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Vacancy Interaction Energies in Transition Metal Oxides

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Vacancy interaction energies E_{11} and E_{22} (for vacancies with same sign) and E_{12} (with opposite sign) in transition metal oxides of the NaCl-type structure were determined by studying the variations of the partial free energy of oxygen with composition. In MnO, $E_{22}=1.34 \,\mathrm{eV}$; in FeO, $E_{22}=0.120 \,\mathrm{eV}$; in CoO, $E_{22}=2.08 \,\mathrm{eV}$; in TiO, $E_{11}=E_{22}=0.100 \,\mathrm{eV}$, $E_{12}=-0.140 \,\mathrm{eV}$; in VO, $E_{11}=E_{22}=0.202 \,\mathrm{eV}$, $E_{12}=-0.286 \,\mathrm{eV}$; in NbO, $E_{11}=E_{22}=0.780 \,\mathrm{eV}$, $E_{12}=-1.10 \,\mathrm{eV}$. An attempt was also made to calculate the vacancy interaction energies using the Debye-Hückel theory of strong electrolytes to account for the long-range coulombic interaction. This method gave good results for NaCl and KCl, but failed for the transition metal oxides. A qualitative relationship was derived showing that the logarithm of the vacancy interaction energies should depend on E° the potential for the following reaction:

 $(Metal)^{++} \longrightarrow (Metal)^{+++} + \bigcirc$.

Introduction

Some of the transition metals of Groups IV, V, VII, and VIII form stable monoxides of the NaCl-type structure. Closer examination shows that the structures contain a relatively large concentration of vacancies. The aim of the present work is to obtain some information about these vacancies.

Theory

The theory of compounds with small deviations from stoichiometric composition has been given by Wagner¹⁾ and by Fowler and Guggenheim.²⁾ The theory was expanded by Anderson³⁾ to include larger deviations. However, he considered only the binary compounds AB where the defect is present solely in atom A, either as a vacancy or as an interstitial. In the compounds under present investigation, the defects occur only as vacancies, but both components can show these vacancies.

The theory for FeO, TiO and NbO was given earlier⁴). MnO, CoO and NiO obey the same relations as FeO. The theory of the VO phase is similar to TiO.

Experimental Results

MnO Phase

Davies and Richardson⁵⁾ studied the oxygen activity at 1773, 1848, and 1923°K, using mixtures of H₂, CO₂, and N₂; their data are shown in Fig. 1. The slope of the solid line gives the vacancy interaction energy: E_{22} = 1.34 ± 0.05 eV. Davies and Richardson also calculated a "theoretical" curve, using Wagner's¹⁾ method, which does not consider interaction between vacancies. According to them, when $n_0/n_{\rm Mn} > 1.005$, *i.e.*, the vacancy concentration is larger than 0.0048 per Mn atom, their "theoretical" curve does not fit the data. In Fig. 1, the dotted line ends and the solid line starts at this concentration of vacancies. Thus, above this vacancy concentration, the interaction between vacancies affects noticeably the properties of the MnO phase. The vacancy concentration above which interaction plays an important role will be different in different systems: this limiting vacancy concentration will decrease if the absolute value of the vacancy interaction energy E_{22} increases, and *vice versa*.



Fig. 1. Evaluation of the vacancy interaction energy from the variation of the oxygen partial free energy with composition in MnO.

FeO Phase

Emmett and Schultz¹⁰⁾ measured the oxygen activity in Fe/FeO and FeO/Fe₃O₄ systems using H₂/H₂O mixtures. From their data (and the composition limit of the FeO phase¹¹⁾) $E_{22}=0.122\pm0.009$ eV at 1073°K.

Ariya, Morozova, and Shneider¹² measured the oxygen activity as a function of composition at 1104 and 1182°K, using CO/CO₂ mixtures. A least square analysis of their data gives $E_{22}=0.109\pm0.008$ eV at 1104° and $E_{22}=0.135\pm0.012$ eV at 1182°K.

