Chemical Bonding in Rock Salt Structured Transition Metal Oxides

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For oxides, MO (M = Mg, Ca, Sr, Ba), the basicity moderating parameter of M governs the nature of the combined oxide(-II) ion, specifically (i) its Pauling electronegativity, x_0, and (ii) its electronic polarizability, $\alpha_{O^{2-}}$, so leading to a simple relationship between x_0 and $\alpha_{O^{2-}}$. This relationship is not obeyed by transition metal oxides (M = Mn, Fe, Ni), but the chemical behavior of mixed molten oxide systems (slags) indicates that the discrepancy lies in x_0 and not in $\alpha_{O^{2-}}$. It is argued that this discrepancy arises because of the contribution to the heat of formation of M–M bonding in these oxides. CdO and the metallic oxides TiO and VO are also considered. © 1990 Academic Press, Inc.

The ionic/covalent character of the metal-to-oxygen bonding in metal oxides is interesting for several reasons. For example, it greatly influences the basic strength of the metal oxide, and this vitally affects the chemical properties of technologically important materials such as metallurgical slags (*1–4*) glasses (*5–9*), and oxidic ceramics (*10*).

For many simple compounds of the metals, the ionic/covalent bond character is usefully judged by electronegativity difference, but for oxides this has been shown to be unreliable (*11*). For example, the Pauling electronegativity difference (obtained from heats of formation) for sodium oxide and silica are almost the same (1.65 and 1.67, respectively), yet their chemistries indicate that sodium oxide is much more ionic. Similarly, the contrast between Cs_2O and P_2O_5 is not borne out by the electronegativity difference (1.49 and 1.45, respectively). The ionicity of the oxide(-II) species is better represented by its own electronegativitiy, x_0. This is because as oxide(-II) becomes more negatively charged, so x_0 is observed to decrease (*11*). Thus, it is the decrease in x_0 which indicates increasing ionicity in the M–O bonding.

The influence of the cation on the charge clouds of the oxide(-II) can be expressed by a parameter, γ_M (*4*). Cations with little influence produce oxides of high ionicity, that is, highly basic oxides such as CaO and BaO, whereas cations which interact strongly with the oxide (-II) charge clouds produce oxides of much lower ionicity, e.g., Al_2O_3, or covalent oxides, e.g., SiO_2 and P_2O_5. Reducing the M–O ionicity reduces the basicity, and accordingly γ_M is called the "basicity moderating" parameter. In short, increasing γ_M (Table I) results in increasing covalency and polarization (complying with Fajans' rules).

Values of γ_M are known with certainty only for the alkali and alkaline earth metals, Mg, Al, Si, B, P, and S. It is obtained from data, mainly for glasses, where probe ions,

TABLE I

ELECTRONEGATIVITY DATA AND POLARIZABILITIES FOR OXIDES

Oxide	γ_M	Q/kJ mole^{-1}	$x_0 - x_M{}^a$	x_M	x_0	$\alpha_{O^{2-}}$/Å^3
MgO	1.28	603	1.92	1.16	3.08	1.71
CaO	1.00	635	1.97	0.93	2.90	2.49
SrO	0.91	596	1.91	0.87	2.78	3.03
BaO	0.87	563	1.86	0.82	2.68	3.62
TiO		523	1.81	1.37	3.18	
VO		423	1.66	1.47	3.13	
MnO		387	1.60	1.40	3.00	2.4
FeO		273	1.40	1.66	3.06	2.6
CoO		238	1.34	1.70	3.04	
NiO		241	1.35	1.71	3.06	2.1
CdO		261	1.37	1.52	2.89	2.5

^{a} Using the Pauling relationship (for Q in kJ mole^{-1}) (20): $Q = 96.48(2(x_0 - x_M)^2 - 1.127)$ applicable to monoxides.

such as Tl^+ and Pb^{2+}, have been used to measure the extent of electron donor power in oxidic systems. The method relies on orbital expansion spectroscopy (in the ultraviolet region) of these probe ions, utilizing chiefly the $(s-p)$ $^1S_0 \rightarrow {}^3P_1$ transition (4). Because of the impairment of UV transparency, data are unavailable for assigning γ_M values to transition metal ions. Thus, comparison of transition metal oxides with nontransition metal oxides cannot presently be made using basicity moderating parameters.

