

Defect Complexes and Defect Clusters in $\text{Mn}_{1-\delta}\text{O}$, $\text{Co}_{1-\delta}\text{O}$ and $\text{Ni}_{1-\delta}\text{O}$ Oxides Diagrams of the Concentrations of Point Defects

Andrzej Stokłosa

Faculty of Chemical Engineering and Technology, Cracow University of Technology

ul. Warszawska 24, 31-155 Kraków, Poland

Tel: 48-126-282-753 E-mail: astoklos@chemia.pk.edu.pl

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Abstract

The diagrams of the concentrations of point defects, determined for a series of temperatures, for the oxides: $\text{Mn}_{1-\delta}\text{O}$, (1173-1830 K), $\text{Co}_{1-\delta}\text{O}$ (1223-1673 K) and $\text{Ni}_{1-\delta}\text{O}$ (1273-1673 K), whilst taking into consideration simple defects and defect clusters of type (2:1), (4:1), (6:2), are presented in this work. A new method was used for the calculations of the diagrams and the results of the studies of the deviation from the stoichiometry obtained by many authors were used in the calculations.

The values of ΔG° of the formation of the individual defects and clusters were determined; their temperature dependencies were also determined. The calculations show that in the studied oxides the maximal concentration of defect clusters is lower than the concentration of single-ionized cation vacancies. At the lowest temperatures studied, the concentration of clusters is comparable to the concentration of electroneutral vacancies. The ratio of these concentration decreases with the temperature increase. The presence of defect clusters only slightly decreases the concentration of cation vacancies. The ratio of the concentrations of defect clusters varies with the temperature. This ratio is different for the individual oxides.

Keywords: Diagrams of concentrations of point defects, Defect clusters, Non-stoichiometric oxides, $\text{Mn}_{1-\delta}\text{O}$, $\text{Co}_{1-\delta}\text{O}$, $\text{Ni}_{1-\delta}\text{O}$

1. Introduction

The non-stoichiometric oxides of 3d transition metals: $\text{Mn}_{1-\delta}\text{O}$, $\text{Fe}_{1-\delta}\text{O}$, $\text{Co}_{1-\delta}\text{O}$ and $\text{Ni}_{1-\delta}\text{O}$ have been the subject of numerous studies for many years, due to their potential use and because they are model systems that allow for the verification of the point defects theory (Kröger, 1974; Kofstad, 1972; Rao & Raveau, 1995; Smyth, 2000; Sørensen, 1981; Tilley, 2008). They show a real insufficiency of metal and the defects are present mainly in the cation sublattice. Although the electron structure of metal ions does not differ much, their oxides are significantly different when considering the structure and the concentrations of the point defects. This causes important differences in the transport properties, dependent on the type of defects and on their concentration (diffusion rate, electrical conductivity, Seebeck effect, etc.). The $\text{Ni}_{1-\delta}\text{O}$ oxide shows the lowest concentration of defects, the $\text{Co}_{1-\delta}\text{O}$ oxide - a higher one, and the highest concentration, up to 0.15 mol/mol, is shown by $\text{Fe}_{1-\delta}\text{O}$. On the other hand, the manganese oxide in the range of its existence reaches the stoichiometric composition, and on the $\text{Mn}_{1-\delta}\text{O}/\text{Mn}_3\text{O}_4$ phase boundary the concentration of defects reaches about 0.1 mol/mol (Kofstad, 1972). In the range of small deviations from the stoichiometry, the double-ionized vacancies dominate in the oxides, such as in the $\text{Ni}_{1-\delta}\text{O}$. At higher concentrations of defects, for example in $\text{Co}_{1-\delta}\text{O}$ and $\text{Mn}_{1-\delta}\text{O}$ oxides, there is a mutual interaction between the vacancies and the electron holes, and a significant contribution to the deviation from the stoichiometry is due to the single-ionized vacancies and electroneutral vacancies (these defects could be considered as complexes of a cation vacancy and M^{3+} ($\text{M}_\text{M}^\bullet$) ion. The presence of a significant concentration of single-ionized or electroneutral vacancies is signaled by the nature of the dependence of the deviation from the stoichiometry on the oxygen pressure (the increase of the 1/n exponent in the dependence of δ on p_{O_2}). The effect of the long-range electrostatic interaction between defects is described by the activity coefficient, which can be calculated with the methods of the statistical thermodynamics (Allbat & Cohen, 1964) or using the Debye-Hückel theory for electrolytes. Dieckmann (Dieckmann, 1977), Nowotny et al. (Nowotny et al., 1984, 1989, 1992) and

Constant et al. (Constant et al., 1992). performed the calculations of the concentration of cobalt vacancies in $\text{Co}_{1-\delta}\text{O}$, taking into account the activity coefficients determined according to the Debye-Hückel theory. These authors obtained compatibility between the concentration of vacancies and the experimental values of δ , although the activity coefficient varied, according to the changing oxygen pressure, in a fairly wide range, which leaves room for doubt. Similar calculations for $\text{Mn}_{1-\delta}\text{O}$ were performed by (Keller & Dieckmann, 1985). But in order to obtain an agreement with the experimental results of δ they adjusted the values of the dielectric constant, which strongly varied with the temperature. At higher concentrations of cation vacancies in oxides, an interaction between cation vacancies with different ionization degrees is postulated (i.e. the formation of complexes of $(V_M V_M)'$, $(V_M V_M)^x$ type) (Bransky & Tallan, 1971; Soullard, 1995; Raymaud & Morin, 1985). A large number of studies and computer calculations treated the formation of complexes and larger clusters as a result of interactions between cation vacancies and interstitial cations. The presence of defects of this type was found experimentally in wüstite $\text{Fe}_{1-\delta}\text{O}$ (Roth, 1960; Koch & Cohen, 1969; Cheetham et al., 1971; Andersson & Sletnes, 1977; Battle & Cheetham, 1979; Gartstein et al., 1986; Radler et al., 1990; Schweika et al., 1995) which has been also confirmed by computer simulations (Gartstein et al., 1986; Radler et al., 1990; Schweika et al., 1995; Catlow et al., 1975, 1977, 1979, 1981a, 1981b, 1985a, 1985b, 1989, 1990; Anderson et al., 1984; Grimes et al., 1986, 1987; Tetot & Gerdanian, 1985). The simplest ionic complexes are complexes of type (2:1), $\{(V_M)_2 M_i^{3+}\}'$, proposed by (Roth, 1960) and complexes of type (4:1) $\{(V_M)_4 M_i^{3+}\}^{5'}$, proposed by (Cheetham et al., 1971). More complex clusters were proposed by (Catlow & Fender, 1975), (6:2), and by (Koch & Cohen, 1969), (13:4). The calculations, performed by (Libowitz, 1968) and (Kofstad & Hed, 1968), for the wüstite ($\text{Fe}_{1-\delta}\text{O}$) have shown that the dependence of the deviation from the stoichiometry can be quite well described when assuming the complexes of type (2:1). A wider discussion was put forward by (Rekas & Mrowec, 1987), considering a series of different complexes with different ionization degrees. They obtained the best agreement for (4:1) complexes with a variable ionization degree. A good agreement was also obtained by (Nowotny & Rekas, 1989), with the assumption that (4:1) complexes dominate and after having taken into account the activity coefficients calculated according to the Debye-Hückel theory. However, the activity coefficients varied in a wide range. From the above calculations it transpires, that the assumption of the domination of one type of defect and the consideration of the activity coefficients could falsify the real structure of the defects. A second oxide showing a significant deviation from the stoichiometry, in which the presence of defect clusters should be expected, is $\text{Mn}_{1-\delta}\text{O}$. The neutronographic studies performed by (Schuster et al., 1989) have not confirmed the presence of a significant concentration of defect clusters. However, their presence is indicated by the results of studies and by the calculations performed by (Radler et al., 1992). The structure of defects and the energy of the formation of clusters in the oxides of *3d* metals were widely discussed by (Tomlison et al., 1990). They presented the calculations of mutual concentrations of simple defects and clusters for $\text{Mn}_{1-\delta}\text{O}$, $\text{Co}_{1-\delta}\text{O}$, $\text{Ni}_{1-\delta}\text{O}$ at 1473 K. Also the simulation calculations (Catlow et al., 1977a, 1977b, 1979, 1981a, 1981b, 1985; Tomlison et al., 1985, 1989, 1990; Anderson et al., 1984; Grimes et al., 1986, 1987; Tetot & Gerdanian, 1985) and studies of many other authors (Radler et al., 1992; Schuster et al., 1989; Nowotny & Rekas, 1989; Klowash & Ellis, 1987; Kleine et al., 1979; Raymaud & Morin, 1985; Sykora et al., 1985, 1989; Petot-Ervas et al., 1984, 1985) indicate that in $\text{Mn}_{1-\delta}\text{O}$, $\text{Co}_{1-\delta}\text{O}$, $\text{Ni}_{1-\delta}\text{O}$ oxides the presence of defect clusters should be expected. Despite numerous theoretical calculations and computer simulations (Kröger, 1974; Stoneham et al., 1985; Tomlison et al., 1985, 1989, 1990; Radler et al., 1992) there is no data allowing for a wider verification of the results of the calculations against the experimental results deviations from stoichiometry. Particularly, such data would take into account the coexistence of a few types of defects and defects clusters and would determine the temperature dependence of the equilibrium constants of the reactions of their formation.

In the previous works (Stokłosa, 2011a, 2011b, 2012), the calculations of the diagrams of the concentrations of point defects were performed, for $\text{Co}_{1-\delta}\text{O}$, $\text{Ni}_{1-\delta}\text{O}$ and $\text{Mn}_{1-\delta}\text{O}$, using the results of the studies of the deviation from the stoichiometry by different authors, assuming as a first approximation that there are cation vacancies and interstitial metal ions with different ionization degrees. A new method was used there for the calculations of the diagrams. This method permits, in the range of small deviations from the stoichiometry, the adjustment of the values of ΔG_f° of the formation of intrinsic ionic defects (Frenkel-type) and double-ionized cation vacancies $(\Delta G_{V_M}^\circ)$, and for higher oxygen pressures the value of $(\Delta G_{V_M}^\circ)$ of the formation of single-ionized and electroneutral vacancies $(\Delta G_{V_M^x}^\circ)$ (the equilibrium constants are calculated). In this method, in a series of steps, for the individual ranges of the oxygen pressure, one parameter is adjusted (ΔG_n° of the formation of individual defects). This significantly increases the possibility of their unambiguous determination, which differs from the method of (Brouwer, 1954), where the equilibrium constants for all of the considered defects must be known. As a result, a simplified electroneutrality condition is used. It was also shown (Stokłosa, 2011, 2012) that the inclusion of the interstitial cations (neglected so far) in the model of the defects structure dramatically changes the calculated

dependences of the concentrations of defects on the oxygen pressure in the pure oxide and, particularly, in the oxide doped with M^{+} ions.

This work presents the calculations of concentrations of the defects (diagrams of the concentrations of point defects), performed using the results of the studies of the deviation from the stoichiometry by many authors, for the oxides: $Co_{1-\delta}O$, $Ni_{1-\delta}O$ i $Mn_{1-\delta}O$ whilst taking into consideration all of the types of defects in the cation sublattice, namely: the simple defects and defect clusters of type (2:1), (4:1), (6:2).

2. Method of Determining the Diagrams of the Concentrations of Point Defects

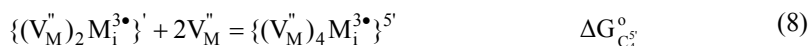
During the calculations of the concentrations of defects it was assumed, according to the point defects theory, that point defects (simple defects and defect clusters) are treated as quasi-particles that form a solution in the oxide and are subject to classical laws of chemical thermodynamics. According to the Kröger-Vink symbolics, the formation of double-ionized cation vacancies and interstitial ions as well as their complexes with electron defects in the $M_{1-\delta}O$ oxide can be described by the following reactions:



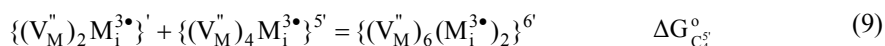
On the other hand, the interactions of cation vacancies with an interstitial ion and with an electron hole leads to the formation of the most simple complex of type (2:1).



