How to Get Ternary Solid Solutions $Fe_{1-x}M'_xO$ (M = Co, Ni)? **A Thermodynamic Concept**

Peer Schmidt^{*[a]}

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The existence ranges of ternary solid solutions $Fe_{1-v}M'_{v}O(M)$ = Co, Ni) have been estimated using thermodynamic modelling by CALPHAD methods: a complete series of mixed crystals Fe_{1-x}Co_xO is stable only at higher temperatures $\vartheta \ge 900$ °C. Below the solid solution shows a miscibility gap due to the different redox potentials $[p(O_2) = f(T)]$ of the binary phases "FeO" and CoO. Hence CoO becomes reduced into metallic cobalt while "FeO" is oxidised into Fe₃O₄. The pseudo binary system FeO/NiO shows solubility ranges only at the border of the binary oxides, the phases built are and $\alpha'(Fe_vNi_{1-v}O)$ (y≤0.60, $\alpha(Fe_{1-x}Ni_xO)$ (x \leq 0.13) $\vartheta \leq 1400$ °C). Due to the broader difference of redox poten-

Introduction

More than 200 publications of the last three years deal with the topic of "multiple component metal oxide combustion catalysts". Above all, the pertinent investigations are enforced with basic hydrocarbons like methane as chemical model systems for combustion. The frequently mentioned oxidic systems comprise one or more of the following components: V2O5, TiO2, ZrO2, CeO2, SnO2, Al2O3, Cr2O3, Mn₂O₃, Fe₃O₄, Fe₂O₃, CoO, Co₃O₄, NiO, CuO, Pt, Pd, Rh or Au.^[1]

Currently oxidic solid solutions of these materials are in evaluation for a fine-tuning of the catalytic behaviour. Thus the catalytic combustion of methane by applying mixed oxides $Co_{1-x}Ni_xO^{[2]}$ achieved a yield of more than 97% $(\vartheta \ge 600 \text{ °C})$, while the yield of the non-catalytic reaction is less than 10%.^[3,4] Thereby the system Co_{1-x}Ni_xO is almost as effective as the system Pd/Al₂O₃ (yield at least 98%, $\vartheta \ge 600$ °C). Based on these results investigations on related chemical systems $M_{1-x}M'_{x}O$ should be continued. Remarkably, the analogous systems of iron with cobalt and nickel, $Fe_{1-x}Co_xO$ and $Fe_{1-x}Ni_xO$, are still unknown.

However, due to the crystallographic conditions the formation of solid solutions $Fe_{1-x}Co_xO$ and $Fe_{1-x}Ni_xO$ could be expected: all three binary oxides crystallise in the halite structure type (space group $Fm\bar{3}m$), no. 225). Since the ionic

tials $[p(O_2) = f(T)]$ of "FeO" and NiO a complete series of mixed crystals cannot exist. In application of the results of thermodynamic modelling the syntheses of mixed crystals Fe_{1-x}Co_xO and their characterisation by X-ray diffraction and thermal analysis succeeds. The mixed phases crystallise in the halite structure type (space group $Fm\bar{3}m$) with a progress of the lattice constants corresponding to the Vegard rule $[a(Fe_{1-x}Co_xO) = 430.0(2) \text{ pm } (x = 0), 427.8(2) \text{ pm } (x = 0.5),$ 425.0(2) pm (x = 1)].

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radii of the metal cations are similar the lattice constants agree with a difference of less than 3%: $Fe_{1-\delta}O[r_{6}(Fe^{II}) =$ 92 pm,^[5] $a(\text{Fe}_{0.925}\text{O}) = 430 \text{ pm}^{[6]}$, CoO $[r_{\text{foll}}(\text{Co}^{\text{II}}) =$ 89 pm,^[5] $a(CoO) = 425 \text{ pm}^{[7]}$, NiO [$r_{[6]}(Ni^{II}) = 83 \text{ pm}^{[5]}$ $a(NiO) = 419 \text{ pm}^{[8]}$]. Thus similar conditions lead to the formation of solid solutions $Co_{1-x}Ni_xO$,^[2] $Fe_{1-x}Mg_xO$ $[r_{[6]}(Mg^{II}) = 86 \text{ pm},^{[5]} a(MgO) = 421 \text{ pm}^{[9]}], \text{ Fe}_{1-x}Mn_xO$ $[r_{16}(Mn^{II}) = 81 \text{ pm},^{[5]} a(MnO) = 445 \text{ pm}^{[9]}, Ni_{1-x}Mn_xO^{[10]}$ and Mg_{1-x}Mn_xO.^[9]

Moreover, the binaries offer shared ranges of thermal stability (Fe_{1- δ}O: $T_{\rm m} \le 1702$ K,^[11] CoO: $T_{\rm m} = 2078$ K,^[11] NiO: $T_{\rm m} = 2228$ K,^[11] MgO: $T_{\rm m} = 3105$ K,^[11] MnO: $T_{\rm m} =$ 2115 K^[11]). The only restriction in temperature is the eutectoid formation reaction of $Fe_{1-\delta}O$ ($T \ge 843$ K, $\vartheta \ge 570 \, ^{\circ}C^{[11]}$, at lower temperatures $Fe_{1-\delta}O$ decomposes into metallic iron and Fe₃O₄.

So why are the phases $Fe_{1-x}Co_xO$ and $Fe_{1-x}Ni_xO$ nonexistent or at least unknown?

We used the concept of the electromotive series of solid oxide^[14,15] for global analyses of the possibility of formation of ternary solid solutions $M_{1-x}M'_{x}O_{a(s)}$. The electrochemical standard potential is computed under the assumption of formal solid electrolyte cells with an standard oxygen electrode of $p^0(O_2) = 1$ bar. The illustration of all the potentials in an electromotive series (compare Figure 1) enables global predictions of equilibria of reduction and oxidation of oxides in any ternary or higher combination: $x \cdot MO_a/y \cdot M'O_b/...z \cdot M''O_c$. Only compounds with the same range of electrochemical or oxygen potential $[E, p(O_2)]$ can be in coexistence under thermodynamic equilibrium condi-

[[]a] Inorganic Chemistry, Dresden University of Technology, Helmholtzstraße 10, 01069 Dresden, Germany Fax: +49-351-463-37287

E-mail: peer.schmidt@chemie.tu-dresden.de http://www.peer-schmidt.de

tions, i.e. the phases appear in one level (on a horizontal line) of the electromotive series diagram. If binary oxides $MO_{a(s)}$ and $M'O_{b(s)}$ are horizontally adjacent, their common solid state reaction can lead to ternary compounds $M_x M'_y O_{xa+yb(s)}$ or solid solution phases $M_{1-x} M'_x O_{a(s)}$, (Figure 1).



