no more than 12.8m NaOH at temperatures of 25 and 75 °C. The calculated hydrogen evolution potential at 25 °C and 1 atm pressure is −0.9262 V versus a Hg/HgO reference electrode at a concentration range from 0.100 to 1.45m NaOH. In a solution of 26 wt.% (8.78m) NaOH at 25 °C for some battery development applications, the Hg/HgO electrode reduction potential changes to $E^{\circ}_{HgO,Hg} = 0.0105$ V versus NHE ($E^{\circ}_{H_2O,H_2} = -0.9228$ V versus NHE). Furthermore, the hydrogen evolution potential changes to −0.9165 V versus an Hg/HgO electrode ($E^{\circ}_{HgO,Hg} = -0.0751$ V versus NHE, $E^{\circ}_{H_2O,H_2} = -0.9916$ V versus NHE) in a solution of 30.0 wt.% (10.71m) NaOH at 80 °C for chlor-alkali electrolysis and hydrogen production process.

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