This limitation is unfortunate because there are many situations where transition metal oxides participate in acid/base reactions and where they are accompanied by, e.g., alkaline earth metal oxides. This happens in metallurgical slags, and it is the basicity which is usually the overriding factor affecting the refining power, for example, in removing sulfur from the molten metal in iron and steel making. Expressing this reaction as

$$\tfrac{1}{2}S_2 + O^{2-}(slag) \rightleftharpoons S^{2-}(slag) + \tfrac{1}{2}O_2$$
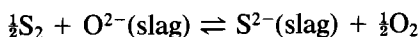
indicates how increasing slag basicity increases its power to remove sulfur. In ex-

traction metallurgy this is expressed numerically as the "sulphide capacity" of the slag (C_S), and previously (4) it has been shown how C_S is correlated to the γ_M values of the Ca^{2+}, Mg^{2+}, Si^{4+}, etc., cations constituting the slag. These correlations are presently being used by the European Coal and Steel Community for slag modeling and involve a data bank covering several hundred slag compositions (12). Among these data are slags containing large amounts of transition metal oxides, and these indicate that MnO and FeO are as basic as CaO and certainly more so than MgO. For example, replacement of CaO by FeO results in insignificant change in the sulfide capacity whereas replacement by MgO produces a marked decrease (Fig. 1). Furthermore, in series of slags based upon $CaO-MgO-SiO_2$ (13), replacement of MgO by MnO or FeO is observed to increase the sulfide capacity, with the C_S values fitting $\gamma_{Fe^{2+}} \approx \gamma_{Mn^{2+}} \approx \gamma_{Ca^{2+}} = 1.00$ (cf. $\gamma_{Mg^{2+}} = 1.28$).

Under aqeous conditions, MnO and FeO are regarded as not very basic because manganese(II) and iron(II) salts undergo (slight) hydrolysis. Thus, to rank these oxides along with CaO, and above MgO, in
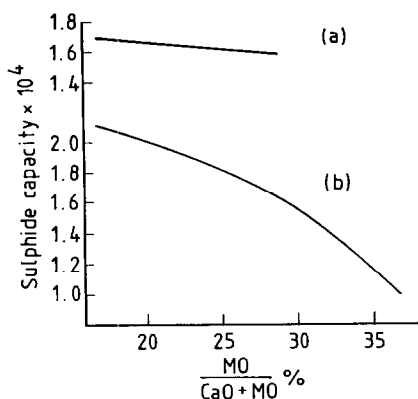
FIG. 1. Decreasing basicity of slags in the CaO–MO–SiO_2 system (constant SiO_2 = 41 mole%) as signalled by decreasing sulfide capacity for (a) MO = FeO and (b) MO = MgO. (Data are for (a) at 1480°C, taken from C. Saint-Jours and M. Alibert, 3rd International Conference on Molten Slags and Fluxes, Institute of Metals, London, 1989; and for (b) at 1500°C, taken from Ref. (4).)

Electronic Polarizability and Electronegativity in Oxides

In principle, the state of ionicity of O^{2-} in inorganic oxides should be reflected in the oxygen electronegativity, x_0, and the oxide(-II) electronic polarizability, $\alpha_{O^{2-}}$. Thus, x_0 and $\alpha_{O^{2-}}$ should each be related simply to the basicity moderating parameter, γ_M. Experimental data (Table I) show that $1/\gamma_M$ varies almost linearly with (i) x_0 and (ii) $1/\alpha_{O^{2-}}$ (14). (The quantity $1/\gamma_M$ is the "optical basicity" value of the oxide (4). It is remarkable that these relationships extend from the most basic oxides known, e.g., BaO, to the most acidic, e.g., P_2O_5 and SO_3 (this is shown for relationship (ii) in Fig. 1 of Ref. (14)), but here we are concerned only with the oxides MgO to BaO (Fig. 2).

basicity may seem surprising. Also, the implication that these oxides are as ionic as CaO (and more so than MgO) seems, at first sight, difficult to reconcile with the significantly greater electronegativity of manganese(II) and iron(II) compared with calcium and magnesium. Furthermore, if the degree of basicity of MnO and FeO extends to NiO, then there is disagreement with the interpretation of the Racah B parameter data that NiO is less ionic than MgO (see below).