Figure 1. Chemical equilibria (\rightarrow) "FeO_(s)" + $M'O_{(s)}$ leading to the formation of solid solutions Fe_{1-x} M'_xO according to the electromotive series of oxides: M' = Mg: Fe_{1-x} Mg_xO ;^[9] Mn: Fe_{1-x}Mn_xO;^[9] Zn: Fe_{1-x}Zn_xO und Fe_yZn_{1-y}O.^[19] Chemical equilibria leading to the formation reactions FeO_(s) + $M'O_{b(s)} =$ Fe $M'O_{1+b(s)}$ or FeO_{a(s)} + $M'O_{b(s)} =$ Fe $M'O_{a+b(s)}$ (in parentheses) according to the electromotive series of oxides: Ca: (Ca^{II}Fe^{III}₂O₄), (Ca^{II}Fe^{III}₂O₅);^[16] Ti: Fe^{II}Ti^{IV}O₃;^[20] Fe^{II}₂Ti^{IV}O₄;^[21] V: Fe^{II}₂V^{III}₂O₄;^[22] Co: (Co^{II}Fe^{III}₂O₄);^[24] Ni: (Ni^{II}Fe^{III}₂O₄);^[8] Cu: (Cu^IFe^{III}O₂), (Cu^{II}Fe^{III}₅O₈), (Cu^{II}Fe^{III}₂O₄);^[25] Sr: (Sr^{II}Fe^{III}₂O₄);^[17] Nb: Fe^{II}Nb^V₂O₆;^[23] Pd: unknown; Cd: (Cd^{II}Fe^{III}₂O₄);^[18] Pb: (Pb^{II}Fe^{III}₁O ₁₉).^[28]

Due to the different conditions of existence $[p(O_2)_T]$ of the compounds Fe₂O₃, Fe₃O₄ as well as "FeO" the system Fe/O is convenient for systematic thermodynamic approaches. The existence of wustite Fe_{1- δ}O thereby is assumed in an idealised composition "FeO",^[12] the divergence of oxygen partial pressures is less than 0.1 orders of magnitude.

In view of the electromotive series of solid oxides mixed crystals $M_{1-x}M'_xO(M = \text{Fe})$ based on "FeO" [s. g. $Fm\bar{3}m$]] are thermodynamically allowed with the isotypic compounds M'O[M' = Mg, Ca, Mn, (Zn), Sr, Ba], i.e. these phases exist under one common oxygen partial pressure and therefore appear in one level of the electromotive series diagram (Figure 1). However, due to the differences in ionic radii [$r_{[6]}(\text{Fe}^{\text{II}}) = 92 \text{ pm}^{[5]}$] there are restraints concerning the formation of solid solutions for $M' = \text{Ca} (r_{[6]} = 114 \text{ pm}^{[5]})$, Sr ($r_{[6]} = 132 \text{ pm}^{[5]}$) und Ba ($r_{[6]} = 149 \text{ pm}^{[5]} \Delta r_{\text{M}} > 15\%$). Shared levels of electrochemical or oxygen potential lead to the formation of ordered compounds as well: $\text{Ca}^{\text{II}}\text{Fe}^{\text{III}}_2\text{O4}$, $\text{Ca}^{\text{II}}\text{Fe}^{\text{III}}_2\text{O5}$, [¹⁶] Sr^{II}Fe^{\text{III}}_2\text{O4}[¹⁷] and Ba^{II}Fe^{III2}O4.

In full agreement with estimation of common existence ranges references for the existence of mixed crystals $Fe_{1-x}Mg_xO^{[9]}$ and $Fe_{1-x}Mn_xO^{[9]}$ as well as partial solutions $Fe_{1-x}Zn_xO$ (halite type) and $Fe_yZn_{1-y}O$ (wurtzite type)^[19] are found.

In ternary systems Fe/*M*'/O where *M*' is titanium, vanadium or niobium, "Fe^{II}O" is in coexistence only with oxidised species $M'^{2b}O_{b(s)}$ (b > 1: TiO₂, V₂O₃, Nb₂O₅, see Figure 1) and forms the compounds: Fe^{II}Ti^{IV}O₃,^[20] Fe^{II}₂Ti^{IV}O₄,^[21] Fe^{II}V^{III}₂O₄,^[22] and Fe^{II}Nb^V₂O₆.^[23] There is no shared range (lg($p(O_2)$ /bar), *E*) of "FeO" with the monoxides *M*'O and therefore no possibility to form solid solutions Fe_{1-x}*M'*_xO (*M'* = Ti, V, Nb). The thermodynamic equilibrium of "FeO" with *M*'O (*M'* = Ti, V, Nb) has to adjust to build metallic iron and oxidised compounds $M'O_{1+\delta}$ (Figure 1).

In correlation with systems $M'/M'O_{(s)}$ (M' = Co, Ni, Cu, Pd, Cd, Sn, Pb) "FeO" is ignoble and reduces the corresponding oxides to the metals M' while itself becomes oxidised. Thermodynamically, this explains the reason for non-existence of solid solutions Fe_{1-x}Co_xO and Fe_{1-x}Ni_xO. Nevertheless further thermodynamic calculations were carried out in order to understand the chemical equilibria in more detail.

Results and Discussion

Thermodynamic Modelling of the System FeO/CoO

As shown, the formation of solid solutions $Fe_{1-x}Co_xO$ and $Fe_{1-x}Ni_xO$ has to be investigated thermodynamically: according to the electromotive series of oxides {lg[$p(O_2)$ / bar], E} the overlap of existence ranges of $Fe_2O_{3(s)}$ and $CoO_{(s)}$ (see Figure 1) leads to the formation of the spinel phase $Co^{II}Fe^{III}{}_2O_4$.^[24] However, the equilibrium between "FeO" and CoO at T = 1000 K results in a redox reaction towards Fe_3O_4 and Co/CoO, Figure 1.

On the other hand, the temperature-dependent presentation of the oxygen potentials $lg[p(O_2)/bar]_T$ of the cobalt and iron oxides (Figure 2) shows, that the gap of potentials $\Delta \{lg[p(O_2)/bar]\}$ between CoO/Co and Fe₃O₄/"FeO" (--- vs. -, Figure 2) decreases with rising temperature: $\Delta \{lg[p(O_2)/bar]\}_{1300} = -1.8$, $\Delta \{lg[p(O_2)/bar]\}_{1500} = -1.0$, $\Delta \{lg[p(O_2)/bar]\}_{1700} = -0.4$. Hence an overlap at temperatures $\vartheta > 1500$ °C is certain (Figure 2). But it is possible to enforce the formation of Fe_{1-x}Co_xO under thermodynamic equilibrium conditions at lower temperatures?

