



Thermodynamic behavior of Ni–Cd and Ni–H₂ batteries over wide ranges of temperatures (0–200°C), KOH concentrations (0.1–20 mol kg⁻¹) and H₂ pressure (0.1–500 bar)

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Abstract

For simulating the full discharged and charged states of nickel–cadmium and nickel–hydrogen batteries, thermodynamic characteristics such as the equilibrium E^e and thermoneutral E^T potentials of the cells have been calculated over wide ranges of temperatures (0°–200°C), potassium hydroxide concentrations (0.1–20 mol kg⁻¹) and hydrogen pressures (0.1–500 bar). The effects of non-ideality of the hydrogen gas phase and potassium hydroxide aqueous solution were taken into account by using available thermodynamic and experimental data. The effect of temperature, potassium hydroxide concentration, and hydrogen pressures on E^e and E^T have been analyzed. © 1998 Elsevier Science S.A.

Keywords: Ni–Cd and Ni–H₂ batteries; Thermodynamic behavior; Equilibrium and thermoneutral potentials

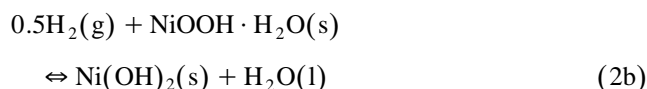
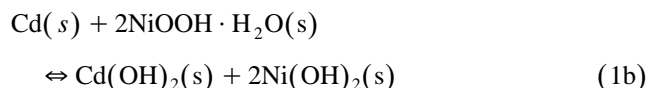
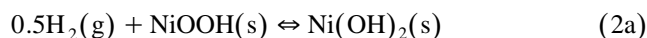
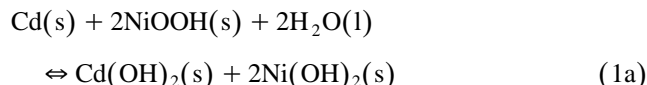
1. Introduction

Nickel–cadmium (Ni–Cd) and nickel–hydrogen (Ni–H₂) batteries have relatively high energy and power densities and exhibit good cycling capabilities and, therefore, have found wide utility in aerospace systems. On the other hand, the cycle life of the batteries under deep discharge conditions is severely limited by the degradation of the electrodes (most notably the nickel electrode), which results in excess battery weight having to be carried into orbit at a cost ~ US\$22400/kg⁻¹. The key to reducing the excess weight would seem to lie in mitigating the degradation of the nickel positive electrode, thereby allowing much deeper discharge without incurring a penalty in terms of decreased cycle life. It is evident, that a complete understanding of the degradation mechanisms requires a careful analysis of the cell thermodynamics, so that the voltage and energy efficiencies can be placed on a rational basis. Thermodynamic data for a variety of alkaline batteries have been published previously by Hodge et al. [1], Pound et al. [2], and Macdonald and Challingsworth [3] for limited ranges of temperatures, hydrogen pressures, and KOH(aq) concentrations. In this work, we expand the

thermodynamic analyses of Ni–Cd and Ni–H₂ batteries to investigate much wider ranges of temperature (0 to 200°C), hydrogen pressure (1 to 500 bar), and KOH(aq) concentration (0.1 to 20 mol kg⁻¹), so as to cover the conceivable sets of conditions that might be experienced in service.

2. Equilibrium and thermoneutral potentials

Following the work of Macdonald and Challingsworth [3], we consider the following cell reactions for Ni–Cd and Ni–H₂ batteries:



where Ni(OH)₂(s), NiOOH(s) or NiOOH · H₂O(s) are as-

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Table 1

The thermodynamic properties of the chemical components of the electrochemical Eqs. (1a), (2a), (1b) and (2b)

Components	$\Delta_f G_i^0(T_0)$ (kJ mol ⁻¹)	$\Delta_f H_i^0(T_0)$ (kJ mol ⁻¹)	$S_i^0(T_0)$ (J mol ⁻¹ K ⁻¹)	a_i (J mol ⁻¹)	$b_i 10^3$ (J mol ⁻¹ K ⁻¹)	$c_i 10^{-5}$ (J K ² mol ⁻¹)
H ₂ (g)	0	0	130.57	27.280	3.263	0.502
Cd(s)	0	0	51.756	22.217	12.30	0
Cd(OH) ₂ (s)	-482.347	-571.642	87.864	12.726	-19.70	1.172
Ni(OH) ₂ (s)	-459.070	-541.799	88.000	18.106	-36.86	1.172
NiOOH(s)	-321.700	-391.231	66.980	30.186	-35.23	1.423
NiOOH · H ₂ O(s)	-564.422	-629.859	150.624	87.388	-82.84	8.661
H ₂ O(l)	-237.183	-285.838	69.923	-	-	-

sumed to be the active materials at the nickel positive electrode [1,3]. The equilibrium voltages for these four reactions are given the Nernst equation as

$$E_1^e(T, m) = E_1^{e,0}(T) + \frac{RT}{F} \ln a_{\text{H}_2\text{O}}(T, m) \quad (3)$$

$$E_2^e(T, p) = E_2^{e,0}(T) + \frac{RT}{2F} \ln f_{\text{H}_2}(T, p) \quad (4)$$

$$E_{1'}^e(T) = E_{1'}^{e,0}(T) \quad (5)$$

$$E_{2'}^e(T, p, m) = E_{2'}^{e,0}(T) + \frac{RT}{2F} \ln f_{\text{H}_2}(T, p) - \frac{RT}{F} \ln a_{\text{H}_2\text{O}}(T, m) \quad (6)$$

where $f_{\text{H}_2}(T, p)$ is the fugacity of hydrogen, which is a function of temperature (T) and pressure (p), and $a_{\text{H}_2\text{O}}(T, m)$ is the activity of water, which is a function of the molal KOH concentration (m) and temperature. The values of $E_1^{e,0}(T)$, $E_2^{e,0}(T)$, $E_{1'}^{e,0}(T)$, $E_{2'}^{e,0}(T)$ are the standard cell voltages, respectively, for Eqs. (1a), (2a), (1b) and (2b). These values can be calculated from a knowledge of the standard molar Gibbs energies, $\Delta_r G_i^0$, of the i -th