The interaction of the (2:1) complex with two cation vacancies causes the formation of the (4:1) complex, yet with higher symmetry:

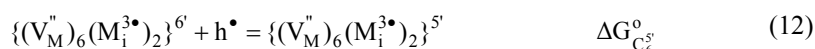
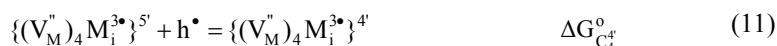


The above complexes could form more complex clusters, e.g.:



where ΔG_n^0 are the standard Gibbs energies of the processes of the formation of individual defects. The indices C_2' , $C_4^{5'}$ and $C_6^{6'}$ denote the clusters: $\{(V_M'')_2 M_i^{3\bullet}\}'$ - (2:1)', $\{(V_M'')_4 M_i^{3\bullet}\}^{5'}$ - (4:1)^{5'} and $\{(V_M'')_6 (M_i^{3\bullet})_2\}^{6'}$ - (6:2)^{6'}, respectively.

If we assume that there is an interaction between cation vacancies and electron holes (Eqs. (2) and (3)), then their interaction with defect complexes and defect clusters should be also be considered in the model of defects. The formation of the individual clusters with a lower ionization degree is presented by the reactions:



The formation of more complex defect clusters, which were found in $Fe_{1-\delta}O$, can be expressed by a series of reactions where there are interactions of increasingly complex clusters that are formed, starting from (6:2), with the complexes C_2' or $C_4^{5'}$. The formation of these types of clusters will cause a change in the concentration of simple complexes, but they will not influence the concentration of vacancies and the deviation from the stoichiometry.

Therefore, in the equilibrium state, there are many equilibria in the oxide that are mutually coupled (Eqs. (1) - (12)). A change in the oxygen pressure causes a change of relative concentrations of the defects and the setting of a new equilibrium state. To describe this process it is necessary to determine a reference state, which could be, for

example, the stoichiometric composition. Quite expanded relations describing the above process are presented in the Appendix. On the other hand, from the analysis of the above equations it transpires that the description of the equilibrium state existing near the stoichiometric composition comes down to simple Eqs. (A36) and (A38), which are obtained as a result of simplification and compensation of the concentrations of the defects. They relate ΔG_i^0 of the formation of intrinsic electron defects and ΔG_F^0 of ionic defects and $\Delta G_{V_M}^0$ of the formation of vacancies, $\Delta G_{\text{def}}^{0(\delta \cong 0)}$ of the formation of defects when $\delta \cong 0$, and the oxygen pressure where the oxide reaches the stoichiometric composition; they are the basis of the method used.

Therefore, in order to determine the values of ΔG_F^0 and $\Delta G_{V_M}^0$ (equilibrium constants), the Eq. (A40), resulting from the Eqs. (A36) and (A38), is used. Knowing the value of ΔG_i^0 , obtained after having been based on the studies of the electrical properties, such values of ΔG_F^0 and $\Delta G_{V_M}^0$ are adjusted, fulfilling the Eq. (A40), whereby, in the range of small deviations from the stoichiometry the dependence of the deviation from the stoichiometry on p_{O_2} is consistent with the experimental results of δ . When the concentrations of $[V_M'']$ and $[M_i^{**}]$ are determined, in the proceeding steps the next defects' equilibria are taken into account, as well as the resulting couplings from the reactions (1) - (12). Therefore, the values of ΔG_C^0 of the formation of the individual complexes, $\Delta G_{C_2}^0$, $\Delta G_{C_4}^0$, $\Delta G_{C_6}^0$ etc., are adjusted in order to obtain, in a possibly wide range of p_{O_2} , the accordance of the dependence of δ on p_{O_2} with the experimental results of δ . The increase of the concentration of clusters causes the decrease of the concentration of vacancies $[V_M'']$; their concentration becomes independent from p_{O_2} . This limits the possibility of increasing the value of ΔG_C^0 of the formation of individual clusters. If the obtained dependence of δ on p_{O_2} differs from the experimental values of δ , in the next steps of the calculations the values of $\Delta G_{V_M}^0$ of the formation of single-ionized vacancies and $\Delta G_{C_2}^0$, $\Delta G_{C_4}^0$, $\Delta G_{C_6}^0$ of the formation of clusters with a lower ionization degree are adjusted. The calculations for all of the defects with a lower ionization degree assumed the same values of ΔG_C^0 of their formation ($\Delta G_{V_M}^0 = \Delta G_{C_2}^0 = \Delta G_{C_4}^0 = \Delta G_{C_6}^0$), assuming that the energy of their interaction with M_M^* (h^*) ions is similar (it could be only lower). As a result of the performed calculations it was found that the introduction of vacancies V_M' into the model of the defects structure required the decrease of the values of ΔG_C^0 of the formation of complexes, which was previously adjusted, besides a small correction of $\Delta G_{V_M}^0$. Therefore, such maximal values of $\Delta G_{C_2}^0$, $\Delta G_{C_4}^0$, $\Delta G_{C_6}^0$ and $\Delta G_{V_M}^0 = \Delta G_{C_2}^0 = \Delta G_{C_4}^0 = \Delta G_{C_6}^0$ were chosen that, in the possibly widest range of p_{O_2} , the accordance of the dependence of δ on p_{O_2} with the experimental results of δ was obtained. When there was no accordance, the values of $\Delta G_{V_M}^0$ of the formation of electroneutral vacancies were adjusted in order to obtain a full accordance with the values of δ . When considering the defects with lower ionization degrees it was assumed that $\Delta G_{V_M}^0 = \Delta G_{M_i^*}^0$ and $\Delta G_{V_M}^0 = \Delta G_{M_i^*}^0$. Clusters with even lower degrees of ionization were not taken into account because their concentration was small.

The concentration of the electron defects vs. $[V_M'']$ was calculated after considering the concentrations of all ionic defects in the electroneutrality condition and solving a quadratic equation. The equilibrium oxygen pressure was calculated using the equilibrium constant ($\Delta G_{V_M}^0$ value) for the reaction of the formation of vacancies V_M' (Eq. (1)), their concentration, and the concentration of electron holes.

The description of the equilibrium state with the concentration of defects, presented in the Appendix, suggests that the defects form an ideal solution. Thus, it could be doubtful whether the obtained results, especially when the concentration of defects is significant, are not charged with excessive errors. The method of calculation presented above to a certain extent takes into account the influence of long-range interactions between the defects. Namely, the values of ΔG_F^0 and $\Delta G_{V_M}^0$ are performed for the range of low concentrations of defects and, as such, it can be assumed that the activity coefficient is close to one. In the case of higher concentrations of defects it can be assumed that in the individual ranges of oxygen pressures the mean value of the activity coefficient for a given type

of defect (f_n), is approximately constant. The logarithm of the equilibrium constant ($\ln K_n$) will be decreased by the value of the term $\ln(f_n)$ in this instance. Thus, choosing the values of ΔG_n^0 of the formation of individual clusters and defects with lower ionization degrees, for the individual ranges of higher concentrations of defects, the mean value of the activity coefficient is taken into account ($\overline{\Delta G}_n^0 = \Delta G_n^0 - RT \ln(\overline{f}_n)$). Therefore, the determined equilibrium constants are the effective constants.

3. Results of Calculations and Discussion

3.1 Concentrations of Simple Defects and Defect Clusters in $Mn_{1\pm\delta}O$

In the previous work (Stokłosa, 2012) the calculations of diagrams of point defects in $Mn_{1\pm\delta}O$ were presented, assuming in the first approximation the presence of manganese vacancies and interstitial ions with the highest ionization degree and lower ionization degrees. The obtained character of the dependence of $\Delta G_{V_{Mn}}^0$ and $\Delta G_{V_{Mn}}^x$ on the temperature (a strong increase with the temperature), the high concentration of vacancies and electron holes, besides the calculations of (Tomlison et al., 1989, 1990) and other authors (Grimes et al., 1986, 1987; Tetot & Gerdanian, 1985), indicate that in $Mn_{1-\delta}O$ not only should simple defects be present, but also complexes (clusters) of ionic defects. Therefore, in these calculations, concerning the defect structure model both simple complexes $\{(V_{Mn}''')_2 Mn_i^{3\bullet}\}^{\cdot}$ - (2:1) $^{\cdot}$, $\{(V_{Mn}''')_4 Mn_i^{3\bullet}\}^{5\cdot}$ - (4:1) $^{5\cdot}$, and more complex clusters, $\{(V_{Mn}''')_6 (Mn_i^{3\bullet})_2\}^{6\cdot}$ - (6:2) $^{6\cdot}$, also with lower ionization degrees, formed according to the reactions (7) - (12) were taken into account. The values ΔG_i^0 of the formation of electronic defects were determined according to the relation (Stokłosa, 2012):

$$\Delta G_i^0 = -2RT \ln \frac{V_{MnO} \sigma_{min}}{2F\mu_h b^{1/2}} \quad (13)$$

where V_{MnO} is the molar volume of the oxide (13.32 cm^3), F - the Faraday constant, and $b = \mu_e/\mu_h$ the ratio of the mobility of electrons to the mobility of electron holes. In the calculations the values of the minimum in the electrical conductivity (σ_{min}) and the mobility of electron holes (μ_h) were used, as obtained by (Error & Wagner, 1971) and it was assumed that the mobility of electrons is not dependent on the temperature and it is $\mu_e = 10 \text{ cm}^2/\text{Vs}$ (Kleinpenning, 1976).

According to the method presented above, in the first stage of the calculation the existence of defects in the highest degree of ionization (V_{Mn}''' and $Mn_i^{3\bullet}$) was assumed. When choosing the values of ΔG_F^0 and $\Delta G_{V_{Mn}}^0$ it was concluded that the change in the value of ΔG_F^0 of the formation of intrinsic ionic defects, in a fairly wide range of p_{O_2} does not affect the dependence of δ on p_{O_2} (in the range where the experimental values of δ were determined). However, the change of ΔG_F^0 affects the nature of the dependence of the sum of concentrations of holes and electrons near the minimum of the sum ($[h^{\bullet}] + b[e^{\cdot}]$) as a function of p_{O_2} . Therefore, the values ΔG_F^0 were chosen in order to obtain symmetrical dependences of the concentrations of electrons and holes on p_{O_2} (the dependence of the derivative $d \log p_{O_2} / d \log [h^{\bullet}] + b[e^{\cdot}]$ on $d \log p_{O_2}$ was analyzed). From the calculations performed it transpired that the dependence of the deviation from the stoichiometry on p_{O_2} was compliant with the values of δ obtained by (Keller & Dieckmann, 1985) only within the range of the lowest oxygen pressures. Next, the values of $\Delta G_{C_2}^0$, $\Delta G_{C_4}^0$ and $\Delta G_{C_6}^0$ of the formation of individual clusters were sequentially chosen. Compatibility was obtained at a wider range of oxygen pressures, although there was still no agreement at the highest pressures (at the range of two orders of magnitude near the phase boundary $Mn_{1-\delta}O/Mn_3O_4$). Due to this, in the next step the values of $\Delta G_{V_M}^0 = \Delta G_{C_2}^0 = \Delta G_{C_4}^0 = \Delta G_{C_6}^0$ of clusters with a lower ionization degree were chosen. In the last step, the value of $\Delta G_{V_{Mn}}^x$ was adjusted in order to obtain a full consistency with the values of δ .

Figure 1 presents the dependence of ΔG_i^0 of the formation of electronic defects ((Δ) points) on the temperature, calculated according to the equation (13) and ΔG_F^0 of the formation of intrinsic Frenkel defects (($\blacktriangle$) points), which were obtained according to the method presented above, using the results of studies by: (Keller & Dieckmann, 1985) for the temperature range of 1173-1673 K and (Bransky & Tallan, 1971) for 1773 K.

Figure 2 presents the dependence of $\Delta G_{V_{Mn}}^0$ of the formation of vacancies ((comp) solid points) on the temperature, obtained using the results of studies by: (Keller & Dieckmann, 1985) for the temperature range of 1173-1673 K,

(Bransky & Tallan, 1971) for 1773 K ((▲) points), and (Hed & Tannhauser, 1967a; 1967b) (HT) for the temperature range of 1523-1830 K ((♦) points). Empty points denote the values obtained for the model of the structure of simple defects (vac) without complexes (Stokłosa, 2012). As shown in Figure 2, in the temperature range of 1173-1473 K the introduction of defect clusters into the model of the defects structure practically does not change the adjusted value of $\Delta G_{V_{Mn}}^o$. Slightly larger differences are present at higher temperatures. The obtained change of the nature of the dependence of $\Delta G_{V_{Mn}}^o$ on the temperature above 1500 K could indicate the presence of two phases of the $Mn_{1-\delta}O$ oxide. Different properties of $Mn_{1-\delta}O$ above 1400 K are suggested by (Hed & Tannhauser, 1967a, 1967b) and (Fender & Riley, 1970), as well as by (Carel, 1982; Gavarri et al., 1985).