It has to be considered, that the oxygen potential $p(O_2)$ of the mixed phases $\text{Fe}_{1-x}\text{Co}_x\text{O}$ is dependent on the molar ratio x due to the stabilisation of mixed crystals by $\Delta_{\text{mix}}G_{298}^0 < 0$. The chemical potentials of mixed phases $\mu(\text{Fe}_{1-x}\text{Co}_x\text{O})$ and therewith also the oxygen potentials $p(O_2)$ are influenced by the excess entropy $\Delta_{\text{mix}}S_{298}^0 = R[x\cdot\ln x + (1-x)\cdot\ln(1-x)]$, whose maximum value is reached at x = 0.5 with $\Delta_{\text{mix}}S_{298}^0 = 5.76 \text{ J}\cdot\text{mol}^{-1} \text{ K}^{-1}$.

The change in oxygen potential $\Delta \{ \lg[p(O_2)/bar]_T \}$ due to the formation of mixed crystals [Equation (1)] can be estimated by means of an easy scheme (1)–(4), dependent on the stoichiometry of the gas-phase reactions (2) and (3). Thereby the amount of the excess entropy $\Delta_{mix}S_{298}^0$ of reaction (1) has to be normalised by $(2/x\cdot\delta)$ for the gas phase reaction (3) of mixed crystals. Then the change of partial pressure depends on the shift of oxygen content δ of the



Figure 2. Phase barogram of the system Fe/Co/O with representation of the temperature dependent oxygen partial pressure $p(O_2)_T$ in chemical equilibrium of the binary compounds $Fe_2O_{3(s)}$ (-), $Fe_3O_{4(s)}$ (-) and "FeO" (-) respectively $Co_3O_{4(s)}$ (--), $CoO_{(s)}$ (--) and the metals. The existence ranges ($p(O_2)$; T) of the binary compounds are marked by the arrows (\uparrow) between the equilibrium lines.

product $M'O_{a-\delta(s)}$ of the gas phase reactions (2), (3), the composition x of the solid solution phase $M_{1-x}M'_xO_a$ and the entropy $\Delta_{mix}S_{298}^{0}$ reaction (4). This way, the lowering of partial pressure $p(O_2)$ can be estimated for the mixed phase Fe_{0.5}Co_{0.5}O as about two orders of magnitude. Therewith the intersection of $lg[p(O_2)/bar]$ functions of equilibria CoO/Co and Fe₃O₄/"FeO" and the overlap of existence ranges of CoO and "FeO" shift from 1500 °C to about 900 °C so that the phase formation of Fe_{0.5}Co_{0.5}O can be expected at this temperature.

$$(_{\text{mix}}) (1-x) M \mathcal{O}_{a(s)} + x M' \mathcal{O}_{a(s)} = M_{1-x} M'_x \mathcal{O}_{x(s)}$$
$$\Delta_{\text{mix}} G_T^0 = \Delta_{\text{mix}} H_T^0 - T \cdot \Delta_{\text{mix}} S_T^0$$
(1)

$$(_{gas1}) \frac{2}{\delta} M' O_{a(s)} = \frac{2}{\delta} M' O_{a-d(s)} + O_{2(g)}$$
$$lg[p(O_2)_{MO_a} / bar] = \frac{\Delta_{gas1} S_T^0}{2.303 \cdot R} - \frac{\Delta_{gas1} H_T^0}{2.303 \cdot R} \cdot \frac{1}{T}$$
(2)

$$(_{gas2})\frac{2}{x\cdot\delta}M_{1-x}M'_{x}O_{a(s)} = \frac{2(1-x)}{x\cdot\delta}MO_{a(s)} + \frac{2}{\delta}M'O_{a-\delta(s)} + O_{2(g)}$$
$$\lg(p(O_{2})_{M_{1-x}M'_{x}O_{a}}/bar) =$$

$$\frac{\Delta_{\text{gas}1} S_T^0 - \frac{2}{x \cdot \delta} \Delta_{\text{mix}} S_T^0}{2.303 \cdot R} - \frac{\Delta_{\text{gas}1} H_T^0 - \frac{2}{x \cdot \delta} \Delta_{\text{mix}} H_T^0}{2.303 \cdot R} \cdot \frac{1}{T}$$
(3)

$$\Delta \{ \lg[p(O_2)/bar] \} = \{ \lg[p(O_2)_{M : O_a}] - \lg[p(O_2)_{M_{1-x}M'_x O_a}] \}$$
$$= -\frac{2}{x \cdot \delta} \cdot \frac{\Delta_{\min} G_T^0}{2.303 \cdot R} \cdot \frac{1}{T}$$
(4)



The actual stabilisation by $T \cdot \Delta_{\min} S_T^0$ can be calculated and visualised by the chemical potential $\mu = f(T)$ of the mixed crystals Fe_{1-x}Co_xO (-, Figure 3) vs. the chemical potential of the physical mixture "FeO" + CoO (---, Figure 3). The comparison shows that the representative phase Fe_{0.5}Co_{0.5}O becomes thermodynamic stable at $\vartheta \ge 810$ °C while the *G*-function of the mixture of Fe₃O₄, Co and α' (Fe_{1-x}Co_xO, x > 0.5) represents the minimum of free gibbs enthalpy at temperatures $\vartheta < 810$ °C (Figure 3).



Figure 3. Temperature-dependent behaviour of the *G*-function of the mixture "FeO" + CoO; (---) compared with the function of the mixture $1/_3$ (Fe₃O₄ + Co + 2 CoO); (---) and the chemical potential of the solid solution Fe_{0.5}Co_{0.5}O (-). Representation of the minimum of the free Gibbs energy $G_{Sys-min} = f(T)$ at $\vartheta \ge 810$ °C: Fe_{0.5}Co_{0.5}O.

As the calculation of chemical potentials of solid state reactions is based on the same thermodynamic standard data used for computation of partial pressures and electrochemical potentials equivalent results are obtained. The determination of phase formation temperature by the means of equation (4) is just an estimation, nevertheless the obtained value is in good agreement with the calculated temperature (Figure 3). It is easy to imagine that the G-functions of further mixed phases with varying composition $Fe_{1-x}Co_xO$ can be calculated and presented identically as shown in Figure 3. The two dimensional projection of characteristic temperatures vs. the composition parameter xwould result in the T-x phase diagram of the pseudo binary line "FeO"/CoO. That way the phase relations and the phase diagram "FeO"/CoO has been calculated using the program ChemSage^[33] (see Figure 4).

