DIAGRAMS E_r–m_{KOH} FOR COBALT AT 25–125 °C AND AT TOTAL PRESSURE OF 1–30 BAR*

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Diagrams E_r–m_{KOH} for cobalt were calculated in the range of molality m_{KOH} = 2–18 mol kg^{-1}, temperature t = 25–125 °C and total pressure P = 1–30 bar (0.1–3.0 MPa) on the basis of recent reliable data for individual reaction components. The water activity a_{H_2O}, the equilibrium pressure of the water vapour p_{H_2O} in or above the KOH solutions was considered. The results displayed differences from the original E–pH diagram for cobalt after Pourbaix. The direct oxidation of Co_3O_4 to CoO_2 without any intermediate stage of Co(III) oxo compounds was found to be thermodynamically more favourable. Consideration of the reduced water activity in concentrated KOH solutions led to the finding that solid $Co(OH)_2$ can be dehydrated to CoO at elevated temperatures in contact with KOH solutions. With rising temperature, dehydration can occur at lower KOH molality. CoO_2, not known in a pure form, was assumed to exist as a pure substance in mixtures with other solid Co oxo compounds in lower states of oxidation.

Key words: Corrosion; Cobalt oxo compounds; Alkaline water electrolysis.

The original E–pH diagram for cobalt according to Pourbaix[1] was based on the thermodynamic data of individual compounds, of which some differ more or less from those given in the recent data sources. This can be clearly seen from the summary Table I. Surprisingly large differences can be found for the standard data for Co_3O_4, and smaller deviations were found also for CoO and $Co(OH)_2$. If the individual data in Table I are compared to each other, then the ΔH_f^0 data given in ref.[5] for CoO, $Co(OH)_2$ and Co_3O_4 apparently can be regarded as ΔG_f^0 data. Correspondingly, it can be assumed that the value given in Table I for ΔH_f^0(CoOOH) = –369.36 kJ mol^{-1} according to ref.[5] actually represents ΔG_f^0(CoOOH) since it is close to the difference of $\Delta G_f^0(Co(OH)_3) - \Delta G_f^0(H_2O)$. At the same time this value is quite different from the difference $\Delta H_f^0(Co(OH)_3) - \Delta H_f^0(H_2O)$, calculated, for example, with the aid of standard data for $Co(OH)_3$ and H_2O according to ref.[2]. The completely different ΔH_f^0 values of Co^{2+}(aq)

* 1 bar = 10^5 Pa.

TABLE I
Thermodynamic standard values of single Co-substances at 25 °C

Substance	$-\Delta H_f^0$, kJ mol^{-1}	$-\Delta G_f^0$, kJ mol^{-1}	S^0, J mol^{-1} K^{-1}	Reference
α-Co(s)	0	0	**30.04**	2
	0	0	30.067	3
	0	0	30.041	4, 6
	0	0	28.5	5
Co^{2+}(aq)		53.56		1
	58.2	54.4	–113	2
	2 916(?)			5
Co^{3+}(aq)		–120.9		1
	–92	–134	–305	2
	5 996(?)			5
CoO(s)	–	205.02	–	1
	237.94	**214.20**	**52.97**	2
	237.735	213.988	52.993	3
	237.944	**214.198**	**52.969**	4
	211.3(?)	–	43.9	5
	238.91	215.104	52.72	6
$Co(OH)_2$(s)	–	456.06	–	1
(blue, pptd.)	–	450.1	–	2
	–	449.36	–	6
(pink, pptd.)	539.7	454.3	79	2
	539.698	454.168	78.998	3
	539.74	452.71	–	6
(pink, aged)	–	458.1	–	2
	541.364	**457.31**	**83.7**	6
	453.5(?)	–	82.0	5
	–	459.654	85	7
Co_3O_4(s)	–	702.22	–	1
	891	774	102.5	2
	910.020	**794.871**	**114.286**	3
	910.020	794.901	114.307	4
	745(?)	–	149.8	5
	887.01	768.563	–	6
$Co(OH)_3$(s)	–	596.64	–	1
	716.7	–	–	2
	725.5	**596.417**	**101.07**	6
		596.417	100	7
$Co(OH)_3$(s)	369.36(?)	–	–	5
CoO_2(s)	272.3[a]	**216.9**	–	1
$HCoO_2^-$(aq)	–	347.15	–	1
	–	**345.5**[b]	72.76[c]	
$Co(OH)_3^-$(aq)	–	585.55	–	6
	–	**585.55**	**20**	7
$Co(CO)_4^-$(aq)	–	**725**	**25**	7

