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Chemical Bonding in the Oxides of the Elements: A New Appraisal

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The role of electronegativity in the bonding of binary compounds is discussed and it is concluded that the usual electronegativity criteria for ionic, covalent, and metallic bonding do not apply to the oxides of the elements. One of the reasons for this is the wide variation observed in the electronegativity value of oxygen; for example, it is 3.5 in SiO_2 but 2.5 in Na_2O. It is argued that the electronegativity of oxygen is a better indication of ionicity (falling with decreasing covalency) than the electronegativity difference. Metallic bonding in oxides is treated from the point of view of polarization, and it is shown how experimental parameters of polarization and of band theory are closely related. These parameters are used for charting the proximity of oxides to the onset of metallization, while, simultaneously, the oxygen electronegativity is used for charting ionic/covalent bonding.

Introduction

Oxidic materials are generally compounds or systems where the sole atomic anion is the oxide(-II) species. They exist in stoichiometric form, e.g., as oxides such as MgO and as oxyanion salts, or in nonstoichiometric form, e.g., as glasses or as defect crystalline systems such as Fe_xO ($x <$ unity). Oxidic materials are interesting from both the theoretical and technological point of view, especially since they can have important electrical, electronic, magnetic, and optical properties either in the solid phase or the liquid.

The more "traditional" types of property, for example the durability of a glass or the scavanging power of a blast furnace slag, are also important and still receive much attention. These traditional properties have been rationalized, over the years, in terms of chemical bonding which has been developed, roughly speaking, along two distinct lines:

(i) Polarization of ions approach. In this approach, all elements in the system are regarded as in the form of ions; for example, in a calcium silicate glass, melt, or crystal, the species present are Ca^{2+} and Si^{4+} cations and O^{2-} anions. The cations exert a polarizing effect on the O^{2-} ions which leads to what Weyl and Marboe (*1*) aptly describe as a "tightening" of the negative charge clouds of the O^{2-}. Cations have different powers of polarization, the effect usually being more powerful the higher the cation charge. One of the most obvious properties of a material which is accountable for in terms of the polarization approach is refractive index: the greater the polarization of the O^{2-}, the lower is the oxide molar refractivity. Indeed, one of the experimental methods of determining polarizability is through measurement of refractive index.

(ii) Covalent-ionic bonding approach. The starting point in this approach is either (a) a model consisting of cations and anions

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(the same as for the polarization approach) followed by the introduction of covalent character into the ionic bonding, or (b) a model consisting of atoms covalently bound and followed by the introduction of ionicity. Either model is used, and often both are used simultaneously, especially in glass chemistry where the terms "network breaker" and "network former" refer, respectively, to elements which interact ionically or covalently with oxygen. For example, in a calcium silicate glass, melt, or crystal, the bonding between the silicon and oxygen is regarded as covalent (but with substantial ionic character) and resulting in silicate anions, the charges of which are balanced by the Ca^{2+} ions which interact with the silicate anions through electrovalency (with some covalent character). When describing these bonding situations, the words "atom" and "ion" have the same meaning: in the above example, the silicon can be described as present in the form of silicon(IV) atoms or silicon(IV) ions.

Acidic and Basic Oxides

It has been customary in the more applied areas of oxide chemistry to express the pattern of chemical bonding, or of ion polarization, in terms of the acidic or basic nature of the constituent oxides. If we choose to list a set of oxides in order of decreasing covalency in the bonding, or decreasing polarization of the O^{2-} ion, (for example, as in Table I) then the progression is regarded as increasing in basicity and decreasing in acidity. The electron donor power of the O^{2-} species increases in such a series, and this property can be measured from shifts in the ultraviolet spectra of acceptor probes such as Pb^{2+}. The spectral shifts make it possible for the basicity (or acidity) to be numerically expressed in terms of a quantity called the "optical basicity," Λ (*2, 3*). Values of Λ for some oxides are in Table I, and it can be seen that oxides having Λ less than approximately 0.5 are those usually described as "acidic" and those above approximately 0.7 are "basic"; Al_2O_3 has a value of 0.6 and can be described as "amphoteric."

