E_r–pH AND E_r–m_{KOH} DIAGRAMS FOR NICKEL AT 25 °C

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Based on the conclusion that no Ni(III) oxo compounds can exist in oxidized nickel oxide electrodes with the total oxidation number $2.0 < z_{Ni} <$ approx. 3.6 and that non-ideal solid solutions with a formal composition $(1 - X_2)$ $Ni(OH)_2 . X_2 NiO_2 . x H_2O$ are involved, E_r–pH and E_r–m_{KOH} diagrams at 25 °C were calculated and graphically represented using the thermodynamic standard data determined for hypothetical $NiO_2 . x H_2O$. The calculations were performed assuming $a_{H_2O} = 1$ in the entire pH range (E_r–pH diagram) and considering the true water activity in KOH solutions of various concentrations (E_r–m_{KOH} diagram).

Key words: Nickel oxide electrodes; E_r–pH diagram; E_r–m_{KOH} diagram.

For the construction of the original E_r–pH diagram for the nickel–water system according to Pourbaix[1] (Fig. 1) the solid substances Ni, NiO, Ni_3O_4, Ni_2O_3 and NiO_2 and their hydrated forms $Ni(OH)_2$, $Ni_3O_4 . 2 H_2O$, $Ni_2O_3 . H_2O$ (= 2 NiOOH) and $NiO_2 . 2 H_2O$ were considered. In these substances, nickel was regarded as zero-, bi-, tri- and/or tetravalent. This view was also shared in later studies (e.g. ref.[2]), although Latimer[3] had already expressed certain doubts about the existence of Ni_2O_3 as chemical individual. After previous experimental results[4], Novakovskii and Uflyand have proved that the assumption of the existence of Ni_3O_4 and $Ni_3O_4 . 2 H_2O$ was unjustified[5]. Accordingly, Silverman published a revised E_r–pH diagram for Ni (ref.[6]). However, this diagram did not include the existence region of NiO_2 and/or $NiO_2 . 2 H_2O$ due to the unsufficient reliability of thermodynamic data for these substances, although the existence of systems with the average oxidation number of nickel in the range of $2.0 \leq z_{Ni} \leq$ approx. (3.7 ± 0.1) is uncontested. The E_r–pH diagram according to Silverman (Fig. 2) must therefore be regarded as too much simplified. In spite numerous publications on this problem (for a survey see e.g. refs[7–14]), there still is the question whether or not Ni(III) oxo compounds also exist as defined chemical individuals in these solid oxo systems in addition to Ni(II) and Ni(IV). Results were found in recent studies affirming (e.g. refs[15–18]) and also contesting[19,20,44,45] the existence of Ni(III) substances. Unclearness is also reflected by the fact that higher valent Ni oxo compounds have not been specified at all in well-known recent tables of thermodynamic data[21–23], with the exception of

Ni_2O_3 and $Ni(OH)_3$ in ref.[21]. Moreover, higher valent solid Ni oxo compounds have been found in several evidently metastable modifications not always precisely defined[7–14,42].

In our previous studies[24,25] on the composition and thermodynamics of higher Ni oxo compounds we were able to show by reevaluating earlier measurements by other

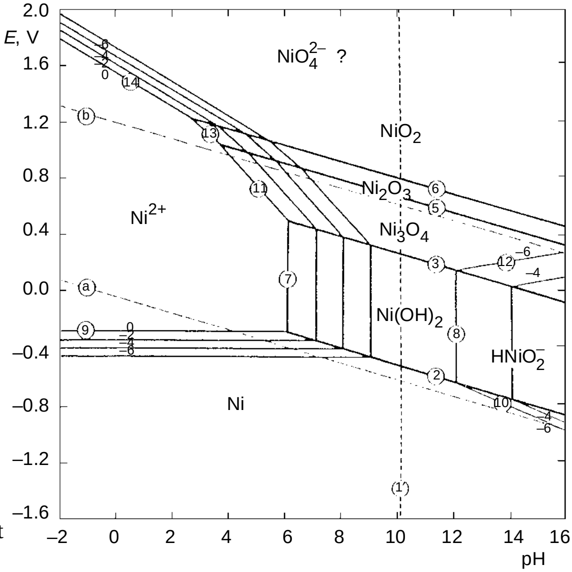

FIG. 1
Original E_r–pH diagram for nickel at 25 °C according to Pourbaix[1]

