

Relationship between Cationic Charge, Coordination Number, and Polarizability in Oxidic Materials

J. A. Duffy[†]

Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen, AB24 3UE, U.K.

Received: April 30, 2004; In Final Form: June 30, 2004

An investigation made into the variation of oxide(−II) electronic polarizability, $\alpha_{\text{oxide}(-\text{II})}$, for glasses covering a wide range of composition shows that there is an almost linear relationship between $\alpha_{\text{oxide}(-\text{II})}$ and glass basicity (expressed as optical basicity, Λ). However, systematic deviations pinpoint the role of coordination number on the polarizing power of cations such as Al^{3+} , Ge^{4+} , and Mg^{2+} . Data for glasses containing these cations indicate that the oxide(−II) atoms of the glass undergo the same degree of polarization regardless of whether these cations exercise a coordination number of four or six. The results of previous studies on cationic charge trends for Fe^{3+} in glass are now explicable on this basis. Furthermore, it is shown that when the effect of coordination number is taken into account in the calculation of Λ for crystalline metal oxides (such as Al_2O_3 or GeO_2) and also metal silicates and aluminosilicates, there is good agreement with the $\alpha_{\text{oxide}(-\text{II})}/\Lambda$ trend already established for glasses. The optical basicity model is currently applied to technical problems concerned with metallurgical slag performance and also glass melts, and the present findings are expected to have important implications for these materials.

Introduction

Most elements, in a given oxidation state, are able to exercise more than a single coordination number. For example, Na^+ and K^+ are sixfold coordinated in their crystalline halides under normal conditions, but when these are vaporized, monomeric molecules are produced where the metal ion is singly coordinated. For such extremes of coordination, it seems likely that there would be a difference in the ionic/covalent nature of the cation–halide bonding. Pauling's electroneutrality principle implies that, with just a single cation–halide interaction for the molecules, greater electron donation is required for the metal ion, resulting in more covalency.¹ For less extreme changes in coordination, as when the Co^{2+} ion is converted from $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ to $[\text{CoCl}_4]^{2-}$, again Pauling's principle suggests more covalency in the Co–Cl bond than in the Co–OH₂ bond.

These aspects of inorganic chemistry were put on a more quantitative footing by Jørgensen in the 1960s with the application of ligand field theory.² This allowed assignment of an orbital expansion (nephelauxetic) parameter, h , to a ligand, which gave an indication of its electron-donating ability. The extent of orbital expansion was assessed by measuring the fall in the Racah parameter from that of the free ion, B_f , such that

$$(B_f - B)/B_f = h \times k \quad (1)$$

where B is for the complexed metal ion (obtained from its d–d absorption spectrum) and k is a parameter specific to the metal ion. Values of h were found to be consistent regardless of the metal ion and served to rank ligands in order of the extent of their nephelauxetic effect. This ranking supports the view that the Co–OH₂ bond is less covalent than the Co–Cl bond in the above complexes.

There is thus an indication that covalency increases with decreasing coordination number of the cation. Nevertheless, this

idea has certain difficulties that have not been fully resolved, and the present paper discusses these difficulties and their importance.

Metal Ions in Glass

Metal ions are coordinated when present not only in crystals but also in glass. An advantage of the glassy environment is that it is possible to generate gradual changes in the electron donor power of the ligands (which, for a glass, are silicate, germanate, etc., groups) simply by changing the chemical composition. This is observed, for example, for the Co^{2+} ion, which exists in glass as the pink octahedral CoO_6 chromophore or as the blue tetrahedral CoO_4 , the equilibrium between the two species being adjustable through small changes in the glass acid/base composition.³

Although the electron donor power of the silicate, etc., groups can be obtained by studying the nephelauxetic effect, some idea of its extent is also gained by measuring electronic polarizability (refractivity). The molar electronic polarizability of a glass, α_m , can be obtained from the refractive index, n , and density, d , by using the Lorentz–Lorenz relationship:^{4,5}

$$\alpha_m = \frac{3M}{4\pi Nd} \frac{n^2 - 1}{n^2 + 2} \quad (2)$$

where N is the Avogadro number and M is the molecular weight assumed for the glass; for example, for a soda-lime-silica glass of composition $10\text{Na}_2\text{O}-15\text{CaO}-75\text{SiO}_2$, M could be chosen as $10 \times M(\text{Na}_2\text{O}) + 15 \times M(\text{CaO}) + 75 \times M(\text{SiO}_2)$, i.e., $(10 \times 61.98) + (15 \times 56.08) + (75 \times 60.08) = 5967.00$.