Figure 3a-3c illustrates the results of the calculations, which included simple defects and defect clusters, also with lower ionization degrees. From the comparison of the obtained results with the diagrams determined for the model of simple defects (Stokłosa, 2012) it can be concluded that both the concentrations of the vacancies $[V_{Mn}']$ and $[V_{Mn}^x]$ and the character of the dependence on p_{O_2} are practically the same. As illustrated in Figure 3a, at 1173 K the concentrations of the individual clusters are lower than the concentration of vacancies $[V_{Mn}']$, and only near the $Mn_{1-\delta}O/M_3O_4$ phase boundary are they close to the concentration of vacancies $[V_{Mn}^x]$. When the temperature increases, the concentration of manganese vacancies increases significantly. The concentration of clusters increases to a small extent with the temperature increase. At 1173 K near the $Mn_{1-\delta}O/M_3O_4$ phase boundary there is the highest concentration of (6:2) clusters, and the lowest - of (2:1) clusters. However, the concentration of (2:1) complexes is significantly higher at lower oxygen pressures. When the temperature increases, the concentration of (2:1) complexes increases (higher than the concentration of (4:1) and (6:2) complexes). At 1773 K (see Figure 3c), the concentrations of complexes with lower ionization degrees increase so much that near the phase boundary $Mn_{1-\delta}O/Mn_3O_4$ they are higher than the concentration of fully ionized complexes, in a similar way to the concentration of vacancies $[V_{Mn}^x]$ being higher than $[V_{Mn}']$ and $[V_{Mn}^{\prime\prime}]$. The obtained change of the type and character of the dependence of the concentrations of individual complexes with the increase of the temperature is in line with the predictions. Figure 3 shows the dependence of the sum of the concentrations of electronic defects ($[h^{\bullet}] + b[e^{\prime}]$) on p_{O_2} ((- -) line) which, as can be seen, is compatible with the analogic sum calculated from the value of the electrical conductivity ((●,○) points) (Stokłosa, 2012). The minimum of this function overlaps with the minimum of the electrical conductivity (Error & Wagner, 1971; Hed & Tannhauser, 1967).

Figure 4 presents the temperature dependence of $\Delta G_{C_2}^o$ ((♦,◇) points), $\Delta G_{C_4}^o$ ((■,□) points), $\Delta G_{C_6}^o$ ((▲,△) points) of the formation of clusters and cation vacancies and clusters with lower ionization degrees $\Delta G_{V_{Mn}}^o = \Delta G_{C_2}^o = \Delta G_{C_4}^o = \Delta G_{C_6}^o = \Delta G_{V_{Mn}}^x$ ((●,○) points). In Figure 4 the values of $\Delta G_{V_{Mn}}^o$ ((×) points) and $\Delta G_{V_{Mn}}^x$ ((+) points) obtained for the model without defect clusters (Stokłosa, 2012) are also plotted. As indicated, the presence of defect clusters causes small but significant changes in the values of $\Delta G_{V_{Mn}}^o$ and $\Delta G_{V_{Mn}}^x$. The obtained dependences, using the results of (Hed & Tannhauser, 1967) (empty points) and (Keller & Dieckmann, 1985) (solid points), are similar. The negative values of ΔG_C^o indicate a decrease in the energy of the system due to the formation of complexes. As can be seen in Figure 4, similar to where $\Delta G_{V_{Mn}}^o$ is concerned, a distinct change of the character of the above dependencies on the temperature also occurred in the case of ΔG_C^o of the formation of complexes above 1500 K. It could indicate that at the temperatures below and above 1500 K the properties of $Mn_{1-\delta}O$ could be different.

In Table 1 the values of enthalpies and entropies of the formation of simple defects and defect clusters, resulting from the relations presented in Figures 1, 2 and 4, are given.

3.2 Concentrations of Simple Defects and Defect Clusters in $Co_{1-\delta}O$

In the previous work (Stokłosa, 2011a) the calculations of diagrams of point defects in $Co_{1-\delta}O$ were presented, assuming in the first approximation the presence of cobalt vacancies and interstitial ions with the highest ionization degree and lower ionization degrees. The obtained character of the dependence of $\Delta G_{V_{Co}}^o$ and $\Delta G_{V_{Co}}^x$ on the temperature (a strong increase with T), the high concentration of vacancies and electron holes, besides the calculations of (Stoneham et al., 1985; Tomlison et al., 1990) and other authors (Nowotny & Rekas, 1989; Klowash & Ellis, 1987; Kleine et al., 1979; Raymaud & Morin, 1985; Sykora et al., 1985, 1989; Petot-Ervas et al., 1984, 1985) indicate that in $Co_{1-\delta}O$ simple defects should not be present alone, but also complexes (clusters) of ionic defects. Similar to the case of $Mn_{1-\delta}O$, in the defect structure model, simple complexes $\{(V_{Co})_2Co_i^{3+}\}^{\prime}$, (2:1)',

$\{(V_{Co}')_4Co_i^{3\bullet}\}^{5'}$, $(4:1)^{5'}$ and more complex clusters, $\{(V_{Co}')_6(Co_i^{3\bullet})_2\}^{6'}$, $(6:2)^{6'}$, also with lower ionization degrees, (Eqs. (7) - (12)), were taken into account.

The calculations used the values of ΔG_i^0 of the electronic defects formation obtained by (Nowotny & Rekas, 1989). According to the method of calculation presented above, in the first stage of the calculation the existence of defects in the highest degree of ionization (V_{Co}'' and $Co_i^{2\bullet}$) was assumed. As a result of the performed calculations it was found that the change of the ΔG_F^0 value influences the curve of δ vs. p_{O_2} practically in the range of oxygen pressures below $p_{O_2} < 10^{-5}$ atm. At low oxygen pressures the studies have been performed mainly by (Söckel & Schmalzried, 1968; Hölscher & Schmalzried, 1984). The results of the above authors, obtained in the temperature range 1273-1473 K, and the results of (Bransky & Wimmer, 1972) and (Fisher & Tannhauser, 1966) at higher temperatures, were used to determine the values of ΔG_F^0 and $\Delta G_{V_{Co}''}^0$ and their temperature dependence. Next, the values of $\Delta G_{C_2}^0$ of the formation of the complex $\{(V_{Co}')_2Co_i^{3\bullet}\}^{4'}$, $\Delta G_{C_4}^0$ of the formation of $\{(V_{Co}')_4Co_i^{3\bullet}\}^{5'}$ and $\Delta G_{C_6}^0$ of the formation of clusters $\{(V_{Co}')_6(Co_i^{3\bullet})_2\}^{6'}$ were sequentially chosen. In the next stages, the adjusted values were: $\Delta G_{V_{Co}'}^0$ and $\Delta G_{C_2}^0 = \Delta G_{C_4}^0 = \Delta G_{C_6}^0$ of the formation of clusters with lower ionization degree. As no satisfying results were obtained, the values of $\Delta G_{V_{Co}''}^0$ in the next stage were chosen in order to obtain a full consistency of the dependence of δ vs. p_{O_2} with the experimental results of δ .

Figure 1 shows the dependencies of ΔG_i^0 of the formation of electronic defects on the temperature ((○) points), determined by (Nowotny & Rekas, 1989) and ΔG_F^0 of the formation of intrinsic Frenkel defects ((●) points).

Figure 2 shows, in turn, the dependence of $\Delta G_{V_{Co}''}^0$ on the temperature ((●) points). The points ((○) vac) denote the values obtained for the model of the structure of simple defects (Stokłosa, 2011a). As shown in Figure 2, the introduction of defect clusters into the model of the defects virtually did not change the adjusted value of $\Delta G_{V_{Co}''}^0$. Above 1473 K a change of the character of the dependence of $\Delta G_{V_{Co}''}^0$ on T was obtained.

Figures 5a - 5c present the results of the calculations of the concentrations of the defects. As demonstrated in Figure 5, similar to the case of $Mn_{1-\delta}O$, a full agreement of the dependence of δ on p_{O_2} with the experimental results of δ was obtained after introducing the vacancies $[V_{Co}']$ and $[V_{Co}^x]$ into the structure of the defects. By comparing the obtained results with the diagrams determined for the model of simple defects (Stokłosa, 2011a) it can be concluded that both the concentrations of the vacancies $[V_{Co}']$ and $[V_{Co}^x]$ and the character of the dependence on p_{O_2} are practically the same. As can be seen in Figure 5a, at 1273 K, in the range of higher oxygen pressures (about 1 atm), the concentration of complexes (4:1) is higher than the concentration of vacancies $[V_{Co}']$; the concentration of these vacancies is comparable with the concentration of (2:1) complexes. The concentration of (6:2) clusters and the concentration of clusters with a lower ionization degree is similar to the concentration of vacancies $[V_{Co}^x]$. When the temperature increases, the concentration of vacancies $[V_{Co}^x]$ and (2:1) complexes increases, and the concentration of (4:1) complexes is relatively lower. The obtained character of the changes of the concentrations of complexes with the temperature increase is different than where $Mn_{1-\delta}O$ is concerned. However, it is in line with the expectations.

Figure 6 presents the temperature dependence of $\Delta G_{C_2}^0$ - (◆) points, $\Delta G_{C_4}^0$ - (■) points, $\Delta G_{C_6}^0$ - (▲) points of the formation of complexes and clusters, also with lower ionization degrees, and vacancies V_{Co}' and V_{Co}^x ($\Delta G_{V_{Co}'}^0 = \Delta G_{C_2}^0 = \Delta G_{C_4}^0 = \Delta G_{C_6}^0$ ((●) points) and $\Delta G_{V_{Co}''}^0$ ((○) points)). A significantly different character of the dependence of ΔG_C^0 on the temperature was obtained at the temperature range of 1170 - 1400 K and above 1473 K. In Figure 6 the values of $\Delta G_{V_{Co}'}^0$ ((×) points) and $\Delta G_{V_{Co}''}^0$ ((+) points) obtained for the model of defects without defect complexes (Stokłosa, 2011a) are plotted. As noted, the presence of defect complexes causes significant changes of the adjusted values of $\Delta G_{V_{Co}'}^0$ and $\Delta G_{V_{Co}''}^0$ when compared to the model without complexes.

The change in the nature of the dependence of ΔG^0 of the formation of simple defects and complexes indicates that different properties of $\text{Co}_{1-\delta}\text{O}$ can be expected below and above 1400 K.

In Table 2, the values of enthalpies and entropies of the formation of simple defects, complexes and defect clusters, resulting from the relations presented in Figures 1, 2 and 6, are given.

3.3 Concentrations of Simple Defects and Defect Clusters in $\text{Ni}_{1-\delta}\text{O}$

In the previous work (Stokłosa, 2011b), the calculations of the diagrams of concentrations of point defects in $\text{Ni}_{1-\delta}\text{O}$ were presented, assuming in the first approximation the presence of nickel vacancies and interstitial ions with the highest ionization degree and lower ionization degrees. As a result of these calculations, it has been found that in the temperature range of 1273-1673 K, taking into account only V_{Ni}'' and Ni_i^{3+} , a good match of the dependence of the deviation from the stoichiometry on p_{O_2} to the experimental results of δ is obtained (also at higher oxygen pressures). Despite a good match of the calculations with the experimental results of δ , according to the suggestion of (Catlow et al., 1981; Stoneham et al., 1985; Tomlison et al., 1985, 1989, 1990), simple complexes $\{(V_{\text{Ni}})_2\text{Ni}_i^{3+}\}'$ and $\{(V_{\text{Ni}})_4\text{Ni}_i^{3+}\}^{s'}$ and clusters, $\{(V_{\text{Ni}})_6(\text{Ni}_i^{3+})_2\}^{6'}$ together with vacancies and complexes with lower ionization degrees, were also considered in the calculations. When calculating the concentrations of the defects, the values of ΔG_i^0 of the formation of electronic defects, determined by (Osburn & Vest, 1971), were used. As a result of these calculations, it was found that the change of the value ΔG_F^0 of the formation of intrinsic ionic defects influences the curve of δ vs. p_{O_2} practically in the range of oxygen pressures below $p_{\text{O}_2} < 10^{-4}$ atm. At low oxygen pressures, at 1473 K, the studies have only been performed by (Söckel & Schmalzried, 1968). Due to this, the values of ΔG_F^0 and their temperature dependence were determined using the results of studies of (Söckel & Schmalzried, 1968) for 1473 K, and then (Osburn & Vest, 1971) and (Mrowec & Grzesik, 2004) for higher temperatures. When adjusting the values of ΔG_F^0 above 1473 K it was assumed that when the temperature increases, their values decrease, and that the discrepancies between the values of δ obtained by different authors are caused mainly by a systematic error, related to the method of determination of the absolute values of δ . The values of ΔG_C^0 of the formation of individual complexes and the values: $\Delta G_{V_{\text{Ni}}}^0$ and ΔG_C^0 of clusters with a lower ionization degree, and $\Delta G_{V_{\text{Ni}}}^0$ ($\Delta G_{V_{\text{Ni}}}^0 \geq \Delta G_{V_{\text{Ni}}}^0$) (were chosen in order not to go against the match of the calculated dependence of δ on p_{O_2} with the experimental values of δ).