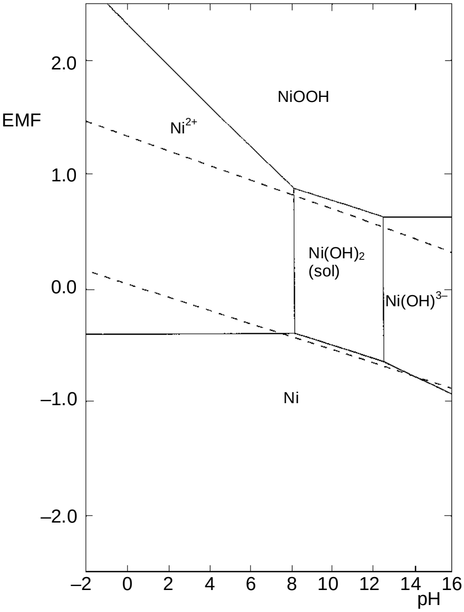

FIG. 2
Revised E_r–pH diagram for nickel at 25 °C according to Silverman[6]

authors of reversible and quasireversible electrode potentials of solid nickel oxo systems in the wide range of $z_{\mathrm{Ni}} = 2.0–3.6$ that such systems can be considered as nonideal solid solutions of Ni(II) and Ni(IV) components with unlimited miscibility and that any Ni(III) oxo compounds do not occur under these conditions. At the same time, we derived and estimated with a sufficient reliability standard values of ΔG_f^0, ΔH_f^0 and S^0 of hypothetical pure $NiO_2 . x\ H_2O$ compounds (with x = 0, 1 or 2) at 25 °C. These results enabled us also to recalculate the E_r–pH and E_r–m_{KOH} diagrams for nickel at 25 °C, which will be reported in more detail in the following.

RESULTS AND DISCUSSION

Thermodynamic Data of Individual Components Considered

The following solid substances were considered in the calculations: Ni, NiO, $Ni(OH)_2$ and hypothetical $NiO_2 . x\ H_2$) (x = 1 or 2); solid nickel oxohydroxo compounds with variable total oxidation number $2.0 < z_{\mathrm{Ni}} \leq$ approx. (3.7 ± 0.1) were regarded as solid solutions of $Ni(OH)_2$ and $NiO_2 . x\ H_2O$ with the formal composition $(1 - X_2)\ Ni(OH)_2 . X_2\ NiO_2 . x\ H_2O$ on the basis of previous studies[24,25] in which $Ni(OH)_2$ was assumed as being completely undissociated and $NiO_2 . x\ H_2O$ as completely dissociated according to

$$NiO_2 . x\,H_2O \quad = \quad H^+ + NiO_2 . (x - 1)\ H_2O . OH^- \quad . \qquad (A)$$

Any possible alkali metal cations, which were only found in the crystal lattice of such systems at higher total oxidation number $z_{\mathrm{Ni}} >$ approx. 3–3.3 (depending on the concentration of the alkali hydroxide solution with which they were in contact)[14,20,26,27], were not taken into consideration due to their unknown influence on the thermodynamic values ΔG_f and S of the solid solutions concerned.

The dissolved substances considered were Ni^{2+} in the acidic range, and $HNiO_2^-$ and $Ni(OH)_3^-$ ions in the alkaline range. In the limited medium pH range, $Ni(OH)^+$ and undissociated $Ni(OH)_2$ (aq) may be additionally considered according to Tremaine and Leblanc[28], but these substances were not taken into consideration in the present calculations for the sake of simplicity and also due to insufficient reliability of the thermodynamic data. Since according to solubility measurements of NiO at 423–573 K (ref.[28]) the molality of $Ni(OH)^+$ below 400 K is statistically insignificant, the mentioned simplification at 25 °C may be considered as justified. Not completely clarified is the question whether Ni(II) anions also occur as $Ni(OH)_3^-$ or $HNiO_2^-$ in alkaline solutions. In most studies (e.g. refs[1,3,29]) dehydrated $HNiO_2^-$ anions were assumed, Tremaine and Leblanc[28] considered the hydrated $Ni(OH)_3^-$ only. Simple inorganic oxo and oxohydroxo anions with higher nickel valence are so far unknown, although complex and metal-organic Ni(III) compounds and their non-aqueous solutions have already been reported (e.g. refs[30,31]).

The thermodynamic standard data of individual substances at 25 °C used in the present calculations are compiled in Table I.

For the reaction

$$Ni(OH)_3^- \,(aq) \quad = \quad HNiO_2^- \,(aq) \; + \; H_2O\,(liq) \qquad (B)$$

these data provided $\Delta G^0_{(2)} = –0.93$ kJ mol^{-1}, which can be considered as $\Delta G^0_{(2)} \approx 0.0$ kJ mol^{-1} in view of the experimental scattering range (see refs[28,29]). This clearly leads to the conclusion that the $HNiO_2^-$ and $Ni(OH)_3^-$ anions may be regarded as thermodynamically equivalent. Their concentration ratio is only influenced by the water activity so that in more concentrated alkaline solutions with reduced water activity ($a_{H_2O} < 1.0$) the dehydrated form, $HNiO_2^-$ (aq), can be assumed as the more probable one. The present calculations therefore considered only this form. Our previous studies[25] also revealed that the differently hydrated forms of hypothetical pure $NiO_2 \,.\, x\,H_2O$ are thermodynamically equivalent to each other. For reasons of simplification, hypothetical monohydrate, $NiO_2 \,.\, H_2O$, was therefore considered in the calculations.