Hoch, Iyer, and Nelken⁴⁾ measured the difference between the partial free energy of oxygen of oxygen-rich and oxygen-poor FeO, using the electromotive force method. Cells of the type Fe, FeO/electrolyte (0.8 ZrO_2 0.2 CaO)/FeO, Fe₃O₄ were used, and measurements carried out between 1173 and 1440°K They found E_{22} =0.112±0.004 eV.

The average for the three investigators is $E_{22}=0.120 \text{ eV}.$

CoO Phase

Carter and Richardson⁶⁾ measured the oxygen activity at 1273, 1423, and 1623°K as a function of composition using nitrogen and

oxygen gas mixtures. Least square treatment of their data gives $E_{22}=2.08\pm0.21\,\mathrm{eV}.$

NiO Phase

Shimomura, Tsubokawa, and Kojima¹³⁾ prepared NiO_{1.20} by decomposition of Ni (NO₃)₂. This method, however, gives only metastable material, and thus their results are not suitable for evaluation of E_{22} .

Mitoff⁷⁾ studied the conductivity of NiO as a function of the concentration of vacancies. As his results can be explained by Wagner's¹⁾ theory, and the highest concentration of vacancies at 1573°K was only 1.6×10^{-4} per Ni atom, it must be concluded that in NiO the interaction between vacancies does not affect the properties of the material, and thus the interaction energy cannot be determined from thermodynamic considerations.

TiO Phase

Hoch, Iyer, and Nelken⁴ measured the difference between the oxygen partial free energy of oxygen-rich and oxygen-poor TiO, using electromotive cells of the type Ti, TiO /electrolyte (0.8 ZrO₂ 0.2 CaO)/TiO, Ti₂O₃. The measurements extended over the temperature range 1235–1445°K; they found $(2E_{11}-E_{12})=$ 7.18 kcal. Thus $E_{11}=0.100 \text{ eV}$, $E_{12}=-0.140 \text{ eV}$. *VO Phase*

Hoch and Ramakrishnan¹⁴⁾ studied the difference between the oxygen partial free energy of VO in equilibrium with V and VO in equilibrium with V_2O_3 , in the temperature range 1200-1490°K, using also the electromotive force cell technique. At 1073 and 1173°K, this difference in oxygen partial free energy is 14.73 kcal/mole of O₂ and 15.65 kcal/mole of O₂, respectively. According to Westman and Nordmark⁸⁾, and Schonberg⁹⁾, the VO phase extends from VO_{0.90} to VO_{1,20} at 1073°K, and from VO_{0.89} to VO_{1.20} at 1173° K. With these data $(2E_{11}-E_{12})=15.94$ kcal and $E_{11}=$ $0.202 \text{ eV}, E_{12} = -0.286 \text{ eV}.$

NbO Phase

Hoch, Iyer, and Nelken⁴ also measured the difference between the oxygen partial free energy of oxygen-rich and oxygen-poor NbO, using again the electromotive force cell technique. They obtained for the ordered vacancies, $(16E_{11}-9E_{12})=515.8$ kcal, giving $E_{11}=0.780$ eV and $E_{12}=-1.10$ eV.

All the above results are given in Table I under "Experimental values."

Substance	Experimental values			Calculated values				
			Vacancy concentration V/N	Coulombic		Eq. (1)		E°
	$E_{22}(E_{11})$ eV	$-E_{12}$ eV		${E_{22}(E_{11}) \over { m eV}}$	$-E_{12} \\ \mathrm{eV}$	$E_{22}(E_{11}) = eV$	$-E_{12} eV$	Volts
FeO	0.120		0.086	1.32		0.386		-0.77
MnO	1.34		0.021	1.28		0.377		-1.51
CoO	2.08		0.006	1.34		0.393		-1.81
TiO	0.100	0.140	0.15	1.34	1.89	0.393	0.798	+0.37
VO	0.202	0.286	0.12	1.39	1.97	0.410	0.830	+0.26
NbO	0.780	1.10	0.25	1.35	1.91	0.397	0.806	

Table I. Vacancy interaction energies in FeO, MnO, CoO, TiO, VO, and NbO.

