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Ionic−Covalent Character of Metal and Nonmetal Oxides

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The acid−base properties of oxidic media are quantified in terms of the optical basicity concept, which serves to correlate many properties with chemical constitution. Optical basicity values, Λ, have been assigned to 25 oxides such that they relate to Λ for crystalline CaO being taken as unity. Since Λ for an oxide is proportional to the degree of negative charge borne by the oxide−(-II) atom or ion, it follows that optical basicity should go hand-in-hand with the ionic/covalent nature of the cation-oxide−(-II) bonding. Unfortunately, this assumption produces many anomalies and trends that do not fit normal inorganic trends. The problem is resolved by adjusting the influence of ionic forms to the bonding by taking into account the heats of formation. In contrast to the (Pauling) electronegativity treatment of oxides, this procedure allows assignment of percentage ionicity to the bonding, and the trends in these in the Periodic Table are as expected for inorganic oxides.

Introduction

Acid−base theory pervades many aspects of chemistry. Technological inorganic applications are in the areas of glass manufacture, geochemistry, extraction metallurgy, catalysis, optical properties, redox equilibria, and many others. These applications are very often concerned with oxidic compounds (metal or nonmetal oxides and ones containing oxyanions), and their acid−base properties were originally handled in terms of oxide−(-II) ion activity.[1] This method proved unsatisfactory in many instances, primarily because of the difficulties in assigning single ion O^{2-} activities,[2] for example, in attempting to compare the basicities of sodium silicate melts and potassium silicate melts.

These problems are largely overcome by using the Lewis theory where a base is a donor of electrons and an acid is an acceptor.[3] Quantitative adoption of the Lewis theory became possible through the establishment of a scale that expressed the extent of electron donation by oxide−(-II) when an oxidic medium was probed by small concentrations of (acidic) metal ions such as Tl^+ or Pb^{2+}.[4] The ultraviolet $^1S_0 \rightarrow {}^3P_1$ absorption frequencies of these ions were red-shifted (as compared with gaseous, free ion values) increasingly with increasing basicity of the probed medium. The red-shifts paralleled the trends previously quantified by Jørgensen[5] in the nephelauxetic effect for transition metal complexes, although the s → p transitions in Tl^+ and Pb^{2+} probably decrease by a somewhat different mechanism than just orbital expansion. The $^1S_0 \rightarrow {}^3P_1$ frequency red-shifts observed for different media (silicates, borates, etc. of various metal ions) were compared with the red-shift observed for Tl^+ or Pb^{2+} in crystalline calcium oxide to produce what was called the optical basicity value, symbolized by Λ.[4] Calcium oxide was defined as having unit optical basicity, and on this basis, the red-shifts for the probe ions yielded values of Λ for a wide range of oxidic media. Subsequently, other methods of optical basicity determination have been developed, for example, using far-infrared spectroscopy,[6] oxygen 1s binding energies,[7] and measurements of electronic polarizability.[8]

The optical basicity method has found wide applications, especially in the technological areas quoted previously. It has been especially successful for correlating the properties of an oxidic medium with its chemical composition. In glass science, these properties have included refractive index,[9,10] ultraviolet transparency,[11−14] hosting properties toward dissolved metal ions,[15−17] redox behavior of glass melts,[18−21] and dependence of viscosity on temperature.[22] In extraction metallurgy, optical basicity is used for dealing with the refining power of slags, expressed as their capacities for removing sulfur, phosphorus, alkali metals, etc. from the molten metal and has also been used in the computer management of blast furnaces.[23−25] The optical basicity method has been applied to demonstrate how enthalpies of formation of silicates can be calculated from chemical composition[26] and also to show how basicity is affected by changes in the coordination number.[27]

One reason for the success of the optical basicity method in dealing with the previous areas is that it expresses the ionic state of the oxide−(-II) atom (or ion). In other words, Λ represents the extent of negative charge residing on the oxide−(-II), $-q_O$,[28] and also its electronic polarizability.[29] The importance of this feature of optical basicity is emphasized by workers concerned with the acid−base nature of surface sites of oxide catalysts,[30−32] and the problem of ionic−covalent bonding and its relationship to optical basicity has been considered.[33−35] In this connection, the following long-standing paradox of the optical basicity model must be resolved. The difficulty is that since Λ is proportional to q_O (the relationship is $q_O = -1.15\Lambda$),[28] there is an implication that metal oxides having similar optical basicities have similar degrees of covalency/ionicity in the bonding. For example, FeO, MnO, and CaO have very close basicities, as is evidenced from slag performance data in the iron and steel industry.[25] Their Λ values are, respectively, 0.93, 0.95, and 1.00 (see Table 1), and therefore, the oxide−(-II) ions of these oxides should bear similar negative charges. However, it does not necessarily follow that the ionic/covalent character of the metal−oxygen bonding is similar for the three oxides. After all, Fe^{2+} and Mn^{2+} are transition metal