It is more instructive to focus on the polarizability of the oxide(−II) atoms rather than on the silicate, etc., groups. For glasses, and oxidic compounds generally, it has been noted that there is poor additivity when the values of α_m , obtained from eq 2, are compared with the atomic polarizabilities of the cations

[†] E-mail: j.a.duffy@abdn.ac.uk.

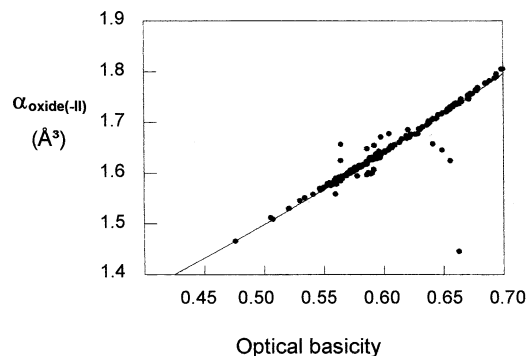


Figure 1. Plot of oxide polarizability, $\alpha_{\text{oxide}(-\text{II})}$, versus optical basicity, Λ , obtained for glass systems $\text{Li}_2\text{O}-\text{SiO}_2$, $\text{Na}_2\text{O}-\text{SiO}_2$, $\text{K}_2\text{O}-\text{SiO}_2$, $\text{CaO}-\text{SiO}_2$, and $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$. Equation 3 is used to calculate Λ taking γ appropriate values (see text). (The deviation, observed for a few points, has no explanation other than it arises from abnormal or defective refractivity data used in ref 5.)

and oxide ions composing the glass or compound.^{5,6} This is in contrast to most inorganic substances, e.g., alkali halides, where good additivity is usually observed.⁴ It has been argued that the reason for poor additivity arises because the oxide(-II) species has a variable polarizability, depending on the polarizing power of surrounding cations.⁵

The oxide(-II) polarizability, $\alpha_{\text{oxide}(-\text{II})}$, is obtained from α_m by subtracting the sum of the cationic polarizabilities and dividing by the number of oxygen atoms contained in the formula adopted for calculating M (for the above glass, oxygen atoms total: $10 + 15 + (2 \times 75) = 175$). The results follow a trend such that the values of $\alpha_{\text{oxide}(-\text{II})}$ appear to increase with increasing basicity of the glass. For example, $\alpha_{\text{oxide}(-\text{II})}$ in vitreous SiO_2 equals 1.466 \AA^3 , but in a $\text{CaO} \cdot \text{SiO}_2$ (2:3) glass it is 1.646 \AA^3 , whereas for the more basic $\text{Na}_2\text{O} \cdot \text{SiO}_2$ (2:3) glass it is 1.688 \AA^3 . When the glass basicity is expressed quantitatively as optical basicity, Λ (see below), an almost linear relationship with $\alpha_{\text{oxide}(-\text{II})}$ is observed.⁵ This can be idealized in the form:

$$\alpha_{\text{oxide}(-\text{II})} = 1.431\Lambda + 0.783 \quad (3)$$

and the proximity to this line of approximately 450 data points is shown in Figure 1. The points refer to glasses in the lithium, sodium, potassium, and calcium binary silicate systems as well as for glasses in the $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$ and $\text{K}_2\text{O}-\text{CaO}-\text{SiO}_2$ systems.

A quantitative relationship between electronic polarizability and optical basicity is to be expected. This is because the optical basicity value, Λ , represents the ability of the oxide(-II) species to donate negative charge when probed by a suitable cation.⁷⁻¹⁰ It represents the electronic state of the oxide(-II) species in a way similar to how it is represented by the electronic polarizability. The optical basicity model has its origins in Jørgensen's nephelauxetic parametrization, having been devised on the basis of electron donation to cations such as Tl^+ and Pb^{2+} and the resulting degree of charge reduction experienced by these ions.¹¹ This reduction was measured using optical spectroscopy, which, for these cations, is expressed by the red shifts in the $^1\text{S}_0 \rightarrow ^3\text{P}_1$ ultraviolet frequencies. For a particular glass (or other oxidic material), the red shift is compared with that for the cations in a very basic environment taken as crystalline calcium oxide. Simple molecular orbital theory shows that the ratio of the red shifts (glass/ CaO) can be taken as a sensible expression of basicity, especially in terms of the Lewis concept, and this ratio (which, in effect, is the ratio of h for the glass to h for CaO) has been termed the "optical basicity".¹¹