The binary phase "FeO" only exists above 570 °C, at lower temperatures (T < 843 K, $\vartheta < 570$ °C) the decomposition into metallic iron and Fe₃O₄ takes place. Between partial solutions a, a' a miscibility gap includes the ternary mixture Fe₃O₄ + Co which is formed in consequence of different redox potentials [$p(O_2) = f(T)$] of the binary phases "FeO" and CoO in agreement with the electromotive series of this system. Hence CoO becomes reduced into metallic cobalt while FeO is oxidised into Fe₃O₄. From the formation of "FeO" up to 900 °C FeO-rich mixed crystals $a(Fe_{1-x}Co_xO, x < 0.25)$ are built. The formation of CoO-



Figure 4. Existence range of the solid solution $Fe_{1-x}Co_xO_{(s)}$ and resulting phase relations on the pseudo-binary line "FeO"/CoO dependent on the temperature and the composition, calculation using thermodynamic standard data of compounds (Table 1) and the program ChemSage.^[33]

rich mixed crystals occurs from room temperature $\alpha'(\text{Fe}_{1-x}\text{Co}_x\text{O}, x = 0.9998)$ with a rise of the composition parameter *x* with increasing the temperature up to 900 °C; $\alpha'(\text{Fe}_{1-x}\text{Co}_x\text{O}, x > 0.25)$.

According to the modelling of the phase diagram at temperatures $\vartheta \ge 902$ °C a complete series of mixed crystals $\alpha(\text{Fe}_{1-x}\text{Co}_x\text{O}, 0 \le x \le 1)$ exists (Figure 3). The extremum of the miscibility gap lies at x = 0.25 (= Fe₃O₄ + Co) and $\vartheta = 902$ °C (T = 1175 K). At composition x = 0.5 the miscibility gap ends at $\vartheta = 812$ °C (T = 1085 K) with formation of the solid solution phase Fe_{0.5}Co_{0.5}O.

An idealised assumed homogeneous melt $Fe_{1-x}Co_xO_{(1)}$ completes the phase diagram at high temperatures between T_m ("FeO") = 1645 K and T_m (CoO) = 2078 K, the T_m according to.^[11]



Figure 5. Phase diagram of the ternary system Fe/Co/O at T = 1000 K. The pseudo-binary line "FeO"/CoO is characterized by the solubilities α_{1000} (Fe_{1-x}Co_xO; $x \le 0.04$) and α'_{1000} (Fe_{1-x}Co_xO; $x \ge 0.60$) as well as their phase relations with Fe₃O₄ and metallic cobalt, calculation using thermodynamic standard data of compounds (Table 1) and the program TRAGMIN.^[34]

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Consistent with the calculations of the binary phase diagram "FeO"/CoO the phase relations of the ternary area Fe/Co/O can be modelled using the program TRAG-MIN,^[34] Figure 5. Thereby the description of the coexistence areas of as well binary and ternary phases (T =1000 K, Figure 5) agrees completely the estimation of the phase relations according to the electromotive series (Figure 1): the ternary spinel phase CoFe₂O₄ exists on the pseudo binary section Fe₂O₃/CoO as Co^{II}Fe^{III}₂O₄. Further, the binary oxide Fe₃O₄ is in coexistence with CoO and metallic cobalt. The iron oxide "FeO" coexists with cobalt, too.

The pseudo binary section "FeO"/CoO exists only partially. Mixtures within the miscibility gap between α (Fe_{1-x}Co_xO, $x \le 0.04$) and α '(Fe_{1-x}Co_xO, $x \ge 0.60$, T =1000 K) (see Figure 4) undergo the redox reaction towards Fe₃O₄ + Co.

Phase Formation and Characterisation of Mixed Crystals $Fe_{1-x}Co_xO$

In application of the results of thermodynamic modelling controlled syntheses of mixed crystals $Fe_{1-x}Co_xO$ and their characterisation by X-ray diffraction and thermal analysis succeed. With reference to the modelling solid state reactions in the temperature range $\vartheta = 500-1100$ °C ($\Delta T =$ 100 K) have been performed to analyse as well the expected miscibility gap as the solid solution. At room temperature metastable products have been obtained by quenching with ice water. First of all, the results of investigations concerning the composition Fe_{0.5}Co_{0.5}O shall be presented here. The results of phase analysis of the reaction products in Equation (5) by powder X-ray diffraction are shown in Figure 6.

$$1/3 \operatorname{Fe}_{(s)} + 1/3 \operatorname{Fe}_2 O_{3(s)} + \operatorname{CoO}_{(s)} \rightleftharpoons 2 \operatorname{Fe}_{0.5} \operatorname{Co}_{0.5} O_{(s)}$$
 (5)

At synthesis temperature $\vartheta = 700$ °C a multi phase mixture of iron oxide Fe₃O₄ (see * in Figure 6), cobalt-rich oxide $\alpha'(Fe_{1-x}Co_xO)$ and metallic cobalt (see # in Figure 6) is



Figure 6. Phase analysis by X-ray powder diffraction (Cu- K_a) of samples with the initial composition 1/2 "FeO" + 1/2 CoO obtained by solid state reactions at synthesis temperatures $\vartheta = 700$, 900, 1100 °C.

found. At $\vartheta = 900$ °C the completed formation of Fe_{0.5}Co_{0.5}O can be observed – the diffraction diagram displays only characteristic reflexes of the halite type structure. The positions of reflexes of the solid solution phase $\alpha'(\text{Fe}_{1-x}\text{Co}_x\text{O})$ becomes shifted with increasing the temperature to smaller diffraction angles (higher *d* values). This is the result of the change of the composition parameter whereby the lattice constants increase with decrease of the CoO-content $x [a(\text{Fe}_{0.925}\text{O}) = 430 \text{ pm},^{[6]} a(\text{CoO}) = 425 \text{ pm}^{[7]}]$. Hence for the obtained phase $\alpha'(\text{Fe}_{1-x}\text{Co}_x\text{O})$ the lattice parameters $a(\text{Fe}_{1-x}\text{Co}_x\text{O}) = 426.8(5) \text{ pm}$ ($\vartheta = 700$ °C) and 427.8(5) pm ($\vartheta = 1100$ °C) result.

