# DIAGRAMS $E_r$–$m_{KOH}$ FOR IRON AT 25–125 °C AND AT TOTAL PRESSURE OF 1–30 Bar*

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Taking into consideration the water activity $a_{H_2O}$, the equilibrium pressure of water vapour $p_{H_2O}$ in or above KOH solutions of different molality (2–18 mol kg$^{-1}$) and temperature (0–200 °C), the relations for the quantitative evaluation of the equilibrium conditions of individual reactions in the Fe–KOH–$H_2O$ system were derived in potential range from –0.3 to +1.8 V (RHE). With the aid of standard thermodynamic data for individual reaction components, $E_r$–$m_{KOH}$ diagrams were constructed for iron at 25, 100 and 125 °C and a total pressure of 1, 10 and 30 bar (0.1, 1 and 3 MPa). Under standard conditions ($a_{H_2O}$ = 1.0), $Fe(OH)_2$(s) may result at temperatures of up to 63.1 °C, while at higher temperatures solid magnetite, $Fe_3O_4$, is directly formed as the thermodynamically stable primary corrosion product. The region of existence of solid $Fe(OH)_2$ is influenced by the molality and temperature of KOH solutions in contact with metallic iron. For example, at 25 °C $Fe(OH)_2$ can only arise as the primary corrosion product in KOH solutions $m_{KOH} \leq 6.34$ mol kg$^{-1}$, which cannot be concluded from the usual $E_r$–pH diagram after Pourbaix.

**Key words:** Iron oxo compounds; Iron corrosion products.

In previous works on $E_r$–pH diagrams for iron[1–7] the water activity was considered to be equal to 1.0 in the pH range from –2 to +16, as usual for Pourbaix diagrams[1]. This simplifying assumption deviates, particularly in highly acid or alkaline solutions, quite considerably from reality and may have led to distorted results. In order to elucidate the catalytic effect of Fe(III) substances on the anodic oxygen evolution at Ni anodes and their further behaviour under conditions of advanced water electrolysis with an intermittent operating mode appropriate calculations have been done in which the water activity and water vapour partial pressure in and over KOH solutions of various molality and temperature[8] were taken into account. In "classical" Pourbaix diagrams potentials are related to the potential of the standard hydrogen electrode (SHE) (at pH 0). In our calculations potentials were related to more practical and experimentally easily achiev-

* 1 bar = $10^5$ Pa.

able reference hydrogen electrode (RHE) placed into experimental electrolyte solution at given temperature and total pressure. The details were already described in our previous paper[9].

The present work deals with calculations of the equilibrium conditions of metallic iron and its oxo compounds in contact with KOH solutions in the molality range of 2–18 mol $kg^{-1}$ at 25–125 °C and 1–30 bar total pressure in dependence on the electrode potential range from –0.3 to +1.8 V (RHE). The results which may be of interest not only for the above given purposes but undoubtedly also for other technical as well as theoretical applications are presented in this paper.

## CALCULATIONS

According to preliminary calculations, only metallic α-Fe and furthermore $Fe(OH)_2$, $Fe_3O_4$ and α-$Fe_2O_3$ were considered as solid, thermodynamically stable substances of the system under study, and $Fe(OH)_3^-$, $Fe(OH)_4^-$ and $FeO_4^{2-}$ as soluble ions. Solid FeO was not taken into account since it disproportionates spontaneously to $Fe_3O_4$ and Fe at temperature below 155.5 °C. Both $Fe(OH)_3$ and α-FeOOH need not be considered either, due to their dehydration to α-$Fe_2O_3$ which is the only thermodynamically stable solid Fe(III) oxo compound. This conclusion is valid for standard conditions ($a_{H_2O} = 1.0$) as well as for concentrated KOH solutions with reduced water activity in the entire temperature range considered. Calculations were thus restricted to the following chemical and electrochemical cell reactions with hydrogen reference electrode placed in common solution (with $n$ denoting the number of exchanged electrons):