Figure 1 shows the dependencies of ΔG_i^0 of the formation of electronic defects on the temperature ((□) points), obtained by (Osburn & Vest, 1971) and ΔG_F^0 of the formation of Frenkel defects ((■) points).

Figure 2 then presents the dependences of $\Delta G_{V_{\text{Ni}}}^0$ on the temperature, obtained using the results of the studies by (Osburn & Vest, 1971; Mrowec & Grzesik, 2004) ((■) points) and (Söckel & Schmalzried, 1968) ((*) points). The points ((□) vac) denote the values obtained for the model of the structure of simple defects (Stokłosa, 2011b). As shown in Figure 2, the introduction of defect clusters into the model of the structure of defects does not change the adjusted value of $\Delta G_{V_{\text{Ni}}}^0$.

Figure 7 illustrates the results of the calculations, which included both the simple defects and defect clusters, also with lower ionization degrees. Figures 7a and 7b compare the diagrams of the concentrations of defects, using the results of (Osburn & Vest, 1971) at 1273 K and 1673 K. Taking into account defect clusters changed the concentrations of nickel vacancies only slightly. As can be seen in Figure 7a and 7b, the concentration of (2:1) complexes is comparable with the concentration of vacancies V_{Ni}' . The concentrations of (4:1) complexes and (6:2) clusters are lower. Figure 7c shows the diagram of the concentrations of defects obtained using the results of (Söckel & Schmalzried, 1968), obtained at 1473 K; they obtained relatively higher values of δ than (Osburn & Vest, 1971). As a result, the adjusted value of $\Delta G_{V_{\text{Ni}}}^0$ is smaller (see Figure 2), which meant that higher absolute values of $|\Delta G_{C_2}^0|$, $|\Delta G_{C_4}^0|$, $|\Delta G_{C_6}^0|$ could be adjusted (Figure 8). This caused significant changes in the concentrations of complexes. At high oxygen pressures, near 1 atm, the concentration of (6:1) is higher than the concentration of $[V_{\text{Ni}}]$, while the concentration of (4:1) clusters is slightly lower, and the lowest concentration is the concentration of (2:1) clusters. As indicated in Figure 7, the systematic error, which could be the reason for the

difference in the values of the deviation from the stoichiometry, can significantly affect the values and the mutual ratios of the calculated concentrations of simple defects and complexes.

Figure 8 presents the temperature dependence of $\Delta G_{C_2}^0$ (($\diamond$, $\diamond$) points), $\Delta G_{C_4}^0$ (($\blacksquare$, $\square$) points), $\Delta G_{C_6}^0$ (($\blacktriangle$, $\triangle$) points) of the formation of clusters and nickel vacancies and clusters with lower ionization degrees $\Delta G_{V_{Ni}}^0 = \Delta G_{C_2}^0 = \Delta G_{C_4}^0 = \Delta G_{C_6}^0 = \Delta G_{V_{Ni}^x}^0$ (($\bullet$, $\circ$) points). In Figure 8, the values of $\Delta G_{V_{Ni}}^0 = \Delta G_{V_{Ni}^x}^0$ (($+$) points) obtained for the model of the defects structure without clusters are plotted. As noted, the presence of defect clusters causes a small change in the adjusted values of $\Delta G_{V_{Ni}}^0$ and $\Delta G_{V_{Ni}^x}^0$ (about 10 kJ). A small difference in the values of δ between the results of studies by (Osburn & Vest, 1971) (solid points) and the results of studies by (Mrowec & Grzesik, 2004) (empty points) also causes small differences in the values of $|\Delta G_C^0|$. On the other hand, a significantly bigger difference was obtained when using the results of (Söckel & Schmalzried, 1968) (($*$) points). In Table 3 the values of enthalpies and entropies of the formation of simple defects and defect clusters, resulting from the relations presented in Figures 1, 2 and 8, are given.

4. Summary

The obtained point defects diagrams for $Mn_{1-\delta}O$, $Co_{1-\delta}O$, $Ni_{1-\delta}O$ oxides indicate that the proposed theoretical approach, from which the determined relations between ΔG^0 of the formation of the defects result, together with the proposed method of calculation, allows for fully interpreting the studies of the deviation from the stoichiometry (in the entire range of the oxide's existence) plus permits us the chance to consider not only simple defects, but also complexes and defect clusters: (2:1) - $\{(V_M)_2 M_i^{3+}\}'$, (4:1) - $\{(V_M)_4 M_i^{3+}\}^{5'}$ and (6:2) - $\{(V_M)_6 (M_i^{3+})_2\}^{6'}$.

Using the results of the studies of the deviation from the stoichiometry for $Mn_{1-\delta}O$, $Co_{1-\delta}O$, $Ni_{1-\delta}O$ oxides, obtained by several authors, the diagrams of the concentrations of point defects were determined in the whole range of existence of the individual oxides. The values ΔG_F^0 of the formation of the Frenkel defects, $\Delta G_{V_M}^0$ of the formation of cation vacancies with different ionization degrees and ΔG_C^0 of the formation of complexes and clusters were determined, as well as their temperature dependence. The values of ΔG_C^0 of the formation of complexes are the maximal values whereby an agreement between the dependence of the deviation from the stoichiometry and the experimental results of δ was obtained. This means that the concentrations of complexes and clusters calculated with the above method are maximal. Accordingly, they could be lower – and in this case the concentration of single ionized vacancies and electroneutral vacancies would be higher.

From the performed calculations it transpires that in the $Mn_{1-\delta}O$ oxide, at 1173 K, the concentrations of complexes are lower than the concentrations of single-ionized vacancies. When the temperature increases, the concentrations of single-ionized vacancies (V_{Mn}') and electroneutral vacancies (V_{Mn}^x) significantly increase; these defects start to dominate above 1373 K, near the $Mn_{1-\delta}O/Mn_3O_4$ phase boundary. Therefore, the influence of the concentration of defect complexes on the values of the deviation from the stoichiometry significantly decreases. At 1173 K the concentrations of (6:1) and (4:1) clusters is similar to the concentration of electroneutral vacancies. On the other hand, at higher temperatures, the concentration of (2:1) complexes is higher than the concentrations of the remaining complexes.

In the case of the $Co_{1-\delta}O$ at 1273 K is concerned, the highest concentration of (4:1) complexes occurs and this is higher than the concentrations of vacancies $[V_{Co}']$, which is then itself close to the concentration of (2:1) complexes. Above 1473 K, the concentrations of $[V_{Co}']$ and $[V_{Co}^x]$ significantly increase and they are higher than the concentration of defect complexes. The highest concentration is the concentration of complexes (2:1)' and electroneutral complexes (2:1)^x, while the concentration of more complex clusters decreases significantly.

In the case of $Mn_{1-\delta}O$ and $Co_{1-\delta}O$, near 1500 K, a change in the character of the temperature dependence of $\Delta G_{V_M}^0$ and ΔG_C^0 of the formation of complexes was obtained. A change in the character of the above dependence could be related to the influence – on the value of the effective equilibrium constant – of the term containing the activity coefficient, ($RT \ln f_c$), which causes a decrease of the value of ΔG^0 of the formation of defects when their concentration increases. The change in the character of the dependence of ΔG^0 on T could also indicate a change of the properties of $Mn_{1-\delta}O$ and $Co_{1-\delta}O$ oxides above 1500 K (the existence of different "phases"). The introduction of defect clusters into the model of the defects structure decreases the $\Delta G_{V_M}^0$ of the formation of single-ionized vacancies and to a small extent changes the character of the temperature dependence. Above 1500 K the absolute

values of $|\Delta G_{V_M'}^0|$ and $|\Delta G_{V_M^x}^0|$ decrease when the temperature increases, which is consistent with expectations. On the other hand, in the range of lower temperatures this relation is inverted.

In the case of the $Ni_{1-\delta}O$ oxide, where the concentration of defects is by over one order of magnitude lower than the concentrations in $Mn_{1-\delta}O$ and $Co_{1-\delta}O$ oxides, in the whole range of its existence, the dependence of the deviation from the stoichiometry on the oxygen pressure can be described if it is assumed that double-ionized nickel vacancies are present. The eventual concentration of complexes of type (2:1) is similar to the concentration of single-ionized vacancies which is by over than two orders of magnitude lower than the deviation from the stoichiometry. The introduction of defect complexes into the model of the defects structure decreases the absolute values of $|\Delta G_{V_{Ni}}^0|$ of the formation of vacancies V_{Ni}' . The character of the temperature dependence of ΔG_C^0 of

the formation of clusters is similar and the absolute values of $|\Delta G_C^0|$ slightly decrease when the temperature increases. Due to a low concentration of defects in $Ni_{1-\delta}O$, the differences in the values of the deviation from the stoichiometry could significantly affect the calculated distribution of the concentrations of defects, which is clearly seen when the results of (Osburn & Vest, 1971) and (Söckel & Schmalzried, 1968) were used for the calculations.

5. Appendix

5.1 Standard Gibbs Energy of the Formation of Defects in a $M_{1-\delta}O$ Oxide

As already mentioned in the methodology, the calculations of the diagrams of the defects' concentrations assumed that defects in $M_{1-\delta}O$ oxides are present mainly in the cation sublattice. The concentration of defects in the oxygen sublattice has a small influence on the concentration of cation defects. The initial state for calculating the concentrations of defects was the stoichiometric composition of the oxide, which is where there is a certain concentration of intrinsic electronic defects, ionized ionic defects (Frenkel), simple defects with lower ionization degrees and defect complexes and defect clusters with the highest and lower ionization degrees. As a result of the oxygen pressure increase and the formation of the deviation from the stoichiometry δ , the increase of the concentration of cation vacancies and defect clusters and the decrease of the concentration of interstitial cations in $M_{1-\delta}O$ oxide is expressed by the following equations that can be obtained through the multiplication of the elementary reactions (1) - (12) by the respective changes Δy_n in the concentrations of individual defects relative to their concentrations present at the stoichiometric concentration (y_n^0):

$$\Delta y_{V_M''}/2 O_2 = \Delta y_{V_M''} O_O + \Delta y_{V_M''} V_M'' + 2\Delta y_{V_M''} h^\bullet \quad \Delta y_{V_M''} \Delta G_{V_M''}^0 \quad (A1)$$

$$\Delta y_{C_2'} M_i^{\bullet\bullet} + 2\Delta y_{C_2'} V_M'' + \Delta y_{C_2'} h^\bullet = \Delta y_{C_2'} \{(V_M'')_2 M_i^{3\bullet}\}' \quad \Delta y_{C_2'} \Delta G_{C_2'}^0 \quad (A2)$$

$$\Delta y_{C_4'} \{(V_M'')_2 M_i^{3\bullet}\}' + 2\Delta y_{C_4'} V_M'' = \Delta y_{C_4'} \{(V_M'')_4 M_i^{3\bullet}\}^{5'} \quad \Delta y_{C_4'} \Delta G_{C_4'}^0 \quad (A3)$$

$$\Delta y_{C_6'} \{(V_M'')_2 M_i^{3\bullet}\}' + \Delta y_{C_6'} \{(V_M'')_4 M_i^{3\bullet}\}^{5'} = \Delta y_{C_6'} \{(V_M'')_6 (M_i^{3\bullet})_2\}^{6'} \quad \Delta y_{C_6'} \Delta G_{C_6'}^0 \quad (A4)$$

$$\Delta y_{M_i^{\bullet\bullet}} M_i^{\bullet\bullet} + \Delta y_{M_i^{\bullet\bullet}}/2 O_2 = \Delta y_{M_i^{\bullet\bullet}} O_O + \Delta y_{M_i^{\bullet\bullet}} M_M^x + 2\Delta y_{M_i^{\bullet\bullet}} h^\bullet - \Delta y_{M_i^{\bullet\bullet}} \Delta G_{M_i^{\bullet\bullet}}^{0(h)} \quad (A5)$$