The process of phase formation has been characterised by the means of difference thermal analyses (DTA) in the temperature range $\vartheta \le 1100$ °C with a heating rate $\Delta T/t =$ 10 K min⁻¹. The sample of the formal composition Fe_{0.5}Co_{0.5}O has been synthesised in a sealed evacuated silica ampoule up to 500 °C and cooled down slowly. DTA measurements were done in sealed evacuated silica micro ampoules with several cycles of heating and cooling. At heating and cooling mode characteristic thermal effects could be detected (Figure 7). From temperatures $\vartheta > 700 \text{ }^{\circ}\text{C}$ a continuous rising endothermic effect occurs. This slight signal within the temperature range up to 850 °C can be assigned to the continuous formation of CoO-rich mixed crystals $\alpha'(\text{Fe}_{1-x}\text{Co}_x\text{O}, x < 0.5)$ with a appreciable decrease of the composition parameter x. The complete transformation of the ternary mixture of the miscibility gap (Fe₃O₄ + $Co + \alpha'$) to $Fe_{0.5}Co_{0.5}O_{(s)}$ proceeds with an intense endothermic effect at $\vartheta_{onset} = 870(10)$ °C and $\vartheta_{max} = 910(10)$ °C (Figure 7). The melting of the sample $[\vartheta_m(\text{Fe}_{0.5}\text{Co}_{0.5}\text{O}) \approx$ 1600 °C, see Figure 4] could not be detected with the used measurement program.



Figure 7. Thermal analysis (DTA) of a sample with the initial composition 1/2 "FeO" + 1/2 CoO, measured in the temperature range from room temperature up to $\vartheta = 1000$ °C in the heating mode (--) with $\Delta T/t = 10 \text{ K min}^{-1}$ and the cooling mode (---) with $\Delta T/t =$ 10 K min⁻¹ as well. Measurement of sealed silica micro ampoule containing the powder sample with the initial composition 1/2"FeO" + 1/2 CoO preheated at 500 °C and cooled down slowly.

With cooling the sample the thermal effects have been reproduced with reversal of heat flux and a hysteresis of about 50 K. Down from high temperatures an intense exo-



thermic effect at $\vartheta_{onset} = 810(10)$ °C for the decomposition of Fe_{0.5}Co_{0.5}O_(s) can be detected. Below 750 °C a slight exothermic signal indicates the further decomposition of mixed crystals α' to Fe₃O₄ + Co + Fe_{1-x}Co_xO ($x \le 1$).

The process proceeds absolutely reversible in several cycles. Although there is a hysteresis of about 50 K between heating and cooling mode the thermodynamic motivation of formation of the solid solution $Fe_{1-x}Co_xO$ and their decomposition can be proved. Hence the results of thermodynamic modelling have been generally confirmed, The temperature shift of 60 K between $T_{f,calc}$ and $T_{f,exp}$ of $Fe_{0.5}Co_{0.5}O_{(s)}$ can be explained by kinetic problems of phase formation. Furthermore the fact of a slight non-ideal behaviour of the solid solution series $Fe_{1-x}Co_xO$ has to be considered.

Finally the presented results can be verified by temperature-dependent X-ray powder diffractometry (Figure 8). The sample of the formal composition "Fe_{0.5}Co_{0.5}O" has been synthesised as described before. From a starting temperature of $\vartheta = 400$ °C in steps of $\Delta T = 50$ K up to 850 °C the existence of a mixture Fe₃O₄ + Co + a' can be observed (Figure 8). The positions of reflexes change to smaller diffraction angles (higher *d* values) due to the thermal expansion of crystal lattices. At temperatures $\vartheta \ge 900$ °C the characteristic reflexes of the spinel phase disappear, the reflex of metallic component ($2\theta \approx 39^\circ$) remains with minor intensity as an artefact of the sample furnace environment. The intensities of the solid solution phase Fe_{1-x}Co_xO (see ' in Figure 8) rise significantly at temperatures $\vartheta \ge 800$ °C, at $\vartheta \ge 900$ °C Fe_{0.5}Co_{0.5}O_(s) represents the main phase.



Figure 8. Temperature dependent phase analysis by high-temperature X-ray powder diffraction (Mo- K_{α}) of samples with the initial composition 1/2 "FeO" + 1/2 CoO. Measurements at temperatures $\vartheta = 400-1050$ °C; $\Delta T = 50$ K; $\Delta t = 30$ min. Attribution of phases: * for Fe₃O_{4(s)}; # for Co_(s); ' for α' (Fe_{1-x}Co_xO_(s); $x \ge 0.5$) and Fe_{0.5}Co_{0.5}O (900 < $\vartheta \le 1050$ °C).

While cooling the sample the thermodynamic equilibrium of decomposition of the mixed phase $Fe_{0.5}Co_{0.5}O_{(s)}$ is adjusted between 800 and 750 °C. Below the characteristic reflexion scheme of the mixture $Fe_3O_4 + Co + \alpha'$ can be observed (Figure 8).

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As shown, the results of phase analyses and thermal analysis prove the predictions made by thermodynamic modelling concerning the phase relations at different temperature ranges very well, the conditions of formation of solid solution $Fe_{1-x}Co_xO$ and the existence ranges of mixed crystals have been confirmed experimentally in full agreement with our calculations.

The lattice constants *a* (halite structure type, space group $Fm\bar{3}m$) of powder samples of different compositions $Fe_{1-x}Co_xO$ show an almost linear progress corresponding to the Vegard rule [$a(Fe_{1-x}Co_xO) = 430.0(2) \text{ pm } (x = 0)$, 427.8(2) pm (x = 0.5), 425.0(2) pm (x = 1), $\vartheta = 1000$ °C], Figure 9. This ideal crystallographic behaviour can be rated as a sign for the homogeneity of the solid solution $Fe_{1-x}Co_xO$ at $\vartheta > 900$ °C. Assuming this ideal behaviour, the composition parameter x = 0.65(1) can be calculated from the lattice constant a = 426.8(5) pm of the $a'(Fe_{1-x}Co_xO)$ phase in the mixture $Fe_3O_4 + Co + a'$ ($\vartheta = 700$ °C, Figure 6). This value is in full agreement with the calculation of the phase diagram ($Fe_{1-x}Co_xO$, x = 0.657, Figure 4).



Figure 9. Progress of lattice constants *a* of samples $Fe_{1-x}Co_xO_{(s)}$ (*x* = 0.0, 0.25, 0.50, 0.75, 1.0) synthesized at ϑ = 1000 °C and quenched to room temperature; trend corresponding to the Vegard rule (- -).