chemical compounds involved in the reactions using the expressions

$$E_1^{e,0}(T) = -\frac{1}{2F} \Delta_r G_1^0 = -\frac{1}{2F} (\Delta G_{\text{Cd(OH)}_2}^0 + 2\Delta G_{\text{Ni(OH)}_2}^0 - \Delta G_{\text{Cd}}^0 - 2\Delta G_{\text{NiOOH}}^0 - 2\Delta G_{\text{H}_2\text{O}}^0) \quad (7)$$

$$E_2^{e,0}(T) = -\frac{1}{F} \Delta_r G_2^0 = -\frac{1}{F} (\Delta G_{\text{Ni(OH)}_2}^0 - \Delta G_{\text{NiOOH}}^0 - \frac{1}{2} \Delta G_{\text{H}_2}^0) \quad (8)$$

$$E_{1'}^{e,0}(T) = -\frac{1}{2F} \Delta_r G_{1'}^0 = -\frac{1}{2F} (\Delta G_{\text{Cd(OH)}_2}^0 + 2\Delta G_{\text{Ni(OH)}_2}^0 - \Delta G_{\text{Cd}}^0 - 2\Delta G_{\text{NiOOH} \cdot \text{H}_2\text{O}}^0) \quad (9)$$

$$E_{2'}^{e,0}(T) = -\frac{1}{F} \Delta_r G_{2'}^0 = -\frac{1}{F} (\Delta G_{\text{Ni(OH)}_2}^0 + \Delta G_{\text{H}_2\text{O}}^0 - \Delta G_{\text{NiOOH} \cdot \text{H}_2\text{O}}^0 - \frac{1}{2} \Delta G_{\text{H}_2}^0) \quad (10)$$

where $\Delta_r G_i^0$ is the change in the standard Gibbs energy for the i -th Eqs. (1a), (1b) and (2a) or Eq. (2b).

Table 2

The calculated values of $\Delta_r G_i^0$ (kJ mol⁻¹) and $\Delta_r H_i^0$ (kJ mol⁻¹) for the electrochemical Eqs. (1a), (2a), (1b) and (2b) for temperatures between 0 and 200°C

Thermodynamic characteristic	Temperature, °C					
	0	25	50	100	150	200
$\Delta_r G_1^0$	-284.127	-282.694	-280.928	-276.396	-270.532	-263.335
$\Delta_r G_2^0$	-138.457	-137.364	-136.224	-133.806	-131.203	-128.415
$\Delta_r G_{1'}^0$	-273.780	-271.612	-271.612	-296.212	-257.296	-249.948
$\Delta_r G_{2'}^0$	-121.725	-131.825	-130.368	-127.469	-124.588	-121.725
$\Delta_r H_1^0$	-296.303	-301.092	-305.938	-315.797	-325.881	-336.188
$\Delta_r H_2^0$	-149.888	-150.568	-151.249	-152.614	-153.981	-155.352
$\Delta_r H_{1'}^0$	-391.848	-395.508	-399.095	-406.048	-412.709	-419.076
$\Delta_r H_{2'}^0$	-197.661	-197.776	-197.828	-197.740	-197.396	-196.798

Table 3
The numerical values of parameters b_i , c_i and d_i of Eqs. (24)–(26)

i	Empirical parameter		
	b_i	c_i	d_i
0	$9.6700 \cdot 10^{-4}$	$6.5393 \cdot 10^{-3}$	$-2.9122 \cdot 10^{-4}$
1	$5.8146 \cdot 10^{-4}$	$1.2106 \cdot 10^{-4}$	$3.4688 \cdot 10^{-6}$
2	$3.4800 \cdot 10^{-6}$	$3.9615 \cdot 10^{-7}$	$-9.6179 \cdot 10^{-9}$

For a comprehensive understanding of the thermodynamics and thermal performance of a battery, the thermoneutral potentials for Eqs. (1a), (1b), (2a) and (2b) must be calculated using the following thermodynamic expressions:

$$E_1^T(T, m) = E_1^{T,0}(T) - \frac{RT^2}{F} \left(\frac{\partial \ln a_{\text{H}_2\text{O}}(T, m)}{\partial T} \right), \quad (11)$$

$$E_2^T(T, p) = E_2^{T,0}(T) - \frac{RT^2}{2F} \left(\frac{\partial \ln f_{\text{H}_2}(T, p)}{\partial T} \right) \quad (12)$$

$$E_V^T(T) = E_V^{T,0}(T) \quad (13)$$

$$E_2^T(T, p, m) = E_2^{T,0}(T) + \frac{RT^2}{F} \left(\frac{\partial \ln a_{\text{H}_2\text{O}}(T, m)}{\partial T} \right) - \frac{RT^2}{2F} \left(\frac{\partial \ln f_{\text{H}_2}(T, p)}{\partial T} \right) \quad (14)$$

where the standard values of the thermoneutral potentials, $E_1^{T,0}(T)$, $E_2^{T,0}(T)$, $E_V^{T,0}(T)$, and $E_2^{T,0}(T)$ can be calculated from values of the standard molal enthalpies, ΔH_i^0 , of the i -th chemical compounds involved in the reactions. Thus,

$$E_1^{T,0}(T) = -\frac{1}{2F} \Delta_r H_1^0 = -\frac{1}{2F} \left(\Delta H_{\text{Cd}(\text{OH})_2}^0 + 2\Delta H_{\text{Ni}(\text{OH})_2}^0 - \Delta H_{\text{Cd}}^0 - 2\Delta H_{\text{NiOOH}}^0 - 2\Delta H_{\text{H}_2\text{O}}^0 \right) \quad (15)$$

$$E_2^{T,0}(T) = -\frac{1}{F} \Delta_r H_2^0 = -\frac{1}{F} \left(\Delta H_{\text{Ni}(\text{OH})_2}^0 - \Delta H_{\text{NiOOH}}^0 - \frac{1}{2} \Delta H_{\text{H}_2}^0 \right) \quad (16)$$

$$E_V^{T,0}(T) = -\frac{1}{2F} \Delta_r H_V^0 = -\frac{1}{2F} \left(\Delta H_{\text{Cd}(\text{OH})_2}^0 + 2\Delta H_{\text{Ni}(\text{OH})_2}^0 - \Delta H_{\text{Cd}}^0 - 2\Delta H_{\text{NiOOH} \cdot \text{H}_2\text{O}}^0 \right) \quad (17)$$

$$E_2^{T,0}(T) = -\frac{1}{F} \Delta_r H_2^0 = -\frac{1}{F} \left(\Delta H_{\text{Ni}(\text{OH})_2}^0 + \Delta H_{\text{H}_2\text{O}}^0 - \Delta H_{\text{NiOOH} \cdot \text{H}_2\text{O}}^0 - \frac{1}{2} \Delta H_{\text{H}_2}^0 \right) \quad (18)$$

where $\Delta_r H_i^0$ is change in standard enthalpy for the i -th Eqs.