$$4\ Fe(OH)_2 = Fe_3O_4 + Fe + 4\ H_2O \qquad (1)$$

$$Fe(OH)_2 + OH^- = Fe(OH)_3^- \qquad (2)$$

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

$$Fe(OH)_3^- + H_2 = Fe + 2\ H_2O + OH^-\ , \quad n = 2 \qquad (4)$$

$$Fe_3O_4 + 4\ H_2 = 3\ Fe + 4\ H_2O\ , \quad n = 8 \qquad (5)$$

$$Fe_3O_4 + H_2 + 2\ H_2O = 3\ Fe(OH)_2\ , \quad n = 2 \qquad (6)$$

$$Fe_3O_4 + H_2 + 2\ H_2O + 3\ OH^- = 3\ Fe(OH)_3^-\ , \quad n = 2 \qquad (7)$$

$$Fe_2O_3 + H_2 + H_2O + 2\ OH^- = 2\ Fe(OH)_3^- , \quad n = 2 \qquad (8)$$

$$Fe_2O_3 + 2\ OH^- + 3\ H_2O = 2\ Fe(OH)_4^- \qquad (9)$$

$$Fe(OH)_4^- + 0.5\ H_2 = Fe(OH)_3^- + H_2O , \quad n = 1 \qquad (10)$$

$$3\ Fe_2O_3 + H_2 = 2\ Fe_3O_4 + H_2O , \quad n = 2 \qquad (11)$$

$$3\ Fe(OH)_4^- + 0.5\ H_2 = Fe_3O_4 + 3\ OH^- + 5\ H_2O , \quad n = 1 \qquad (12)$$

$$2\ FeO_4^{2-} + 3\ H_2 = Fe_2O_3 + H_2O + 4\ OH^- , \quad n = 6 \qquad (13)$$

$$FeO_4^{2-} + 1.5\ H_2 + H_2O = Fe(OH)_4^- + OH^- , \quad n = 3 . \qquad (14)$$

The thermodynamic standard data of most reaction components at 25 °C were taken from refs[10–14], data for $FeO_4^{2-}$(aq) were taken from the original literature[15]. All used data are compiled in Table I. The coefficient of the general form of the temperature dependence of the molar heat capacity for pure substances

$$C_p^0 = a + b\ .\ 10^{-3}\ T + c\ .\ 10^{-6}\ T^2 + d\ .\ 10^5\ T^{-2} \quad (J\ mol^{-1}\ K^{-1}) \qquad (15)$$

TABLE I
Thermodynamic standard values of single Fe-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-Fe(s) | 0.0 | 0.0 | 27.085 | 10 |
| $Fe(OH)_2$(s) | 574.045 | 491.969 | 87.864 | 11 |
| α-$Fe_2O_3$(s) | 825.503 | 743.523 | 87.4 | 11 |
| $Fe_3O_4$(s) | 1 118.383 | 1 015.227 | 146.147 | 12 |
| $Fe(OH)_3^-$(aq) | – | 614.9 | 299 | 13, 16 |
| $Fe(OH)_4^-$(aq) | – | 842.2 | 24.5 | 14 |
| $Fe(OH)_4^{2-}$(aq) | 481.16 | 322.17 | 37.7 | 15 |
| $H_2$(g) | 0.0 | 0.0 | 130.684 | 13 |
| $H_2O$(liq) | 285.830 | 237.129 | 69.91 | 13 |
| $OH^-$(aq) | 229.994 | 157.244 | –10.75 | 13 |

calculated from JANAF Tables[11] are given in Table II. Relations for mean molar heat capacity of ions, $\overline{C_P^0} \mid_{T_1}^{T}$, in the temperature range $T_1$ and $T$, where $T_1$ = 298.15 K, according to the "correspondence principle" of Criss and Cobble[17] are summarized in Table III.

The calculated values of $\Delta G_{(i)}^0$ and $E_{(i)}^0$ of individual reactions in the temperature range from 25 to 125 °C are compiled in Tables IV and V, respectively.

For reaction (*1*), $\Delta G_{(1)}^0$ changes from slightly positive to negative with rising temperature. The value $\Delta G_{(1)}^0$ = 0 J mol$^{-1}$ is reached at $T_c$ = 336.25 K. At this critical temperature all three solid reaction components may coexist in contact with pure water ($a_{H_2O}$ = 1.0). Below this temperature $Fe(OH)_2$ remains stable and above this temperature it disproportionates spontaneously to $Fe_3O_4$ and Fe. This result is in agreement with the $E_r$–pH diagram after Silverman[6], according to which $Fe(OH)_2$ is formed as the primary corrosion product of iron in pure water at 25 °C. Equilibrium established between metallic iron and concentrated KOH solutions may be influenced significantly because the