The lattice constant of "FeO" deviates from the straight line because of the non-ideal composition of wustite $Fe_{1-\delta}O_{(s)}$ ($\delta \ge 0.04$). The same behaviour has been described for the existence of mixed crystals $Fe_{1-x}Mg_xO^{[9]}$

Considering this background the problem of the actual composition of obtained samples of the solid solution $(Fe_{1-x}Co_x)_{1-\delta}O_{(s)}$ $(0 \le x \le 1)$ should be discussed. We used thermogravimetric measurements for the experimental proof: cobalt oxide $Co_{1-\delta}O_{(s)}$ has been confirmed with the composition $Co_{1.0}O_{(s)}$. Samples of "FeO" have been synthesised with stoichiometric amounts of $Fe_{(s)} + Fe_2O_{3(s)}$ by solid state reactions at 900 °C. Measured in an oxidising mode the phase pure samples have shown a mass growth $\Delta m/m^0 = 10.0(1)\%$ (Figure 10) which is less than the ideal value $\Delta m/m^0_{\text{theor}} = 11.1\%$ (7), see Equation (6).



Figure 10. Thermal analyses (thermogravimetry $\Delta m/m^0$) of samples "FeO" = Fe_{1- δ}O_(s) and (Fe_{0.5}Co_{0.5})_{1- δ}O_(s) synthesized at ϑ = 1000 °C in sealed, evacuated silica ampoules and quenched to room temperature; measured in the temperature range from room temperature up to ϑ = 1050 °C in the heating mode with $\Delta T/t$ = 10 K min⁻¹.

$$2 \text{ FeO}_{(s)} + \frac{1}{2} \text{ O}_{2(g)} \iff \text{Fe}_2 \text{ O}_{3(s)}$$

$$71.844 \quad 31.999 \qquad 159.688 \text{ g·mol}^{-1}$$

$$\Delta m/m^0_{\text{ theor.}} = 11.1 \% \tag{6}$$

From the experimental mass difference $\Delta m/m^0 = 10.0(1)\%$ a composition of the wustite phase results: Fe_{0.955(5)}O_(s). This composition represents the iron-rich phase boundary of the wustite Fe_{1- δ}O_(s) (0.04 $\leq \delta < 0.15^{[29]}$).

Samples of the mixed crystal $Fe_{0.5}Co_{0.5}O_{(s)}$ react in oxidising atmosphere by the formation of a mixture $Fe_2O_{3(s)}$ + $Co_3O_{4(s)}$ with a mass growth $\Delta m/m^0 = 8.9(1)\%$ (Figure 10). The first step takes place up to 750 °C, above this temperature the reduction of the intermediate $Co_3O_{4(s)}$ occurs. Hence a mass reduction by release of oxygen leads to the formation of $Fe_2O_{3(s)} + CoO_{(s)}$ respectively $Fe_2CoO_{4(s)}$. From the experimental mass difference $\Delta m/m^0 = 8.9(1)\%$ a composition of the mixed crystal results: $(Fe_{0.5}Co_{0.5}O_{(s)})_{0.99(1)}$ - $O_{(s)}$. In consequence the composition $Fe_{0.5}Co_{0.5}O_{(s)}$ can be assumed as ideal, see Equation (7).

$$4 \operatorname{Fe}_{0.5}\operatorname{Co}_{0.5}\operatorname{O}_{(s)} + 5/6 \operatorname{O}_{2(g)} \iff \operatorname{Fe}_{2}\operatorname{O}_{3(s)} + 2/3 \operatorname{Co}_{3}\operatorname{O}_{4(s)}$$

$$146.777 \quad 31.999 \quad 159.688 \quad 240.797 \text{ g} \cdot \text{mol}^{-1}$$

$$\Delta m/m^{0}_{\text{ theor.}} = 9.08 \%$$
(7)

Phase Formation and Characterisation of Mixed Crystals $Fe_{1-x}Ni_xO$

Because of the broader difference of redox potentials $[p(O_2) = f(T)]$ of "FeO" and NiO (Figure 1) a complete series of mixed crystals cannot exist. Hence the pseudo bi-



nary system FeO/NiO shows solubility ranges only at the border of the binary oxides $\alpha(\text{Fe}_{1-x}\text{Ni}_x\text{O})$ ($x \le 0.13$) and $\alpha'(\text{Fe}_y\text{Ni}_{1-y}\text{O})$ ($y \le 0.60$, $\vartheta \le 1400$ °C), see Figure 11.



Figure 11. Existence range of the partial solid solutions Fe_{1-x} - $Ni_xO_{(s)}$ and $Fe_yNi_{1-y}O_{(s)}$ and resulting phase relations on the pseudo-binary line "FeO"/NiO dependent on the temperature and the composition, calculation using thermodynamic standard data of compounds (Table 1) and the program ChemSage.^[33]

Above the formation temperature of "FeO" up to 900 °C FeO-rich mixed crystals $\alpha(\text{Fe}_{1-x}\text{Ni}_x\text{O}, x \le 0.13)$ are formed. The formation of NiO-rich mixed crystals occurs from room temperature $\alpha'(\text{Fe}_y\text{Ni}_{1-y}\text{O}, y = 0.0001)$ with a rise of the composition parameter *y* with increasing temperature up to 1400 °C ($\alpha'(\text{Fe}_y\text{Ni}_{1-y}\text{O}), y \le 0.60$). Between the partial solutions α , α' a miscibility gap includes the ternary mixture Fe₃O₄ + Ni which is formed in consequence of different redox potentials [$p(O_2) = f(T)$] of the binary phases "FeO" and NiO in agreement with the electromotive series of this system. Hence NiO becomes reduced into metallic nickel while FeO is oxidised into Fe₃O₄, Figure 11.

According to the modelling of the phase diagram at temperatures $\vartheta \ge 1400$ °C (1673 K) the mixture Fe₃O₄ + Ni melts [compare: $T_{\rm m}$ (Fe₃O₄) = 1870 K, $T_{\rm m}$ (Ni) = 1728 K]. Depending on the interaction model of different melts L_1 (Fe₃O₄ + Ni) and L_2 ("FeO" + NiO) different case scenarios can be modelled. As there are no experimental clues, the behaviour of the liquidus line can be given only as a speculation presented by the dashed line shown in Figure 11.