Analysis of accumulated spectroscopic data for many glasses has indicated that Λ can be calculated from chemical composition by the empirical formula

$$\Lambda = \frac{X(\text{AO}_{a/2})}{\gamma_A} + \frac{X(\text{BO}_{b/2})}{\gamma_B} + \dots \quad (4)$$

where $X(\text{AO}_{a/2})$, $X(\text{BO}_{b/2})$, ... are the proportions of oxygen atoms contributed by these constituent oxides (that is their equivalent fractions), and γ_A , γ_B , ... are specific to each cation and express quantitatively their effect in reducing the basicity of the oxide(-II) ions.¹² They were therefore called "basicity moderating parameters", although they may also be regarded as a measure of the polarizing power of each cation, especially in view of the relationship between $\alpha_{\text{oxide}(-\text{II})}$ and Λ shown in Figure 1. For a glass, for example, of mole percentage composition $x\text{Li}_2\text{O} \cdot y\text{Al}_2\text{O}_3 \cdot z\text{SiO}_2$, $X(\text{Li}_2\text{O}) = x/(x + 3y + 2z)$, $X(\text{Al}_2\text{O}_3) = 3y/(x + 3y + 2z)$, and $X(\text{SiO}_2) = 2z/(x + 3y + 2z)$, and from eq 4, Λ is given by

$$\Lambda = \left(\frac{x}{\gamma_{\text{Li}}} + \frac{3y}{\gamma_{\text{Al}}} + \frac{2z}{\gamma_{\text{Si}}} \right) / (x + 3y + 2z) \quad (5)$$

The Λ values used in Figure 1 were obtained using eq 4 together with the following γ values: Li, 1.23; Na, 0.905; K, 0.76; Ca, 1.00; Si, 2.10.⁵ (These values are slightly different from those obtained originally using spectral shifts for Ti^{4+} and Pb^{2+} ,^{8,12} but are a somewhat better fit for optical basicities derived from refractivity data.) It should be noted that for a single oxide eq 4 indicates that Λ is simply $1/\gamma$, a relationship that is important when dealing with metal oxides later.

Coordination Number

Although for many glass systems there is a close relationship between $\alpha_{\text{oxide}(-\text{II})}$ and Λ (Figure 1), investigation of several other glass systems has indicated exceptional behavior.⁵ Putting aside discrepancies arising from faulty experimental data, it is apparent that deviations from the normal trend are often not random but are systematic; for example, they rely closely on changes in glass composition. These deviations are particularly apparent in those glass systems where a change in coordination number can occur, principally those systems containing boron, germanium, and aluminum. It is well known that the coordination number of these elements depends on the glass composition, boron switching between threefold and fourfold coordination, while germanium and aluminum switch between fourfold and sixfold.

The deviations in the optical basicity occurring for these stereochemical changes are usually attributable to a change in the basicity-moderating parameter. For example, it has been shown for the $\text{K}_2\text{O}-\text{GeO}_2$ glass system⁶ that when the coordination number of germanium increases from four to six, γ_{Ge} changes from 1.64 to 2.5 (approximately). Similarly for aluminum, for four-coordination γ_{Al} is 1.65 but 2.5 for six-coordination.¹³ More recently, it has been noted that γ for magnesium, normally 1.10 when in fourfold coordination,⁵ increases in sodium magnesium silicate glasses as the MgO content decreases, and again this probably arises owing to Mg^{2+} increasing its coordination to sixfold (see next section). The situation for borate glasses is less straightforward, probably owing to the removal of π -bonding ability when boron switches from three- to four-coordination, and a treatment must await further developments.