Calculation of Vacancy Interaction Energies

The vacancy interaction energies can be calculated if it is assumed that they are due to coulombic forces. Fumi¹⁵⁾ made extensive calculations on the interaction energies of vacancies in NaCl and KCl; Reitz and Gammel¹⁶⁾ and Kurosawa¹⁷⁾ also carried out similar calculations. Their results are summarized in Table II. For the oxides investigated in the present work, data are not available to carry out detailed calculations. Therefore a simpler approximation has to be made.

Table II. Calculated vacancy interaction energy $-E_{12}$ in NaCl and KCl

		NaCl eV	KCl eV
1.	Coulombic interaction energy	0.91	0.98
2.	Fumi ²¹⁾	0.60	0.72
3.	Reitz and Gammel ²²⁾	0.89	
4.	Kurosawa ²³⁾	0.44	0.58
	This research		
5.	1000°K	0.79	0.88
6.	1300°K	0.66	0.74
7.	Limit	0.39	0.42
	Average of 2, 3, 4	0.625	
	Average of 2, 4		0.65
	Average of 1, 7	0.65	0.70

Lidiard¹⁸⁾ has used the Debye-Hückel theory of strong electrolytes to evaluate the interaction energy between a vacancy and an impurity atom in NaCl. This method will be applied here to calculate the interaction energy of vacancies. The interaction energy can then be expressed as

$$E = \frac{e^2}{\varepsilon} \left(\frac{1}{r_0} - \frac{\kappa}{1 + \kappa a} \right) \tag{1}$$

where ε is the dielectric constant, *e* the charge of the "vacancy" (charge of the missing ion), r_0 the distance of closest approach, κ the Debye-Hückel screening constant, and *a* the next closest distance of approach. The screening constant κ is expressed as $\kappa^2 = 8\pi me^2/kTW$, where *m* is the number of vacancies and *W* equals the volume of the crystal. The necessary data (dielectric constant, lattice parameter) are taken from the "Handbook of Chemistry and Physics".¹⁹⁾ The dielectric constants of TiO, VO, MnO, CoO, and NbO were taken as equal to that of FeO.



Fig. 2. Relation between the vacancy interaction energy E_{vv} and the potential E° for the reaction Me⁺⁺ \rightarrow Me⁺⁺⁺+ \bigcirc .

NaCl and KCl

To check the approximation, the interaction energy between vacancies in KCl and NaCl will be evaluated first.

Calculating the number of vacancies from the data of Stone,²⁰⁾ (Eq. 8 and Table I), the screening constant and the interaction energy can be calculated. The screening constant is dependent on the concentration of vacancies, which in NaCl and KCl is very strongly dependent on the temperature. In the second half of Table II the screening constant and the interaction energy at 1000 and 1300°K were evaluated. As the temperature is raised, κ increases due to the exponential increase of vacancies. Correspondingly, $-E_{12}$ decreases. The limiting value is obtained when $\kappa_a \gg 1$: then

$$E_{vv} = \frac{e^2}{\varepsilon} \left(\frac{1}{r_0} - \frac{1}{a} \right). \tag{2}$$

This value is also given in Table II. It is interesting to note that for NaCl, the average of Fumi's, Reitz and Gammel's, and Kurosawa's values is 0.625 eV, the average between the coulombic and the limit of the Debye-Hückel approximation is 0.65 eV. Similarly for KCl, the average of Fumi's and Kurosawa's data is 0.65 eV, that between coulombic and Debye-Hückel limit 0.70 eV.

Oxide Phase

In these phases, the vacancy concentration is independent of temperature. In the evaluation of the screening constant the vacancy concentration in the middle of the experimental range is used. As the concentration of vacancies is so large, the difference in calculating E's using Eq. (1) or Eq. (2) is very small.

The agreement between calculated and experimental values is not very good. In the formation of the defects in the transition metal oxides a certain number of ions have to carry excess charges because of the deviation from stoichiometry. For example, in the case of FeO, the introduction of an Fe vacancy creates two Fe³⁺ ions, to maintain electrical neutrality. Similarly, when TiO deviates from stoichiometry, the excess charge will be carried either by Ti⁺ or Ti³⁺ ions (the oxygen will always be divalent). A qualitative relation between the vacancy interaction energy and the potential E° of the reactions of the type

$$Fe^{++} \rightarrow Fe^{+++} + \bigcirc$$
 (3)

is as follows.