TABLE I
Thermodynamic standard data of individual substances considered at 25 °C

Substance	$-\Delta H^0_f$, kJ mol^{-1}	$-\Delta G^0_f$, kJ mol^{-1}	S^0, J mol^{-1} K^{-1}	Reference
Ni(s)	0.0	0.0	29.87	21
NiO(s)	239.7	211.7	37.99	21
$Ni(OH)_2$(s)	540.26	457.7	88.77	25
$NiO_2 \,.\, H_2O$(s)[a]	545.	439.16	94.6	25
$NiO_2 \,.\, 2\,H_2O$(s)[a]	844.	676.30	139.	25
Ni^{2+}(aq)		45.03	–128.9	21, 25
$HNiO_2^-$(aq)	441.49[b]	353.6[c]	70.94[d]	
$Ni(OH)_3^-$(aq)		589.8		28
H_2(g)	0.0	0.0	130.684	21
H^+(aq)	0.0	0.0	0.0	21
H_2O(liq)	285.830	237.129	69.91	21
OH^-(aq)	229.994	157.244	–10.75	21

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[a] Hypothetical pure substance; [b] recalculated from $\Delta G^0_f(HNiO_2^-$ aq$) = –82.0$ kcal mol^{-1} (= –343.09 kJ mol^{-1}) according to ref.[32] using the corrected value for $\Delta G^0_f(Ni(OH)_2$,s) according to ref.[25]; [c] calculated according to Couture and Laidler[39] for $r_{Ni–O} = 2.058$ Å (ref.[40]); [d] calculated from ΔG^0_f and S^0 values of this compound and corresponding data of $Ni(OH)_2$, H_2O and OH^-.

Calculation of the E_r*–pH Diagram*

According to the above, for the calculation of E_r–pH in the valence range Ni(0)–Ni(II) the following reactions were taken into account (electrochemical reactions are written for the reduction process).

$$Ni^{2+} + 2\ e = Ni \tag{C}$$

$$NiO + 2\ H^+ + 2\ e = Ni + H_2O \tag{D}$$

$$Ni(OH)_2 + 2\ H^+ + 2\ e = Ni + 2\ H_2O \tag{E}$$

$$NiO + H_2O = Ni(OH)_2 \tag{F}$$

$$Ni(OH)_2 = HNiO_2^- + H^+ \tag{G}$$

$$Ni^{2+} + 2\ H_2O = HNiO_2^- + 3\ H^+ \tag{H}$$

$$HNiO_2^- + 3\ H^+ + 2\ e = Ni + 2\ H_2O \tag{I}$$

The calculated values of standard Gibbs energies ΔG^0, standard potentials E^0 and equilibrium constants (as log K) of individual reactions are compiled in Table II.

The pH and activity dependence of the equilibrium states in systems under consideration are given by the corresponding equations (*1*)–(*6*); the water activity was assumed as $a_{H_2O} = 1.0$ in the whole pH region, as is usual for Pourbaix diagrams[1].

$$E_{r(C)} = -0.23335 + 0.2953 \log a_{Ni^{2+}} \tag{1}$$

$$E_{r(D)} = 0.13178 - 0.05916\ pH \tag{2}$$

$$E_{r(E)} = 0.08581 - 0.05916\ pH \tag{3}$$

$$\log a_{HNiO_2^-} = -18.2337 + pH \tag{4}$$

$$\log (a_{HNiO_2^-}/a_{Ni^{2+}}) = -29.0275 + 3\ pH \tag{5}$$

$$E_{r(I)} = 0.62527 + 0.02958 \log a_{HNiO_2^-} - 0.088739 \text{ pH} \qquad (6)$$

The negative value of $\Delta G^0_{(F)} = -8.871$ kJ mol^{-1} for the hydration of NiO to $Ni(OH)_2$ shows that under standard conditions, i.e. involving pure water with $a_{H_2O} = 1.0$, NiO is thermodynamically instable and should be spontaneously hydrated to $Ni(OH)_2$. A theoretical coexistence of the two pure phases in the form of a solid two-phase mixture is only possible if the relation $a_{H_2O} = 1/K_{(F)}$ is fulfilled, i.e. at 25 °C the water activity in the aqueous phase would have to be $a_{H_2O} = 0.0279$. However, since the driving force of NiO hydration is not excessively strong even in pure water and it further decreases with increasing temperature, the velocity of this process is practically zero as the hydration of separately prepared NiO to $Ni(OH)_2$ was never observed[33,34]. This fact was also veryfied by the application of NiO diaphragms for advanced water electrolysis[35–38].