TABLE I
OPTICAL BASICITIES OF SOME OXIDES M_mO_n

Oxide	x_M	$\Lambda(M_mO_n)$
SO_3	2.5	0.33
P_2O_5	2.1	0.40
B_2O_3	2.0	0.42
SiO_2	1.8	0.48
Al_2O_3	1.5	0.60
MgO	1.2	0.78
CaO	1.0	1.00
BaO	0.9	1.15
Na_2O	0.9	1.15
K_2O	0.8	1.4
Cs_2O	0.7	1.7

Note. Optical basicities, $\Lambda(M_mO_n)$, are from Ref. (*7*).

When acidic and basic oxides react, for example to form a glass, the optical basicity of the glass is simply given by

$$\Lambda(\text{glass}) = X_1\Lambda_1 + X_2\Lambda_2 + \ldots \quad (1)$$

where $X_1, X_2 \ldots$, are the equivalent fractions of the component oxides each with an optical basicity of $\Lambda_1, \Lambda_2 \ldots$. The properties of molten and vitreous oxide systems have been correlated quite successfully with their optical basicities by several workers (e.g., Refs. (*4–10*).

Electronegativity

Although chemical bonding is a subject which is often dealt with in terms of quantum theory, there is much to be gained by using an approach based on semiempirical parameters which relate to individual atoms or ions. The best known of these approaches, among chemists and physicists, is that based upon electronegativity, and this has become increasingly popular in the field of solid state chemistry (*11*, *12*). Both the polarization approach and the covalent–ionic approach to oxidic materials can be rationalized (and therefore, to some extent, united) by electronegativity. The concept of electronegativity has undergone many refinements and there are now several definitions and scales in use. However, in the present treatment, it is important to note that we use electronegativity in the same sense as originally introduced by Pauling, and also that electronegativity values used here are derived from heats of formation by the Pauling method (*13*).

Electronegativity originated with the idea of the introduction of ionicity into the bonding of essentially covalent molecules (*13*), the degree of ionicity increasing with increasing electronegativity difference between the bonded atoms in the molecule. However, electronegativity has also been useful at the other end of the ionic-covalent scale, that is, the introduction of covalency into essentially ionic solids, where a decreasing electronegativity difference between atoms is taken to indicate increasing covalency. Thus, in calcium silicate the electronegativity differences of 2.5 for Ca–O and 1.7 for Si–O (obtained using $x_O = 3.5$) are taken to indicate ionic bonding between oxygen and calcium, but a more covalent type of bonding between oxygen and silicon. This can be seen to fit the usually accepted description of Ca^{2+} ions and silicate anions.

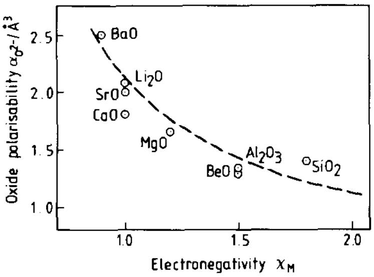

FIG. 1. Plot of oxide(-II) polarizability versus Pauling electronegativity of M for some oxides, M_mO_n, (data from Ref. (*15*). The curve is of Eq. (2).

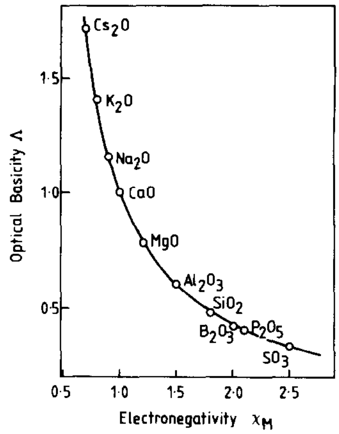

FIG. 2. Plot of optical basicity, Λ, of oxides (general formula, M_mO_n) versus Pauling electronegativity of M, x_M. The curve is of Eq. (3).

The relationship between electronegativity and polarization is more tenuous (see Ref. (*14*), for example). As far as oxides of the s block and the lighter p block elements are concerned, the polarizability, $\alpha_{O^{2-}}$, of the oxide(-II) species increases with decreasing electronegativity, x_M, of the cation, as shown in Fig. 1, where the curve fits Eq. (2):

$$\alpha_{O^{2-}} = \frac{1.3}{x_M - 0.25} + 0.4. \qquad (2)$$

This equation is derived from relationships (*15*) arising from studies previously made on the orbital expansion effects experienced by probe ions in oxidic systems (*2*).