The results of thermodynamic modelling can be verified by X-ray diffractometry of samples of the formal composition "Fe_{0.5}Ni_{0.5}O" synthesised at different temperatures (Figure 12). From starting temperature at $\vartheta = 900$ °C in steps of $\Delta T = 100$ K up to 1200 °C the existence of a mixture Fe₃O₄ + Ni + a' can be observed. The positions of reflexes (* in Figure 12) only shift slightly to smaller diffraction angles (higher *d* values) due to the thermal expansion of crystal lattices. The characteristic reflexes of the spinel phase never disappear but the intensities of the solid solution phase $a'(Fe_yNi_{1-y}O)$ rise significantly with increasing temperature. Moreover the positions of reflexes of the solid solution phase $a'(Fe_yNi_{1-y}O)$ shift explicit to smaller diffraction angles (higher *d* values). This is the result of the change of the composition parameter whereby the lattice constants increase with decrease of the NiO-content *y* $[a(\text{Fe}_{0.925}\text{O}) = 430 \text{ pm},^{[6]} a(\text{NiO}) = 419 \text{ pm}^{[8]}]$. Hence for the obtained phase $a'(\text{Fe}_y\text{Ni}_{1-y}\text{O})$ the lattice parameters $a(\text{Fe}_y\text{Ni}_{1-y}\text{O}) = 420.0(5) \text{ pm}$ ($\vartheta = 900 \text{ °C}$) and 422.9(5) pm ($\vartheta = 1200 \text{ °C}$) result. Assuming an ideal crystallographic behaviour the composition parameters $y_{700} = 0.10(1)$ respectively $y_{1000} = 0.36(1)$ can be calculated from the lattice constant $a(\text{Fe}_y\text{Ni}_{1-y}\text{O})$ in the mixture $\text{Fe}_3\text{O}_4 + \text{Ni} + a'$ ($\vartheta = 700 \text{ °C}$, Figure 12). These values are lower than the ones obtained by the calculation of the phase diagram ($\text{Fe}_y\text{Ni}_{1-y}\text{O}$, $y_{700} = 0.29$, $y_{1000} = 0.53$, Figure 11). Thus it has to be accepted, that the model of an ideal solid solution is invalid for the thermodynamic modelling of the partial solutions $\text{Fe}_{1-x}\text{Ni}_x\text{O}$ and $\text{Fe}_y\text{Ni}_{1-y}\text{O}$.



Figure 12. Phase analysis by X-ray powder diffraction (Cu- K_{α}) of samples with the initial composition 1/2 "FeO" + 1/2 NiO obtained after solid-state reactions at synthesis temperatures $\vartheta = 900$, 1000, 1100, 1200 °C.

Conclusions

In spite of the almost perfect crystallographic conditions for the formation of mixed phases $Fe_{1-x}Co_xO$ and $Fe_{1-x}Ni_xO$ no homogeneous solid solutions series exist. Hence the phase formation is driven only by the thermodynamic properties of binary compounds and their interaction: Due to the different redox potentials $[p(O_2) = f(T)]$ of the binary phases "FeO" and CoO the solid solution shows a miscibility gap, by reason of the broader difference of redox potentials $[p(O_2) = f(T)]$ of "FeO" and NiO a complete series of mixed crystals cannot exist. Global estimations and predictions of this behaviour can be done by using the concept of an *electromotive series of solid oxides*.

By the means of detailed thermodynamic modelling the existence ranges of ternary solid solutions $\alpha(\text{Fe}_{1-x}\text{Co}_x\text{O})$ ($\vartheta \ge 902 \,^{\circ}\text{C}$), $\alpha(\text{Fe}_{1-x}\text{Ni}_x\text{O})$ ($x \le 0.13$) and $\alpha'(\text{Fe}_y\text{Ni}_{1-y}\text{O})$ ($y \le 0.60$, $\vartheta \le 1400 \,^{\circ}\text{C}$) have been calculated. The experimental proof succeeded using different analytical methods. Thereby the solid solution $\alpha(\text{Fe}_{1-x}\text{Co}_x\text{O})$ shows an almost ideal behaviour concerning as well the crystallographic as the thermodynamic properties.

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Even if syntheses of mixed crystals $Fe_{1-x}Co_xO$ ($0 \le x \le 1$, $\vartheta > 900$ °C) have been realised, their use as metal oxide combustion catalysts is unfeasible, since the thermodynamic equilibrium adjusts rapidly towards the miscibility gap at the reaction temperatures of combustion of hydrocarbons ($\vartheta \approx 600$ °C). Only members of the partial solid solution $\alpha'(Fe_{1-x}Co_xO)$, x > 0.75 are thermodynamic stable under the required condition. For applications the formation of the respective metal carbides has to be regarded experimentally although the oxygen partial pressure is very high. The application of the partial solutions $\alpha(Fe_{1-x}Ni_xO)$ and $\alpha'(Fe_yNi_{1-y}O)$ as metal oxide combustion catalysts does not seem to be realistic.

In respect of syntheses of multiple component metal oxide combustion catalysts the *electromotive series of solid oxides* can be taken as an easy, far-reaching tool for a systematic design of new materials. As only compounds with shared ranges of electrochemical or oxygen potential can interact and form new phases, a combinational solution of synthesis results.

Experimental Section

Preparation: Starting materials used were iron powder (ABCR, 99.9%), iron oxide Fe₂O₃ (Riedel-de Haën, 99%), cobalt oxide Co₃O₄ (p.a. quality, Merck) and nickel oxide NiO (99%, Chempur). The defined components of syntheses Fe, Fe₂O₃ and CoO have been obtained by further preparation under controlled conditions of oxygen partial pressure: Fe has been reduced by hydrogen at ϑ = 500 °C (t = 3 h). Fe₂O₃ has been treated with oxygen for complete oxidation of iron oxide powder at ϑ = 500 °C (t = 3 h). Cobalt oxide CoO has been obtained by thermal degradation of Co₃O₄ at 900 °C under argon atmosphere. The composition of obtained "FeO", CoO and Fe_{1-x} Co_xO, i.e. the oxygen content, has been proved by thermogravimetric measurements in an oxidising atmosphere. All starting materials have been handled in an argon-filled glove box (c(O₂, H₂O) < 0.1 ppm). The starting materials Fe/ Fe₂O₃/CoO(NiO) were mixed together in the molar ratio of defined

compositions (1-x) "FeO" + x M'O (7) and sealed in evacuated silica ampoules, see Equation (8).

$$(1-x)/3 (Fe_2O_{3(s)} + Fe_{(s)}) + x M'O_{(s)} \rightleftharpoons Fe_{1-x} M'_xO_{(s)}$$
 (8)

Adherent moisture has been removed by heating under dynamic vacuum prior to use. The mixtures were heated at different temperatures $\vartheta = 500-1100$ °C with steps of $\Delta T = 100$ K in furnaces for 3–4 d and rapidly cooled to room temperature with ice water. The products are micro-crystalline powders and, at room temperature, not sensitive to oxygen and moisture.

Phase Analysis: Samples of $Fe_{1-x}Co_xO$ and $Fe_{1-x}Ni_xO$ (x = 0.0, 0.25, 0.5, 0.75, 1.0), quenched from different reaction temperatures, have been analysed by X-ray powder diffraction using a Siemens D5000 diffractometer (Cu- K_{α} radiation, reflexion mode) at room temperature.