[a] Calculated according to ref.[23]. [b] Corrected value according to the private communication of Dr R. L. Nuttall (NBS) replacing the uncorrect original NBS-value[2] of $\Delta G_f^0(HCoO_2^-, aq) = -407.5$ kJ mol^{-1}. [c] Calculated according to ref.[8].

and Co^{3+}(aq) from ref.[5] in comparison to the NBS data[2] cannot be conclusively explained without the original literature in question. All the ΔH_f^0 data according to ref.[5] in Table I should be therefore taken as unsufficiently reliable.

In connection with proposed application of Co(II) or Co(III) for electrocatalytic oxygen evolution from alkaline solutions at nickel anodes[9,10], we calculated the thermodynamic stability of cobalt oxo compounds in question under conditions of advanced alkaline water electrolysis[11] in the intermittent operating mode, as it was also done for iron[12]. It became apparent that the new standard data used for Co_3O_4 and other Co substances altered the shape of the E_r–m_{KOH} diagram distinctly in comparison to the original E–pH diagram[1]. In contrast to the original Pourbaix method[1], the present calculations consider the water activity a_{H_2O} and the equilibrium pressure of water vapour p_{H_2O} in or above KOH solutions for given KOH molality and temperature.

The equilibrium potentials of all cell reactions were related to the hydrogen reference electrode (RHE) in the common solution[13]. In this manner, any liquid junction potential difference is avoided, in contrast to the standard hydrogen reference electrode (SHE) used in Pourbaix diagrams[1].

In this paper we present the results obtained for the molality range m_{KOH} = 2–18 mol kg^{-1}, potential range from –0.3 to 2.0 V (RHE), temperature range of 25–125 °C and the total pressure range of 1–30 bar, which may have a significance for their eventual technical applications.

THEORETICAL AND CALCULATIONS

It follows from the original E–pH diagram after Pourbaix[1] that solid $Co(OH)_3$ arises from the anodic oxidation of Co_3O_4. However, Benson and co-workers[14] have demonstrated that rather CoOOH is formed instead of $Co(OH)_3$. This was also confirmed in further papers[15,16]. In the present calculations, we therefore took metallic α-Co and also CoO, $Co(OH)_2$, Co_3O_4, CoOOH and CoO_2 into consideration as solid substances, and $HCoO_2^-$, $Co(OH)_3^-$ and $Co(OH)_4^-$ as dissolved ions existing in alkaline media. Co(II)-tetrahydroxoanion, $Co(OH)_4^{2-}$, also detected in alkaline solutions[17], was not taken into consideration in our calculations, since its thermodynamic data are not available. The thermodynamic standard data used in our calculations are printed bold in Table I.

Due to the lack or reliable standard data for CoOOH(s) it was assumed, as usual in similar cases[1], that this oxyhydroxide is thermodynamically equivalent to partially dehydrated $Co(OH)_3$(s) so that

$$\Delta G_f^0(\text{CoOOH}) = \Delta G_f^0(\text{Co(OH)}_3) - \Delta G_f^0(\text{H}_2\text{O}) = -359.28 \text{ kJ mol}^{-1} \qquad (A)$$

and

$$\Delta H_f^0(\text{CoOOH}) = \Delta H_f^0(\text{Co(OH)}_3) - \Delta H_f^0(\text{H}_2\text{O}) = -439.67 \text{ kJ mol}^{-1} \qquad (B)$$

resulting to ΔS_f^0(CoOOH) = –269.6 J mol^{-1} K^{-1} and the standard entropy, S^0(CoOOH) = 30.9 J mol^{-1} K^{-1}, all at 25 °C. Standard data for other reaction components H_2(g), H_2O(liq) and OH^-(aq) were taken from refs[2,3]. The coefficients of the temperature dependence of the molar heat capacity of pure substances,

$$C_p^0 = a + b \,.\, 10^{-3}\, T + c \,.\, 10^{-6}\, T^2 + d \,.\, 10^5\, T^{-2} \quad (\text{J mol}^{-1}\ \text{K}^{-1}) \qquad (1)$$

were calculated from available C_p^0 data[3,4] by the least squares method. The values for CoOOH and CoO_2 were estimated from the corresponding values of similar substances given in ref.[18]. All these data are given in Table II. The relations for the temperature dependence of the mean molar heat capacity of individual ions according to the "corresponding principle" after Criss and Cobble[19,20] are given in Table III.