3. Calculation of the thermodynamic data and cell voltages

The standard molal Gibbs energy ΔG_i^0 , and enthalpy, ΔH_i^0 , contained in Eqs. (7)–(10) and Eqs. (15)–(18) were calculated by using the well known expressions

$$\Delta G_1^0 = \Delta_f G_i^0(T_0) - S_i^0(T_0)(T - T_0) + \int_{T_0}^T C_{P,i}^0(T) dT - T \int_{T_0}^T C_{P,i}^0(T) d \ln T \quad (19)$$

$$\Delta H_i^0 = \Delta_f H_i^0(T_0) + \int_{T_0}^T C_{P,i}^0(T) dT \quad (20)$$

where $\Delta_f G_i^0(T_0)$ and $\Delta_f H_i^0(T_0)$ are the standard molal Gibbs energy and enthalpy of formation of the i -th chemical compound from its elements in their stable phase at the reference temperature, T_0 , $S_i^0(T_0)$ is the standard molal entropy of the i -th chemical compound at the same reference temperature, T_0 , and $C_{P,i}^0(T)$ is the standard molal isobaric heat capacity of the i -th chemical compound. The values of $C_{P,i}^0(T)$ are commonly expressed as a power function

$$C_{P,i}^0(T) = a_i + b_i T + c_i T^{-2} \quad (21)$$

where a_i , b_i , and c_i are empirical regression coefficients. The values of $\Delta_f G_i^0(T_0)$, $\Delta_f H_i^0(T_0)$, $S_i^0(T_0)$, a_i , b_i , and c_i were taken from the paper of Macdonald and Challingsworth [3] and are given in Table 1. The thermodynamic properties of water (ΔG_i^0 and ΔH_i^0) at elevated temperatures were calculated by using the HGK Equation of State [4] via the SUPCRT92 computer code [5].

By using the data given in Table 1, we calculated values for $\Delta_r G_i^0$ and $\Delta_r H_i^0$ over the temperature range between 0 and 200°C, and the results are given in Table 2.

Table 4

The calculated values of water activity $a_{\text{H}_2\text{O}}(T, m)$ over wide range of temperature and KOH(aq) concentrations

Temperature °C	$a_{\text{H}_2\text{O}}$ at concentration m (mol kg ⁻¹)					
	0.1	1	5	10	15	20
0	0.996	0.962	0.753	0.437	0.207	0.100
25	0.996	0.962	0.753	0.449	0.227	0.117
50	0.996	0.962	0.754	0.462	0.248	0.136
100	0.996	0.962	0.761	0.493	0.293	0.177
150	0.996	0.963	0.775	0.531	0.342	0.220
200	0.997	0.964	0.795	0.576	0.395	0.263

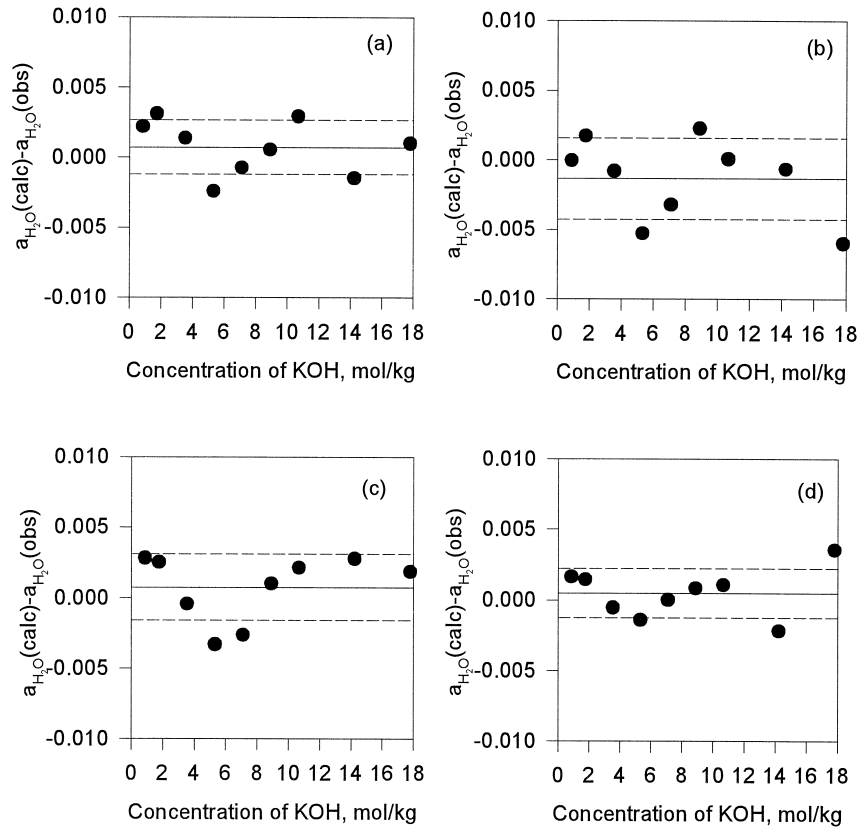


Fig. 1. The regression analysis results for the isobaric activity of water in KOH aqueous solution: (a) 0°C, (b) 20°C, (c) 40°C, (d) 60°C.