Since electronegativity is such an important factor affecting the covalent/ionic character of bonding, it might be expected that a simple relationship exists between the electronegativity, x_M, and the optical basicity of the oxide, $\Lambda(M_mO_n)$. Oxides whose optical basicities are known are restricted to those in Table I and a simple relationship with electronegativity, Eq. (3), has been found (see Fig. 2):

$$\Lambda(M_m\mathrm{O}_n) = \frac{0.75}{x_M - 0.25}. \quad (3)$$

It would be very valuable to know the relationship between Λ and x for oxides of other elements, especially transition metal oxides.

Thus, electronegativity is an important factor when considering oxidic systems, and it is useful, at this point, to summarize the situation for binary compounds generally. Denoting the electronegativities of cation and anion by x_{M} and x_A, respectively, the following principles hold:

1. High ionicity if $(x_A - x_M)$ is large, and ionicity decreases in a series of binary compounds ranked in order of decreasing $(x_A - x_M)$.
2. Predominantly covalent bonding when $(x_A - x_M)$ is small (usually below approximately 1.7) but with x_A greater than 2.0.
3. Predominantly metallic bonding when $(x_A - x_M)$ is small (usually below approximately 1.0) but with x_A and x_M less than 2.0.

Principles 2 and 3, above, are illustrated for the extreme condition of $(x_A - x_M) = 0$ by the covalent CI_4 ($x_{\mathrm{C}} = 2.5$, $x_{\mathrm{I}} = 2.5$) and a metal alloy such as pewter ($x_{\mathrm{Pb}} = 1.8$, $x_{\mathrm{Sn}} = 1.8$).

For oxides the trend from ionic to covalent bonding, accompanying decreasing $(x_{\mathrm{O}} - x_M)$, is illustrated by the series:

	CaO	MgO	Al_2O_3	SiO_2	P_2O_5
$(x_{\mathrm{O}} - x_M) =$	1.97	1.92	1.86	1.67	1.47

(The values of $(x_{\mathrm{O}} - x_M)$ are calculated by the Pauling method (*13*) from heats of formation in Ref. (*16*).) However, although many oxides seem to fit into this pattern of ionic–covalent bonding, there are some metal oxides which behave as metals, and their properties dictate that the bonding is metallic. It would be anticipated (point 3, above) that for these oxides the electronegativity difference $(x_{\mathrm{O}} - x_M)$, would be quite small, but this is found to be not necessarily so. For example, TiO is a well-known metal, yet the value of $(x_{\mathrm{O}} - x_{\mathrm{Ti}})$, which is 1.81, places it close to Al_2O_3 in the above ionic–covalent series.

It is known that the electronegativity of oxygen varies over an enormous range in oxides (*17*), and it is possible that metallic bonding can be related more to trends in x_{O} rather than in $(x_{\mathrm{O}} - x_M)$. In Table II, values of x_{O} have been obtained by adding x_M to the difference $(x_{\mathrm{O}} - x_M)$ for each oxide. It is important to note that for this purpose x_M was calculated from data for the chlorides, bromides and iodides (but not the fluorides (*15*)), and this sometimes had the effect of slightly raising x_M from its "normal" value (as in Fig. 2), which is obtained by, as is usual, ignoring any variation in x_{O}. The values of x_{O} are plotted against the electronegativity of the cation in Fig. 3, and it can be seen that the usually assigned value of around 3.5 for x_{O} operates mainly in nonmetal oxides, but in metal oxides x_{O} is somewhat below this figure. The curve in Fig. 3 is for the relationship Eq. (4),

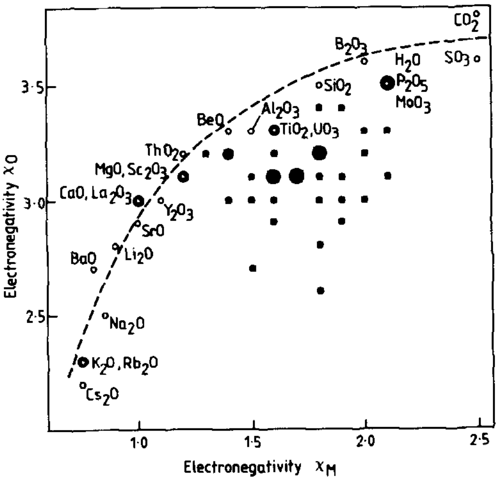

FIG. 3. Plot of oxygen electronegativity, x_{O}, versus electronegativity of element, M, for oxides, $M_m\mathrm{O}_n$, using data in Table II. Labeled points (open circles) are when $M^{(2n/m)+}$ cations have the s^2p^6 outer configuration; unlabeled points (filled circles) are for other configurations. (Larger circles are for two or more oxides.) The curve is of Eq. (4).