On the other hand, the formation of clusters and defects with a lower ionization degree is presented by the reactions:

$$\Delta y_{C_2'} \{(V_M'')_2 M_i^{3\bullet}\}' + \Delta y_{C_2'} h^\bullet = \Delta y_{C_2'} \{(V_M'')_2 M_i^{3\bullet}\}^x \quad \Delta y_{C_2'} \Delta G_{C_2'}^0 \quad (A6)$$

$$\Delta y_{C_4'} \{(V_M'')_4 M_i^{3\bullet}\}^{5'} + \Delta y_{C_4'} h^\bullet = \Delta y_{C_4'} \{(V_M'')_4 M_i^{3\bullet}\}^{4'} \quad \Delta y_{C_4'} \Delta G_{C_4'}^0 \quad (A7)$$

$$\Delta y_{C_6'} \{(V_M'')_6 (M_i^{3\bullet})_2\}^{6'} + \Delta y_{C_6'} h^\bullet = \Delta y_{C_6'} \{(V_M'')_6 (M_i^{3\bullet})_2\}^{5'} \quad \Delta y_{C_6'} \Delta G_{C_6'}^0 \quad (A8)$$

$$\Delta y_{V_M'} V_M' + \Delta y_{V_M'} h^\bullet = \Delta y_{V_M'} V_M^x \quad \Delta y_{V_M'} \Delta G_{V_M'}^0 \quad (A9)$$

$$\Delta y_{M_i^{\bullet}} M_i^{\bullet} = \Delta y_{M_i^{\bullet}} M_i^{\bullet\bullet} + \Delta y_{M_i^{\bullet}} e' \quad -\Delta y_{M_i^{\bullet}} \Delta G_{M_i^{\bullet}}^0 \quad (A10)$$

$$\Delta y_{V_M^x} V_M^x + \Delta y_{V_M^x} h^\bullet = \Delta y_{V_M^x} V_M^{\bullet\bullet} \quad \Delta y_{V_M^x} \Delta G_{V_M^x}^0 \quad (A11)$$

$$\Delta y_{M_i^x} M_i^x = \Delta y_{M_i^x} M_i^{\bullet} + \Delta y_{M_i^x} e' \quad -\Delta y_{M_i^x} \Delta G_{M_i^x}^0 \quad (A12)$$

where ΔG_n^0 are the standard Gibbs energies of the individual reactions.

By adding the equations (A1)-(A12) and then dividing them by the total quantity of the incorporated oxygen ($\Delta y_{V_M''} + \Delta y_{M_i^{**}} = \Delta y_O$), we get the equation describing the formation and decay of the determined quantities of point defects (mole fractions) as a result of the incorporation of 1 mole of oxygen atoms (into a determined, sufficiently big quantity (volume) of the oxide):

$$\frac{1}{2} O_2 + \frac{\Delta y_{M_i^{**}}}{\Delta y_O} M_i^{**} + \frac{\Delta y_{M_i^{\bullet}}}{\Delta y_O} M_i^{\bullet} + \frac{\Delta y_{M_i^x}}{\Delta y_O} M_i^x = O_O^x + \frac{\Delta y_{M_i^{**}}}{\Delta y_O} M_M^{x(surf)} + \frac{\Delta y_{V_M''}}{\Delta y_O} V_M'' + \frac{\Delta y_{V_M^{\bullet}}}{\Delta y_O} V_M^{\bullet} + \frac{\Delta y_{V_M^x}}{\Delta y_O} V_M^x + \frac{\Delta y_{C_2^{'}}}{\Delta y_O} C_2^{' } + \frac{\Delta y_{C_2^x}}{\Delta y_O} C_2^x + \frac{\Delta y_{C_4^{S'}}}{\Delta y_O} C_4^{S'} + \frac{\Delta y_{C_4^{4'}}}{\Delta y_O} C_4^{4'} + \frac{\Delta y_{C_6^{6'}}}{\Delta y_O} C_6^{6'} + \frac{\Delta y_{C_6^{S'}}}{\Delta y_O} C_6^{S'} + \left(2 - \frac{\Delta y_{V_M''} + 2\Delta y_{V_M^x} + \Delta y_{C_2^{'}} + 2\Delta y_{C_2^x} + \Delta y_{C_4^{4'}} + \Delta y_{C_6^{S'}}}{\Delta y_O} \right) h^{\bullet} + \frac{\Delta y_{M_i^{\bullet}} + 2\Delta y_{M_i^x}}{\Delta y_O} e^{\bullet} \quad \Delta G_{def}^{(o(\delta))} \quad (A13)$$

The standard Gibbs energy of the above process ($\Delta G_{def}^{(o(\delta))}$) (the resultant standard Gibbs energy of the defects' formation per one mole of oxygen atoms) is the sum ΔG_n^0 of processes (A1) - (A12) and is expressed by the equation:

$$\Delta G_{def}^{(o(\delta))} = \frac{\Delta y_{V_M''}}{\Delta y_O} \Delta G_{V_M''}^0 - \frac{\Delta y_{M_i^{**}}}{\Delta y_O} \Delta G_{M_i^{**}}^0 + \frac{\Delta y_{V_M^{\bullet}}}{\Delta y_O} \Delta G_{V_M^{\bullet}}^0 - \frac{\Delta y_{M_i^{\bullet}}}{\Delta y_O} \Delta G_{M_i^{\bullet}}^0 + \frac{\Delta y_{V_M^x}}{\Delta y_O} \Delta G_{V_M^x}^0 - \frac{\Delta y_{M_i^x}}{\Delta y_O} \Delta G_{M_i^x}^0 + \frac{\Delta y_{C_2^{'}}}{\Delta y_O} \Delta G_{C_2^{'}}^0 + \frac{\Delta y_{C_2^x}}{\Delta y_O} \Delta G_{C_2^x}^0 + \frac{\Delta y_{C_4^{S'}}}{\Delta y_O} \Delta G_{C_4^{S'}}^0 + \frac{\Delta y_{C_4^{4'}}}{\Delta y_O} \Delta G_{C_4^{4'}}^0 + \frac{\Delta y_{C_6^{6'}}}{\Delta y_O} \Delta G_{C_6^{6'}}^0 + \frac{\Delta y_{C_6^{S'}}}{\Delta y_O} \Delta G_{C_6^{S'}}^0 \quad (A14)$$

On the other hand, the dependence of the concentration of the defects on the oxygen pressure in the equilibrium state, resulting from the condition of equality of chemical potentials of the components from the Eq. (A13), has the following form after its rearrangement:

$$\frac{\Delta y_{V_M''}}{\Delta y_O} \ln[V_M''] + \frac{\Delta y_{V_M^{\bullet}}}{\Delta y_O} \ln[V_M^{\bullet}] + \frac{\Delta y_{V_M^x}}{\Delta y_O} \ln[V_M^x] + \frac{\Delta y_{C_2^{'}}}{\Delta y_O} \ln[C_2^{'}] + \frac{\Delta y_{C_2^x}}{\Delta y_O} \ln[C_2^x] + \frac{\Delta y_{C_4^{S'}}}{\Delta y_O} \ln[C_4^{S'}] + \frac{\Delta y_{C_4^{4'}}}{\Delta y_O} \ln[C_4^{4'}] + \frac{\Delta y_{C_6^{6'}}}{\Delta y_O} \ln[C_6^{6'}] + \frac{\Delta y_{C_6^{S'}}}{\Delta y_O} \ln[C_6^{S'}] + \left(2 - \frac{\Delta y_{V_M''} + 2\Delta y_{V_M^x} + \Delta y_{C_2^{'}} + 2\Delta y_{C_2^x} + \Delta y_{C_4^{4'}} + \Delta y_{C_6^{S'}}}{\Delta y_O} \right) \ln[h^{\bullet}] + \frac{\Delta y_{M_i^{\bullet}} + 2\Delta y_{M_i^x}}{\Delta y_O} \ln[e^{\bullet}] - \frac{\Delta y_{M_i^{**}}}{\Delta y_O} \ln[M_i^{**}] - \frac{\Delta y_{M_i^{\bullet}}}{\Delta y_O} \ln[M_i^{\bullet}] - \frac{\Delta y_{M_i^x}}{\Delta y_O} \ln[M_i^x] - \frac{1}{2} \ln p_{O_2} = \frac{-\Delta G_{def}^{(o(\delta))}}{\Delta y_O} \quad (A15)$$

where the concentrations of the individual point defects, resulting from the change of the concentration (Δy_n) in relation to the concentration at the stoichiometric composition (y_n^0) (per one mole of the oxide), are:

$$[V_M''] = y_{V_M''}^0 + \Delta y_{V_M''} - \Delta y_{V_M^{\bullet}} - 2\Delta y_{C_2^{'}} - 2\Delta y_{C_4^{S'}} = y_{V_M''}^0 + \Delta y_{V_M''} \quad (A16)$$

$$[C_2^{'}] = y_{C_2^{'}}^0 + \Delta y_{C_2^{'}} - \Delta y_{C_2^x} - \Delta y_{C_4^{S'}} - \Delta y_{C_6^{6'}} = y_{C_2^{'}}^0 + \Delta y_{C_2^{'}} \quad (A17)$$

$$[C_4^{S'}] = y_{C_4^{S'}}^0 + \Delta y_{C_4^{S'}} - \Delta y_{C_4^{4'}} - \Delta y_{C_6^{6'}} = y_{C_4^{S'}}^0 + \Delta y_{C_4^{S'}} \quad (A18)$$

$$[C_6^{6'}] = y_{C_6^{6'}}^0 + \Delta y_{C_6^{6'}} - \Delta y_{C_6^{S'}} = y_{C_6^{6'}}^0 + \Delta y_{C_6^{6'}} \quad (A19)$$

$$[C_2^x] = y_{C_2^x}^0 + \Delta y_{C_2^x} \quad (A20)$$

$$[C_4^{4'}] = y_{C_4^{4'}}^0 + \Delta y_{C_4^{4'}} \quad (A21)$$

$$[C_6^{5'}] = y_{C_6^{5'}}^0 + \Delta y_{C_6^{5'}} \quad (A22)$$

$$[V_M^{\cdot}] = y_{V_M^{\cdot}}^0 + \Delta y_{V_M^{\cdot}} - \Delta y_{V_M^x} = y_{V_M^{\cdot}}^0 + \Delta y_{V_M^{\cdot}} \quad (A23)$$

$$[V_M^x] = y_{V_M^x}^0 + \Delta y_{V_M^x} \quad (A24)$$

$$[M_i^{\bullet\bullet}] = y_{M_i^{\bullet\bullet}}^0 - \Delta y_{M_i^{\bullet\bullet}} + \Delta y_{M_i^{\cdot}} - \Delta y_{C_2} = y_{M_i^{\bullet\bullet}}^0 - \Delta y_{M_i^{\bullet\bullet}} \quad (A25)$$

$$[M_i^{\cdot}] = y_{M_i^{\cdot}}^0 - \Delta y_{M_i^{\cdot}} + \Delta y_{M_i^x} = y_{M_i^{\cdot}}^0 - \Delta y_{M_i^{\cdot}} \quad (A26)$$

$$[M_i^x] = y_{M_i^x}^0 - \Delta y_{M_i^x} \quad (A27)$$

The description of the changes of the concentrations of defects, presented above, takes into account the very important fact that the change of the concentration of defects (see Eq. (A13) and (A15)) is smaller than the real quantity of defects that are formed (see Eq. (A1) - (A12) and (A14)). The reason for this is that a part of them contributes to the increase of the concentration of clusters and vacancies with a lower ionization degree. For example, the change of the concentration of vacancies $\Delta y_{V_M^{\cdot}}$ is lower than the amount of vacancies that are formed $\Delta y_{V_M^{\cdot}}$. From Eq. (A16) it transpires that it is:

$$\Delta y_{V_M^{\cdot}} = \Delta y_{V_M^{\cdot}}^{\cdot} + \Delta y_{V_M^{\cdot}}^{\cdot} + 2\Delta y_{C_2} + 2\Delta y_{C_4^{5'}} \quad (A28a)$$

And taking into account Eqs. (A17) - (A19) and (A23) and (A24) we get:

$$\Delta y_{V_M^{\cdot}} = \Delta y_{V_M^{\cdot}}^{\cdot} + \Delta y_{V_M^{\cdot}}^{\cdot} + \Delta y_{V_M^x} + 2y_{C_2}^{\cdot} + 2\Delta y_{C_2}^x + 4\Delta y_{C_4^{5'}}^{\cdot} + 4\Delta y_{C_4^{5'}}^x + 4\Delta y_{C_6^{5'}}^{\cdot} + 4\Delta y_{C_6^{5'}}^x \quad (A28b)$$

By analogy, the changes of the concentrations of the remaining defects can be written.