For construction of the E_r–m_{KOH} diagrams under the above mentioned reaction conditions, the following chemical and electrochemical reactions were taken into consider-

TABLE II
Coefficients of the Eq. (*1*) of individual pure substances

Substance	*a*	*b*	*c*	*d*
α-Co(s)	17.47	25.536	–8.98	0.46263
CoO(s)	9.189	116.21	–0.80453	16.367
$Co(OH)_2$(s)	82.42	49.142	–1.3448	0.10301
Co_3O_4(s)	209.89	–171.25	190.27	–46.866
CoOOH	62.6	41.5	–	–
CoO_2	53.63	46	–23.3	–12
H_2(g)	26.2164	4.3911	–0.23311	1.4327
H_2O(liq)	109.91	–189.11	273.87	2.1831

TABLE III
Relations for the average values of molar heat capacities $\overline{C_P^0}\,|\,_{T_1}^{T}$ of the considered ions between T_1 = 298.15 K and *T*, using the "corresponding principle" according to Criss and Cobble[19]

Ion	$\overline{C_P^0}\,|\,_{T_1}^{T}$ J mol^{-1} K^{-1}
OH^-(aq)	(215.01 – 0.72104*T*)/ln (*T*/T_1)
$HCoO_2^-$(aq)	(185.272 – 0.621037*T*)/ln (*T*/T_1)
$Co(OH)_3^-$(aq)	(362.02 – 1.21406*T*)/ln (*T*/T_1)
$Co(OH)_4^-$(aq)	(345.27 – 1.15786*T*)/ln (*T*/T_1)

ation (in electrochemical cell reactions related to the reference hydrogen electrode in the same solution, n denotes the number of exchanged electrons):

$$CoO + H_2 = Co + H_2O , \quad n = 2 \qquad (2)$$

$$Co(OH)_2 + H_2 = Co + 2\ H_2O , \quad n = 2 \qquad (3)$$

$$4\ CoO = Co_3O_4 + Co \qquad (4)$$

$$4\ Co(OH)_2 = Co_3O_4 + Co + 4\ H_2O \qquad (5)$$

$$Co_3O_4 + H_2 = 3\ CoO + H_2O , \quad n = 2 \qquad (6)$$

$$Co_3O_4 + H_2 + 2\ H_2O = 3\ Co(OH)_2 , \quad n = 2 \qquad (7)$$

$$Co_3O_4 + H_2 + 3\ OH^- = 3\ HCoO_2^- + H_2O , \quad n = 2 \qquad (8)$$

$$Co_3O_4 + H_2 + 3\ OH^- + 2\ H_2O = 3\ Co(OH)_3^- , \quad n = 2 \qquad (9)$$

$$Co(OH)_2 = CoO + H_2O \qquad (10)$$

$$Co(OH)_3^- = HCoO_2^- + H_2O \qquad (11)$$

$$Co(OH)_2 + OH^- = Co(OH)_3^- \qquad (12)$$

$$Co(OH)_3^- + H_2 = Co + 2\ H_2O + OH^- , \quad n = 2 \qquad (13)$$

$$Co(OH)_2 + OH^- = HCoO_2^- + H_2O \qquad (14)$$

$$CoO + OH^- = HCoO_2^- \qquad (15)$$

$$HCoO_2^- + H_2 = Co + H_2O + OH^- , \quad n = 2 \qquad (16)$$

$$3\ CoOOH + 0.5\ H_2 = Co_3O_4 + 2\ H_2O\ ,\quad n = 1 \qquad (17)$$

$$CoOOH + 0.5\ OH^- = Co(OH)_3^-\ ,\quad n = 1 \qquad (18)$$

$$CoOOH + 0.5\ H_2 + OH^- = HCoO_2^- + H_2O\ ,\quad n = 1 \qquad (19)$$

$$CoOOH + OH^- + H_2O = Co(OH)_4^- \qquad (20)$$

$$Co(OH)_4^- + 0.5\ H_2 = Co(OH)_3^- + H_2O\ ,\quad n = 1 \qquad (21)$$

$$Co(OH)_4^- + 0.5\ H_2 = HCoO_2^- + 2\ H_2O\ ,\quad n = 1 \qquad (22)$$

$$3\ Co(OH)_4^- + 0.5\ H_2 = Co_3O_4 + 5\ H_2O + 3\ OH^-\ ,\quad n = 1 \qquad (23)$$