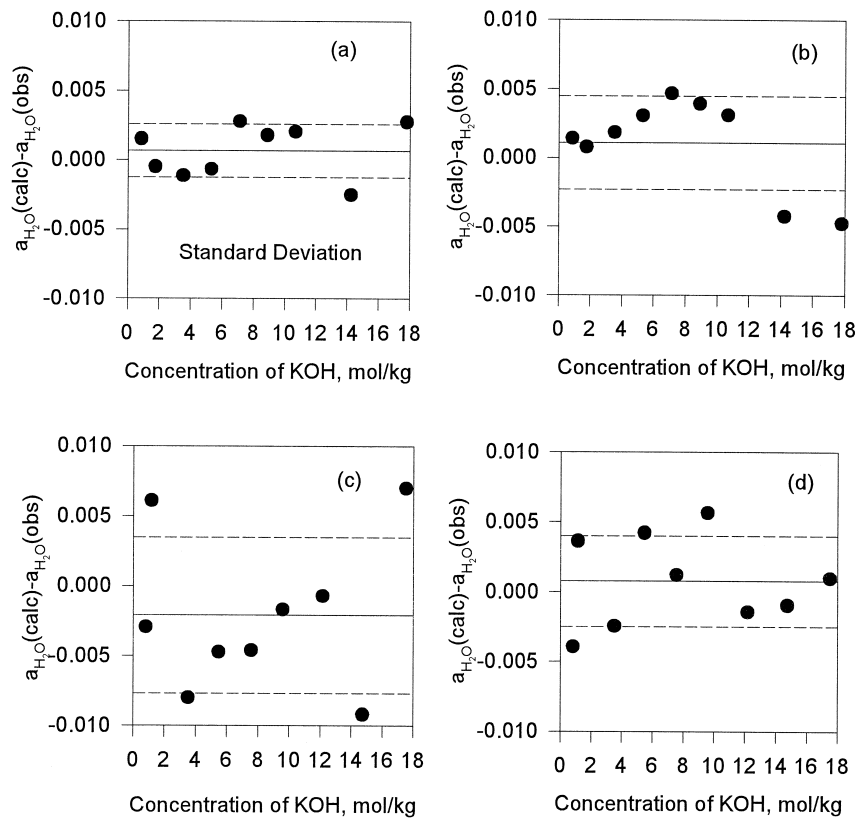


Fig. 2. The regression analysis results for the isobaric activity of water in KOH aqueous solution: (a) 80°C, (b) 100°C, (c) 150°C, (d) 200°C.

Table 5

The calculated values of fugacity coefficient $f_{\text{H}_2}(T,p)/p$ over wide range of temperature and pressure

Temperature °C	$f_{\text{H}_2}(T,p)/p$ at pressure (bar)					
	1	50	100	200	300	500
0	0.995	0.997	1.023	1.083	1.153	1.309
25	0.995	0.996	1.020	1.076	1.139	1.280
50	0.995	0.994	1.017	1.068	1.126	1.253
100	0.995	0.991	1.011	1.055	1.103	1.205
150	0.995	0.989	1.006	1.044	1.084	1.165
200	0.995	0.986	1.001	1.034	1.068	1.134

Calculation of the equilibrium cell voltages of Eqs. (1a), (2a) and (2b) requires a knowledge of the activity of water $a_{\text{H}_2\text{O}}(T,m)$ in the potassium hydroxide solutions, as well as the values for the fugacity of hydrogen, $f_{\text{H}_2}(T,p)$. In addition, calculation of the thermoneutral cell voltages for Eqs. (1a) and (2b) requires information on the temperature derivative of the activity of water, $(\partial \ln a_{\text{H}_2\text{O}}(T,m))/\partial T$, whereas estimation of the thermoneutral cell voltages for Eqs. (2a) and (2b) requires a knowledge of the temperature derivative of the hydrogen fugacity, $(\partial \ln f_{\text{H}_2}(T,p))/\partial T$.