TABLE II
Coefficients of the Eq. (*15*) of individual pure substances

| Substance | *a* | *b* | *c* | *d* |
|---|---|---|---|---|
| α-Fe(s) | 23.765 | 5.4841 | 14.888 | –1.457 |
| $Fe(OH)_2$(s) | 75.092 | 74.777 | –25.304 | 1.7212 |
| α-$Fe_2O_3$(s) | 98.269 | 77.822 | – | –14.853 |
| $Fe_3O_4$(s) | 252.84 | –226.91 | 296.91 | –54.101 |
| $H_2$(g) | 26.2164 | 4.3911 | –0.2331 | 1.4327 |
| $H_2O$(liq) | 109.91 | –189.11 | 273.87 | 2.1831 |

TABLE III
Relations for the average values of molar heat capacities $\overline{C_P^0} \mid_{T_1}^{T}$ of ions between $T_1$ = 298.15 K and *T*, according to the "corresponding principle" by Criss and Cobble[17]

| Ion | $\overline{C_P^0} \mid_{T_1}^{T}$, J mol$^{-1}$ K$^{-1}$ |
|---|---|
| $OH^-$(aq) | (215.01 – 0.72104*T*)/ln (*T*/$T_1$) |
| $Fe(OH)_3^-$(aq) | (328.85 – 1.1028*T*)/ln (*T*/$T_1$) |
| $Fe(OH)_4^-$(aq) | (345.27 – 1.158*T*)/ln (*T*/$T_1$) |
| $FeO_4^{2-}$(aq) | (341.97 – 1.147*T*)/ln (*T*/$T_1$) |

equilibrium constant of the reaction (*1*) is given by the equilibrium water activity at the given temperature:

$$\log K_{(1)} = -\Delta G^0_{(1)}/2.3\boldsymbol{R}T = 4 \log a_{H_2O} \ . \qquad (16)$$

From the dependence of water activity in KOH solutions on $m_{KOH}$ and temperature[8]

$$\log a_{H_2O} = -0.02255\, m_{KOH} + 0.001434\, m^2_{KOH} + \\ + (1.38\, m_{KOH} - 0.9254\, m^2_{KOH})/T \qquad (17)$$

the associated KOH molality, at which all three solid phases may coexist with KOH solution at the given temperature, can be calculated on the basis of relations (*16*) and (*17*) for $T < T_c$:

$$m_{KOH,r} = \{0.02255 - 1.38/T - [(0.02255 - 1.38/T)^2 + \\ + \log K_{(1)}(0.001434 - 0.9254/T)]^{0.5}\} / (0.002868 - 1.8508/T) \ . \qquad (18)$$

The values of log $K_{(1)}$, $a_{H_2O,r}$ and the associated KOH molality, $m_{KOH,r}$, are given in Table IV for some temperatures. The regions of existence of individual solid phase as a function of KOH molality and temperature are shown in Fig. 1. With increasing KOH molality the point of transition of $Fe(OH)_2$ to $Fe_3O_4$ and Fe is shifted to lower temperatures. Thus, $Fe(OH)_2$ cannot exist at $m_{KOH} > 6.346$ mol kg$^{-1}$ at 25 °C. In accordance with these conclusions $E^0_{(3)} = E^0_{(5)}$ at $T_c$ = 336.25 K (63.1 °C). Below this temperature $E^0_{(3)} < E^0_{(5)}$ and above this temperature $E^0_{(3)} > E^0_{(5)}$. This means that at $t$ < 63.1 °C, solid

TABLE IV
Calculated values of individual parameters for chemical reactions (*1*), (*2*) and (*9*) for the temperature range of 25–125 °C

| Reaction | parameters | $t$, °C | | | | |
|---|---|---|---|---|---|---|
| | | 25 | 50 | 75 | 100 | 125 |
| (*1*) | $\Delta G^0$, J mol$^{-1}$ | 4 133 | 1 477.6 | –1 389.5 | –4 454 | –7 704 |
| | log $K$ | –0.72410 | –0.23884 | 0.20848 | 0.62349 | 1.01076 |
| | $a_{H_2O,r}$ | 0.6591 | 0.8715 | (1.1275) | (1.4318) | (1.7893) |
| | $m_{KOH,r}$ | 6.3473 | 2.6974 | – | – | – |
| (*2*) | $\Delta G^0$, J mol$^{-1}$ | 34 313 | 35 722 | 37 571 | 39 857 | 42 578 |
| (*9*) | $\Delta G^0$, J mol$^{-1}$ | 84 998 | 91 326 | 98 948 | 107 828 | 117 941 |