$$CoO_2 + 0.5\ H_2 = CoOOH\ ,\quad n = 1 \qquad (24)$$

$$CoO_2 + 0.5\ H_2 + H_2O + OH^- = Co(OH)_4^-\ ,\quad n = 1 \qquad (25)$$

$$3\ CoO_2 + 2\ H_2 = Co_3O_4 + 2\ H_2O\ ,\quad n = 1 \qquad (26)$$

$$CoOOH + 0.5\ H_2 = Co(OH)_2\ ,\quad n = 1 \qquad (27)$$

$$CoOOH + 0.5\ H_2 = CoO + H_2O\ ,\quad n = 1\ . \qquad (28)$$

Data of standard Gibbs energies for chemical reactions and standard cell reaction potentials are summarized in Tables IV and V. In calculations of equilibrium data at non-standard reaction conditions, water activities and equilibrium water vapour pressures (in bar) in and over KOH solution were expressed according to following relations[21]:

$$\log a_{H_2O} = -0.02255\, m_{KOH} + 0.001434\, m_{KOH}^2 + (1.38\, m_{KOH} - 0.9254\, m_{KOH}^2)/T \qquad (29)$$

and

$$\log p_{H_2O} = -0.01508\, m - 0.001679\, m^2 + 2.25887 \,.\, 10^{-5}\, m^3 + (1 - 0.001206\, m + \\ + 5.6024 \,.\, 10^{-4}\, m^2 - 7.8228 \,.\, 10^{-6}\, m^3)\,(35.44623 - 3\,343.93/T - \\ - 10.9 \log T + 0.004164\, T)\ , \qquad (30)$$

where $m = m_{KOH}$ and the pressure is in bar.

Both Eqs (*29*) and (*30*) are valid for the range of m_{KOH} = 2–18 mol kg^{-1} in the temperature range T = 293.15–473.15 K. The fugacity coefficients of gaseous hydrogen in the considered temperature and total pressure range is expressed by the simplified relation

$$\log \gamma_{H_2} = (3.796 \,.\, 10^{-4} - 4.233 \,.\, 10^{-7}\, T)\, P\ , \qquad (31)$$

where P is in bar. For the pressure range of 1–30 bar see ref.[22].

TABLE IV
Calculated values of ΔG^0 of individual chemical reactions in the temperature range of 25–125 °C

Reaction	ΔG^0, J mol^{-1}				
	25 °C	50 °C	75 °C	100 °C	125 °C
(*4*)	61 929	63 722	65 699	67 842	70 139
(*5*)	85 802	83 513	81 071	78 486	75 770
(*11*)	2 909	–428.80	–4 304.8	–8 719.7	–13 676
(*12*)	29 004	30 583	32 674	35 276	38 389
(*14*)	31 913	30 169	28 426	26 686	24 948
(*15*)	25 944	25 383	25 258	25 608	26 474
(*20*)	28 665	30 589	33 098	36 182	39 833

TABLE V
Potential- and pressure-independent equilibrium molality of $Co(OH)_3^-$, $-\log m_{Co(OH)_3^-}$ in the existence region of solid $Co(OH)_2$ at 25 and 50 °C for KOH molality ranging from 2 to 18 mol kg^{-1}

t, °C	$-\log m_{Co(OH)_3^-}$ at m_{KOH}								
	2	4	6	8	10	12	14	16	18
25	4.780	4.479	4.303	4.178	4.081	4.002	3.935	3.877	3.826
50	4.642	4.341	4.165	4.040	3.943	3.864	3.797	3.739	3.688

Evaluation of the individual reactions under non-standard conditions revealed that the disproportionation reaction (*4*) and (*5*) cannot proceed from left to right, since their Gibbs energies display positive values not only at standard conditions (a_{H_2O} = 1.0) but also in whole range of m_{KOH} = 2–18 mol kg^{-1} at 25–125 °C. This conclusion is in clear contrast to the similar system Fe–KOH–H_2O where the disproportionation of $Fe(OH)_2$ to Fe_3O_4 and Fe at m_{KOH} > 6.35 mol kg^{-1} can proceed spontaneously at 25 °C (see ref.[12]).