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TABLE 1: Optical Basicities,[a] Heats of Formation, Q,[b] and Ionicity Data of Oxides

oxide	$\Lambda(M_aO_b)$	q_O	Q (kJ mol^{-1})	$x_O - x_M$	% ionicity
Cs_2O	1.55	−1.78	245.8	1.53	80
Rb_2O	1.45	−1.67	339.0	1.52	73
BaO	1.35	−1.55	548.0	1.85	74
K_2O	1.30	−1.50	361.5	1.56	66
In_2O_3	1.25	−1.44	922.8	1.47	40
La_2O_3	1.20	−1.38	1805	1.92	67
Na_2O	1.10	−1.27	414.2	1.65	54
SrO	1.05	−1.21	592.0	1.91	59
CaO	1.00	−1.15	634.9	1.96	58
Y_2O_3	1.00	−1.15	1757	1.90	56
MnO	0.95*	−1.09	387.7	1.60	44
FeO	0.93*	−1.07	273.5	1.41	37
ZnO	0.91	−1.05	348.2	1.54	39
Ag_2O	0.91*	−1.05	32.4	0.86	20
Sc_2O_3	0.91	−1.05	1716	1.88	50
Li_2O	0.81	−0.93	597.9	1.91	45
Ga_2O_3	0.71	−0.82	1073	1.56	30
Fe_2O_3	0.69*	−0.79	837.4	1.42	25
Cr_2O_3	0.69*	−0.79	1150	1.60	30
MgO	0.61	−0.70	601.6	1.92	34
SiO_2	0.48	−0.55	910.7	1.71	22
P_4O_{10}	0.48	−0.55	2979.0	1.45	17
GeO_2	0.41	−0.47	535.2	1.40	21
Al_2O_3	0.40	−0.46	1675.7	1.86	21
B_2O_3	0.40	−0.46	1274	1.66	18

[a] Except those asterisked, values of Λ apply to crystalline or vitreous solids and are derived from refractivity measurements.[29] Asterisked values were obtained by pragmatic means[25] (see text). From Cs_2O to Y_2O_3, figures are quoted to the nearest 0.05. [b] Values of Q are taken from ref 43.

ions, and their behavior is greatly influenced by the availability of d-orbitals, which is not the case for the Ca^{2+} ion.

What is the connection between the acid−base properties of oxides and the nature of chemical bonding? This question is considered here, and a model is proposed that provides numerical ranking of ionicity for oxides within the context of optical basicity usage.

Optical Basicity Background. It is important to note that, owing to experimental difficulties, direct probe ion optical basicity measurements of crystalline metal oxides have not been made (apart from CaO and one or two other oxides), and the assignment of Λ values to individual oxides was originally made using data of probe ions in media such as vitreous silicates and borates. This became possible through the establishment of the following empirical relationship.[36,37]

$$\Lambda = \frac{X(AO_{a/2})}{\gamma_A} + \frac{X(BO_{b/2})}{\gamma_B} + ... \qquad (1)$$

where $X(AO_{a/2})$, $X(BO_{b/2})$, ... are the molar proportions of oxide−(-II) atoms contributed by the oxides $AO_{a/2}$, $BO_{b/2}$, ... and γ_A, γ_B, ... are basicity moderating parameters that express the power of the cations A^{a+}, B^{b+}, ... to attenuate the (average) electron donor power of the oxide−(-II). For a single oxide, $MO_{m/2}$, eq 1 is simply $\Lambda(MO_{m/2}) = 1/\gamma_M$, and the relationship, eq 1, becomes

$$\Lambda = X(AO_{a/2})\Lambda(AO_{a/2}) + X(BO_{b/2})\Lambda(BO_{b/2}) + ... \qquad (2)$$

Examination of probe ion Λ values for a variety of calcium silicate glasses, together with substitution for Λ(CaO) (equals 1.00) in eq 2, allowed calculation of the optical basicity of SiO_2 [$\Lambda(SiO_2) = (\Lambda_{glass} - X(CaO))/X(SiO_2)$], which was found to be 0.48. The Λ values of other metal oxides were similarly determined through probe ion examination of their silicates (in vitreous form). With the development of newer methods of optical basicity determination, it became possible to make direct measurements on binary oxides, and these were found usually to agree with ones derived from probe ion measurements (i.e., see ref 29).