$Fe(OH)_2$ is the thermodynamically stable product of iron corrosion in pure water whereas at $t > 61.3$ °C $Fe_3O_4$ is formed. With increasing KOH molality, however, the temperature limit for the formation of $Fe_3O_4$ instead of $Fe(OH)_2$ is shifted towards lower temperatures, as can be seen from Fig. 1. The equilibrium cell reactions potential corresponding to reactions (*3*) and (*5*) is given by expressions

$$E_{(3)} = E^0_{(3)} - (2.3\boldsymbol{R}T/2\boldsymbol{F}) \log (a^2_{H_2O}/a_{H_2}) \qquad (19)$$

and

$$E_{(5)} = E^0_{(5)} - (2.3\boldsymbol{R}T/2\boldsymbol{F}) \log (a_{H_2O}/a_{H_2}) \ , \qquad (20)$$

where the dependence of both water and hydrogen activities on the reaction conditions has to be taken into consideration. The gaseous activity at hydrogen reference electrode is given by the relation

$$a_{H_2} = (P - p_{H_2O})\, \gamma_{H_2} \ , \qquad (21)$$

where $p_{H_2O}$ represents the equilibrium pressure of water vapour over the KOH solution at $m_{KOH}$ and given temperature, and $\gamma_{H_2}$ is the fugacity coefficient of hydrogen at given total pressure $P$ and temperature. The water vapour equilibrium pressure for $m_{KOH}$ =

TABLE V
Calculated values of $E^0$ for electrochemical reactions (*3*)–(*8*) and (*10*)–(*14*) for the temperature range of 25–125 °C

| Reaction | $E^0$, V | | | | |
|---|---|---|---|---|---|
| | 25 °C | 50 °C | 75 °C | 100 °C | 125 °C |
| (*3*) | –0.09178 | –0.09812 | –0.10389 | –0.10914 | –0.11823 |
| (*4*) | 0.08604 | 0.08691 | 0.09063 | 0.09713 | 0.10636 |
| (*5*) | –0.08643 | –0.09622 | –0.10570 | –0.11492 | –0.12390 |
| (*6*) | –0.07036 | –0.09047 | –0.11110 | –0.13223 | –0.15384 |
| (*7*) | –0.60381 | –0.64569 | –0.69492 | –0.75146 | –0.81528 |
| (*8*) | –0.33860 | –0.36778 | –0.40172 | –0.44040 | –0.48381 |
| (*10*) | 0.10187 | 0.10533 | 0.11046 | 0.11718 | 0.12541 |
| (*11*) | 0.19182 | 0.18809 | 0.18476 | 0.18181 | 0.17922 |
| (*12*) | 1.51324 | 1.60735 | 1.72121 | 1.85444 | 2.00678 |
| (*13*) | 1.66743 | 1.65204 | 1.63633 | 1.62028 | 1.60386 |
| (*14*) | 1.52060 | 1.49514 | 1.46889 | 1.44190 | 1.41422 |

2–18 mol kg$^{-1}$ and the temperature range of 0–200 °C can be taken from ref.[8], with $m_{KOH} = m$ and pressure in bar:

$$\log p_{H_2O} = -0.01508\, m - 0.001679\, m^2 + 2.25887 \,.\, 10^{-5} m^3 + (1 - $$
$$- 0.001206\, m + 5.6024 \,.\, 10^{-4} m^2 - 7.8228 \,.\, 10^{-6} m^3)(35.44623 - $$
$$- 3\,343.93/T - 10.9 \log T + 0.0041645 T) \quad . \qquad (22)$$

The expression for the fugacity coefficient $\gamma_{H_2}$ in the same temperature range and the pressure from 1 to 200 bar can be taken from ref.[18]. For the temperature range of 0–150 °C and $P$ = 1.0–50 bar it can be substituted by a simple relation

$$\log \gamma_{H_2} = (3.77 \,.\, 10^{-4} - 4.23 \,.\, 10^{-7} T)\, P \quad . \qquad (23)$$

In order to evaluate correctly equilibrium conditions for reactions with the participation of soluble ionic substances it is necessary to know the activity coefficients of these ions under real reaction conditions. Unfortunately, this prerequisite is not sufficiently fulfilled for concentrated multicomponent solutions of the system under study both at room and at elevated temperatures. Therefore, in the case of reactions (*2*), (*4*), (*7*), (*8*), (*9*), (*10*) and (*12*), where equal number of moles of anions carrying equal charge appears on both sides of reaction equations, the ratio of the activity coefficients of these anions can be regarded as equal to 1.0 since a common solution with the same ionic strength is involved in the equilibrium state. Furthermore, due to the fact that $m_{Fe(OH)^{3-}} << m_{OH^-}$ as well as $m_{Fe(OH)_4^-} << m_{OH^-}$, it may be assumed that $m_{OH^-} = m_{KOH}$.