The work (Stokłosa, 2011a) also demonstrated that the standard Gibbs energy of the formation of vacancies $V_M^{\cdot}$ ($\Delta G_{V_M^{\cdot}}^0$) is the sum of the -ergonic effects related to the incorporation of one mole of oxygen ($\Delta G_O^0 + 2\Delta G_i^0$) and $\Delta G_{V_M^{\cdot}}^{0*}$ of the proper process of the formation of cation vacancies:

$$\Delta G_{V_M^{\cdot}}^0 = (\Delta G_O^0 + 2\Delta G_i^0) + \Delta G_{V_M^{\cdot}}^{0*} \quad (A29)$$

where ΔG_O^0 and ΔG_i^0 denote the standard Gibbs energy of the oxygen incorporation and the formation of electronic defects, respectively.

Analogically, the standard Gibbs energy of the formation of interstitial cations can be expressed by the equation:

$$\Delta G_{M_i^{\bullet\bullet}}^0 = -(\Delta G_O^0 + 2\Delta G_i^0) + \Delta G_{M_i^{\bullet\bullet}}^{0*} \quad (A30)$$

where $\Delta G_{M_i^{\bullet\bullet}}^{0*}$ is the standard Gibbs energy of the formation of interstitial cations $M_i^{\bullet\bullet}$. $\Delta G_{V_M^{\cdot}}^{0*}$ and $\Delta G_{M_i^{\bullet\bullet}}^{0*}$ can be related to the ΔG_F^0 of the formation of intrinsic ionic defects of Frenkel type, because by adding the Eqs. (A29) and (A30) we get:

$$\Delta G_{V_M^{\cdot}}^0 + \Delta G_{M_i^{\bullet\bullet}}^0 = \Delta G_{V_M^{\cdot}}^{0*} + \Delta G_{M_i^{\bullet\bullet}}^{0*} = \Delta G_F^0 \quad (A31)$$

Therefore, $\Delta G_{V_M^{\cdot}}^{0*}$ and $\Delta G_{M_i^{\bullet\bullet}}^{0*}$ are expressed by the equations:

$$\Delta G_{V_M^{\cdot}}^{0*} = 1/2(\Delta G_F^0 + D) \quad (A32)$$

$$\Delta G_{M_i^{\bullet\bullet}}^{0*} = 1/2(\Delta G_F^0 - D) \quad (A33)$$

where the D parameter is the difference between them:

$$\Delta G_{V_M^{\cdot}}^{0*} - \Delta G_{M_i^{\bullet\bullet}}^{0*} = D \neq 0 \quad (A34)$$

As a result, the standard Gibbs energy of the process (A13) (Eq. (A14)) has the form of:

$$\Delta G_{\text{def}}^{0(\delta)} = \Delta G_O^0 + 2\Delta G_i^0 + \frac{1}{2}D + \frac{\Delta y_{V_M^{\cdot}} - \Delta y_{M_i^{\bullet\bullet}}}{\Delta y_O} \Delta G_F^0 + \frac{\Delta y_{V_M^{\cdot}}}{\Delta y_O} \Delta G_{V_M^{\cdot}}^{0*} - \frac{\Delta y_{M_i^{\bullet\bullet}}}{\Delta y_O} \Delta G_{M_i^{\bullet\bullet}}^{0*} + \frac{\Delta y_{V_M^x}}{\Delta y_O} \Delta G_{V_M^x}^0 - \frac{\Delta y_{M_i^x}}{\Delta y_O} \Delta G_{M_i^x}^0$$

$$+ \frac{\Delta y_{C_2'}}{\Delta y_O} \Delta G_{C_2'}^0 + \frac{\Delta y_{C_2''}}{\Delta y_O} \Delta G_{C_2''}^0 + \frac{\Delta y_{C_4'}}{\Delta y_O} \Delta G_{C_4'}^0 + \frac{\Delta y_{C_4''}}{\Delta y_O} \Delta G_{C_4''}^0 + \frac{\Delta y_{C_6'}}{\Delta y_O} \Delta G_{C_6'}^0 + \frac{\Delta y_{C_6''}}{\Delta y_O} \Delta G_{C_6''}^0 \quad (A35)$$

5.2 Standard Gibbs Energy of the Formation of Defects in an Oxide Near the Stoichiometric Composition

Near the stoichiometric composition there is a low concentration of intrinsic defects. The highest concentration will be the concentration of double-ionized ionic defects, and their concentrations will be equal ($y_{V_M''}^0 \cong y_{M_i''}^0$). The concentrations of defects with lower ionization degrees will be much lower. If $\Delta G_{V_M''}^0 \cong \Delta G_{M_i''}^0$ and $\Delta G_{V_M'}^0 \cong \Delta G_{M_i'}^0$, then also the concentrations of these defects will be equal ($y_{V_M'}^0 \cong y_{M_i'}^0$) and ($y_{V_M}^0 \cong y_{M_i}^0$). Due to a low concentration of defects, the concentrations of defect complexes and defect clusters will also be low. It could be demonstrated very clearly that near the stoichiometric composition ($\delta \cong 0$) the changes of the concentrations of the defects are infinitesimally small, yet are of the same order of magnitude (Stokłosa, 2011a). This is why the changes of the concentrations of defects (mole fractions) in Eqs. (A13) - (A15) and (A35) will tend to the values occurring at the stoichiometric composition (Stokłosa, 2011a). As such, if we assume that near the stoichiometric composition the concentration of complexes can be neglected, then the assumed approximation and the compensation of the concentrations of defects cause that the Eq. (A15) has the following, simple form:

$$2\ln[h^\bullet] - \frac{1}{2}\ln(p_{O_2}^{(s)}) = \frac{-\Delta G_i^0}{RT} - \frac{1}{2}\ln(p_{O_2}^{(s)}) = \frac{-\Delta G_{def}^{0(\delta \approx 0)}}{RT} \quad (A36)$$

On the other hand, the Eq. (A35) will be simplified to the relation:

$$\Delta G_{def}^{0(\delta \approx 0)} \cong \Delta G_O^0 + 2\Delta G_i^0 + 1/2D \quad (A37)$$

Taking into account the Eqs. (A36) and (A31) - (A35), the Eqs. (A29) and (A30) assume the form of:

$$\Delta G_{V_M''}^0 \cong \Delta G_{def}^{0(\delta \approx 0)} + 1/2\Delta G_F^0 \quad (A38)$$

$$\Delta G_{M_i''}^0 \cong -\Delta G_{def}^{0(\delta \approx 0)} + 1/2\Delta G_F^0 \quad (A39)$$

Near the stoichiometric composition the value of $\Delta G_{def}^{0(\delta \approx 0)}$, according to the Eq. (A36), depends on the ΔG_i^0 of the formation of the electronic defects and on the value of $p_{O_2}^{(s)}$ whereby the oxide reaches the stoichiometric composition. On the other hand, the $\Delta G_{V_M''}^0$ of the formation of vacancies depends on the values of $\Delta G_{def}^{0(\delta \approx 0)}$ and ΔG_F^0 of the formation of intrinsic defects. Therefore, they must fulfill the condition resulting from Eqs. (A36) and (A38):

$$\Delta G_{V_M''}^0 - (\Delta G_i^0 + 1/2RT\ln(p_{O_2}^{(s)}) + 1/2\Delta G_F^0) = 0 \quad (A40)$$

Thus, it is possible to choose such values of ΔG_F^0 and $\Delta G_{V_M''}^0$, fulfilling the Eq. (A40) (at the adjusted value of $p_{O_2}^{(s)}$) that, for the range of small deviations from the stoichiometry (in the range where double-ionized vacancies dominate), make it possible to obtain the compatibility between the dependence of the deviation from the stoichiometry on p_{O_2} and the experimental results of δ . The Eqs. (A36) and (A38), together with the condition (A40), are the basis of the method of calculation of the values of ΔG_F^0 and $\Delta G_{V_M''}^0$ and $p_{O_2}^{(s)}$ (the oxygen pressure whereby the oxide reaches or could reach the stoichiometric composition).

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Table 1. The values of the enthalpy ΔH and entropy ΔS of the formation of intrinsic Frenkel-type defects, manganese vacancies V_{Mn}'' , V_{Mn}' and V_{Mn}^x , complexes C_2' - (2:1), $C_4^{5'}$ - (4:1), $C_6^{6'}$ - (6:2) and clusters with lower ionization degrees $\Delta H_{C_2^x} = \Delta H_{C_4^{4'}} = \Delta H_{C_6^{6'}}$, determined using the dependences shown in Figures 1, 2, 4

Equilibr.	ΔH /(kJ/mol)	ΔS /(J/mol)	ΔT /(K)	[Ref]
Frenkel (Eq. (A31))	309±1	50±1	1173-1773	
(V_{Mn}'')	-88±10	-124±7	1173-1473	(KD)
Eq.(1)	152±15	25±9	1573-1773	(KDBT)
-''-	87±6	-1±4	1523-1830	(HT)
$(V_{Mn}'), (V_{Mn}^x)$	54±8	74±6	1173-1473	(KD)
Eqs. (2), (3)	-184±27	-78±16	1573-1773	(KDBT)
-''-	-132±19	-56±11	1523-1830	(HT)
$\{(V_{Mn}'')_2 Mn_i^{3\bullet}\}'$	-316±6	-41±5	1173-1473	(KD)
(C_2') Eq. (7)	-375±5	-80±3	1573-1773	(KDBT)
(2:1)'	-322±11	-50±7	1523-1830	(HT)
$\{(V_{Mn}'')_4 Mn_i^{3\bullet}\}^{5'}$	-157±5	-30±3	1173-1473	(KD)
$(C_4^{5'})$ Eq.(8)	-249±5	-80±3	1573-1773	(KDBT)
(4:1) ^{5'}	-149±8	-24±5	1523-1830	(HT)
$\{(V_{Mn}'')_6 (Mn_i^{3\bullet})_2\}^{6'}$	-129±4	-32±3	1173-1473	(KD)
$(C_6^{6'})$ Eq. (9)	-190±15	-65±9	1573-1773	(KDBT)
(6:2) ^{6'}	-157±7	-48±4	1523-1830	(HT)
$\{(V_{Mn}'')_2 Mn_i^{3\bullet}\}^x$	54±8	74±6	1173-1473	(KD)
(C_2^x) Eqs. (10)-(12)	-184±27	-78±16	1573-1773	(KDBT)
(2:1) ^x	-132±19	-56±11	1523-1830	(HT)

(KD), (KDBT), (HT) denote the results of the deviation from the stoichiometry studies (used in the calculations in the present work), obtained by: (Keller & Dieckmann, 1985) and (Bransky & Tallan, 1971) and (Hed & Tannhauser, 1967), respectively.

Table 2. The values of the enthalpy ΔH and entropy ΔS of the formation of intrinsic Frenkel-type defects, cobalt vacancies V_{Co}'' , V_{Co}' and V_{Co}^x , complexes and clusters C_2' - (2:1), $C_4^{5'}$ - (4:1), $C_6^{6'}$ - (6:2) and clusters with lower ionization degrees $\Delta H_{C_2^x} = \Delta H_{C_4^x} = \Delta H_{C_6^x}$, determined using the dependences shown in Figures 1, 2, 6

Equilibr.	ΔH /(kJ/mol)	ΔS /(J/mol)	ΔT /(K)
Frenkel (Eq. (A31))	336±2	89±1	1223-1673
(V_{Co}'')	8±10	-122±8	1223-1400
Eq. (1)	228±5	25±3	1223-1673
(V_{Co}')	140±32	138±24	1173-1400
Eq. (2)	228±5	25±3	1473-1673
(V_{Co}^x)	140±32	138±24	1173-1400
Eq. (3)	-240±64	-130±40	1473-1673
$\{(V_{Co}'')_2 Co_i^{3\bullet}\}'$	-293±7	-32±5	1173-1400
(C_2') Eq. (7)	-257±7	-13±4	1473-1673
$\{(V_{Co}'')_4 Co_i^{3\bullet}\}^{5'}$	-168±7	-15±5	1173-1400
($C_4^{5'}$) Eq.(8)	-153±7	-10±1	1473-1673
$\{(V_{Co}'')_6 (Co_i^{3\bullet})\}^{6'}$	-112±7	-36±3	1173-1400
($C_6^{6'}$) Eq. (9)	-62±1	-5±1	1473-1673
$\{(V_{Co}'')_2 Co_i^{3\bullet}\}^x$	140±32	138±24	1173-1400
(C_2^x) Eqs. (10)-(12)	228±5	25±3	1473-1673