TABLE 1: Values of γ , Density, and Refractive Index^a for Oxides with Sixfold Coordinated Cations

oxide	structure	n	d	α_m (Å)	$\alpha_{M^{Z+}}$ (Å)	$\alpha_{\text{oxide}(-II)}$ (Å)	$\gamma_{(4)}^b$	$\gamma_{(6)}^b$	$1/\gamma_{(6)}$
SiO ₂	stishovite	1.799	4.35	2.34	0.0165	1.16	2.10	3.15	0.317
α -Al ₂ O ₃	corundum	1.769	4.00	4.19	0.052	1.36	1.65	2.475	0.404
γ -Al ₂ O ₃	see note c	1.696	3.47	4.48	0.052	1.46	1.65	2.20 ^c	0.455 ^c
GeO ₂	rutile	1.99	6.24	3.30	0.60	1.35	1.64	2.46	0.407
MgO	rocksalt	1.737	3.56	1.80	0.094	1.71	1.1	1.65	0.606

^a Refractivity data from refs 23 (SiO₂) and 24 (Al₂O₃, MgO, and GeO₂). ^b Subscript denotes coordination number; $\gamma_{(6)} = 6\gamma_{(4)}/4$ (eq 6) except for γ -Al₂O₃ (note c). Values of $\gamma_{(4)}$ are from ref 5. ^c γ for γ -Al₂O₃ is calculated for 1/3 Al³⁺ in four-coordination and 2/3 in six-coordination (see text).

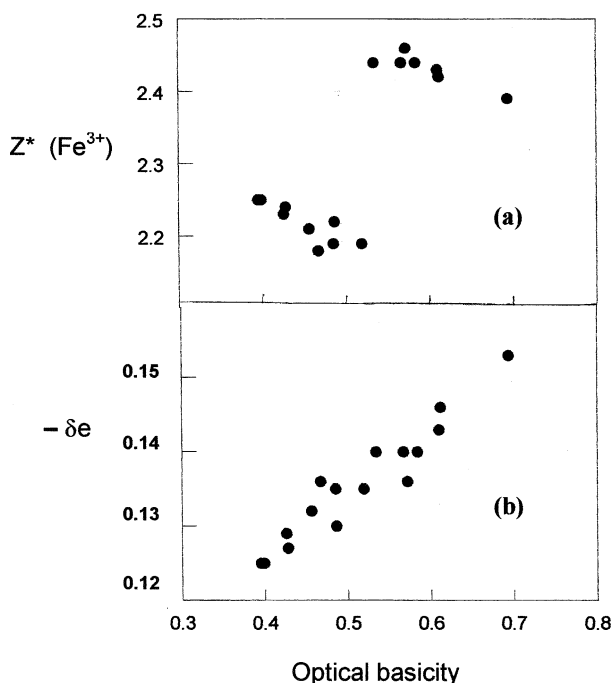


Figure 2. (a) Plotted points showing the trend in positive charge, Z^* , borne by Fe³⁺ with increasing glass basicity, Λ , for alkali phosphate (lower set) and alkali silicate systems (upper set); the sudden increase in Z^* is when the coordination number of Fe³⁺ changes from six to four. (b) Trend for the amount of electron charge, $-\delta e$, donated to the Fe³⁺ ion, on average, by each oxide(−II) in the glass; note that there is no discontinuity corresponding to the coordination number change for Fe³⁺.

If γ is viewed in terms of cation polarizing power, these results can be interpreted to suggest that the polarizing effect that the cation has on oxide(−II) is not significantly diminished by an increase in the number of oxide(−II) atoms/ions with which the cation interacts. The overall polarizing power of the cation appears to increase to take account of the extra number of oxide(−II) atoms that it polarizes. In terms of chemical bonding, cation polarization of oxide(−II) corresponds to a partial transfer of negative charge from oxide(−II) to the cation, thereby reducing the charge of the cation, M^{Z+} , from Z to Z^* . (This is the principle on which the spectroscopic determination of optical basicity was based, see earlier.) With this in mind, consideration is given to previously published results for the Fe³⁺ ion when hosted in glass.¹⁰ It has been shown that observed frequency shifts in its d–d absorption spectrum can be used to assess trends in Z^* as the glass composition is varied. It is also possible to assess the amount of negative charge, $-\delta e$, on average, donated by each oxide(−II). Results of such studies for two series of glasses, the Na₂O–SiO₂ system and the Na₂O–P₂O₅ system, are shown in Figure 2, where the trend in Z^* for Fe³⁺ and $-\delta e$ for each oxide(−II) are plotted against the optical basicity of each glass in the two series.