Λ values are known for several oxides (see Table 1), and their availability means that calculation of optical basicity is possible for the media they may constitute (e.g., a $Na_2O-CaO-SiO_2$ glass or a $CaO-Al_2O_3-SiO_2$ metallurgical slag). It was this facility that made the optical basicity model available for application to such a wide range of technological problems. Making measurements in molten inorganic oxide media at 1400−1600 °C is usually extremely difficult. However, for optimum technological performance, it is necessary to have available data for such media, for example, concerning redox equilibria of the Fe^{2+}/Fe^{3+} couple in molten glass or the phosphorus/phosphate couple in molten slags. The facility for calculating optical basicity provides the means for avoiding much of this experimental work since a set of results obtained for one system (e.g., Na_2O-SiO_2) can be correlated with optical basicity, and the relationship is then conveniently transferred to many other systems. The optical basicity method has even shown how redox data in aqueous solution at 25 °C can be used for making quantitative predictions of redox equilibria in oxidic melts at 1400 °C.[38]

Ionic−Covalent Character of Oxides. Before embarking on a strategy for assessing ionic character in binary oxides, it is necessary to consider the implications of arguments based on optical basicity and also electronegativity.

The optical basicity, Λ, of an oxide or oxidic system represents the tendency for the oxide−(-II) atoms (or ions) (i) to donate electronic charge to a hosted metal ion and thereby provide an environment of appropriate charge for stability (e.g., Fe^{3+} over Fe^{2+} or vice versa)[16,18] and (ii) to partake in reactions such as (in metallurgical slags)[25,39]

$$S(metal) + O^{2-}(slag) = S^{2-}(slag) + 1/2O_2(gas) \qquad (3)$$

These types of behavior are examples of how Λ is related to the degree of negative charge borne by oxide−(-II), $-q_O$.

The assessment of ionic/covalent character in the bonding of binary compounds can usually be made, at least in semi-quantitative terms, through application of electronegativity arguments. In general, the larger the electronegativity difference, the more ionic the bonding. For oxides of general formula, M_aO_b, the (Pauling) electronegativity difference, $x_O - x_M$, is obtained from the heat of formation, Q, as follows: [40]

$$x_O - x_M = \sqrt{\frac{Q + 1.13b}{2b}} \qquad (4)$$

Q is in electronvolts (1 eV ≡ 96.48 kJ/mol) and is corrected for the π-bonding in O_2 by adding 1.13 eV (or 101.3 kJ) per mol of oxide−(-II).

The resulting values of $x_O - x_M$ for the oxides in Table 1 show several anomalies, and these arise owing to the variability in the oxide−(-II) electronegativity: as the negative charge on oxide−(-II) increases, so there is a decrease in x_O.[41] It can be seen (Table 1) that the oxides SiO_2, Al_2O_3, MgO, and CaO follow the expected increasing trend in line with increasing ionicity. However, the reverse is the case for CaO, Na_2O, K_2O, and Rb_2O, where, instead of the expected increase in $x_O - x_M$, there is a decrease. There are further anomalies, for example,

TABLE 2: Percentage of Ionicity in Oxides[a]

IA	IIA	IIIA	IIIB	IVB	VB
Li_2O			B_2O_3		
45			18		
Na_2O	MgO		Al_2O_3	SiO_2	P_2O_5
54	34		21	22	17
K_2O	CaO	Sc_2O_3	Ga_2O_3	GeO_2	
66	58	50	30	21	
Rb_2O	SrO	Y_2O_3	In_2O_3		
73	59	56	40		
Cs_2O	BaO	La_2O_3			
80	74	67			

[a] d-Block metal oxides:Cr_2O_3 30; MnO 44; FeO 37; Fe_2O_3 25; ZnO 39; and Ag_2O 20.

$x_{O}–x_{M}$ for Na_2O is similar to that for B_2O_3. Clearly, the (Pauling) electronegativity model does not apply straightforwardly to oxides.

Results

Calculation of Ionicity. Often in chemistry, the assignment of numerical parameters for a particular property is made on an arbitrary basis: examples include ionic radii and polarizabilities. Nevertheless, such parameters are very useful, especially for the purposes of ranking, and this could be the case for arbitrarily assigned ionicities for metal oxides, where there are likely to be applications such as in ion migration studies or catalysis.