$$x_O = 4.1 - \frac{0.86}{x_M - 0.25} \qquad (4)$$

and the oxides of Groups IA, IIA, and IIIA (B to La) and the first and second row p block elements lie close to this line. Eq. (4) seems to apply when the cation has the noble gas electronic configuration but usually not otherwise. The highly electropositive metals have remarkably small values of x_O (for example, 2.5 for Na_2O and 2.2 for Cs_2O), and in view of the principles of electronegativity discussed earlier, this fall in x_O predicts metallic properties for oxides of elements of very high electropositiveness (not achieved in the natural elements). In other words, as the O^{2-} ion becomes more negatively charged, there is a growing tendency for its electrons to become itinerant. it is noteworthy that the value of x_O for the metallic TiO is much greater than the alkali metal oxides and is very close to the values for the insulating oxides Al_2O_3 and Sc_2O_3. Thus, for TiO neither the electronegativity x_O nor the electronegativity difference (x_O − x_M) appear to signal metallic bonding.

TABLE II

DATA RELATING TO ELECTRONEGATIVITY, OPTICAL ABSORPTION EDGE, AND REFRACTIVITY FOR OXIDES M_mO_n

Oxide	Δx	x_M	x_O	E	$\sqrt{E}$	$(1 - R_m/V_m)$
SO_3	1.12	2.5	3.6			
CO_2	1.25	2.5	3.8			
SeO_2	1.08					<0.39
H_2O	1.43	2.1	3.5			0.79
P_2O_5	1.45	2.1	3.5			0.71
TeO_2	1.19	2.1	3.3			0.45
B_2O_3	1.66	2.0	3.6			0.65
As_2O_3	1.23	2.0	3.2			0.55
SiO_2	1.67	1.8	3.5	10	3.2	0.68
GeO_2	1.40	1.8	3.2	5.4	2.3	0.5
Sb_2O_3	1.35	1.9	3.4	3.25	1.8	0.41
Sb_2O_5	1.24	2.0	3.3			
HgO	1.02	1.9	2.9	2.2	1.5	0.36
Hg_2O	1.02	1.8	2.8			
Bi_2O_3	1.25	1.8	3.1	2.6	1.6	0.36
PbO	1.30	1.6	2.9	2.0	1.4	0.32
PbO_2				4.45	2.1	0.41
SnO	1.43	1.6	3.1			
SnO_2	1.44	1.8	3.2	3.8	1.9	0.49
Tl_2O	1.19	1.5	2.7			
Tl_2O_3	1.14	1.9	3.0			
In_2O_3	1.48	1.6	3.1	2.8	1.7	
Ga_2O_3	1.56	1.8	3.4	4.4	2.1	0.52
CdO	1.37	1.6	3.0	2.3	1.5	0.37
ZnO	1.54	1.5	3.0	3.4	1.8	0.49
Al_2O_3	1.86	1.5	3.3	8.3	2.9	0.59
BeO	1.93	1.4	3.3			0.60
Sc_2O_3	1.88	1.2	3.1	5.4	2.3	0.50
Y_2O_3	1.90	1.1	3.0			0.52
La_2O_3	1.97	1.0	3.0			0.53
CeO_2	1.76			3.2	1.8	0.41
MgO	1.92	1.2	3.1	7.3	2.7	0.60
CaO	1.97	1.0	3.0	6.8	2.5	0.56
SrO	1.91	1.0	2.9	5.3	2.3	0.57
BaO	1.86	0.8	2.7	4.8	2.2	0.51
Li_2O	1.91	0.9	2.8			0.64
Na_2O	1.65	0.85	2.5			
K_2O	1.56	0.75	2.3			
Rb_2O	1.51	0.75	2.3			
Cs_2O	1.49	0.75	2.2	2–3	1.4–1.7	
TiO	1.81	1.4	3.2	0.0	0.0	
TiO_2	1.71	1.6	3.3	3.0	1.7	0.32
V_2O_3	1.63	1.6	3.2	0.1	0.3	
Cr_2O_3	1.59	1.4	3.0	3.4	1.8	0.36
MnO	1.60	1.5	3.1	3.8	1.9	0.45
FeO	1.40	1.7	3.1			0.41
Fe_2O_3	1.41	1.8	3.2	2.0	1.4	0.28
CoO	1.34	1.7	3.1	2.7	1.6	0.40
NiO	1.35	1.7	3.1	3.8	1.9	0.44
CuO	1.17	1.9	3.1	1.95	1.4	0.34
Cu_2O	1.20	1.8	3.0	2.2	1.5	0.32
ZrO_2	1.84	1.4	3.2			0.45
MoO_2	1.41	2.1	3.5			
MoO_3	1.37	2.1	3.5	3.8	1.9	0.37
WO_3	1.42			2.8	1.7	0.37
Rh_2O_3	1.03	2.1	3.1			
PdO	1.00	2.0	3.0			
Ag_2O	0.85	1.8	2.6	1.2–1.6	1.1–1.3	
ThO_2	1.93	1.2	3.2			0.44
UO_2	1.87	1.3	3.2			
UO_3	1.66	1.6	3.3			0.61