In accordance with the fact that $Ni(OH)_2$ occurs as a thermodynamically stable substance compared to NiO in contact with alkaline non-complexing aqueous solutions, $Ni(OH)_2$ was observed almost exclusively as a product of the anodic oxidation or cor-

TABLE II
Calculated values of the standard Gibbs energies ΔG^0, standard potentials E^0, and equilibrium constants log K of individual reactions at 25 °C

Reaction	ΔG^0, kJ mol^{-1}	E^0, V	log K
(*C*)	45.03	–0.23335	–
(*D*)	–25.429	0.13178	–
(*E*)	–16.558	0.08581	–
(*F*)	–8.871	–	1.5541
(*G*)	104.10	–	–18.2377
(*H*)	165.668	–	–29.0275
(*I*)	–120.66	0.62527	–
(*J*)	–317.26	1.6441	–
(*K*)	–255.68	1.3250	–
(*L*)	–246.8	1.2790	–
(*M*)	–151.57	0.7855	–
(*N*)	–16.558	0.08581	–
(*O*)	–40.773	0.21129	–
(*P*)	–255.68	1.3250	–
(*R*)	–231.45	1.1994	–
(*S*)	24.215	–	–4.24231

rosion of metallic nickel at not too positive anodic potentials, since the standard potential for its formation according to Eq. (*E*) is by about 46 mV more negative than for the formation of NiO (see Table II). Nickel(II) hydroxide also occurs as the end product during the reduction of the charged nickel oxide electrodes with $z_{Ni} > 2.0$ in different types of nickel batteries (Ni–Fe, Ni–Cd, Ni–Zn or Ni–H_2)[8,10–14].

Additional oxidation of Ni(II) compounds to the Ni(IV) can be formally expressed by the following equations with the hypothetical pure $NiO_2 \,.\, H_2O$ as final product (for $x = 1$) (all reactions are written in the reversed direction).

$$NiO_2 \,.\, H_2O + 4\ H^+ + 2\ e = Ni^{2+} + 3\ H_2O \qquad (J)$$

$$NiO_2 \,.\, H_2O + 2\ H^+ + 2\ e = Ni(OH)_2 + H_2O \qquad (K)$$

$$NiO_2 \,.\, H_2O + 2\ H^+ + 2\ e = NiO + 2\ H_2O \qquad (L)$$

$$NiO_2 \,.\, H_2O + H^+ + 2\ e = HNiO_2^- + H_2O \qquad (M)$$

The standard data of these reactions at 25 °C are also listed in Table II. As is also shown by these data, $Ni(OH)_2$ can be considered as thermodynamically more stable in comparison to NiO under standard conditions at 25 °C since a higher potential would be necessary for its oxidation to $NiO_2 \,.\, H_2O$.

In fact, hypothetical pure $NiO_2 \,.\, H_2O$ does not take part in reactions (*J*)–(*M*), but its nonideal solid solutions with the already mentioned formal composition $(1 - X_2)$ $Ni(OH)_2 \,.\, X_2\ NiO_2 \,.\, x\ H_2O$ (refs[24,25]). Accordingly, the real activities of individual components of the solid solutions must be included in the respective Nernst equations. Due to the relations and results in ref.[25] and under the mentioned simplifying assumption of $a_{H_2O} = 1.0$ in the entire pH range, the following is obtained after corresponding conversion.

$$E_{r(J)} = 1.6441 - 0.02958 \log a_{Ni^{2+}} - 0.1183\ pH + $$
$$+ 0.05916 \log (X_2/(1 + X_2)) + 0.05044/(1 + X_2)^2 \qquad (7)$$

$$E_{r(K)} = 1.3250 - 0.05916\ pH - 0.02958 \log ((1 - X_2^2)/X_2^2)) - $$
$$- 0.05044\ (2X_2^2 - 1)/(1 + X_2)^2 \qquad (8)$$

$$E_{r(M)} = 0.7855 - 0.02958 \log a_{HNiO_2^-} - 0.02958\ pH + $$
$$+ 0.05918 \log (X_2/(1 + X_2)) + 0.05044/(1 + X_2)^2 \qquad (9)$$

Here, X_2 denotes the molar fraction of the hypothetical pure $NiO_2 . x H_2O$ in its solid solution with $Ni(OH)_2$. Since the solid solution is considered to consist of $Ni(OH)_2$ and $NiO_2 . x H_2O$, the Nernst equation for reaction (*L*) was not taken into account.

All necessary relations are thus available which are required for constructing the E_r–pH diagram at 25 °C. The diagram under the usual assumption of $a_{H_2O} = 1.0$ in the entire pH range is shown in Fig. 3. In the range of existence of Ni(0) and Ni(II) the diagram is practically of the same design as the original one according to Pourbaix[1] (Fig. 1) with only slight alterations due to correct standard data of Ni^{2+}(aq) and $Ni(OH)_2$(s) (ref.[25]).