With this in mind, the following method has been devised, which incorporates the Pauling method that was originally used for obtaining electronegativity values of the elements by using heats of formation of binary compounds (other than oxides). However, the difficulties arising from the variability of oxide−(-II) electronegativity are circumvented by considering the problem from the viewpoint of optical basicity. The charge on oxide−(-II), $-q_O$, obtained from the relationship $q_O = -1.15\Lambda$ represents the portion of the dinegative charge that is used for electrovalency. It follows that the portion of negative charge available for covalency (e.g., for a 1:1 oxide) amounts to $2 - |q_O|$. For crystalline calcium oxide, $\Lambda = 1.00$ (by definition), and therefore, $q_O = -1.15$, $q_{Ca} = +1.15$, and 0.85 electron-worth of charge is used for covalency. The ionicity for CaO is then taken as $q_{Ca}/(q_{Ca} + 0.85)$ (i.e., 1.15/2 = 58%) and this, it should be noted from Table 1, is associated with a corrected heat of formation, Q', of 634.9 + 101.3 (= 736.2) kJ/mol.

For dealing with other oxides, CaO is chosen as the standard state since this oxide was adopted for the original optical basicity scale.[4] With an ionicity of 58% corresponding to $Q' = 736.2$ kJ/mol, the positive charge on the metal ion is adjusted assuming linearity between Q' and ionicity. For a metal oxide, MO, with corrected heat of formation, Q'_M, the adjustment for the charge on the metal ion, q_M, is obtained by multiplying by Q'_M/Q'_{Ca} (i.e., $Q'_M/736.2$). The electron worth of charge for covalency is still assumed to be $2 - |q_O|$, and the ionicity is taken as $(Q'_M/736.2)/[(Q'_M/736.2) + 2 - |q_O|]$. The following calculations illustrate the method.

Zinc Oxide. The optical basicity of ZnO is 0.91, and q_O is $-1.15 \times 0.91 = -1.05$, so that formally $q_{Zn} = +1.05$ and there is a quantity $(2 - 1.05) = 0.95$ electron worth of charge supplied by oxide(-II) for covalency. From Table 1, it is seen that the corrected $Q' = 348.2 + 101.3$ (i.e., 449.5 kJ/mol oxide(-II)). The ionic contribution in ZnO is therefore much less than in CaO, and to take account of this, q_{Zn} (= +1.05) is reduced by a factor of (449.5/736.2); the adjusted q_{Zn} is +0.61. Thus, the ionicity in the ZnO bond is given by 0.61/(0.61 + 0.95) (i.e., 39%).

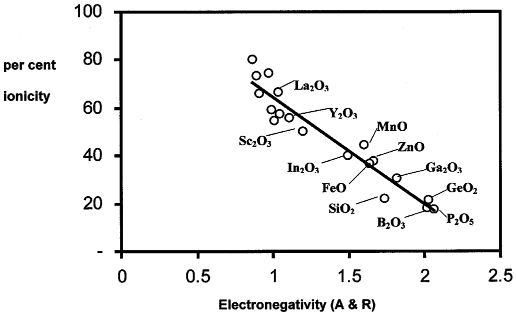

Figure 1. Plot of percentage ionicity of binary oxides versus (Allred-Rochow) electronegativity of the nonoxygen element. The unlabeled cluster of points close to the top-left of the straight line are for alkali and alkaline earth metal oxides.

Sodium Oxide. With $\Lambda(Na_2O) = 1.10$, $q_O = -1.26$. There are two sodium ions for each oxide−(-II), which means that the formal charge q_{Na} is 1/2 × 1.26 (i.e., +0.63). The corrected heat of formation, Q', is 414.2 + 101.3 (Table 1) (i.e., 515.6 kJ/mol oxide−(-II)) and again, with respect to calcium oxide, the adjusted q_{Na} is $(515.6/736.2) \times 0.63 = 0.44$. The electronic charge used for covalency is $2 - 2 \times 0.63 = 0.74$, amounting to 0.37 per Na−O bond, and the ionicity is 0.44/(0.44 + 0.37) (i.e., 54%).

Silicon Dioxide. The corrected heat of formation (Table 1), Q', is $910.7 + 2 \times 101.3 = 1113.3$ kJ/mol SiO_2 (i.e., 556.7 kJ/mol oxide−(-II)). With $\Lambda(SiO_2) = 0.48$, the value of q_O is $-(0.48 \times 1.15) = -0.55$, and although the charge on the silicon is $+(2 \times 0.55)$, as far as the Si−O bond is concerned, the effective q_{Si} is half of this, that is, the +0.55 and adjusted q_{Si} is $(556.7/736.2) \times 0.55 = 0.42$. Since the electronic charge used for covalency (in one Si−O bond) is 2 − 0.55 (i.e., 1.45), the ionicity is 0.42/(0.42 + 1.45) = 22%.

The results for the remaining oxides are in the right-hand column of Table 1.