In the phosphate glasses, the coordination number of the Fe³⁺ ion is six, but in the silicate glasses it is four (this was clearly

shown by the characteristic d–d spectra).¹⁰ The positive charge on the Fe³⁺ ion, Z^* , is seen to decrease with increasing optical basicity (Figure 2), as expected, but when the coordination number changes from six to four, Z^* undergoes a sharp increase before again undergoing a gradual fall. At the optical basicity value where the change in coordination number occurs ($\Lambda = 0.52$, approximately), Z^* increases from +2.21 to +2.47, corresponding to the positive charge decrease, $(Z - Z^*)$, falling from 0.79 to 0.53. It should be noted that this fall corresponds to $(Z - Z^*)$ dropping to 2/3 of the value as the coordination number goes from six to four. Related to this effect is the trend for $-\delta e$ experienced by oxide(−II) in Figure 2, when it is apparent that the amount of negative charge transferred from each oxide(−II) to Fe³⁺ does *not* change during the coordination change for the Fe³⁺.

The significance of these results was only partly understood when they were reported. In light of the present work, they strongly indicate that the cation (Fe³⁺ in Figure 2) effects the same degree of polarization on the oxide(−II) species regardless of whether it interacts with four of them or six. This conclusion profoundly affects the interpretation of the γ parameter being a measure of a cation's "polarizing power", because it means that γ is dependent on the coordination number of the cation and increases with increasing coordination number. However, this is in accordance with the observations made for glass systems that contain Ge⁴⁺, etc., cations; see above. Indeed, the results of Figure 2 imply that when these cations undergo a change in coordination number from four to six, the operational γ value should increase by a factor of 6/4. Denoting the coordination number as a subscript this can be written as

$$\gamma_{(6)} = 6\gamma_{(4)}/4 \quad (6)$$

In the next section, evidence is provided supporting this relationship.

Metal Oxides

It is convenient to consider some crystalline metal oxides that are relevant to the present discussion. These oxides, with their refractive indices and densities (Table 1), are isotropic or nearly so, and therefore eq 2 can be used to calculate the molar polarizability, from which the value of $\alpha_{\text{oxide}(-II)}$ is obtained by subtracting the polarizability contribution of the cation and dividing by the number of oxide(−II)s in the molecular formula. These oxides have been chosen because their cations exist in the crystal with a coordination number of six, whereas when present in glass, they normally exert fourfold coordination. The γ values shown in Table 1 are derived from the "normal" $\gamma_{(4)}$ values,⁵ through multiplication by 6/4: eq 6. The γ form of Al₂O₃ is particularly interesting because one-third of the Al³⁺ is in fourfold coordination and two-thirds are in sixfold, and the operational γ parameter is accordingly taken as $1/3 \gamma_{(4)} + 2/3 \times 6/4 \gamma_{(4)} = 4/3 \gamma_{(4)}$. These "new" γ values can be used for obtaining the optical basicities, Λ , of the metal oxides simply by taking the reciprocal (see earlier). It is interesting to note

TABLE 2: Structural and Refractivity Data^a for Crystalline Silicates, etc.

compound	C.N. ^b	<i>n</i>	<i>d</i> (g/cm ³)	α_m (Å)	$\alpha_{M^{2+}}$ (Å)	$\alpha_{oxide(-II)}$ (Å)	Λ^c
CaSiO ₃		1.63	2.905	5.63	0.49	1.72	0.651
Ca ₂ SiO ₄		1.73	3.28	8.30	0.96	1.84	0.738
SrSiO ₃		1.62	3.65	6.24	0.88	1.79	0.676
BaSiO ₃		1.675	4.399	7.22	1.57	1.88	0.762
MgSiO ₃	6, —	1.654	3.20	4.55	0.11	1.48	0.519 (0.607)
Mg ₂ SiO ₄	6, —	1.69	3.20	6.66	0.20	1.61	0.541 (0.693)
MgCa ₃ Si ₂ O ₈	6, —	1.71	3.15	16.15	1.54	1.83	0.689 (0.727)
MgAl ₂ O ₄	4, 6	1.73	3.55	6.33	0.20	1.53	0.530 (0.682)
Ca ₃ Al ₂ (SiO ₄) ₃	—, 6	1.735	3.53	20.27	1.56	1.56	0.589 (0.640)
CaMgSi ₂ O ₆	6, —	1.67	3.275	9.78	0.56	1.53	0.590 (0.704)
Ca ₂ Al ₂ SiO ₇	—, 4	1.669	3.04	13.33	1.06	1.75	0.682 (0.595)
CaAl ₂ Si ₂ O ₈	—, 4	1.585	2.74	13.47	0.61	1.61	0.590 (0.515)

^a From ref 24. ^b C.N.: coordination number of Mg²⁺ and Al³⁺, respectively. ^c Λ is calculated using γ value appropriate to coordination number of Mg²⁺ or Al³⁺ (see Table 1); values in parentheses are obtained by using the “incorrect” γ value.