Similar conclusion is valid for the dehydration of $Co(OH)_2$ to CoO (reaction (*10*)) for which at standard conditions the $\Delta G^0_{(10)}$ values in the range of 25–125 °C are weakly positive. However, in contact with KOH solutions the dehydration temperature of $Co(OH)_2$ may apparently be shifted towards lower values. Combining Eq. (*29*) with the relation for the temperature dependence of the equilibrium constant of reaction (*10*),

$$\log K_{(10)} = \log a_{H_2O} = -\Delta G^0_{(10)}/(2.3\boldsymbol{R}T) \qquad (32)$$

the following equation was obtained:

$$m_{KOH,r} = \{0.02255 - 1.38/T - [(0.02255 - 1.38/T)^2 + \\ + 4 \log K_{(10)}(0.001434 - 0.9254/T)]^{0.5}\} / (0.002868 - 1.8508/T) \ , \qquad (33)$$

where $m_{KOH,r}$ denotes the KOH molality at which $Fe(OH)_2$ can coexist with solid CoO. The dependence of the dehydration temperature on the KOH molality is shown in Fig. 1. The theoretical dehydration in pure water can proceed at T = 424.77 K under appropriate total pressure. From Fig. 1 it can be seen that $Co(OH)_2$ can exist at m_{KOH} = 10 mol kg^{-1}

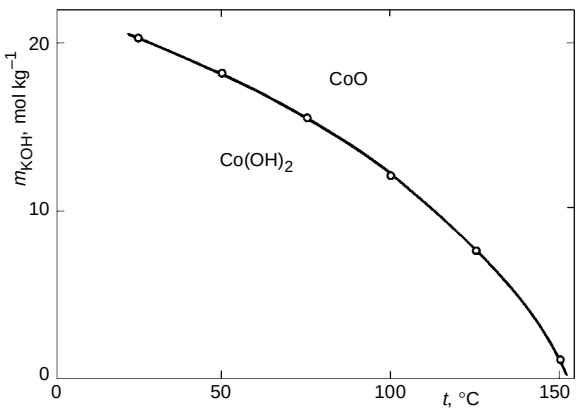

FIG. 1
Thermodynamic stability regions of solid $Co(OH)_2$ and CoO in contact with aqueous KOH solutions in dependence on their molality and temperature

up to 50 °C since its dehydration to CoO can only proceed t this temperature and $m_{KOH} >$ 18.11 mol kg^{-1} (assuming that relation (*29*) can be extrapolated for this m_{KOH} value). It must be emphasized that the results given in Fig. 1 could not be obtained using the Pourbaix method[1] based on the simplified assumption of $a_{H_2O} = 1.0$ in the entire pH range.

The temperature dependence of $\Delta G^0_{(11)}$ showed $\Delta G^0_{(11)} = 0$ J mol^{-1} at $T = 320.15$ K, while above this temperature it displays negative values (Table IV). This means that at $t > 47$ °C, the dehydrated form $HCoO_2^-$ should be present as the predominant form in alkaline solutions, whereby with increasing KOH molality the molar ratio $m_{HCoO_2^-} / m_{Co(OH)_3^-}$ should continue to rise in accordance with the relation

$$\log (m_{HCoO_2^-}/m_{Co(OH)_3^-}) = -\Delta G^0_{(11)}/2.3\boldsymbol{R}T - \log a_{H_2O} \quad . \qquad (34)$$

These results lead to simplified conclusion that at $t > 60$ °C only $HCoO_2^-$ is present as the sole Co(II) anionic form in the entire range of $m_{KOH} = 2$–18 mol kg^{-1}. At lower temperatures, both forms should in principle be taken into consideration in calculation of the equilibrium solution composition as a function of the reaction conditions. At 25 °C, when merely solid $Co(OH)_2$ can exist in the entire concentration region, the molar ratio $m_{HCoO_2^-} / m_{Co(OH)_3^-} = 1.0$ is reached at $m_{KOH} = 12.91$ mol kg^{-1}. It was assumed for the sake of simplicity, that the potential-independent molality of $Co(OH)_3^-$ can represent the total equilibrium solubility of Co(II) anions in the range of existence of solid $Co(OH)_2$.