These problems are a symptom of the inadequacy of current theories of chemical bonding to account comprehensively in a unifying manner for major properties of transition metal oxides, for example, their magnetic, spectroscopic, and electronic properties. Our objective in addressing the problems described above is to gain insight into the chemical bonding of these compounds. The opportunity is taken for including other rocksalt structured oxides (see Table I).
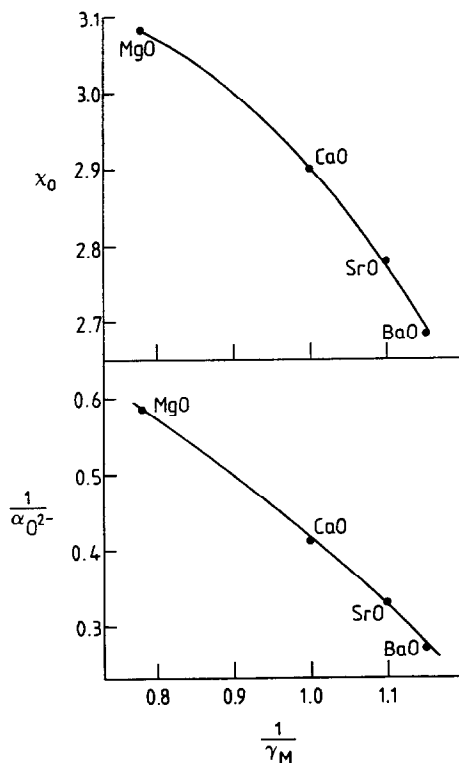

FIG. 2. Relationships of (a) oxygen electronegativity, x_0, and (b) oxide electronic polarizability, $1/\alpha_{O^{2-}}$, with basicity moderating parameter, $1/\gamma_M$.
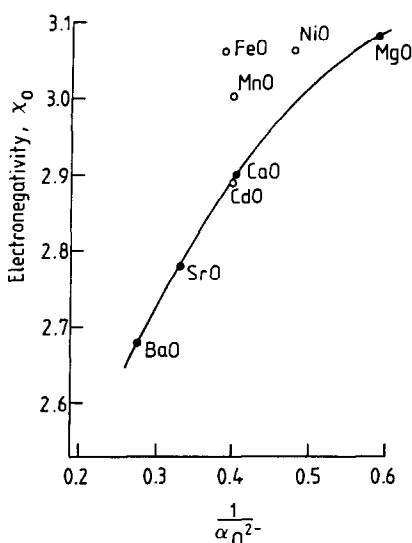
FIG. 3. Plot of x_0 versus $1/\alpha_{O^{2-}}$ for oxides designated.

Figure 2 anticipates a simple relationship between x_0 and $1/\alpha_{O^{2-}}$ (Fig. 3), and since this eliminates the need for γ_M values, it is possible to include data for transition metal oxides from Table I. For MnO and FeO, $\alpha_{O^{2-}}$ indicates very similar ionicity to CaO, but x_0 indicates lower ionicity. In view of the chemical similarity of MnO and FeO to CaO, in terms of their basicity in molten oxide systems (see above), it appears that $\alpha_{O^{2-}}$ is a reliable signal for ionicity; the electronegativity, x_0, as far as transition metal oxides are concerned, is not. The $\alpha_{O^{2-}}$ value for NiO indicates an ionicity or basicity between CaO and MgO, but no "chemical" data are available to confirm this.

With the γ_M values of Mn^{2+} and Fe^{2+} virtually the same as for Ca^{2+}, it is necessary to explain why x_0 for MnO and FeO is greater than for CaO. The bonding role of Mn^{2+} and Fe^{2+}, expressed by γ_M, requires x_0 for MnO and FeO (and NiO) to fit the plot for the oxides MgO to BaO in Fig. 3. The larger x_0 values arise from greater heats of formation, Q, and therefore there must

be an additional contribution to the bonding in the transition metal oxides.

The most obvious contribution, apparent when using the Mott and Hubbard model for transition metal oxides (15), is from the $d-d$ ($t_{2g}-t_{2g}$) orbital overlapping between adjacent metal ions. In this model the $d-d$ bonding is a very important factor for the transition metal oxides, but is absent in MgO, CaO, SrO, and BaO (Fig. 4). If it is assumed that other contributory factors are negligible, then the difference between the experimental value of x_0 and the "corrected" x_0 (obtained by using the value of $1/\alpha_{O^{2-}}$ and interpolating in Fig. 3) represents the contribution of intermetal ion $d-d$ orbital overlapping to the heat of formation of the metal oxide. Figure 3 therefore can be used for estimating what proportion of the metal oxide heat of formation arises from metal-to-metal bonding.

Metal-to-Metal Bonding

The results obtained from Fig. 3 by this means, admittedly very rough, indicate that the contribution of $d-d$ overlapping to the heat of formation is small for NiO and negligible for CdO, but significantly greater for MnO and FeO (Table II).