However, fundamental changes occur in the range of existence of higher nickel oxo compounds. In accordance with the assumed non-existence of solid Ni(III) oxohydroxy compounds[24], no existence region of Ni(III) containing compounds is found either. The formation of solid solutions with the mentioned formal composition at various total oxidation number $z_{Ni} = 2 X_2 + 2$ only begins under reversible conditions near or above the equilibrium potential of the oxygen electrode in the same solution (e.g. solid solution with $X_2 = 0.005$, i.e. with $z_{Ni} = 2.01$ is formed at $E_r = 1.239$ V (SHE) at 25 °C and pH 0). The displacement of the equilibrium potential of the formation of solid solutions with increasing total oxidation number z_{Ni} is plotted in Fig. 3 by solid lines together with corresponding z_{Ni} values. Different slopes of these lines in acidic and alkaline solutions correspond to different pH dependences of the formation of solid solutions with the same composition from acid and alkaline solutions (see Eqs (*7*)–(*9*)). The rather small displacement of the equilibrium potentials towards more positive values

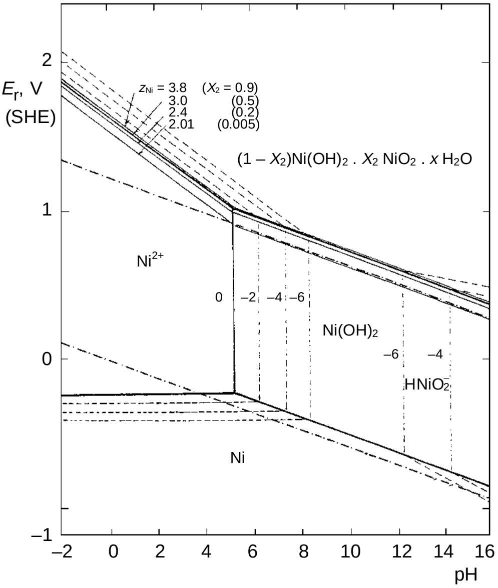

FIG. 3
E_r–pH diagram for nickel at 25 °C calculated from the data of this work

with increasing z_{Ni} in the rather large range from approx. 2.4 to 3.8 is apparently attributable to the nonideal behaviour of solid solutions of $Ni(OH)_2 + NiO_2 . x H_2O$ (ref.[25]). The equilibrium activities of the ions, Ni^{2+}(aq) and $HNiO_2^-$ (aq), whose logarithm in the molality scale is indicated numerically, are plotted by dotted lines.

Calculation of E_r–m_{KOH} Diagram

The representation of the E_r–pH diagram according to Pourbaix[1] under the assumption of a_{H_2O} = 1.0 in the entire pH range has certain advantages, but also disadvantages. The greatest advantage is the general validity of the diagram for arbitrary non-complexing aqueous solution and its simple construction due to the corresponding Nernst equations, without the necessity to know actual concentration and pH dependence of the activities of individual reactants. The disadvantages of this form of representation include:

1) the invalidity of the simplifying assumption of a_{H_2O} = 1.0 especially at extreme pH values (e.g. in 12 M KOH, i.e. approx. 10 M KOH, a_{H_2O} = 0.350 at 25 °C (ref.[41]);

2) the necessity to know activities and activity coefficients of individual reacting ions and undissociated substances as well as of water for a given solution composition in case when the E_r–pH diagram should be applied for solving concrete real problems as exact as possible;

3) E_r values relative the standard hydrogen electrode (SHE) at pH 0 can differ less or more pronouncely from the experimentally measured values if these include liquid-junction potentials not defined in more detail.

In order to eliminate these disadvantages, we have used the form of the E_r–m_{KOH} diagram for the application pursued by us (problem of advanced alkaline water electrolysis). The equilibrium potential of the system studied, related to the equilibrium potential of the hydrogen electrode in the same solution (RHE), can be easily achieved experimentally and precisely determined with the aid of this one or another easily achievable reference electrode with the same pH dependence of the reversible potential, e.g. $Hg/HgO/OH^-$ electrode. Such a system is not accompanied with any liquid-junction potential difference. A further advantage of this type of representation is the pH independence of the equilibrium potential differences of most cell reactions against the hydrogen reference electrode in the same solution. In order to include the variable water activity in KOH solutions of various molality in this representation mode, the following earlier derived relation was used[41]:

$$\log a_{H_2O} = -0.02255 m_{KOH} + 0.001434 m_{KOH}^2 + (1.38 m_{KOH} - 0.9254 m_{KOH}^2)/T \qquad (10)$$

or for T = 298.15 K (= 25 °C):

$$\log a_{H_2O} = -0.01792 m_{KOH} - 0.0016698 m_{KOH}^2 \qquad (11)$$

valid for m_{KOH} = 2–18 mol kg^{-1} (H_2O).