Note. Δx values are calculated from heats of formation (*16*) by the Pauling method (*13*). x_M is Pauling-type electronegativity, based upon data for chlorides, bromides, and iodides (see text), expressed to one decimal place except for the alkali metals for which it is to the nearest 0.05. As far as possible, E (in eV) is taken as the optical absorption edge, but if spectra are unavailable, then in appropriate cases it is taken as the band gap. The data are derived from references quoted in Ref. (*28*) and Landoldt-Bornstein, series III/17 (Springer, Berlin). Other sources are: M. R. TUBBS, *Phys. Sol. Stat. A*, **21**, 253 (1974) for MoO_3 and C. WOOD, B. VAN PELT, AND A. DWIGHT, *Phys. Sol. Stat. B*, **54**, 701 (1972) for Sb_2O_3. R_m/V_m is obtained from $(n^2 - 1)/(n^2 + 2)$ where the refractive index, n, (uncorrected for wavelength) is taken from Ref. (*16*), Landoldt-Bornstein (loc. cit.) and Gmelin Handbook (Springer, Berlin).

Proximity of the Nonmetal/Metal Transition

Although it is usually straightforward to distinguish a metallic material from a nonmetallic, it is very difficult to quantify the metallic contribution to bonding in compounds which are nonmetals. The reason for this difficulty is that the change from nonmetallic to metallic is not gradual but very sudden: the valence electrons are either localized or itinerant (*18*). It therefore seems unprofitable to refer to "a partial metallic component" in the bonding of compounds. Instead, we shall regard compounds in terms of their proximity to the nonmetal/metal transition.

Discussion concerning the relationship between polarizability and the onset of metallization (*19–21*) have indicated that if the molar volume, V_m, is below a certain critical value, then a polarization, or dielectric, catastrophe occurs, at which point the valence electrons become itinerant and there is metallic conduction. Consideration of the Clausius–Mossotti relationship:

$$\alpha_m = \frac{3V_m}{4\pi N}\frac{\varepsilon - 1}{\varepsilon + 2} \qquad (5)$$

(where ε is the dielectric constant arising from the polarizability, N is Avogadro's number, and the Lorentz factor is taken as $4\pi/3$) indicates that when $4\pi N\alpha_m/3V_m$, or, more simply, R_m/V_m (where R_m is the molar refractivity) approaches unity, ε becomes infinite. In other words, a material is nonmetallic for R_m/V_m less than unity, but is metallic when $R_m/V_m = 1$. This has been shown to be the case for the naturally occurring forms of the elements (*22*) and also for simple compounds subjected to pressure. For example, the thallium halides (*23*) become metallic when compressed to the critical value of V_m (*24*).