For determination of temperature dependent phase equilibria high temperature X-ray powder diffraction using a Stoe StadiP diffractometer (Mo- K_{a1} radiation, capillary, transmission mode) was carried out. Starting material with the initial compositions Fe_{0.5}Co_{0.5}O and Fe_{0.5}Ni_{0.5}O were preheated in tubular furnaces for 3–4 d at 500 °C and rapidly cooled to room temperature. In order to avoid oxidation or reduction from the atmosphere samples were measured in sealed capillaries. Measurements ran from a starting temperature $\vartheta = 400$ °C up to 1050 °C, one diffraction pattern was recorded every 50 K with a hold time $\Delta t = 30$ min for the adjustment of thermal equilibrium. To prove the reversibility of chemical equilibria, the samples were cooled from $\vartheta = 1050$ down to 400 °C in the same manner ($\Delta T = 50$ K, $\Delta t = 30$ min). The obtained data were analysed using the programm WinX^{POW[30]} and compared to the PDF-2 data base.^[31]

Thermal Analysis: Thermogavimetric measurements have been performed under different atmospheres (argon, air, oxygen) on a Netzsch STA 409 Luxx with a heating rate of 10 K min⁻¹ in the temperature range from room temperature up to 1100 °C.

The process of phase formation has been characterised by means of difference thermal analyses (DTA) of initial mixtures of different compositions (1–*x*) "FeO" + *x* CoO in the temperature range $\vartheta \le 1100$ °C with a heating rate $\Delta T/t = 10$ K min⁻¹ on a Seteram

Table 1. Thermodynamic data of condensed phases in the systems Fe/Co/O and Fe/Ni/O.

Compound	ΔH^0_{298} [kJ mol ⁻¹]	S_{298}^0 [J K ⁻¹ mol ⁻¹]	$\frac{C_p^{[a]}}{[JK^{-1}mol^{-1}]}$			Ref.
			а	b	С	
Fe ₂ O _{3(s)}	-823.4	87.4	98.3	77.8	-1.5	[12]
$Fe_3O_{4(s)}$	-1115.5	146.2	140.0	90.0		[12]
$Fe_3O_{4(1)}$	-1115.2	146.2	213.4			[11]
"FeO(s)"	-266.0	59.4	44.7	12.0		[12]
"FeO ⁽⁾ "	-247.4	58.5	65.8			[11]
Fe _(s)	0.0	27.3	18.0	22.8		[12]
$Co_3O_{4(s)}$	-918.7	109.3	131.6	66.0	-2.5	[12]
CoO _(s)	-237.9	53.0	48.0	10.0		[12]
CoO	-185.9	71.9	60.7			[11]
Co _(s)	0.0	30.1	20.0	16.0		[12]
NiO(s)	-239.7	38.0	44.0	14.0		[12]
NiO	-178.4	65.3	54.4			[11]
Ni	0.0	29.9	24.8	9.0		[12]
$Fe_{0.75}Co_{0.25}O_{(s)}$	-259.0	62.5	45.5	11.5		[b]
$Fe_{0.50}Co_{0.50}O_{(s)}$	-251.9	61.9	46.4	11.0		[b]
$Fe_{0.25}Co_{0.75}O_{(s)}$	-244.9	59.3	47.2	10.5		[b]

[a] $C_p = a + b \times 10^{-3} T + c \times 10^6 T^{-2}$; optimised for the temperature range $T \le 2200$ K. [b] $\Delta_{mix} H_{298}^0 = 0$; $\Delta_{mix} S_{298}^0 = R[x \cdot \ln x + (1 - x) \cdot \ln(1 - x)]$.



Labsys TM thermal analyser. In order to avoid oxidation or reduction from the atmosphere, DTA measurements were done in sealed evacuated silica micro ampoules.

Thermodynamic Modelling: To understand the complex mechanism of formation of mixed crystals $Fe_{1-x}Co_xO$ and to optimise the synthesis a detailed thermodynamic modelling and description of the ternary system Fe/Co/O was aspired. In this modelling the components as well as the binary compounds $Fe_2O_{3(s)}$, $Fe_3O_{4(s)}$, "FeO_(s)", $Co_3O_{4(s)}$ and $CoO_{(s)}$ respectively NiO_(s) had to be included to reach a realistic picture of the phase relations in the ternary system. The thermodynamic data (Table 1) for the binary compounds are well known, the data set is adopted from.^[11–13] The existence of wustite $Fe_{1-\delta}O$ is assumed in an idealised composition "FeO" as referred.^[11–13]

The estimation of thermodynamic interaction of metal oxides at the formation of mixed crystals $Fe_{1-x}Co_xO$ is based on the assumption of an ideal solid solution, where is $\Delta_{mix}G_{298}^0 = -T\cdot\Delta_{mix}S_{298}^0$ ($\Delta_{mix}H_{298}^0 = 0$) and $\Delta_{mix}S_{298}^0 = R[x\cdot \ln x + (1-x)\cdot \ln(1-x)]$.^[32] The functions of heat capacity were estimated for all compositions according to the rule of Neumann-Kopp.

Thermodynamic modelling of phase equilibria have been performed by using CALPHAD methods based on the Eriksson Gibss energy minimiser implemented in the programs ChemSage^[33] and TRAGMIN.^[34] The binary phase diagrams have been calculated with the *two-dimensional phase mapping* mode (Chemsage^[33]) in the temperature range 300–3000 K. For two-dimensional phase mapping the thermodynamic stable solid mixture of Fe_(s) + Fe₃O_{4(s)} has been introduced with a *G*-function as the sum of chemical potentials $[\mu_T(Fe) + \mu_T(Fe_3O_4) = \mu_T("Fe_4O_{4rt}") = 4 \cdot \mu_T("FeO_{rt}")]$. At temperatures $\vartheta \ge 570$ °C the function of the wustite phase "FeO_{ht}"^[12] was valid. The redox equilibria Fe₃O₄ + *M'* have been introduced with he sum of chemical potentials $[\mu_T(M') + \mu_T(Fe_3O_4)]$ $= \mu_T$ ("*M*'Fe₃O₄")].

Data of the liquid components "FeO₍₁₎" and $M'O_{(1)}$ have been taken in agreement with literature data,^[11,35] the *G*-functions of the liquid phases were adopted for an ideal solution.

Finally the phase relations in the ternary area Fe/Co/O and the solid state – gas phase equilibria have been calculated using the program TRAGMIN^[34] at different given compositions isothermally in the temperature range 800–1500 K with $\Delta T = 100$ K.

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