The contribution of $d-d$ overlapping to Q depends on the magnitude of the overlap integral, $S_{(d_\sigma-d_\sigma)}$ and the number of unpaired
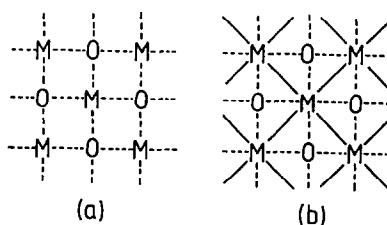

FIG. 4. Contrast between (a) alkaline earth metal oxides and (b) transition metal oxides (with rock salt structure) indicating essentially electrovalent bonding between M^{2+} and O^{2-} ions (----) and, in (b), metal-to-metal d orbital overlapping (—).

TABLE II

DATA RELEVANT TO d–d OVERLAPPING IN METAL OXIDES

Oxide	Correction to x_0	Correction to Q/kJ mole$^{-1\,a}$	Overlap integral $S_{(d_\sigma - d_\sigma)}$
TiO	(0.28)	(180)^b	0.025
VO	(0.23)	(137)^b	0.014
MnO	0.10	60	0.001
FeO	0.18	90	0.001
NiO	0.06	24	0.000
CdO	zero	zero	0.002

^{a} Equal to $96.48[4\delta x_0(x_0 - x_M) - 2\delta x_0^2]$ kJ mole^{-1} (where δx_0 is the correction to x_0) since correction to Q is $96.48[2(x_0 - x_M)^2 - 2(x_0 - \delta x_0 - x_M)^2]$ kJ mole^{-1} (see footnote to Table 1).
^{b} Calculated on the basis of $\alpha_{O^{2-}} = 2.5$ Å^3 (see text).

electrons. For present purposes, use of Slater orbitals for calculating overlap integrals is adequate, and values of $S_{(d_\sigma - d_\sigma)}$ obtained by this means (see Appendix) are in Table II. It is seen that $S_{(d_\sigma - d_\sigma)}$ values are large for TiO and VO (to be discussed presently), but much less for the remaining oxides. Presumably the larger contribution to Q in FeO (amounting to a third of the total Q, see Table II), compared with MnO, arises owing to the smaller exchange energy associated with the high-spin d^6 configuration of Fe^{2+} compared with the high-spin d^5 configuration of Mn^{2+}. For NiO, the t_{2g} level of the d^8 Ni^{2+} ion is full, and d–d overlapping is not expected to contribute to Q; this also holds true for CdO containing the d^{10} Cd^{2+} ion. As seen from Table II, the correction for NiO is small and for CdO it is zero.

TiO and VO differ significantly from the other rock salt structured oxides in being metallic. Although their refractive indices are unknown, it is possible to calculate the molar electronic polarizability, α_m, of each oxide by applying the Clausius–Mossotti relationship on the assumption of a Herzfeld "polarization catastrophe" (16). For this condition, α_m is the molar volume multiplied by $3/4\pi N$, where N is Avogadro's number, and equals 5.14 Å^3 for TiO and

4.61 Å^3 for VO (Table III). The ions undergoing the polarization catastrophe are those in which the electrons become itinerant. Theoretical models for TiO and VO indicate that these are the metal ions, and hence the large values of α_m arise owing to the enormous values of $\alpha_{Ti^{2+}}$ and $\alpha_{V^{2+}}$ for these ions in the metallic regime. Since the oxide electrons remain localized, $\alpha_{O^{2-}}$ is expected to change only slightly.

It is worthwhile proceeding with a "guessed" value for $\alpha_{O^{2-}}$ since, despite the arbitrariness of this step and the semiquantitative nature of any results,[1] the implications are very interesting. Thus, we can obtain an estimate of the electronic polarizabilty of a metal ion (Ti^{2+} or V^{2+}) in a state where previously bound electrons have been set free by mutual polarization of the metal ions. If $\alpha_{O^{2-}}$ is taken as 2.5 Å^3 (that is, similar to that in MnO and FeO), then the polarizabilities for Ti^{2+} and V^{2+} (i.e., α_m – 2.5) are 2.6 and 2.1 Å^3, respectively. These are enormous compared with other dipositive ions of similar size (these have Pauling values <0.05 Å^3 (17)). Indeed, they indicate

[1] A further approximating factor is the uncertainty in Q owing to nonstoichiometry.