Table 3. The values of the enthalpy ΔH and entropy ΔS of the formation of intrinsic Frenkel-type defects, nickel vacancies V_{Ni}'' , V_{Ni}' and V_{Ni}^x , complexes and clusters C_2' - (2:1), $C_4^{5'}$ - (4:1), $C_6^{6'}$ - (6:2) and clusters with lower ionization degrees $\Delta H_{C_2^x} = \Delta H_{C_4^x} = \Delta H_{C_6^x}$, determined using the dependences shown in Figure 1, 2, 8

Equilibr.	ΔH /(kJ/mol)	ΔS /(J/mol)	ΔT (K)
Frenkel Eq. (A31)	358±2	42±1	1273-1673
(V_{Ni}'') Eq.(1)	236±1	-43±1	1273-1673
(V_{Ni}'), (V_{Ni}^x) Eqs. (2), (3)	-71±2	-19±1	1273-1673
$\{(V_{Ni}'')_2 Ni_i^{3\bullet}\}'$ Eq. (7)	-450±7	-74±5	1273-1673
$\{(V_{Ni}'')_4 Ni_i^{3\bullet}\}^{5'}$ Eq. (8)	-233±4	-26±3	1273-1673
$\{(V_{Ni}'')_6 (Ni_i^{3\bullet})_2\}^{6'}$ Eq. (9)	-180±7	-25±5	1273-1673
$\{(V_{Ni}'')_2 Ni_i^{3\bullet}\}^x$ Eqs. (10)-(12)	-71±2	-19±1	1273-1673

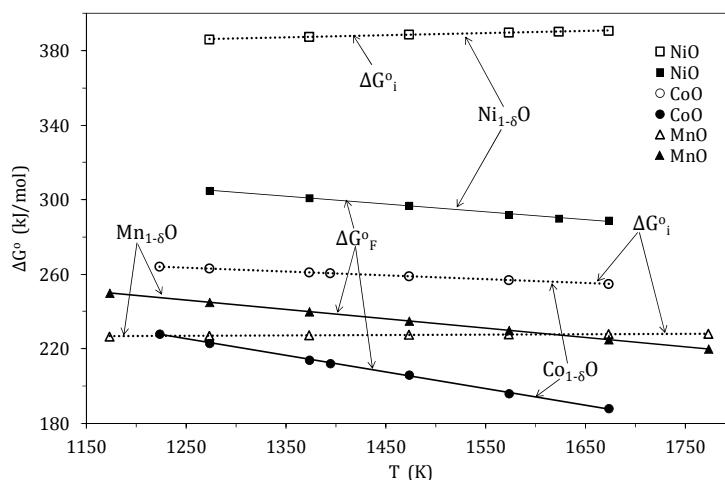


Figure 1.

The temperature dependence of ΔG_i° of the formation of electronic defects for $\text{Ni}_{1-\delta}\text{O}$ determined by (Osburn & Vest 1971) ((□) points), for $\text{Co}_{1-\delta}\text{O}$, determined by (Nowotny & Rekas, 1989) ((○) points), and for $\text{Mn}_{1-\delta}\text{O}$ from the Eq. (13) ((Δ) points) and ΔG_F° of the formation of intrinsic Frenkel-type defects, determined based on the results of the studies of the deviation from the stoichiometry obtained: for $\text{Ni}_{1-\delta}\text{O}$ by (Söckel & Schmalzried 1968) for 1473 K and by (Osburn & Vest 1971; Mrowec & Grzesik, 2004) - (■) points, for $\text{Mn}_{1-\delta}\text{O}$ by (Keller & Dieckmann, 1985; Bransky & Tallan, 1971) - (▲) points and for $\text{Co}_{1-\delta}\text{O}$ obtained by (Söckel & Schmalzried, 1968; Hölscher & Schmalzried, 1984; Fisher & Tannhauser, 1966; Bransky & Wimmer, 1972) - (●) points.

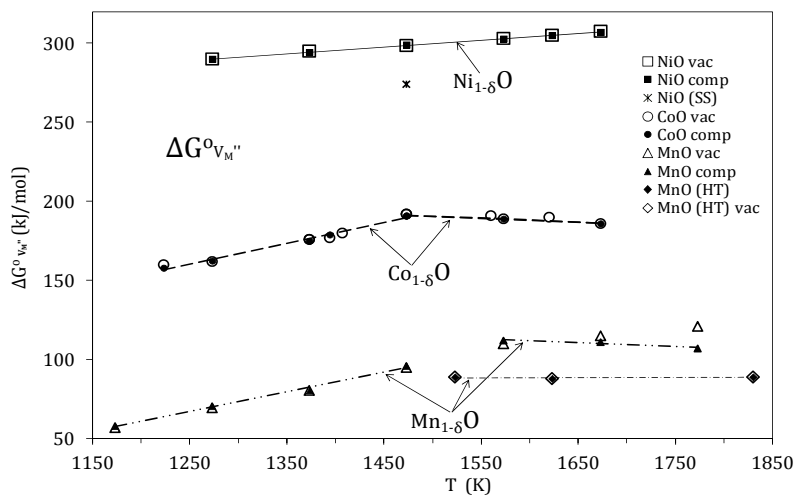


Figure 2.

The temperature dependence of $\Delta G_{V_M^\circ}^\circ$ of the formation of cation vacancies (V_M°) determined after being based on the results of the studies of the deviation from the stoichiometry obtained: for $\text{Mn}_{1-\delta}\text{O}$ by (Keller & Dieckmann, 1985; Bransky & Tallan, 1971) - (Δ, ▲) points, (Hed & Tannhauser, 1967) - (◆, ◇) points, for $\text{Co}_{1-\delta}\text{O}$ obtained by (Söckel & Schmalzried, 1968; Hölscher & Schmalzried, 1984; Fisher & Tannhauser, 1966; Bransky & Wimmer, 1972) - (○, ●) points, for $\text{Ni}_{1-\delta}\text{O}$ obtained by (Söckel & Schmalzried, 1968; Osburn & Vest, 1971; Mrowec & Grzesik, 2004) - (□, ■) points. The empty points denote the values of $\Delta G_{V_M^\circ}^\circ$ obtained in the works (Stokłosa, 2011a, 2011b, 2012), for the simple model of defects, without complexes.

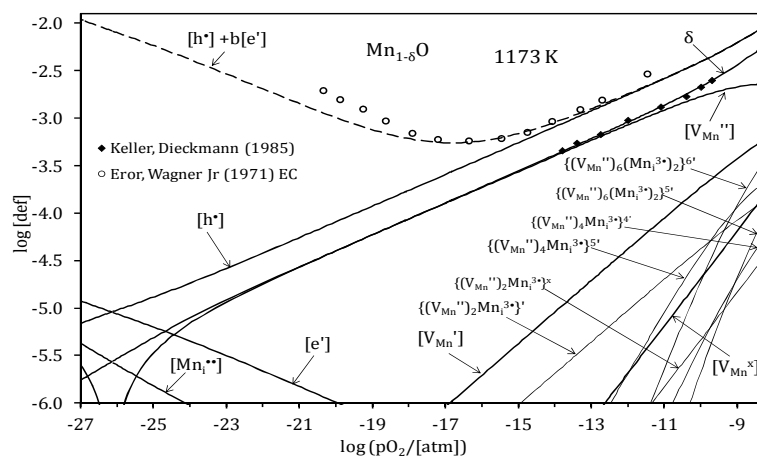


Figure 3a.

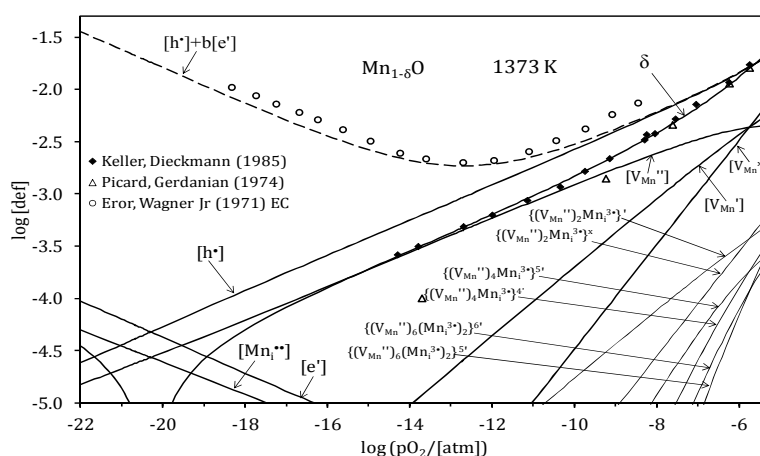


Figure 3b.

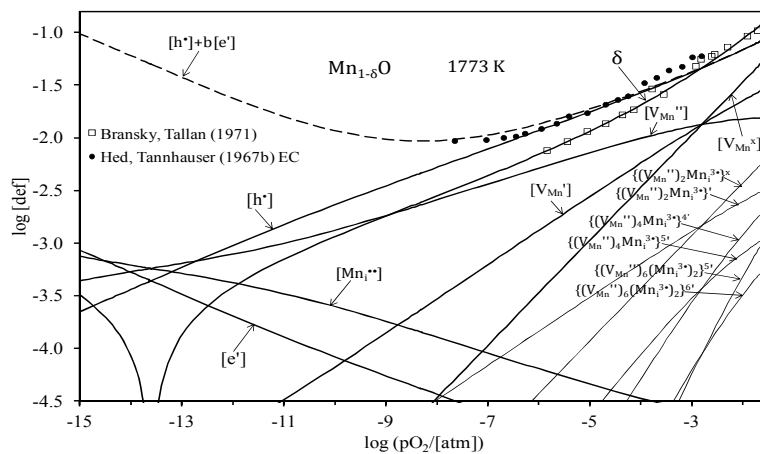
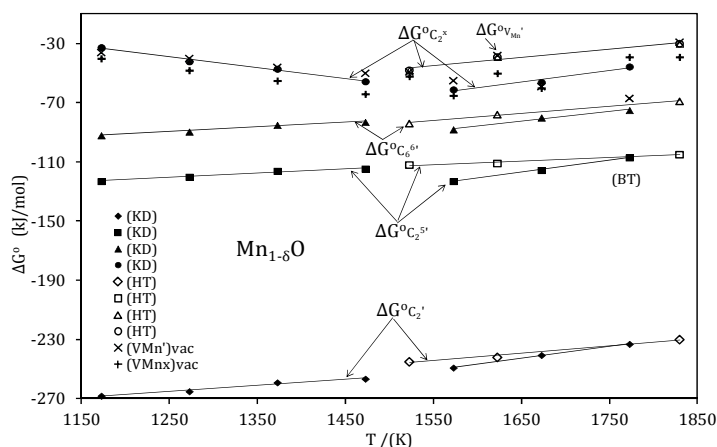


Figure 3c.

The diagrams of the point defects concentrations for the $\text{Mn}_{1-\delta}\text{O}$, taking into account manganese vacancies and interstitial manganese ions as well as complexes: C_2 , C_4 and C_6 , obtained using the results of the studies of the deviation from the stoichiometry by: (Keller & Dieckmann, 1985), a) for 1173 K, b) 1373 K, c) (Bransky & Tallan, 1971) for 1773 K. The (---) line: the values of the sum of the concentrations of electronic defects, $([\text{h}^\bullet] + b[\text{e}^\bullet])$ ($b = \mu_e/\mu_h$ – the ratio of the mobility of electrons to the mobility of electron holes). The points mark the results of the deviation from the stoichiometry studies obtained by: (Keller & Dieckmann, 1985) – (♦), (Bransky & Tallan, 1971) – (□), (Picard & Gerdanian, 1974) – (Δ) and the values of the sum of the concentrations $([\text{h}^\bullet] + b[\text{e}^\bullet])$ calculated from the value of the electrical conductivity obtained by: (Error & Wagner, 1971) – (○) points and by (Hed & Tannhauser, 1967b) – (●) points.



The temperature dependence of $\Delta G_{C_2}^0$, $\Delta G_{C_4}^0$, $\Delta G_{C_6}^0$ of the formation of defect complexes, respectively: $\{(V_{Mn})_2 Mn_i^{3\bullet}\}'$ ($(\diamond, \diamond)$ points), $\{(V_{Mn})_4 Mn_i^{3\bullet}\}^{5'}$ - ($\blacksquare, \square$), $\{(V_{Mn})_6 (Mn_i^{3\bullet})_2\}^{6'}$ - ($\blacktriangle, \triangle$) and with lower ionization degrees ($\Delta G_{V_{Mn}}^0 = \Delta G_{C_2}^0 = \Delta G_{C_4}^0 = \Delta G_{C_6}^0 = \Delta G_{V_{Mn}}^0$) - ($\bullet, \circ$), obtained using the results of the studies of the deviation from the stoichiometry obtained by: (Keller & Dieckmann, 1985; Bransky & Tallan, 1971) - (solid points) and by (Hed & Tannhauser, 1967) - (empty points). The ($\times$) points mark the results of $\Delta G_{V_{Mn}}^0$ and the (+) points the values of $\Delta G_{V_{Mn}}^0$, obtained in the work (Stokłosa, 2012) for the model of defects without defect clusters.