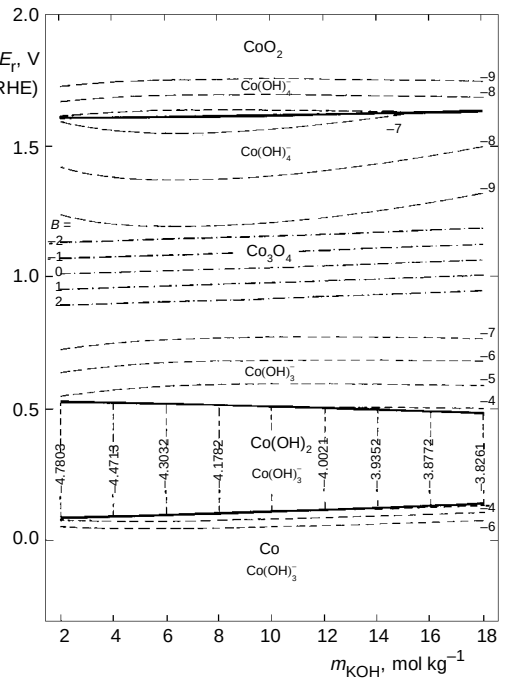

FIG. 2
E_r–m_{KOH} diagram for cobalt at 25 °C and total pressure of 1 bar (meaning of individual lines see in text)

The results of calculations for 25 and 50 °C under the given simplified assumption are summarized in Table V.

The potential-dependent molality of $Co(OH)_3^-$ under corresponding conditions was calculated from the relation, based on the appropriate form of Nernst equation,

$$\log m_{Co(OH)_3^-} = 2\boldsymbol{F}(E^0_{(13)} - E_r)/2.3\boldsymbol{R}T + 2\log a_{H_2O} + \log m_{KOH} - \\ - \log (P - p_{H_2O}) - \log \gamma_{H_2} \qquad (35)$$

in which expressions for a_{H_2O}, p_{H_2O} and γ_{H_2} in dependence on the reaction conditions, *i.e.* Eqs (*29*)–(*31*), were inserted.

In similar manner, the equilibrium molalities of the dehydrated anion form, $HCoO_2^-$, were calculated for temperature $t > 60$ °C. The results of these calculations are depicted (in form of $\log m_{HCoO_2^-}$) in Figs 3 and 4.

As concerns the composition of solutions in equilibrium with solid cobalt spinel Co_3O_4 under various reaction conditions, apart from the Co(II) anions, the $Co(OH)_4^-$ ions also take part in the equilibrium state with rising electrode potential, corresponding to reactions (*21*) and (*22*). The change in the molar ratio of these anions as a function of the reaction conditions was calculated using Nernst equation and repre-

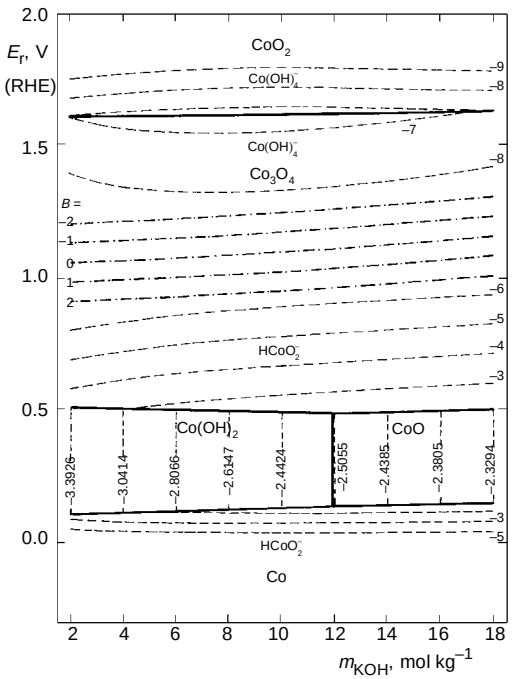

FIG. 3
E_r–m_{KOH} diagram for cobalt at 100 °C and total pressure of 10 bar (meaning of individual lines see in text)