In this way, it was also possible to quantitatively evaluate the equilibrium conditions of individual reactions under study as a function of water activity. Since the results of these calculations can also be applied to other cases, the calculation approach will be discussed here in more detail.

The selected representation of the E_r–m_{KOH} diagram for the system investigated is based on the following electrochemical cell reactions with the hydrogen reference electrode in the common electrolyte (i.e. KOH solution of known molality) and the corresponding cathodic and anodic electron balance (±n e).

$$Ni(OH)_2 + H_2 = Ni + 2\ H_2O\ ,\quad n = 2 \tag{N}$$

$$HNiO_2 + H_2 = Ni + H_2O + OH^- \ ,\quad n = 2 \tag{O}$$

$$NiO_2 . H_2O + H_2 = Ni(OH)_2 + H_2O\ ,\quad n = 2 \tag{P}$$

$$NiO_2 . H_2O + H_2 + OH^- = HNiO_2^- + 2\ H_2O\ ,\quad n = 2 \tag{R}$$

Thermodynamic standard data of these reactions are also specified in Table II. It can be seen that $\Delta G^0_{(N)} = \Delta G^0_{(E)}$ and $\Delta G^0_{(P)} = \Delta G^0_{(K)}$, so that also $E^0_{(N)} = E^0_{(E)}$ and $E^0_{(P)} = E^0_{(K)}$. Corresponding Nernst equations (written for $a_{H_2} = p_{H_2} = 1$) became following forms at 25 °C.

$$E_{r(N)} = 0.08581 - 0.05916 \log a_{H_2O} \tag{12}$$

$$E_{r(O)} = 0.21129 - 0.02958 \log ((a_{H_2O}\ m_{KOH}/m_{HNiO_2^-})\ (\gamma_{OH^-}/\gamma_{HNiO_2^-})) \tag{13}$$

$$\begin{aligned} E_{r(P)} = {} & 1.3250 - 0.02958 (\log a_{H_2O} + \log ((1 - X_2^2)/X_2^2)) - \\ & - 0.05044(2X_2^2 - 1)/(1 + X_2)^2 \end{aligned} \tag{14}$$

$$\begin{aligned} E_{r(R)} = {} & 1.1994 - 0.02958 \log ((a_{H_2O}\ m_{HNiO_2^-}/m_{KOH})\ (\gamma_{HNiO_2^-}/\gamma_{OH^-})) + \\ & + 0.05916 \log (X_2/(1 + X_2)) + 0.05044/(1 + X_2)^2 \end{aligned} \tag{15}$$

In the range of $m_{KOH} \geq 1$ mol/(kg H_2O), $m_{KOH} >> m_{HNiO_2^-}$ is applicable so that the equilibrium molality m_{OH^-} may be kept equal to the total molality m_{KOH}, i.e. $m_{OH^-} = m_{KOH}$. As far as the ratio of the activity coefficients $\gamma_{HNiO_2^-}/\gamma_{OH^-}$ was concerned, it was assumed that it might be equalled to 1.0 since it was the ratio of two equally charged ions in the same solution with the same ionic strength. In Eqs (*12*)–(*15*) the water activity according to Eq. (*11*) is to be substituted for the given total molality m_{KOH} as well as the corresponding value of X_2 in Eqs (*31*) and (*32*) for the given total oxidation number $z_{\mathrm{Ni}} = 2X_2 + 2$.

The course of the E_r–m_{KOH} diagram for the Ni–KOH–H_2O system at 25 °C thus calculated is shown in Fig. 4. As can be seen, the equilibrium potential for the Ni/Ni(OH)$_2$ coexistence is slightly shifted to more positive values with increasing KOH molality due to decreasing water activity $a_{\mathrm{H_2O}}$.

In the existence range of pure Ni(OH)$_2$ the equilibrium molality $m_{\mathrm{HNiO_2^-}}$ is given by the equilibrium of the reaction

$$\mathrm{Ni(OH)_2} \;+\; \mathrm{OH^-} \;=\; \mathrm{HNiO_2^-} \;+\; \mathrm{H_2O} \qquad (S)$$

with $\Delta G^0_{(S)} = 24.215$ kJ mol^{-1} at 25 °C. This gives

$$\log m_{\mathrm{HNiO_2^-}} = -4.2431 + \log m_{\mathrm{KOH}} - \log a_{\mathrm{H_2O}} \ . \qquad (16)$$

The potential-independent equilibrium values of log $m_{\mathrm{HNiO_2^-}}$ are listed numerically in Fig. 4 at verticals for the given KOH molalities. The potential dependent equilibrium values of log $m_{\mathrm{HNiO_2^-}}$ for the coexistence of Ni and Ni(OH)$_2$ at given KOH molalities were derived from Eq. (*13*). These values are shown by dotted lines in Fig. 4. Analogously, potential-dependent equilibrium values of log $m_{\mathrm{HNiO_2^-}}$ in coexistence with solid solutions Ni(OH)$_2$/NiO$_2$. x H$_2$O were calculated from Eq. (*15*) for given values of