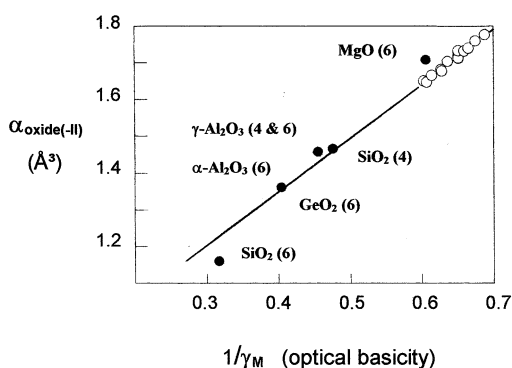


Figure 3. Plot of $\alpha_{oxide(-II)}$ versus $1/\gamma_M$ (i.e., optical basicity) for the oxides containing six-coordinated metal ion (Table 1; note that data for α -Al₂O₃ and GeO₂ overlap). The continuous line is that for the glass systems in Figure 1, slightly extrapolated, and includes data points for glasses (open circles).

that the optical basicity of the oxide is not necessarily the same value with which it operates when present in a glass, a result that might be relevant in the area of oxide catalysis.

At this stage, the plot is made for the oxides in Table 1 of $\alpha_{oxide(-II)}$ versus Λ . The points are judged in comparison with the (almost) linear relationship originally found for the silicate glass systems (Figure 1 and eq 3). As shown in Figure 3, all points lie reasonably close to this line. This is a crucial result and indicates the reliability of the $\gamma_{(6)}$ values assigned to the oxides and, therefore, the validity of eq 7. It is especially gratifying that the data point for γ -Al₂O₃ fits so well, considering that there is a mixture of sixfold and fourfold coordinating aluminum. The fit for stichovite, which contains six-coordinated silicon, should also be noted.

Applications

The type of chemistry discussed here is concerned with bonding interactions between atoms and ions and may seem academic. There are, however, important technical applications, especially for dealing with slag performance in steel-making^{14–16} and the quality control of melts in the glass industry.^{17–19} In both areas, the optical basicity model plays a significant role.

Recent work on the thermodynamics of glass melts has resulted in important developments linking the properties of molten and vitreous silicates with those of crystalline counterparts.^{20,21} Attempts for making an optical basicity link between silicate glass melts and silicate crystals have so far had very limited success. These limitations became apparent when refractivity methods were developed for obtaining optical

basicity values for slags containing large quantities of iron, manganese, and chromium.²² It was found that correlations between $\alpha_{oxide(-II)}$ and Λ for crystalline silicates (and aluminates) existed only to a limited extent, and there appeared to be no overall pattern. In light of the present work it is probable that a major difficulty arose through no account being taken of differences in coordination number. Now, with the availability of γ values for both sixfold and fourfold coordination, the problem can be reconsidered.

Before undertaking this task it is necessary to bear in mind the fundamental difference between crystalline silicates, etc., and those in vitreous form. In the crystalline state, lattice energy effects can give rise to distortions in such a way that the atoms and ions are displaced from their “natural” positions that they can assume in the molten state and that are usually more or less preserved during quenching to a glass. It therefore seems unlikely that a correlation between $\alpha_{oxide(-II)}$ and Λ for crystalline silicates will fit as closely to the trend in Figure 1 (eq 3) as the data for the corresponding glasses. Our task is to investigate whether a meaningful fit does occur.