The isobaric activity of water in a strong electrolyte

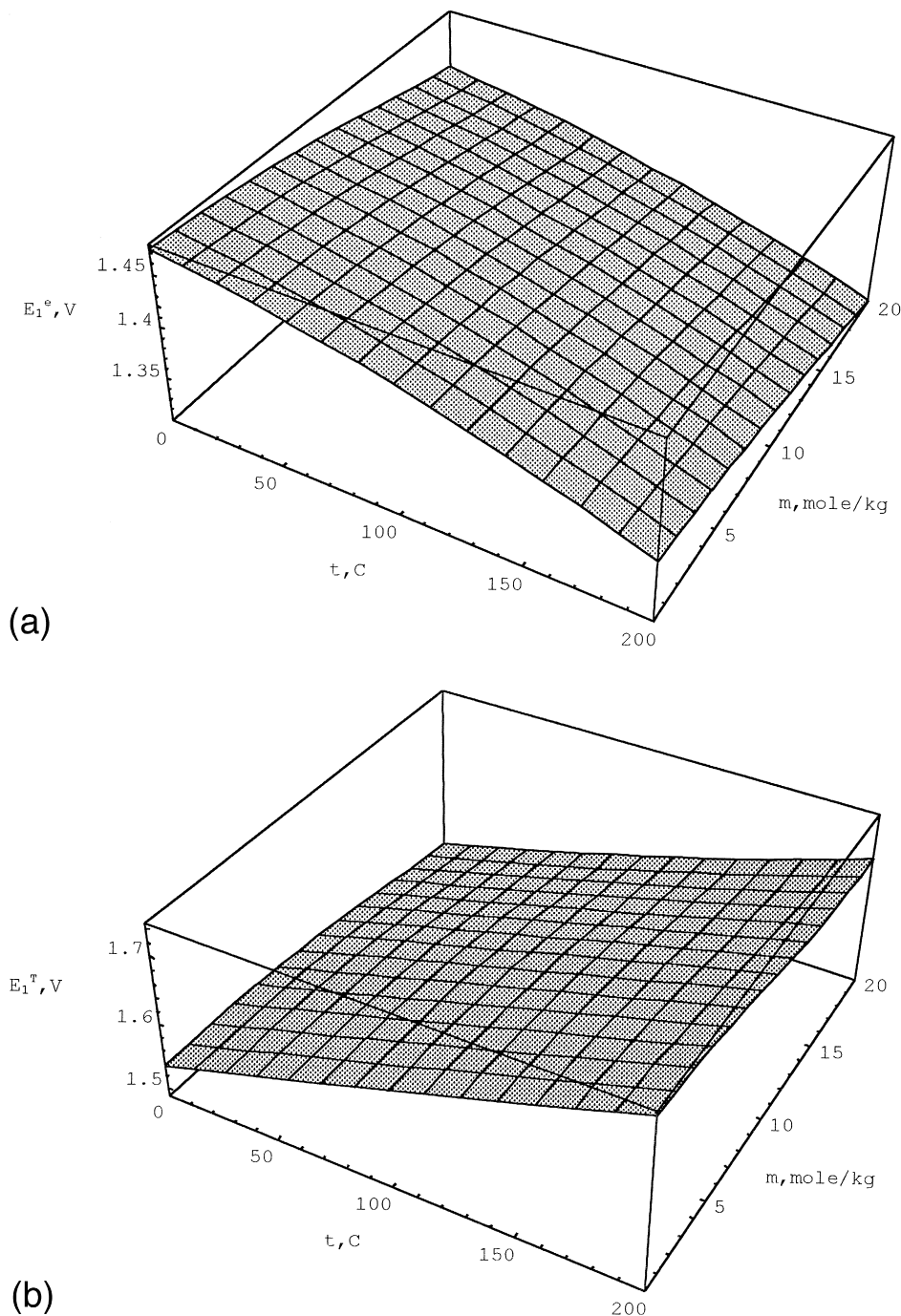


Fig. 3. The temperature–KOH(aq) concentration surfaces of equilibrium $E_1^0(T,m)$ (a) and thermoneutral $E_1^T(T,m)$ (b) cell voltages for Ni–Cd battery.

solutions, such as potassium hydroxide, can be calculated by following expression [6]

$$\ln a_{\text{H}_2\text{O}}(T, m) = \frac{p}{p_0} + \int_p^{p_0} \left(\frac{RT}{p} - V_{\text{H}_2\text{O}} \right) dp + \int_p^{p_0} \bar{V}_{\text{H}_2\text{O}} dp \quad (22)$$

if the extent of vapor pressure lowering and density are known. In Eq. (22), p is the pressure of the steam in

equilibrium with the solution, p_0 is the vapor pressure of pure water at the temperature of the solution, $V_{\text{H}_2\text{O}}$ is the molar volume of pure water in the vapor phase, and $\bar{V}_{\text{H}_2\text{O}}$ is the partial molal volume of water in the solution. We have used experimental data taken from the International Critical Tables [7] and from Zarembo et al. [8] to calculate $a_{\text{H}_2\text{O}}(T, m)$ over wide ranges of temperature (0–200°C) and KOH concentration (0.1–20 mol kg⁻¹) at a pressure equal to 1 bar at temperatures between 0 to 100°C and at the steam pressure of pure water at temperatures above

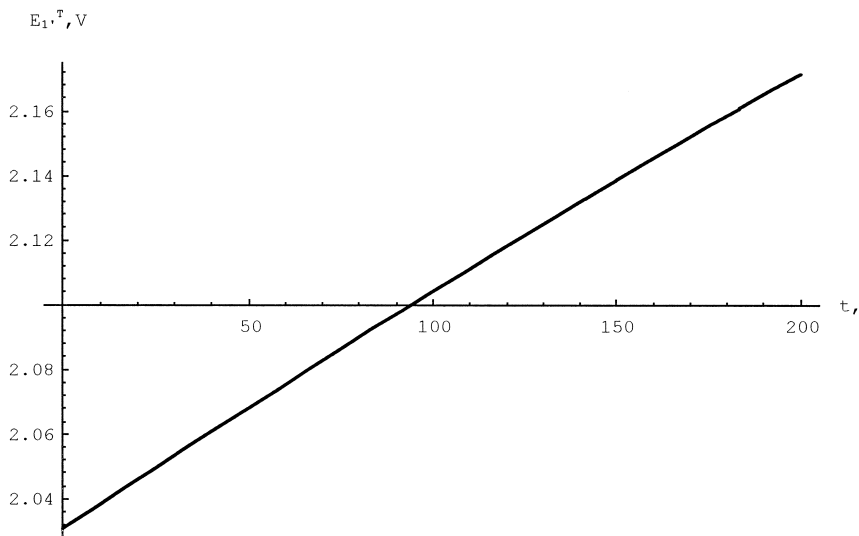
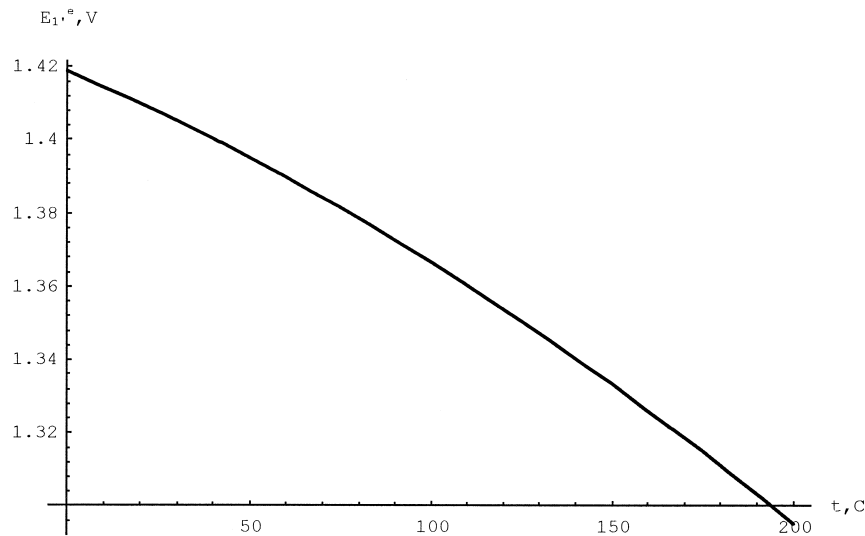


Fig. 4. The temperature dependences of equilibrium $E_1^c(T)$ (a) and thermoneutral $E_1^T(T)$ (b) cell voltage for Ni–Cd battery.