The equilibrium molality of ions $Fe(OH)_3^-$ and $Fe(OH)_4^-$ was calculated by solving relations for equilibrium constants of chemical reactions (*2*) and (*9*) and Nernst equations for electrochemical reactions (*4*), (*7*), (*8*), (*10*) and (*12*), for the given reaction

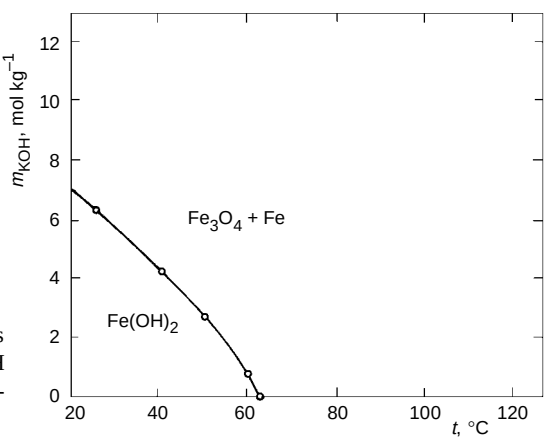


FIG. 1
Thermodynamic stability regions of solids $Fe(OH)_2$, $Fe_3O_4$ and Fe in aqueous KOH solutions in dependence on the KOH molality and temperature

conditions. For example, the potential-independent equilibrium molality $m_{Fe(OH)^{3-}}$ was calculated using the relation

$$\log m_{Fe(OH)_3^-} = -\Delta G^0_{(2)}/2.3\boldsymbol{R}T + \log m_{KOH} \qquad (24)$$

which holds for the quite narrow region of existence of solid $Fe(OH)_2$ (see Figs 2 and 3 for 25 °C). Below the equilibrium potential of cell reaction (*3*), the equilibrium molality of $Fe(OH)_3^-$ is governed by the relation ($P$ and $p_{H_2O}$ is to insert in bar)

$$\log m_{Fe(OH)_3^-} = 2\boldsymbol{F}(E_r - E^0_{(4)})/2.3\boldsymbol{R}T + 2\log a_{H_2O} + \\ + \log m_{KOH} - \log (P - p_{H_2O}) - \log \gamma_{H_2} \ . \qquad (25)$$

The calculated equilibrium data of $\log m_{Fe(OH)_3^-}$ and $\log m_{Fe(OH)_4^-}$ are fitted by dotted lines to the numerical logarithm values in Figs 2–5.

The molar ratio of Fe(II)/Fe(III) anions in saturated KOH solutions was calculated from the relation

$$\log (m_{Fe(OH)_3^-}/m_{Fe(OH)_4^-}) = A = \boldsymbol{F}(E^0_{(10)} - E_r)/2.3\boldsymbol{R}T - \log a_{H_2O} + \\ + 0.5 \log (P - p_{H_2O}) + 0.5 \log \gamma_{H_2} \ . \qquad (26)$$

At positive potentials $E_r \geq 1.5$ V (RHE), when oxygen evolution from aqueous KOH solutions represents the main anodic process, solid $Fe_2O_3$ can be oxidized to soluble

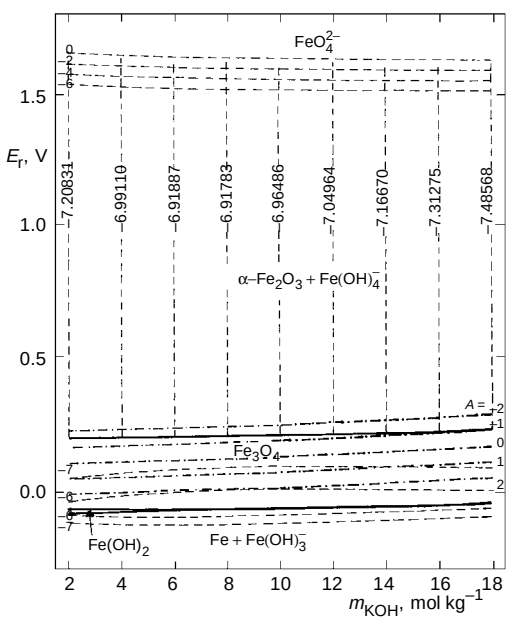


FIG. 2
$E_r$–$m_{KOH}$ diagram for iron at 25 °C and total pressure 1 bar (meaning of individual lines see in text)