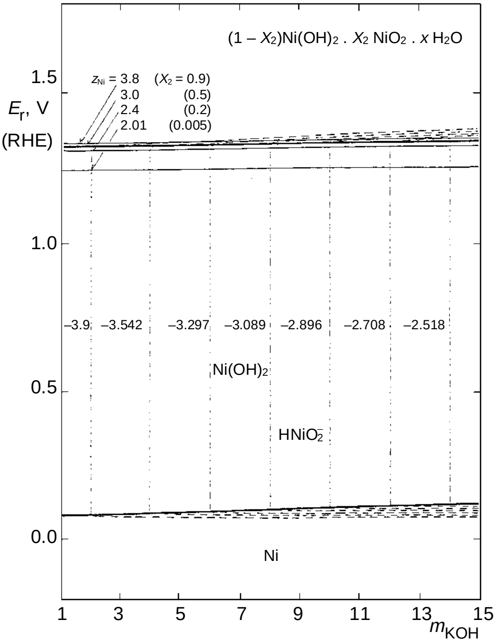

FIG. 4
New E_r–m_{KOH} diagram for nickel at 25 °C calculated from data of this work (RHE scale)

m_{KOH}, a_{H_2O} and z_{Ni} or X_2. For reasons of clarity, these data are only shown by dotted lines in Fig. 4 above the solid line for the coexistence with solid solution with $z_{Ni} = 3.0$ (i.e. for $X_2 = 0.5$).

CONCLUSIONS

The E_r–pH and E_r–m_{KOH} diagrams for nickel at 25 °C constructed by described manner represent well the experimentally observed conditions of the thermodynamically stable existence regions of individual Ni compounds in different valence states and mutual coexistence as a function of the electrode potential (on SHE scale) and pH (in E_r–pH diagram) of aqueous non-complexing solutions, and m_{KOH}, respectively (RHE scale, E_r–m_{KOH} diagram). As already mentioned above, the incorporation of alkaline cations into the crystal lattice of solid solutions $Ni(OH)_2/NiO_2 . x\ H_2O$ was not considered in the present calculations, since the influence of different alkaline cations on the thermodynamic behaviour of solid solutions has so far not been sufficiently determined[43]. In our opinion, however, the experimentally observed incorporation of alkaline cations into the crystal lattice of solid solutions $Ni(OH)_2/NiO_2 . x\ H_2O$ can be regarded as partial neutralization of the Ni(IV) component which can dissociate in the solid solution to mobile H^+ ions and immobile anions $NiO_2 . (x - 1)\ H_2O . OH^-$. According to this concept, no intercalation compound are therefore involved. Also, it was not possible in these calculations to take into consideration any metastable modifications of the nickel oxohydroxo compounds with different total oxidation number $z_{Ni} \geq 2.0$, as often reported in the literature (e.g. refs[8,10–14]), because their thermodynamic properties are known only insufficiently.

The E_r–pH diagram (Fig. 3) is formally similar to the revised EMF–pH diagram according to Silverman[6] (Fig. 2), but the significant difference is that solid solutions $Ni(OH)_2/NiO_2 . x\ H_2O$ with the total oxidation number $2.0 < z_{Ni} \leq 4.0$ are present in the potential region above the equilibrium potential of the oxygen electrode instead of NiOOH. This new revised version of the Pourbaix diagram for nickel can be considered as a thermodynamic completion as well as a support of the recent works of different authors[18–20,44,45], in which the existence of Ni(III) was questioned.

REFERENCES

1. Deltombe E., Zoubov N., Pourbaix M. in: *Atlas d'Equilibres Electrochimiques à 25 °C* (M. Pourbaix, Ed.). Gauthier and Villars, Paris 1963; Engl. Transl. p. 330. NACE, Houston 1974.
2. Macdonald D. D., Syrett B. C.: Corrosion-NACE *35*, 471 (1979).
3. Latimer W. M.: *Oxidation Potentials*, 2nd ed., p. 198. Prentice-Hall, Englewood Cliffs (1952).
4. McEwan R. S.: J. Phys. Chem. *75*, 1782 (1971).
5. Novakowskii A. M., Uflyand N. Y.: Zashch. Met. *13* (11), 22 (1977).
6. Silverman D. C.: Corrosion-NACE *37*, 546 (1981).
7. *Gmelins Handbuch der Anorganischen Chemie*, 8. Aufl., Nickel, Syst. Nr. 57, Teil B, Lief. 2, S. 380, 434, 465. Verlag Chemie, Weinheim 1965.