When a metal (Me) vacancy is created, the first step is

$$Me^{++} \rightarrow Me^{2} + \Box^{++};$$

i.e., a metal atom is removed, and a double positively charged vacancy left behind. The charges from the vacancy tend to form

trivalent metal ions and uncharged vacancies. (A doubly charged vacancy is equivalent to a complex formed by the vacancy and the two trivalent metal ions; in the case of an uncharged vacancy the trivalent metal ions are distributed randomly in the lattice).

$$\Box^{++} + 2\mathrm{Me}^{++} \rightarrow 2\mathrm{Me}^{+++} + \Box \ . \tag{4}$$

This is the same reaction as (3), and the free energy charge for reaction (4) is thus $\Delta F^{\circ}{}_{(3)} = -2 \mathscr{F} E^{\circ} + C_1$ kcal. The constant C_1 is introduced because the E°'s given in Table II are for aqueous solutions.

According to Eq. (2) the vacancy interaction energy is proportional to e^2 , the square of the charge on each vacancy. $(r_0$ and ε do not vary much in the oxides under investigation). From Eq. (4), the concentration of charged vacancies $[\Box^{++}]$ in terms of concentration of all the vacancies $[\Box^{++}+\Box]$ can be obtained. The ratio $2[\Box^{++}]/[\Box^{++}+\Box] = a$ can be interpreted as the average charge on a vacancy (or twice the fraction of complexes). Thus

$$E_{vv} \propto \frac{4[\square^{++}]^2}{[\square^{++}+\square]^2} \simeq \frac{4[\square^{++}]^2}{[\square]^2} . \tag{5}$$

Applying the mass action law to equation (4)

$$\frac{[\Box^{++}][Me^{++}]^2}{[\Box][Me^{+++}]^2} = C_2 e^{\frac{-2\mathscr{F}E^6 + C_1}{RT}}$$
(6)

where C_2 accounts for the use of concentrations, rather than activities. Taking [Me⁺⁺] \simeq 1, (most sites are doubly charged), and 2[Me⁺⁺⁺]=[\Box], and comparing Eqs. (5) and (6), 1n E_{vv} should be a function of E° , 1n E_{vv} is plotted against E° in Fig. 2.

 E° will influence both E_{11} and E_{12} in TiO, VO, and NbO. For these compounds the total vacancy interaction energy $E_{11}+1/2E_{12}$ (there are twice as many sites of similar charge than of opposite charge surrounding a site) is plotted in Fig. 2. In first approximation, $\ln E_{vv}$ is a linear function of E° ; the straight line in Fig. 2, calculated by least squares, is:

$$\ln E_{vv} = -(2.76 \pm 0.24) - (1.85 \pm 0.27) E^{\circ}$$

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DISCUSSION

Lidiard, A. B.: In your evaluation of the partition function to obtain your equilibrium equations you made an assumption that the two kinds of vacancies were randomly distributed ("Bragg-Williams" approximation). Is it not possible that the inferred vacancy interaction energies are in error on account of this approximation?

Hoch, M.: In treating NbO, we assumed ordered vacancies, and also random vacancies. The difference in vacancy interaction energies is only 10 %. This is because when large values of E_{11} are obtained, the difference in oxygen activity is the controling factor. When E_{11} is small, then random (or almost random) distribution of vacancies is present. (See J. Phys. Chem. of Solids (1962), for detailed discussion).

Fukai, **Y**.: As I remember, TiO and VO are more like metals than insulators. So that, I don't think electrons be localized in these crystals, and valence states of metal ions will be defined so simply as you have done in this calculation.

Hoch, M.: In the statistical treatment it is immaterial if we have a metal or an insulator. The theoretical calculation using the Debye-Hückel theory gave no agreement with the experiment; thus the question of type of conduction for our purpose is unimportant.