In terms of the tight binding approach to band theory, the onset of metallization is when the valence band and conduction band merge into each other. Since, for a binary compound, the valence band is composed essentially of anion orbitals and the conduction band of cation orbitals, the merging of the two bands into each other can be thought of as the stage at which the minimum energy, E, of transferring an electron from the anion to the cation becomes zero. In terms of the polarizability approach (see above) this is when the electrons become itinerant and $R_m/V_m = 1$. Thus, for a series of binary compounds, the nonmetal/metal transition is approached more closely as (i) the energy, E, and (ii) the quantity $(1 - R_m/V_m)$ both approach zero. It is remarkable that a good correlation exists between these two distinct quantities, as shown in Fig. 4 where the straight line (for E in eV) is given by

$$E = 20\left(1 - \frac{R_m}{V_m}\right)^2. \qquad (6)$$

Since the origin in Fig. 4 is for $E = 0$ and $R_m/V_m = 1$, progressing along the line (Eq. (6)) away from the origin corresponds to an increasing departure from the nonmetal/

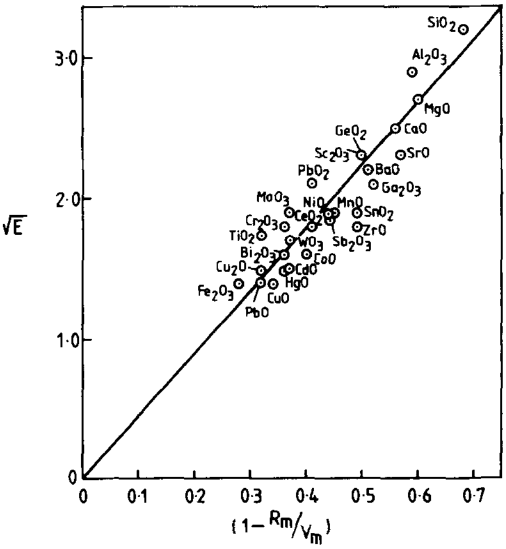

FIG. 4. Plot of $\sqrt{E}$ versus $(1 - R_m/V_m)$ for oxides. The straight line is derived from Eq. (6).

metal transition. In this paper, we therefore use E (or rather $\sqrt{E}$) and $(1 - R_m/V_m)$ as a measure of how near an oxide is to the onset of metallization. Thus, in the following series of oxides, for example, there is what might be described as a growing "tendency towards metallization."

	SiO_2	Al_2O_3	NiO	Cs_2O	Cu_2O	V_2O_3	TiO
E (eV)	10	8.3	3.7	2–3	2.2	0.1	0.0
$(1 - R_m/V_m)$	0.68	0.59	0.44	—	0.32	—	—
	nonmetal						metal

To some extent, the quantities E and $(1 - R_m/V_m)$ are complementary to each other. Values of R_m/V_m are more readily accessible away from the nonmetal/metal transition, whereas E is associated with energy bands of semiconductors but becomes increasingly "unreal" when dealing with insulators which many people regard in terms of molecular orbitals rather than energy bands.

Electron Release and Gain

An electronegativity scale which is significantly different from all others is the "optical" electronegativity scale of Jørgensen (*25*). This is concerned not so much with ionic/covalent character but with the energy involved in transferring an electron from one atom (or ion) to another in a molecule or complex ion. For example, in $[PbCl_6]^{2-}$, the lowest energy electron transfer (from chloride to lead(IV)) absorption band is at 4.05 eV and this energy is regarded as a measure of the optical electronegativity difference between Cl^- and Pb^{4+}. Jørgensen chose the optical electronegativity value of the halide ions to be the same as the Pauling electronegativity for the halogen atoms since it was apparent that the spectroscopic shifts in going from one halogeno complex to another were in proportion to the differences in Pauling electronegativity. The wealth of spectroscopic data for complexes allowed optical electronegativities for other anions and many cations to be assigned, and it became apparent that, apart from the anchor point of the halogens, there was a marked difference between Jørgensen's optical electronegativity values and those of other electronegativity scales.