Strictly, eq 2 applies only to isotropic materials, and in order to minimize error in obtaining $\alpha_{oxide(-II)}$, it is necessary to choose crystalline silicates and aluminates where distortions from cubic symmetry are small. Although there is a vast amount of structural data, the number of compounds for which refractivity data are also available is relatively small. The present study restricts itself to compounds given in ref 24. These include the silicates of calcium, strontium, and barium and also, appropriately, compounds where both magnesium and aluminum have coordination numbers of four and six. Optical basicities calculated from chemical composition, together with values of $\alpha_{oxide(-II)}$ obtained from the refractivity data, are in Table 2. For the magnesium and aluminum compounds, two sets of Λ values were obtained using both $\gamma_{(4)}$ and $\gamma_{(6)}$.

On plotting $\alpha_{oxide(-II)}$ against optical basicity, the silicates where magnesium and aluminum are absent show good fit to the line in Figure 1, eq 3. Furthermore, the points for the magnesium and aluminum compounds also lie reasonably close provided that the γ value appropriate to coordination number is adopted for calculating Λ . Although these points show more scatter than those for calcium, strontium, and barium silicates, nevertheless, all of them (with the very slight exception for MgCa₃Si₂O₈) are greatly improved compared with the results where optical basicities were calculated with the “incorrect” γ value (open circles in Figure 4). Thus, by paying attention to the coordination number of magnesium and aluminum, there is a fairly good correlation between $\alpha_{oxide(-II)}$ and Λ , which is similar to that applying to the glasses in Figure 1. This is a gratifying result, confirming the expectation (never before

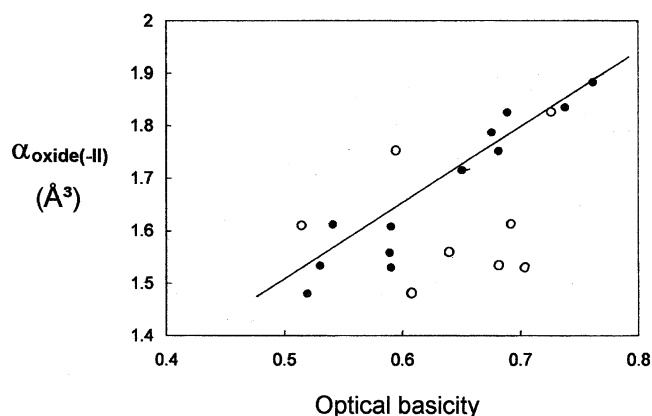


Figure 4. Plot of $\alpha_{\text{oxide}(-\text{II})}$ for silicates in Table 2 versus optical basicity, Λ , which is calculated using γ values of Mg^{2+} and Al^{3+} that are appropriate to coordination number. Open circles are where Λ is calculated using the “wrong” γ value. The line is that for vitreous systems (Figure 1 and eq 3).

demonstrated, however) that the optical basicity model ought to apply more or less equally to both vitreous systems and crystalline materials.

Investigations were extended to observe any effects arising from coordination number changes occurring for the highly ionic cations, Ca^{2+} , Sr^{2+} , or Ba^{2+} . However, it was found that when adjustments were made to the γ values, the optical basicities so obtained showed poor correlation with eq 3. For example, Ca^{2+} has a coordination number of eight in Ca_2SiO_4 , but if γ_{Ca} is taken as 8/6 of its usual value of 1.00 (i.e., 1.33), eq 4 yields $\Lambda = 0.614$, which is a poor fit to eq 3 compared with the value of 0.738, which is obtained taking $\gamma_{\text{Ca}} = 1.00$. Again, in $\text{MgCa}_3\text{Si}_2\text{O}_8$ the Ca^{2+} ion exercises coordination numbers of 10 (two-thirds) and 12 (one-third), and using the appropriately adjusted γ_{Ca} value of 1.78, $\Lambda = (1/1.65 + 3/1.78 + 4/2.10)/8 = 0.524$, which compares badly with $\Lambda = 0.689$ when taking γ_{Ca} as 1.00. It therefore appears that the polarizing effect of cations is modified by coordination number only when there is a significant covalent interaction with oxide(-II). These include the cations Si^{4+} , Ge^{4+} , Al^{3+} , and Mg^{2+} .