TABLE III

DATA FOR POLARIZABILITY[a] AND OVERLAP INTEGRALS

Oxide	d/g cm^{-3}	n	α_m/Å$^{3\,b}$	$\zeta_A(=\zeta_B)$	a/Å	ρ
MgO	3.56	1.737	1.81			
CaO	3.32	1.837	2.96			
SrO	4.75	1.870	3.93			
BaO	5.72	1.980	5.25			
TiO	4.93		5.14^c	2.38	4.177	13.28
VO	5.76		4.61^c	2.60	4.09	14.21
MnO	5.44	2.16	2.84	3.03	4.445	18.00
FeO	5.7	2.32	3.0	3.25	4.307	18.70
NiO	6.67	2.18	2.47	3.68	4.117	20.55
CdO	8.15	2.49	3.96	3.34^d	4.695	20.95

[a] Densities, d, and refractive indices, n, from Refs. (*19*) and (*25*).

[b] From $\sigma_m = \dfrac{3M}{4\pi Nd}\left(\dfrac{n^2-1}{n^2+2}\right)$. No correction is made in taking n for the sodium D line.

[c] Assuming polarization catastrophe (see text).

[d] $4d$ orbital.

that Ti^{2+} and V^{2+}, in the metallic regime, have a "floppiness" similar to that of the much larger (and singly charged) Cs^+ ion ($\alpha_{Cs^+} = 2.42$ Å^3 (*17*). Also, it is worthwhile noting that making $\alpha_{O^{2-}} = 2.5$ Å^3 yields, through Fig. 3, corrections to Q which indicate much larger contributions from d–d overlapping than for the other oxides (Table II), complying with the greater overlap integrals.

Conclusions

1. MnO and FeO are as basic as CaO; NiO has a basicity between CaO and MgO. This is important for their chemistry in the molten or solid state, but is a paradox for their aqueous solution chemistry (see below).

2. Metal-to-metal bonding can be an important factor in transition metal oxides (Fig. 4), and is especially so for TiO and VO, also according with their electron itinerancy.

3. Metal-to-metal bonding in nonmetallic oxides is covalency which means that the oxide ions are more ionic than the individual metal ions. It is this factor which explains why the interelectronic repulsion within the d level (expressed by the Racah B parameter) for Ni^{2+} is lower in NiO than for Ni^{2+}-doped MgO. The values of B are 800 and 865 cm^{-1}, respectively (*19*), and this observation could be taken, mistakenly, to imply that MgO is more basic than NiO.

4. The behavior of Mn^{2+}, Fe^{2+}, and Ni^{2+} salts in aqueous solution implies that the parent oxides are not strong bases. This behavior, however, arises through the covalent tendencies of these cations, used for metal-to-metal bonding in the oxides, reducing the ionicity of the cation-aquo ligand bonding (compared e.g., to that for Ca^{2+}).

Appendix

The electronegativity differences x_O–x_M (Table I) are calculated from heats of formation, Q, of the metal oxides (taken from Ref. (*19*)) by the Pauling method (*20*). Values of x_M, for obtaining x_O, are based on the metal bromide, since it is known that x_{Br}

undergoes little variation from one metal ion to another (11).

Molar polarizabilities of the oxides, α_{MO}, are calculated from refractive index (at 589 nm) and density using the Lorentz-Lorenz relationship (Table III). Values of $\alpha_{O^{2-}}$ (Table II) are obtained by substracting $\alpha_{M^{2+}}$ (Pauling polarizabilities are used (17)). Although $\alpha_{M^{2+}}$ values for transition metal ions are uncertain (0.4 Å^3 is taken for all of them (21)), the error affecting $\alpha_{O^{2-}}$ and consequent correction to Q is relatively small.

The overlap integrals, $S_{(d_\sigma-d_\sigma)}$, were obtained on the basis of Slater orbitals of the form

$$N_n r^{n-1} \exp(-\zeta_{nl} r).$$

The exponent ζ_{nl} is $(Z-S)/n$, where Z is the nuclear charge, S is the screening constant, and r is the distance in atomic units; S was estimated with Burns' rules (22). The overlap integrals require two parameters ρ and τ defined as (23)

$$\rho = (\zeta_A + \zeta_B)R/2$$

and

$$\tau = (\zeta_A - \zeta_B)/(\zeta_A + \zeta_B),$$

where ζ_A and ζ_B are the exponents of the orbitals of ions A and B (identical in the present case, and therefore τ is zero) and R is the internuclear distance in atomic units (equal to $a/\sqrt{2}$ where a is the unit cell dimension of the oxide). Having calculated ρ (Table III), the overlap integrals were obtained from the tables of Ref. (24) and are listed in Table II.

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