$FeO_4^{2-}$. However, an exact evaluation of reactions (*13*) and (*14*) is more complicated since only less reliable thermodynamic standard data of $FeO_4^{2-}$(aq) are available[15] and anions with different charges appear on both sides of reaction equations. Based on the assumption of low solubility (0.00909 M $K_2FeO_4$) in 14.58 M KOH at 20 °C (ref.[19]), $\gamma_{OH^-} = \gamma_{\pm KOH}$, $\gamma_{FeO_4^{2-}} = \gamma^2_{\pm K_2FeO_4}$ and $m_{FeO_4^{2-}} << m_{OH^-}$, *i.e.* $m_{OH^-} = m_{KOH}$, the following relation is obtained for the equilibrium molality $m_{FeO_4^{2-}}$ upon oxidation of $Fe_2O_3$ according to reaction (*14*):

$$\log m_{FeO_4^{2-}} = 3\boldsymbol{F}(E_r - E^0_{(14)})/2.3\boldsymbol{R}T + 2\log m_{KOH} + 0.5\log a_{H_2O} - \\ - 1.5\log(P - p_{H_2O}) - 1.5\log\gamma_{H_2} + \log(\gamma_{\pm KOH}/\gamma_{\pm K_2FeO_4}) \quad . \qquad (27)$$

Since there is a lack of literature data for the dependence of mean activity coefficient ratio on the composition of solution and its temperature, we have assumed that this ratio is close to 1 so that $\log(\gamma_{\pm KOH}/\gamma_{\pm K_2FeO_4}) \approx 0$ and may thus be neglected in Eq. (*27*). The calculated values of $\log m_{FeO_4^{2-}}$ are plotted in Figs 2, 4 and 5 by dotted lines in the potential region of $E_r \geq 1.5$ V (RHE). However, it must be added that the ferrate ions are thermodynamically unstable since they may decompose spontaneously in alkaline solutions to solid $Fe_2O_3$ and/or $Fe(OH)_4^-$ releasing gaseous oxygen according to

$$2\ FeO_4^{2-} + 2\ H_2O \longrightarrow Fe_2O_3 + 1.5\ O_2 + 4\ OH^- \qquad (28)$$

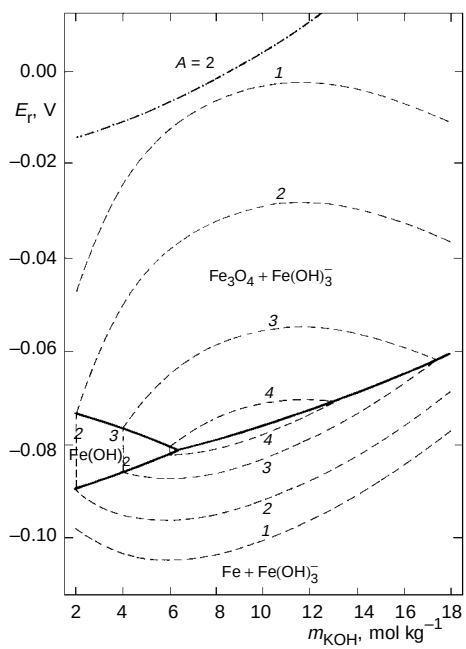


FIG. 3

$E_r$–$m_{KOH}$ diagram for iron in the potential range –0.11 to +0.01 V (RHE) at 25 °C and total pressure 1 bar; $\log m_{Fe(OH)_3^-}$ ($m$ in mol kg$^{-1}$): –6.0 (*1*), –5.71 (*2*), –5.41 (*3*) and –5.233 (*4*)

and

$$2\ FeO_4^{2-} + 5\ H_2O \longrightarrow 2\ Fe(OH)_4^- + 1.5\ O_2 + 2\ OH^- \ . \qquad (29)$$

The decomposition of $FeO_4^{2-}$ ions in strongly alkaline solutions investigated in detail in refs[20,21], was not considered in the present study. Therefore, the course of the calculated equilibrium molality of $FeO_4^{2-}$ ions in Figs 2, 4 and 5 should be taken as tentative.