Compared with complex ions, binary compounds present a much more complicated situation, for instead of discrete energy levels (molecular orbitals) we often must deal with energy bands. For a binary compound which is a nonmetal, the valence electrons completely fill the valence band, and in straightforward cases, the next higher energy band (the conduction band) is empty. Light which has an energy less than the difference between the top of the valence band and the bottom of the conduction band (designated E, see previously) will not be absorbed by the compound, but when the light has a frequency exceeding this energy, there is usually great absorption resulting in a transparency "cut-off." Thus, the energy E can be taken roughly as that corresponding to the frequency of the absorption edge. Since the valence band and conduction band are constructed essentially from orbitals of the anion and of the cation, respectively, the promotion of an electron, by a light photon, from the valence band to the conduction band is analogous to the electron transfer process in a complex ion. Because of this analogy, it is possible to make the assignment of an "electron transfer" electronegativity (denoted χ^*) (*26*), to cations and anions in solids, which is analogous to optical electronegativity for complexes, so that the following relationship holds:

$$E = 3.72[\chi^*(\text{anion}) - \chi^*(\text{cation})]. \quad (7)$$

The constant 3.72 is chosen so that E is in eV and χ^* for Cl^-, Br^-, and I^- is, as in the case of optical electronegativity, the same as the Pauling electronegativity of the halogen atoms. (3.72 arises from the conversion

TABLE III

ELECTRON TRANSFER ELECTRONEGATIVITIES, χ^*

Na^+	Mg^{2+}											Al^{3+}	Si	P^{3-}	S^{2-}	Cl^-
0.95	1.1											0.95		1.75	2.15	3.0
K^+	Ca^{2+}	Sc	Ti	V	Cr^{3+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu	Zn^{2+}	Ga^{3+}	Ge	As^{3-}	Se^{2-}	Br^-
0.95	1.0				2.0	1.45	1.75	2.0	2.0		1.1	1.15		1.55	1.9	2.8
Rb^+	Sr^{2+}										Cd^{2+}	In^{3+}	Sn	Sb^{3-}	Te^{2-}	I^-
1.0	1.0										1.45	1.45		1.35	1.8	2.5
Cs^+	Ba^{2+}										Hg^{2+}					
0.95	1.0										1.55					

from cm^{-1} to eV of Jørgensen's proportionality constant of 30,000 (*25, 26*).) Values of χ^* which have so far been obtained are in Table III. These values can be substituted in Eq. (7) to obtain values of E and this can be done straightforwardly except in the case of Cr^{3+}, Mn^{2+}, Fe^{2+}, Co^{2+}, and Ni^{2+} for which adjustments must be made because of spin–pairing effects (and 10Dq in the case of Ni^{2+}) (*27*). In nontransition metal compounds, E is often the band gap or energy gap, E_g. Experimentally determined values of E_g, for example, those of III–V compounds, II–VI compounds, and I-VII compounds (alkali halides), show very close agreement with values of E obtained from Eq. (7) using χ^* electronegativities (*26*).

The electron transfer electronegativities, χ^*, of the anion and cation characterize the ease with which an electron can be transferred (i) from the anion, the energy for this process *increasing* with increasing χ^*(anion), (ii) to the cation, the energy for this process *decreasing* with increasing χ^*(cation). For a series of binary compounds having a common cation, it follows that if the ordering corresponds to decreasing χ^*(anion), there will be a decrease in [χ^*(anion) − χ^*(cation)] and in E, corresponding to an increasing approach to the nonmetal/metal transition.

For the oxides of the elements, we have already observed how there is a fall in Pauling electronegativity as the metal becomes more electropositive (Fig. 3). This has been taken to indicate an increase not only in the ionicity but also in the tendency for the electrons of oxide(-II) to become itinerant (see previously). Thus, we should expect this increasing tendency for itinerancy to be reflected in a decrease in $\chi^*(O^{2-})$ also, as the cation becomes more electropositive.

There have been no studies of the effect of constitution upon χ^* electronegativity in the oxides of the elements. However, previous work on the shift of charge transfer absorption bands in various oxidic media (*28*) has indicated a correlation between optical electronegativity and optical basicity given by

$$\chi_{opt}(O^{2-}) = 4.3 - 2.0\Lambda. \tag{8}$$

If this relationship were to hold for oxides M_mO_n, then $\chi_{opt}(O^{2-})$ would be replaced by $\chi^*(O^{2-})$, and, because of Eq. (3), the relationship Eq. (8) becomes

$$\chi^*(O^{2-}) = 4.3 - \frac{1.5}{x_M - 0.25}. \tag{9}$$

Since Eq. (3) applies only to certain elements (Table I) and not to, for example, transition elements, it follows that this restriction also applies to Eq. (9). Using the limited data available, values of $\chi^*(O^{2-})$ have been calculated (Table IV) and they are plotted versus x_M in Fig. 5. (Note that for Cs_2O, E is unknown, but taking a rough value between 2 and 3 eV seems justifiable when the color of Cs_2O is compared with that of, for example, CdS for which E = 2.6 eV.) The points for H_2O, Al_2O_3, MgO,