Conclusions

This study has shown that for oxidic materials the oxide(-II) species undergoes more or less the same degree of polarization regardless of whether the polarizing cation, e.g., Al^{3+} or Mg^{2+} , exerts a coordination number of four or six. Data for Fe^{3+} are in accordance with this mechanism since the extent of electron donation in the Fe–O bond is not apparently affected by the change in coordination number (see Figure 2). These conclusions

are unexpected, and they contrast with the more traditional ideas expressed in the Introduction. However, the emergence of “new” basicity-moderating parameters, appropriate to the coordination number that the cation exercises, opens up a wider range of oxidic materials, especially crystalline silicates, amenable to an optical basicity treatment. This result is expected to impinge on important areas of applied chemistry, namely, the refining power of metallurgical slags and the quality control of glass melts. It is possible that there would also be applications to geochemistry.

Acknowledgment. The author is grateful to Dr. E. Lachowski for advice on coordination numbers and also to Professor M. Ingram for useful discussions.

References and Notes

- (1) Pauling, L. *J. Chem. Soc.* **1948**, 1461.
- (2) Jørgensen, C. K. *Oxidation Numbers and Oxidation States*; Springer-Verlag: Berlin, 1969; Chapter 4.
- (3) Paul, A. *Trans. Indian Ceram. Soc.* **1969**, 28, 63.
- (4) Tessman, J. R.; Kahn, A. H.; Shockley, W. *Phys. Rev.* **1953**, 92, 890.
- (5) Duffy, J. A. *J. Non-Cryst. Solids* **2002**, 297, 275.
- (6) Kamitsos, E. I.; Yiannopoulos, Y. D.; Duffy, J. A. *J. Phys. Chem. B* **2002**, 106, 8988.
- (7) Duffy, J. A. In *Electrochemistry of Glasses and Glass Melts, Including Glass Electrodes*; Bach, H., Baucke, F. G. K., Krause, D., Eds.; Springer-Verlag: Berlin, 2000; pp 275–301.
- (8) Duffy, J. A. *Bonding, Energy Levels and Bands in Inorganic Solids*; Longmans: U.K., 1990; Chapters 6 and 8.
- (9) Duffy, J. A. *Geochim. Cosmochim. Acta* **1993**, 57, 3961.
- (10) Duffy, J. A.; Ingram, M. D.; Fong, S. *Phys. Chem. Chem. Phys.* **2000**, 2, 1829.
- (11) Duffy, J. A.; Ingram, M. D. *J. Am. Chem. Soc.* **1971**, 93, 6448.
- (12) Duffy, J. A.; Ingram, M. D. *J. Non-Cryst. Solids* **1976**, 21, 373.
- (13) Duffy, J. A. *Phys. Chem. Glasses* **2003**, 44, 388.
- (14) Yang, Y.; Sommerville, I. D. *Phys. Chem. Glasses* **2002**, 43C, 362.
- (15) Mitchell, F.; Sleeman, D. H.; Duffy, J. A.; Ingram, M. D.; Young, R. W. *Ironmaking Steelmaking* **1997**, 24, 306.
- (16) *3rd Int. Conf. Molten Slags and Fluxes*, Glasgow, 1988; The Institute of Metals: London, 1989; pp 29, 60, 86, 91–94, 107, 146–162, 166–168, 241–245, 277–282, 313–316.
- (17) Karlsson, K. H. *Chemistry of Glass Forming Silicate Melts*; Åbo Akademi University Press: Finland, 1995; pp 1–45.
- (18) Claussen, O.; Rüssel, C. *Phys. Chem. Glasses* **1998**, 39, 200.
- (19) Schreiber, H. D.; Peters, L. J.; Beckman, J. W.; Schreiber, C. W. *Glastechn. Ber.* **1996**, 69, 269.
- (20) Conradt, R. In *Analysis of the Composition and Structure of Glass and Glass Ceramic*; Bach, H., Krause, D., Eds.; Springer-Verlag: Berlin, 1999; pp 232–254 and 435–450.
- (21) Shakhmatkin, B. A.; Vedishcheva, N. M.; Wright, A. C. *XIX Int. Congr. Glass 2001*; Soc. Glass Tech.: Sheffield, U.K., 2001; p 52.
- (22) Duffy, J. A. *Ironmaking Steelmaking* **1989**, 16, 426.
- (23) *Encyclopaedia of Minerals*; Roberts, W. L., Rapp, G. R., Weber, J., Eds.; Van Nostrand: New York, 1974.
- (24) Winchell, A. N.; Winchell, H. *The Microscopical Character of Artificial Inorganic Solid Substances*; Academic Press: New York, 1964; p 59.