Discussion

As indicated previously, the percentage ionicities for the oxides in Table 1 were derived by applying a combination of optical basicity and electronegativity arguments. When the values are inserted into the Periodic Table, as shown in Table 2, it is apparent that the pattern follows closely the chemical trends of the elements. For example, it is seen that on descending each group, there is the expected increase in ionicity, while on moving from left to right along a Period, the ionicity decreases. For the acidic oxides B_2O_3, SiO_2, and P_2O_5, which are regarded as covalent, the ionicities are very low. Also, the ionicities for the d-block metal oxides fit well with the chemical characteristics of the metal ions. When the ionicities of the oxides in Table 1 are plotted against the electronegativity of the nonoxygen element, there is a reasonable straight line relationship (Figure 1), apart from data for Li_2O, MgO, Al_2O_3, and Ag_2O, and they are omitted in Figure 1. It is interesting that for 100% ionicity, the straight line extrapolates to an electronegativity close to zero. The plot in Figure 1 is for Allred−Rochow[42] electronegativity, but the pattern obtained using Pauling electronegativities (not shown) is very similar.

The ionicities assigned to the oxides (Table 2) remove the anomalies referred to in the Introduction. Thus, the overall decrease in (Pauling) electronegativity difference, $x_{O}–x_{M}$, observed from Li_2O to Cs_2O (see Table 1), which might have suggested decreasing ionicity, is resolved. Similarly, the approximate equality of $x_{O}–x_{Na}$ and $x_{O}–x_{B}$ (Table 1) can no longer be imagined to indicate approximately equal ionicity. Further-more, the oxides CaO, MnO, and FeO, which have fairly similar optical basicities (see Introduction), are seen to have (Table 1) distinct ionicities in their bonding (58, 44, and 37%, respectively). The oxides Ag_2O, ZnO, and Sc_2O_3, all with the same optical basicity of 0.91, show a distinct difference in ionicity, that for Ag_2O being very low (20%); again, this is in keeping with the general chemistry of the three metal ions. Another example is seen for In_2O_3, the Λ value of which (1.25) is greater than that for Na_2O (1.10), yet from the position of indium in the Periodic Table, similar ionicities are not expected. The results bear this out: 40% for In_2O_3 as compared with 55% for Na_2O.

It was mentioned in the Introduction that the optical basicity values listed in Table 1 are derived chiefly from refractivity measurements. For most of the oxides, these values differ only slightly from optical basicities originally obtained in vitreous media using spectroscopic Tl^+ and Pb^{2+} probe ions. The exceptions are Li_2O, MgO, and Al_2O_3, which have probe ion Λ values of 1.00, 0.78, and 0.61, respectively.[29] The discrepancies probably arise owing to different coordination numbers in the crystalline oxides as compared with the vitreous environment. Indeed, this has previously been discussed at length for Al_2O_3, and whereas with 6-fold coordination, as in corundum, Λ is 0.40, when coordination is 4-fold, as in aluminosilicate glasses, Λ is 0.61; incidentally, in γ-Al_2O_3, where one-third of the Al^{3+} ions are in 4-fold coordination and two-thirds are in 6-fold, Λ is 0.46, which is close to the mean value.[27] If the probe ion Λ values of Li_2O, MgO, and Al_2O_3 replace the refractivity ones for calculating ionicity, the results are 56, 44, and 33%, respectively. These ionicities lie much closer to the straight line in Figure 1, although it is difficult to understand why they should. No explanation can be offered for Ag_2O lying so far away from the straight line in Figure 1.

Conclusion

In the assessment of ionic/covalent character in the bonding of binary oxides, the optical basicity method is used to calculate the charge on the oxide−(-II) and, hence, by difference, the electron worth of charge used for covalency. The traditional and simplest way of regarding ionicity in the bonding of binary compounds generally is to take the positive charge of the cation and divide it by the sum of this positive charge and the electron worth of charge used for covalency. This method was used for assigning an ionicity of 58% to calcium oxide. However, in considering the oxides of other elements, the method neglects taking into account the effectiveness of the valency electrons in performing their job of binding the atoms or ions, either through the ionic component or through the covalent component.

This defect is corrected here, at least as far as the ionic component is concerned, by following the Pauling method that links the heat of formation, associated with a bond, with the resonance of canonical structures; the greater the heat of formation, the more important the ionic canonical forms are. It is this principle that is used to relate the ionicity of binary oxides to the standard state, chosen as calcium oxide. The percentage ionicities, obtained by this method, are presented in Table 2. They show a ranking for these oxides that conforms with the position of the nonoxygen element in the Periodic Table. The anomalies that arise from electronegativity differences, $x_{O}-x_{M}$ (see Table 1), that were mentioned in the Introduction are also resolved.

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