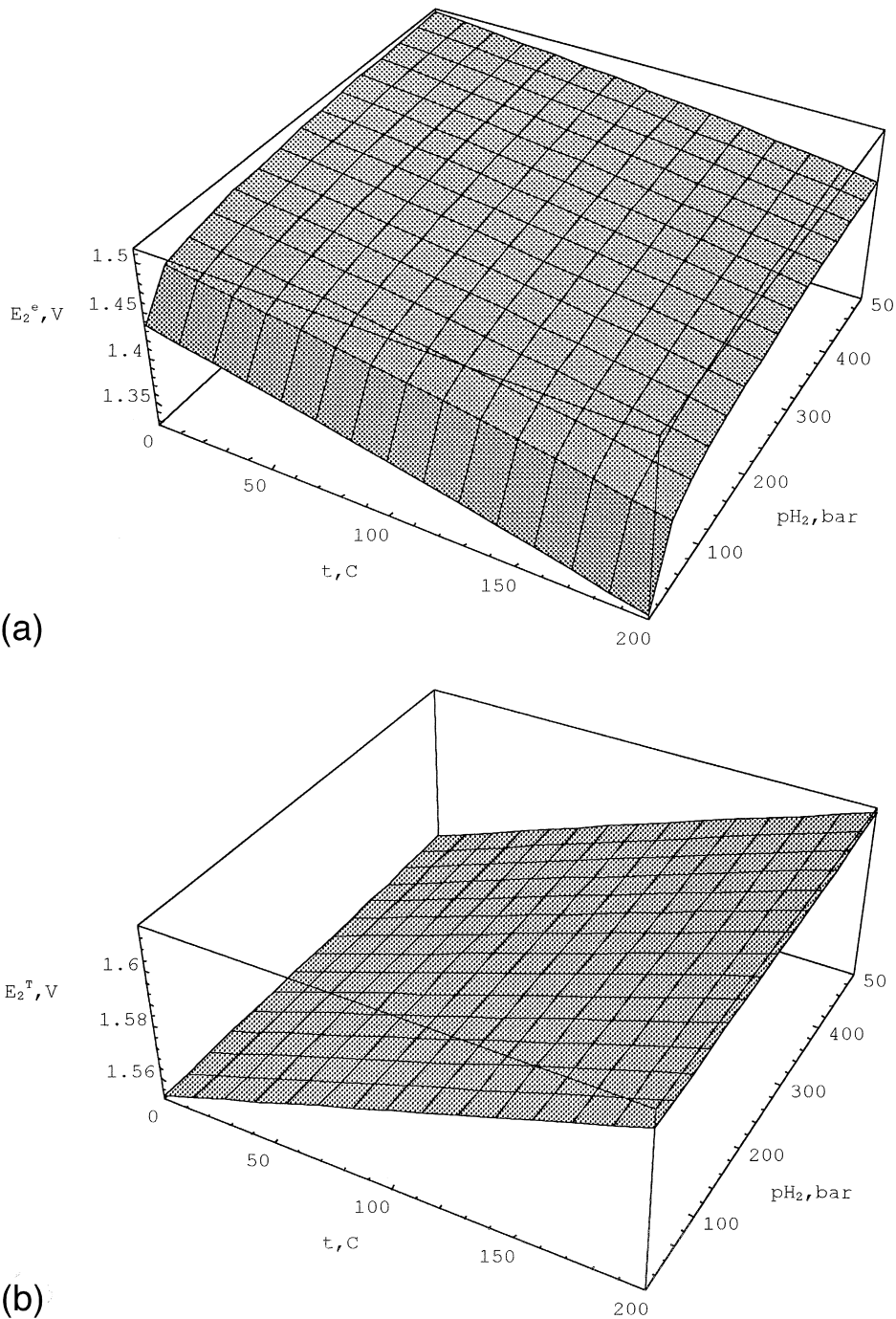


Fig. 5. The temperature–hydrogen pressure surfaces of equilibrium $E_2^e(T, p)$ (a) and thermoneutral $E_2^T(T, p)$ (b) cell voltage for Ni–H₂ battery.

100°C. The derived $a_{\text{H}_2\text{O}}(T, m)$ values were fitted to the following expression [6]

$$a_{\text{H}_2\text{O}}(T, m) = \exp \left\{ (-2m/55.51) \times \left[1 - A_{\text{D-H}} (B_{\text{D-H}}^3 \dot{a}^3 m)^{-1} \left((1 + B_{\text{D-H}} \dot{a} \sqrt{m}) - 2 \ln(1 + B_{\text{D-H}} \dot{a} \sqrt{m}) - (1 + B_{\text{D-H}} \dot{a} \sqrt{m})^{-1} \right) + Bm + Cm^2 + Dm^3 \right] \right\} \quad (23)$$

where $A_{\text{D-H}}$, $B_{\text{D-H}}$, and \dot{a} are the Debye–Huckel theory

parameters and B , C , D are the empirical parameters that are determined by regression analysis. The values of $A_{\text{D-H}}$ and $B_{\text{D-H}}$ were calculated using density and dielectric constant data for water taken from Ref. [4] and \dot{a} was taken as a constant equal to 0.45 nm. The empirical parameters B , C , D were fitted by following polynomial equations

$$B = \sum_0^2 b_i t^i \quad (24)$$

$$C = \sum_0^2 c_i t^i \quad (25)$$

$$D = \sum_0^2 d_i t^i \quad (26)$$

were coefficients b_i , c_i , and d_i are given in Table 3.

Calculated values of water activity for KOH(aq) solutions for temperature between 0 and 200°C and for KOH concentrations between 0.1 and 20 mol kg⁻¹ are given in

Table 4. In Figs. 1 and 2, deviations between the observed [7,8] and calculated $a_{\text{H}_2\text{O}}(T,m)$ values are presented as a function of KOH concentration. The standard deviation of the calculated data from the observed values is also shown in Figs. 1 and 2 by the dotted line. As can be seen these figures, the standard deviations were found to be around 0.002 at low temperatures and around 0.005 at high temperatures. The standard deviations correspond closely to the experimental errors in $a_{\text{H}_2\text{O}}(T,m)$ given in Refs. [7,8].