sented in Figs 2–4 by dash-dotted lines (*B*) corresponding to log ($m_{Co(OH)_3^-} / m_{Co(OH)_4^-}$) or log ($m_{HCoO_2^-} / m_{Co(OH)_4^-}$). As can be seen, the equality of the equilibrium molalities of the two ions with different valences is only achieved above 1.0 V (RHE), and with rising temperature this potential is slightly shifted towards more positive values. However, the total equilibrium molality of Co-anions is very low above about 1.0 V (RHE), as can be seen from the dotted lines for log $m_{Co(OH)_4^-}$ in Figs 2–4. The highest equilibrium molality $m_{Co(OH)_4^-}$ achieved at the equilibrium potential of oxidation of Co_3O_4 to CoO_2, is close to the value of $1 . 10^{-7}$ mol kg^{-1}. As this concentration decreases on both sides of the equilibrium potential of this reaction, it can be regarded as negligibly low, irrespective of further reaction conditions.

Distinctly different results in comparison to the original *E*–pH diagram[1] were, however, obtained for further oxidation of Co_3O_4. According to the present calculations, Co_3O_4 is preferentially oxidized directly to solid CoO_2 according to reaction (*26*) since the standard potential of this cell reaction is much lower than for the oxidation to CoOOH according to reaction (*17*) (see Table VI). The difference in the standard potential of both cell reactions increases with rising temperature. This conclusion also remains valid under non-started reaction conditions. In calculations it was assumed that CoO_2 appears as a pure substance in the reactions considered. In reality, however, only mixtures of CoO_2 with various amounts of lower Co oxo compounds are present, as may be deduced from earlier results compiled in ref.[24]. It is not excluded that

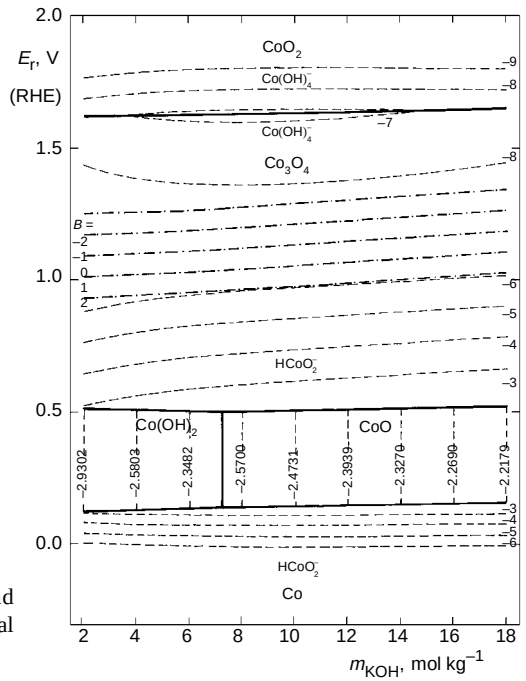

FIG. 4
E_r–m_{KOH} diagram for cobalt at 125 °C and total pressure of 30 bar (meaning of individual lines see in text)

in these mixtures solid solutions of CoO_2 with corresponding cobalt oxo compounds in lower oxidation states (Co_3O_4, CoOOH (?)) are formed, as it is in the case of $NiO_2 \cdot x\ H_2O/Ni(OH)_2$ solid solutions[25].

Thermodynamic calculations on the preferred oxidation of Co_3O_4 to CoO_2 lead to the conclusion that under reversible conditions CoOOH actually cannot exist or it exists as thermodynamically metastable substance only. This conclusion is generally valid for the whole range of considered reaction conditions.

The existence regions of individual solid Co substances calculated in this way as a function of the reaction conditions are shown in the form of E_r–m_{KOH} diagrams for 25 °C and total pressure P = 1 bar in Fig. 2, for 100 °C, P = 10 bar in Fig. 3 and for 125 °C, P = 30 bar in Fig. 4.