## RESULTS AND DISCUSSION

The results of the thermodynamic calculations for the system under study are shown in Figs 2 and 3 for 25 °C and total pressure $P$ = 1 bar, in Fig. 4 for 100 °C and total pressure 10 bar and in Fig. 5 for 125 °C and total pressure of 30 bar. However, on the basis of given relations for $a_{H_2O}$, $p_{H_2O}$ and $\gamma_{H_2}$, the calculations can be performed in the range of $m_{KOH}$ = 2–18 mol kg$^{-1}$ for any reaction conditions in the range of 0–200 °C and pressure range of 1–50 bar (using Eq. (*23*)) or up to 200 bar (using Eq. (*40*) from ref.[18] for fugacity coefficient $\gamma_{H_2}$). The RHE-scale of equilibrium potentials is experimentally easily to realize and completely free of any liquid junction potential; this represents a significant advantage in comparison to the classical Pourbaix diagrams.

Very interesting results not achievable using the usual form of $E_r$–pH diagrams after Pourbaix[1] were obtained for conditions of the spontaneous iron corrosion in KOH solu-

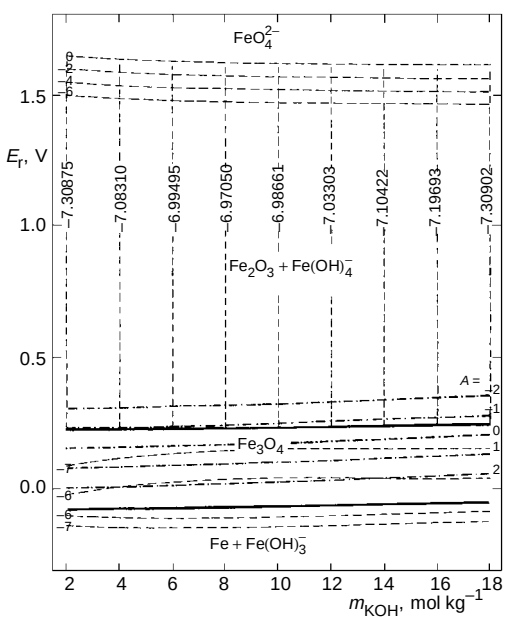


FIG. 4
$E_r$–$m_{KOH}$ diagram for iron at 100 °C and total pressure 10 bar (meaning of individual lines see in text)

tions when the true water activity was taken into account. At potentials from about –0.09 to –0.05 V (RHE) metallic iron is spontaneously corroded at $m_{KOH}$ = 2–6.3 mol kg$^{-1}$ at the room temperature first to solid $Fe(OH)_2$ and at $m_{KOH}$ > 6.35 mol kg$^{-1}$ directly to $Fe_3O_4$, releasing gaseous hydrogen. The region of existence of solid $Fe(OH)_2$ is very narrow and wedge-shaped, as can be seen in the enlarged scale in Fig. 3. The stability limit of metallic iron is shifted towards more positive potentials with increasing KOH molality. On the contrary, equilibrium potential of $Fe(OH)_2$ oxidation to $Fe_3O_4$ is shifted towards more negative values with increasing KOH molality. Dotted lines in the lower potential range show the constant values of the equilibrium molalities of $Fe(OH)_3^-$ as a function of $m_{KOH}$ and electrode potential for the given temperature and total pressure. In the region of existence of solid $Fe(OH)_2$ they run vertically since in this region they are potential-independent. At the triple point with critical molality $m_{KOH}$ = 6.347 mol kg$^{-1}$ and critical potential $E_{cr}$ = –0.0813 V (RHE) at 25 °C, when metallic iron can coexist with solid $Fe(OH)_2$ and magnetite, $Fe_3O_4$, the equilibrium molality of $Fe(OH)_3^-$ is given by log $m_{Fe(OH)_3^-}$ = –5.209. This value also represents the highest equilibrium molality at 25 °C in the entire range of potentials and KOH molality considered.