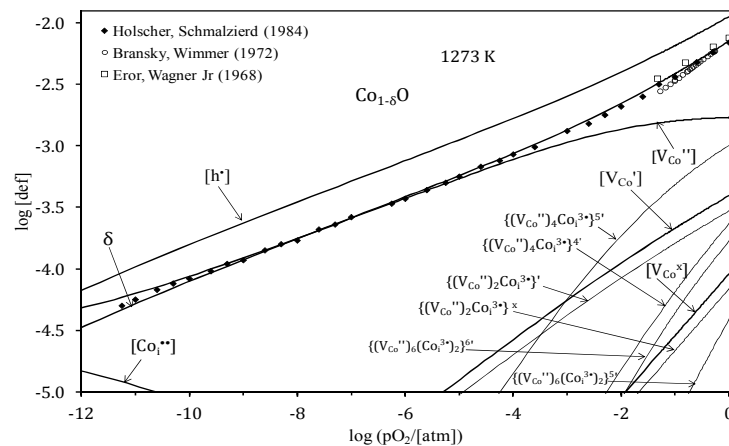


Figure 5a.

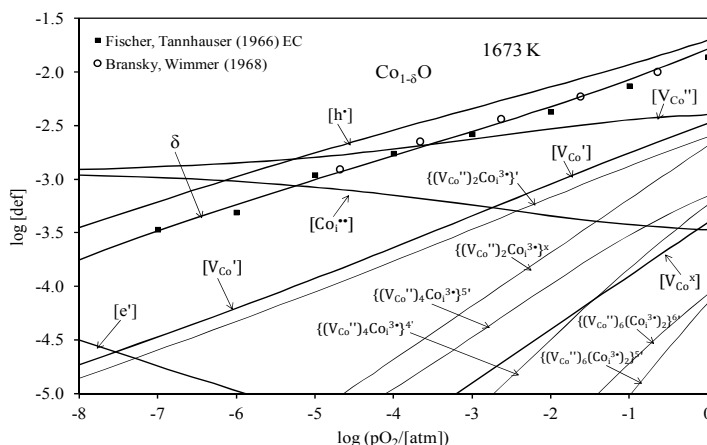


Figure 5c.

The diagrams of the point defects concentrations for the $\text{Co}_{1-\delta}\text{O}$, taking into account simple defects as well as complexes: C_2 , C_4 and C_6 , obtained using the results of the studies of the deviation from the stoichiometry by: (Söckel & Schmalzried, 1968; Hölscher & Schmalzried, 1984), for the temperature: a) 1273 K, b) 1473 K, and by: c) (Bransky & Wimmer, 1972) for 1673 K. The points mark the results of the deviation from the stoichiometry studies obtained by: (Söckel & Schmalzried, 1968; Hölscher & Schmalzried, 1984) – (♦) points, (Bransky & Wimmer, 1972) – (○), (Constant et al., 1992) – (●), (Fisher & Tannhauser, 1966) – (■).

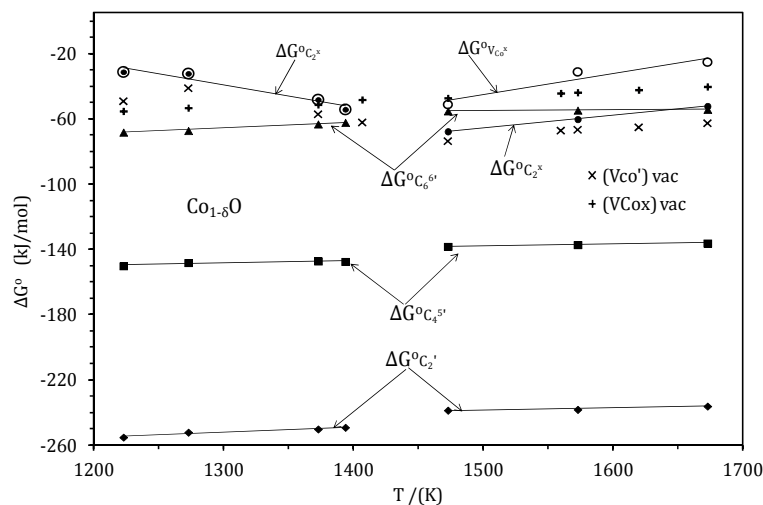


Figure 6.

The temperature dependence of $\Delta G_{C_2}^0$, $\Delta G_{C_4}^0$, $\Delta G_{C_6}^0$, of the formation of defect complexes, respectively: $\{(V_{Co})_2Co_i^{3+}\}'$ - ($\blacklozenge$) points, $\{(V_{Co})_4Co_i^{3+}\}'^{5'}$ - ($\blacksquare$), $\{(V_{Co})_6(Co_i^{3+})\}'^{6'}$ - ($\blacktriangle$), defects with lower ionization degrees ($\Delta G_{C_2}^0 = \Delta G_{C_4}^0 = \Delta G_{C_6}^0 = \Delta G_{V_{Co}}^0$) - ($\bullet$) and $\Delta G_{V_{Co}}^0$ - ($\circ$), obtained using the results of the studies of the deviation from the stoichiometry obtained by (Söckel & Schmalzried, 1968; Hölscher & Schmalzried, 1984; Bransky & Wimmer, 1972). The ($\times$) points mark the results of $\Delta G_{V_{Co}}^0$ and the (+) points the values of $\Delta G_{V_{Co}}^0$, obtained in the work (Stokłosa, 2011a) for the model of simple defects without defect clusters.

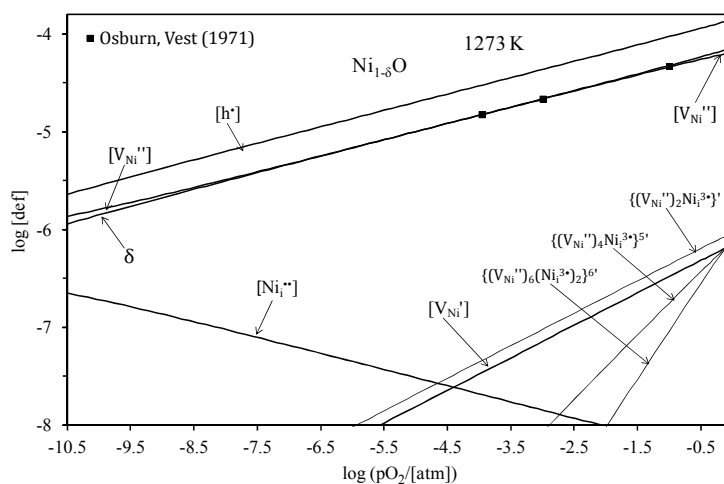


Figure 7a.

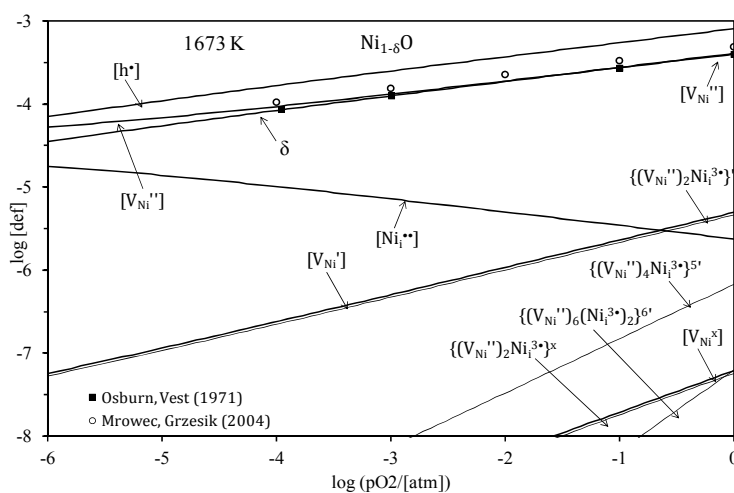


Figure 7b.

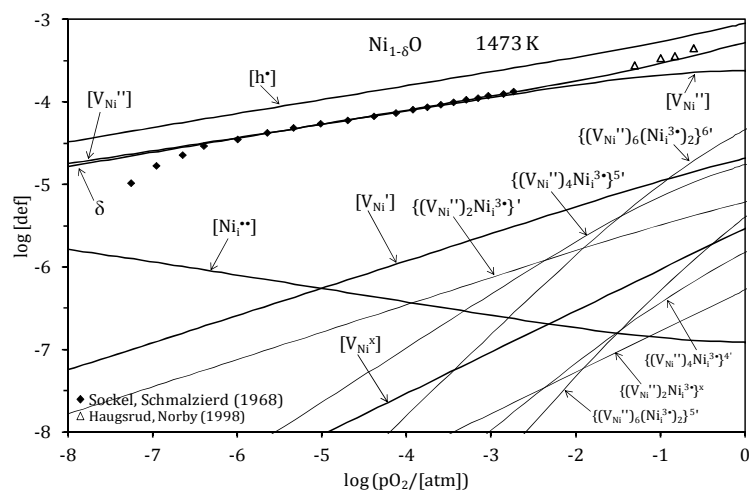


Figure 7c.

The diagrams of the point defects concentrations for the $\text{Ni}_{1-\delta}\text{O}$, taking into account simple defects as well as complexes: C_2 , C_4 and C_6 , obtained using the results of the studies of the deviation from the stoichiometry by: (Osburn & Vest, 1971) a) for 1273 K, b) 1673 K, and by (Söckel & Schmalzried, 1968) (c) for 1473 K. The points mark the results of the deviation from the stoichiometry studies obtained by: (Söckel & Schmalzried, 1968) – (◆) points, (Osburn & Vest, 1971) – (■) points, (Mrowec & Grzesik, 2004) – (○) points, (Hangsrud & Norby, 1998) – (Δ) points.

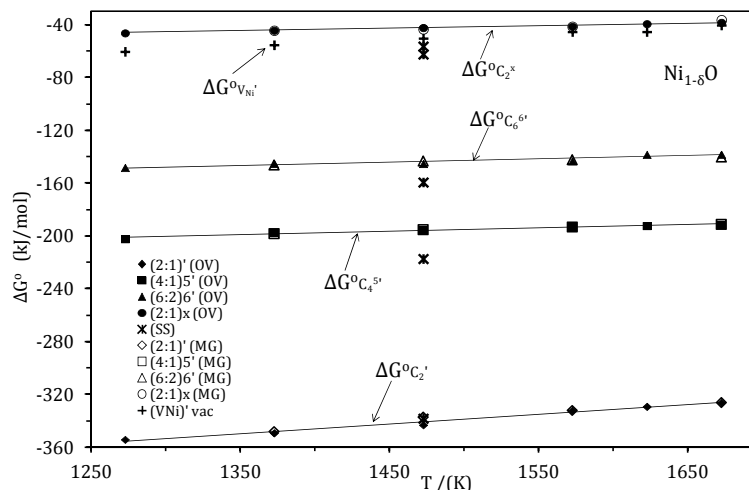


Figure 8.

The temperature dependence of $\Delta G_{C_2}^0$, $\Delta G_{C_4}^0$, $\Delta G_{C_6}^0$ of the formation of defect complexes, respectively: $\{(V_{Ni})_2 Ni_i^{3\bullet}\}'$ - ($\blacklozenge, \blacklozenge$) points, $\{(V_{Ni})_4 Ni_i^{3\bullet}\}^{5'}$ - ($\blacksquare, \square$), $\{(V_{Ni})_6 (Ni_i^{3\bullet})_2\}^{6'}$ - ($\blacktriangle, \triangle$) and with lower ionization degrees ($\Delta G_{C_2}^0 = \Delta G_{C_4}^0 = \Delta G_{C_6}^0 = \Delta G_{V_{Ni}}^0$) - ($\bullet, \circ$), obtained using the results of the studies of the deviation from the stoichiometry obtained by: (Osburn & Vest, 1971) (solid points), (Mrowec & Grzesik, 2004) (empty points) and by (Söckel & Schmalzried, 1968) for $T = 1473$ K - ($\ast$) points. The (+) points mark the values of $\Delta G_{V_{Ni}}^0 = \Delta G_{V_{Ni}}^x$, obtained in the work (Stokłosa, 2011b) for the model of simple defects without defect clusters.