8. Milner P. C., Thomas U. B. in: *Advances in Electrochemistry and Electrochemical Engineering* (C. W. Tobias, Ed.), Vol. 5, p. 1–86. Interscience Publ., New York 1967.
9. Hoare J. P.: *The Electrochemistry of Oxygen*, p. 271. Interscience, New York 1968.
10. Falk U. in: *Electrochemical Power Sources* (M. Barak, Ed.), p. 324. P. Peregrinus, London 1980.
11. Briggs D. V. in: *Electrochemistry*, Vol. 4, p. 35. The Chemical Society, London 1974.
12. Arvia A. J., Posadas D. in: *Encyclopedia of Electrochemistry of Elements* (A. J. Bard, Ed.), Vol. III, p. 211. Dekker, New York 1975.
13. Gunther R. G., Gross S. (Eds): *The Nickel Electrode,* Proc. Vols 82–84. The Electrochemical Soc., Inc., Peddington 1982.
14. Oliva P., Leonardi J., Laurent J. F., Delmas C., Braconnier J. J., Figlarz M., Fievet F., de Guibert A.: J. Power Sources *8*, 229 (1982).
15. Hahn F., Beden B., Croissant M., Lamy C.: Electrochim. Acta *31*, 335 (1986).
16. Hahn F., Floner D., Beden B., Lamy C.: Electrochim. Acta *32*, 1631 (1987).
17. Beden B., Bewick A.: Electrochim. Acta *33*, 1695 (1988).
18. Chaojoing Zhang, Su-Moon Park: J. Electrochem. Soc. *134*, 2966 (1987).
19. Desilvestro J., Corrigan D. A., Weaver M. J.: J. Electrochem. Soc. *135*, 885 (1988).
20. Corrigan D. A., Knight S. L.: J. Electrochem. Soc. *136*, 613 (1989).
21. Wagman D. D., Evans W. H., Parker V. B., Schumm R. H., Halow I., Bailey S. M., Churney K. L., Nuttall R. L.: J. Phys. Chem. Ref. Data *11*, Suppl. No. 2 (1982).
22. Chase M. W., Jr., Davies C. A., Downey J. R., Jr., Frurip D. J., McDonald R. A., Syverud A. N.: J. Phys. Chem. Ref. Data *14*, Suppl. No. 1 (1985).
23. Barin I.: *Thermochemical Data of Pure Substances*. VCH Verlagsges., Weinheim 1989.
24. Balej J., Divisek J.: Ber. Bunsenges. Phys. Chem. *97*, 929 (1993).
25. Balej J., Divisek J.: Ber. Bunsenges. Phys. Chem. *97*, 933 (1993).
26. Bartl H., Bode H., Sterr G., Witte J.: Electrochim. Acta *16*, 615 (1971).
27. Melendres C. A., Paden W., Tani B., Walczak W.: J. Electrochem. Soc. *134*, 762 (1987).
28. Tremaine P. R., Leblanc J. C.: J. Chem. Thermodyn. *12*, 521 (1980).
29. Gayer K. H., Garrett A. B.: J. Am. Chem. Soc. *71*, 2973 (1949).
30. Nag K., Chakravorty A.: Coord. Chem. Rev. *33*, 87 (1980).
31. Bhattacharya S., Mukherjee R., Chakravorty A.: Inorg. Chem. *25*, 3448 (1986).
32. Nuttall R. L.: Privat communicaiton.
33. Hüttig G. F., Peter A.: Z. Anorg. Allg. Chem. *189*, 183, 190 (1930).
34. Cairns R. W., Ott E.: J. Am. Chem. Soc. *55*, 527 (1933).
35. Divisek J., Schmitz H., Mergel J.: Chem.-Ing.-Tech. *52*, 465 (1980).
36. Divisek J., Schmitz H.: Int. J. Hydrogen Energy *7*, 703 (1982).
37. Divisek J., Malinowski P.: J. Electrochem. Soc. *133*, 915 (1986).
38. Divisek J. in: *Electrochemical Hydrogen Technologies* (H. Wendt, Ed.), p. 137. Elsevier, Amsterdam 1990.
39. Couture A. M., Laidler K. J.: Can. J. Chem. *35*, 202 (1957).
40. *International Tables for X-Ray Crystallography* (K. Lonsdale, Ed.), Vol III. Kynoch Press, Birmingham 1968.
41. Balej J.: Int. J. Hydrogen Energy *10*, 233 (1985).
42. Larramona G., Gutierrez C.: J. Electrochem. Soc. *137*, 428 (1990).
43. Barnard R., Randell C. F., Tye F. L.: J. Appl. Electrochem. *11*, 517 (1981).
44. Greaves C., Malsbury A. M., Thomas H. A.: Solid State Ionics *18*/*19*, 763 (1986).
45. Malsbury A. M., Greaves C.: J. Solid State Chem. *71*, 418 (1987).