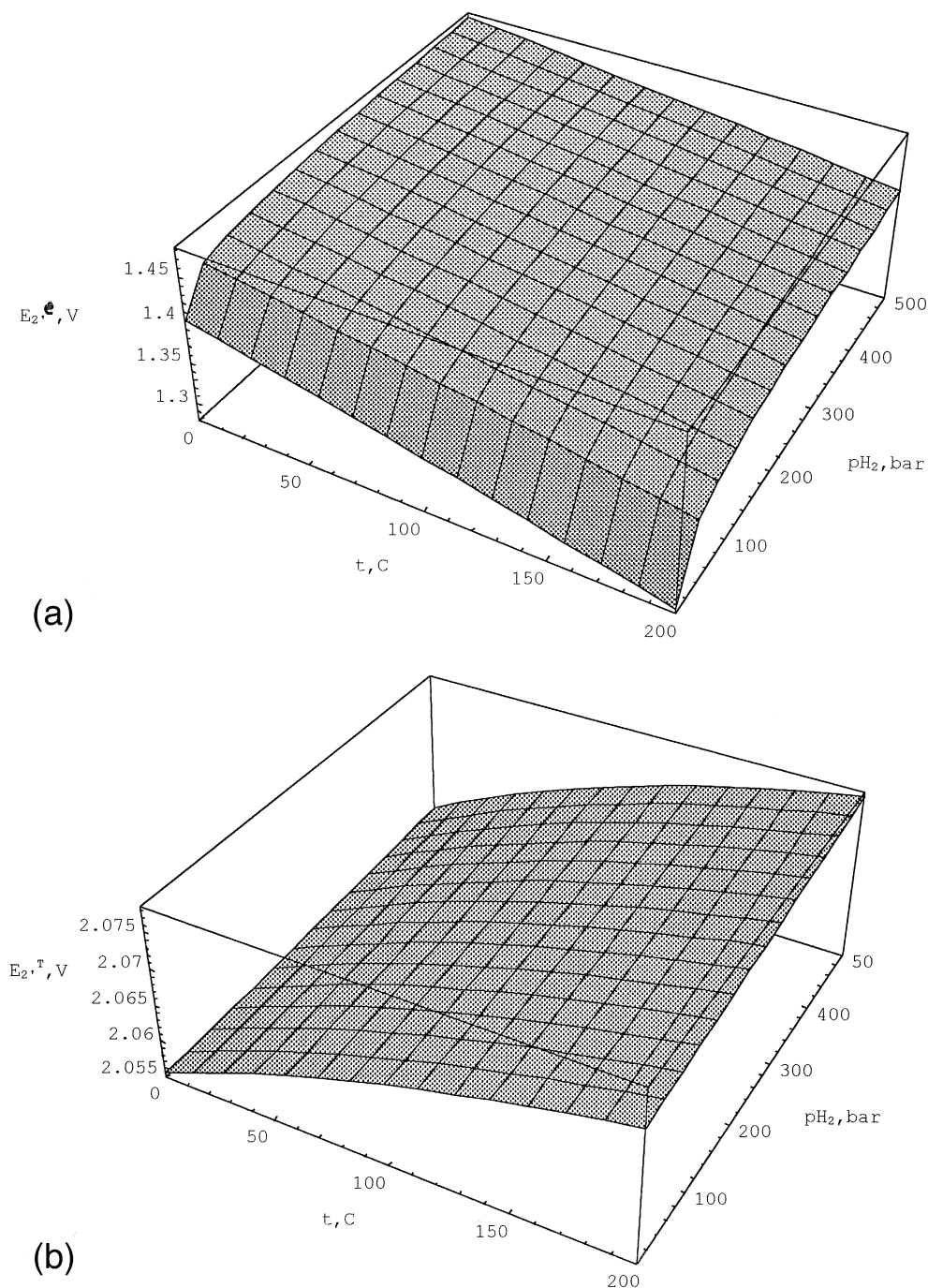


Fig. 6. The temperature–hydrogen pressure surfaces of equilibrium $E_2^e(T,p,m)$ (a) and thermoneutral $E_2^T(T,p,m)$ (b) cell voltage for Ni–H₂ battery at 10 mol kg⁻¹ KOH(aq) concentration.

The hydrogen fugacity, $f_{\text{H}_2}(T, p)$, was estimated over wide ranges of temperatures (0–200°C) and pressures (1–500 bar) from the molar volume of the gas, V_{H_2} , using the following expression:

$$\ln f_{\text{H}_2}(T, p) = \ln p + \frac{1}{RT} \int_0^p \left(V_{\text{H}_2} - \frac{RT}{p} \right) dp \quad (27)$$

The experimental data for V_{H_2} were taken from the paper

of Reynolds [9] and the calculated values of the fugacity coefficients, $f_{\text{H}_2}(T, p)/p$, are given in Table 5.

The derived thermodynamic data were employed to estimate the equilibrium and thermoneutral cell voltages for Ni–Cd and Ni–H₂ batteries as functions of temperature, hydrogen pressure, and KOH(aq) concentration, and these calculations are presented in Figs. 3–7. These surfaces are also expressed in the form of multi-variable equations, so that the reader can calculate equilibrium and thermoneutral potentials for any given set of conditions.