In the region of coexistence of solid magnetite, apart from $Fe(OH)_3^-$ ions, $Fe(OH)_4^-$ anions may also occur to an increasing extent with increasing electrode potential in KOH solutions. The decadic logarithm of molar ratio of both anions, given as *A* (see Eq. (*27*)), is plotted in Figs 2–5 by dash-dotted lines. As can be seen, the fraction of $Fe(OH)_4^-$ at potentials close to 0.0 V (RHE) for all reaction conditions is still fairly low

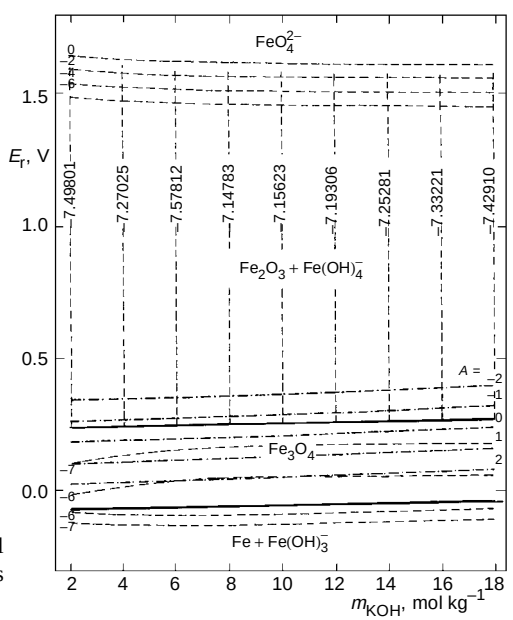


FIG. 5
$E_r$–$m_{KOH}$ diagram for iron at 125 °C and total pressure 30 bar (meaning of individual lines see in text)

and amounts to about one hundredth of the equilibrium molality of $Fe(OH)_3^-$ ions. At potentials of the oxidation of magnetite to haematite, $\alpha$-$Fe_2O_3$, the fraction of $Fe(OH)_3^-$ ions always remains perceptible and actually increases with rising temperature, although $Fe(OH)_4^-$ ions are already in the majority in the solution (see the shift of the curves for $A = -1$ and $-2$ in Figs 2, 4 and 5). Nevertheless, the total quantity of dissolved Fe(II) and Fe(III) ions remains very low. This is also demonstrated by the potential-independent equilibrium molality of $Fe(OH)_4^-$ in the entire region of existence of $\alpha$-$Fe_2O_3$, which for $m_{KOH} = 2$–18 mol kg$^{-1}$ is in the order of $10^{-7}$ to $10^{-8}$ mol kg$^{-1}$ at 25 °C and actually decreases again with rising temperature after reaching the solubility maximum at 8 $m_{KOH}$ of *ca* 8 mol kg$^{-1}$.

Above 1.45 to 1.5 V (RHE), $\alpha$-$Fe_2O_3$ may be oxidized to soluble ferrate ions, $FeO_4^{2-}$. The results calculated for this potential range are, however, apparently less reliable than results obtained at more negative potentials where participation of lowervalency Fe substances is involved. There is a clear discrepancy between the standard data for $FeO_4^{2-}$(aq) after Wood[15] (see Table I) and $\Delta H_f^0(FeO_4^{2-},aq) = -432.44$ kJ mol$^{-1}$ which follows from $\Delta H_f^0(K_2FeO_4,aq) = -973.2$ kJ mol$^{-1}$ and $\Delta H_f^0(K^+,aq) = -252.38$ kJ mol$^{-1}$ at 25°C according to ref.[13]. The value for $\Delta G_f^0(FeO_4^{2-},aq) = -467.29$ kJ mol$^{-1}$ at 25 °C used by Pourbaix[1] (labelled by him with a question mark) displays even greater discrepancy with Wood's data. With respect to the solubility of $K_2FeO_4$, 0.009 M $K_2FeO_4$ in 14.58 M KOH at 20 °C, it could be expected that the existence region of solid $K_2FeO_4$ probably extends at potentials above the curve for log $m_{FeO_4^{2-}}$ close to $-2$ so that the curve for $m_{FeO_4^{2-}}$ seems questionable, at least at room temperature. Thus, there is a need for new, more reliable standard data for $FeO_4^{2-}$(aq) as well as for solid $K_2FeO_4$ or other alkali metal ferrates.

Nevertheless, it can be concluded that the presented results showed clearly that the values of water activity under real reaction conditions must be considered in gathering sufficiently reliable data on equilibrium conditions in the course of chemical and electrochemical reactions in metal–$H_2O$ systems. The usual method of constructing $E$–pH diagrams according to Pourbaix[1] based on the simplified assumption of $a_{H_2O} = 1.0$ in the entire pH range from $-2$ to $+16$ can lead to incorrect results at real reaction conditions deviating more distinctly from those at which this assumption is sufficiently valid.

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