TABLE VI
Calculated values of standard potential of electrochemical cell reactions in the temperature range from 25 to 125 °C

Reaction	E^0, V				
	25 °C	50 °C	75 °C	100 °C	125 °C
(*2*)	0.11888	0.10811	0.09747	0.08696	0.07655
(*3*)	0.08794	0.08246	0.07755	0.07315	0.06924
(*6*)	0.43982	0.43832	0.43796	0.43855	0.44004
(*7*)	0.53261	0.51527	0.49771	0.47992	0.46193
(*8*)	0.03647	0.04637	0.05644	0.06672	0.07725
(*9*)	0.08170	0.03970	–0.01049	–0.06884	–0.13536
(*13*)	0.23826	0.24099	0.24694	0.25604	0.28358
(*16*)	0.25333	0.23877	0.22463	0.21085	0.19739
(*17*)	1.98287	2.00823	2.03453	2.06170	2.08970
(*18*)	0.71540	0.69586	0.67118	0.64136	0.60638
(*19*)	0.68526	0.69834	0.71171	0.72529	0.73906
(*21*)	1.01251	1.01190	1.01037	1.00803	1.00497
(*22*)	0.98235	0.99569	1.00831	1.01986	1.03010
(*23*)	2.87412	2.95933	3.06367	3.18679	3.32842
(*24*)	1.47568	1.45404	1.43255	1.41117	1.38986
(*25*)	1.17858	1.13708	1.08986	1.03704	0.97875
(*26*)	1.60246	1.59257	1.58303	1.57378	1.56480
(*27*)	1.01602	1.01291	1.00996	1.00716	1.00451
(*28*)	0.95415	0.96162	0.97012	0.97957	0.98990

DISCUSSION

There is an obvious disparity between the original *E*–pH diagram for cobalt (in SHE scale) in the alkaline pH range after Pourbaix[1] and present E_r–m_{KOH} diagram (in RHE scale) at 25 °C. According to Pourbaix, the region of existence of solid $Co(OH)_2$ extends from about +0.1 V to about 0.93 C (RHE) when oxidation to Co_3O_4 takes place. The existence region of cobalt spinel, Co_3O_4, is, however, very narrow since even at about 0.97 V (RHE) it should be oxidized to $Co(OH)_3$. Co(III) hydroxide is stable up to about 1.41 V (RHE) and should be oxidized to CoO_2 at this potential.

According to the present calculations, the range of existence of solid $Co(OH)_2$ is not so broad since its oxidation to Co_3O_4 already takes place at about 0.6 V (RHE) (see Fig. 2). The greatest difference from the original Pourbaix diagram is displayed by the existence region of cobalt spinel, Co_3O_4, which, according to the present results, extends up to about 1.6 V (RHE). At this potential it passes into the existence region of CoO_2 (most probably in form of solid solution with some lower cobalt oxo compound). Thus no region of existence of pure Co(III) oxo compounds such as $Co(OH)_3$, Co_2O_3 or CoOOH emerges since under the given reaction conditions they are thermodynamically unstable. This conclusion also applies to higher temperatures, since according to the present calculations the E_r–m_{KOH} diagrams at 100 °C and 10 bar as well as at 125 °C and 30 bar are very similar to that for 25 °C and bar in the potential range considered (Figs 2–4). The premise for this conclusion is, naturally, that the thermodynamic standard data of individual Co substances, especially of Co_3O_4, used in the present calculations are more reliable than those used by Pourbaix[1]. If the formation and existence of different Co(III) oxo compounds (*e.g.* refs[14–16]) should prove to be unambiguously detected under the given reaction conditions, then such substances must be regarded as thermodynamically metastable in the sense of the present results.

The present calculations taking into account the actual water activity a_{H_2O} and the equilibrium pressure of water vapour in or above the KOH solutions also allowed us to state that solid $Co(OH)_2$ can be dehydrated to CoO in concentrated KOH solutions at elevated temperature. Accordingly, under such conditions, apart from the region of existence of $Co(OH)_2$ a region of existence of anhydrous CoO also appears in the E_r–m_{KOH} diagram, and with rising temperature dehydration occurs at lower KOH molalities (see Figs 1, 3 and 4). Such a result would not be possible to obtain under the simplified assumption of $a_{H_2O} = 1.0$ for the entire pH range usually used according to the Pourbaix method[1].

As far as CoO_2 is concerned, due to the lack of thermodynamic data it was assumed that it can coexist as a pure substance with lower Co oxo compounds. It is, however, not excluded that Co(IV) component can be present in form of solid solutions with lower cobalt oxo compounds, similarly as in the case of Ni(IV)/Ni(II) solid solutions[25,26]. Pure CoO_2 as well as pure NiO_2 remain still unknown[24]. Further experimental investigations in this direction are therefore very desirable.

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