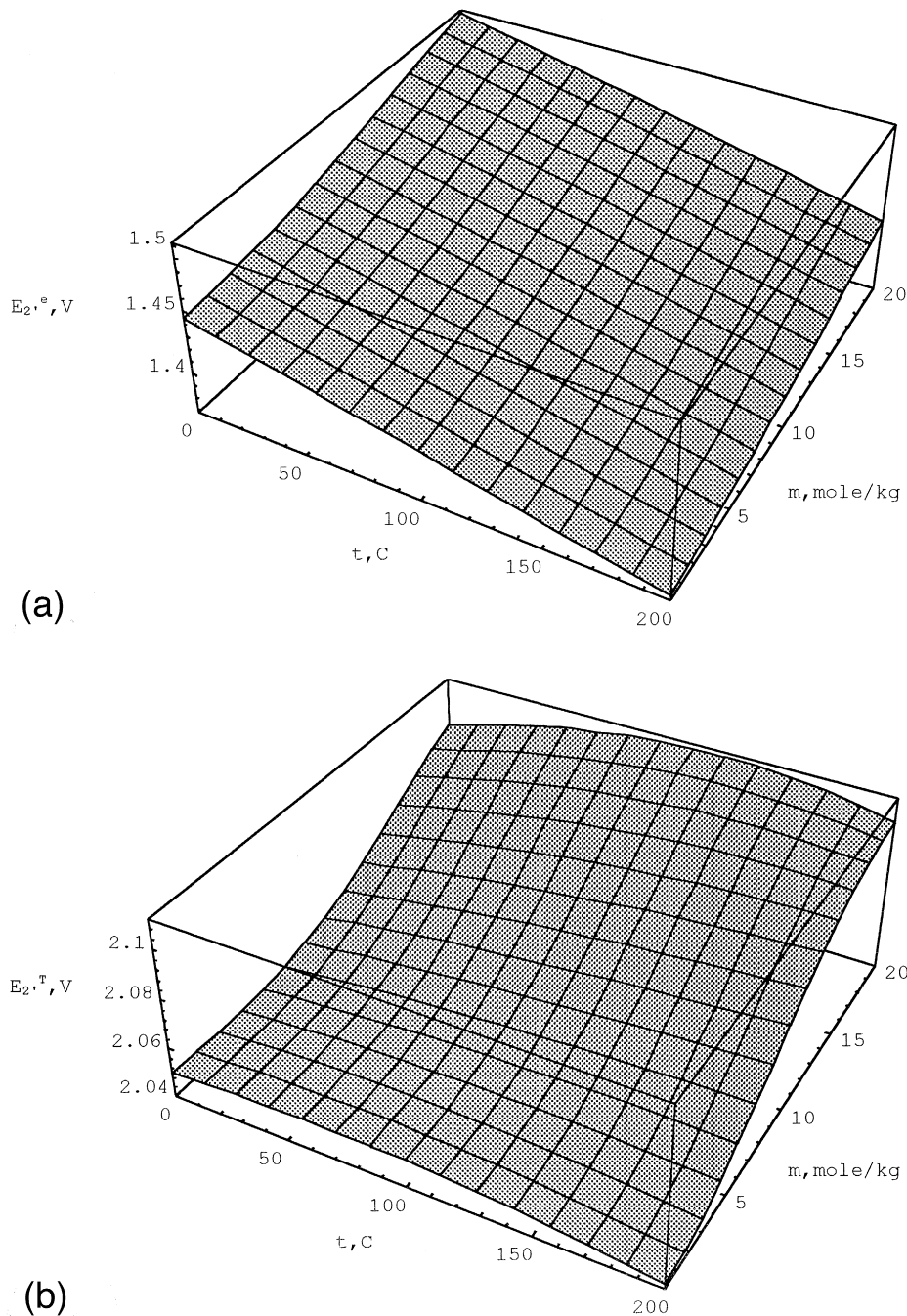


Fig. 7. The temperature–hydrogen pressure surfaces of equilibrium $E_2^E(T, p, m)$ (a) and thermoneutral $E_2^T(T, p, m)$ (b) cell voltage for Ni–H₂ battery at 200 bar hydrogen pressure.

4. Discussion

The present work was undertaken to address shortcomings in previous studies of the thermodynamics of Ni–Cd and Ni–H₂ batteries, particularly with respect to the ranges of the state variables (temperature, hydrogen pressure, and KOH concentration) and with regards to the effect of non-ideality. Thus, particular care has been to include corrections for the non-ideal behavior of H₂ gas at elevated pressures and of KOH solutions at very high solute concentrations. However, as noted previously [3], the data base for the active components in the nickel positive electrode are still uncertain, with respect to both the identity of the phases (e.g., ‘NiOOH’ vs. ‘NiOOH · H₂O’) and the thermodynamic parameters that have been assigned to the assumed compounds.

As can be seen from Figs. 3–7, the equilibrium potentials for both Ni–Cd and Ni–H₂ batteries decrease with increasing temperature and increase with increasing pressure over whole range of investigated temperature, hydrogen pressure, and KOH(aq) concentration. From Figs. 3–7, we note a pronounced effect of KOH(aq) concentration, in that the equilibrium potentials for Eq. (1a) decreases with increasing concentration of KOH(aq) while the equilibrium potentials for Eq. (2b) increases with increasing concentration of KOH(aq).

The thermoneutral potentials, which correspond to the voltages at which the cells would have to operate at so that the entropic dissipation of energy is zero, for both Ni–Cd and Ni–H₂ batteries increases with increasing temperature with exception of Eq. (2b), where there is almost no temperature dependence is observed over whole range of KOH(aq) concentration.

Finally, the equilibrium and thermoneutral potentials for all four cell reactions (Eqs. (1a), (1b), (2a) and (2b)) increase with increasing partial pressure of hydrogen. Typ-

ically, the correction to the potentials due to the non-ideal behavior of hydrogen is of the order of only a few millivolts, but much larger corrections occur because of the non-ideality of the electrolyte. Thus, for Eqs. (1a) and (2b), that are the only reactions in which ‘free’ water appears, the (opposite) correction is given by $(RT/F)\ln\gamma_{\text{H}_2\text{O}}$, where $\gamma_{\text{H}_2\text{O}} = a_{\text{H}_2\text{O}}/x_{\text{H}_2\text{O}}$ is the activity coefficient of water, and $x_{\text{H}_2\text{O}}$ is the mole fraction of water in aqueous KOH solution. The value of $\gamma_{\text{H}_2\text{O}}$ ranges from 0.997 to 0.136 at 0°C and from 0.998 to 0.358 at 200°C, that gives rise to the corrections of 0 to around 50 mV over the entire range of conditions explored.

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