TABLE IV

DATA FOR EVALUATING ELECTRONEGATIVITY, $\chi^*(O^{2-})$, IN OXIDES M_mO_n

Oxide	E (eV)[a]	Correction (eV)[b]	χ^*(cation)	$\chi^*(O^{2-})$
Al_2O_3	8.3	0.6	0.95	3.33
MgO	7.3		1.1	3.06
CaO	6–7		1.0	2.6–2.9
BaO	ca. 6		1.0	ca. 2.6
Cs_2O	2–3[c]	0.6	0.95	1.6–1.9
ZnO	3.4		1.1	2.01
CdO	2.2		1.45	2.04
Ga_2O_3	4.4	0.6	1.15	2.49
In_2O_3	2.8	0.6	1.45	2.36
MnO	3.8	$56B/3$; ($B = 0.099$ eV)	1.45	1.97
NiO	3.7	$14B/3 + 10Dq$; ($B = 0.099$ eV)	2.0	2.58

[a] Values from Refs. (*26*) and (*28*) and "Amer. Inst. Phys. Handbook" (H. P. R. Frederikse, Ed.), p. 9.16–9.25, McGraw-Hill, New York (1972).

[b] In using Eq. (7), E must be adjusted by (i) adding 0.6 eV for oxides, M_nO_m, where $n \neq m$, (*26*) (ii) subtracting spin-pairing energies given in terms of the Racah parameter, B, in Ref. (*27*) for MnO and NiO (values of B cited are from Ref. (*25*) (Ch. 5), and (iii) subtracting $10Dq$ (1.09 eV (Ref. (*25*), Ch. 5) for NiO.

[c] Estimated value (see text).

CaO, BaO, and Cs_2O follow the (broken) curve of Eq. (9) quite closely but the oxides of elements outside the *s* and *p* blocks lie well away. This trend for the *s*- and *p*-block oxides is remarkable when it is remembered that Eq. (9) is based upon a relationship (Eq. (8)) holding for oxidic *systems* rather than simple oxides. Included in Fig. 5 are anions with small χ^* values (whose compounds often have low values of E) in order to emphasize the significance in the observed fall of $\chi^*(O^{2-})$.

Two Types of Metallic Oxide?

The fall in $\chi^*(O^{2-})$ and also in x_0, with increasing electropositive nature of the metal in oxides M_mO_n, are understandable when it is recalled that the overall electron affinity of the O^{2-} ion is negative. The O^{2-} ion is highly unstable and tends spontane-

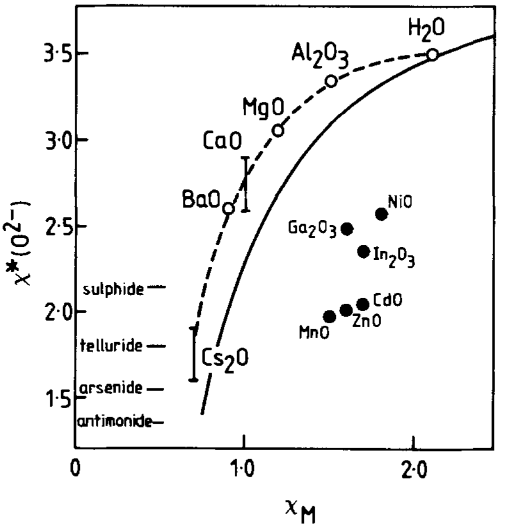

FIG. 5. Plot of electron transfer electronegativity of oxide(-II), $\chi^*(O^{2-})$, versus Pauling electronegativity, x_M, for oxides M_mO_n, using data from Table IV. The unbroken curve is of Eq. (9).

ously to lose an electron. Thus, as the degree of negative charge on the oxide(-II) ion increases (as it would do with increasingly electropositive metals) so there is a growing tendency for it to "discard" an electron, thereby lowering the energy required for transferring an electron to the cation. As discussed above, a low energy of electron transfer corresponds to a low value of χ^*(anion), and this is what is observed for $\chi^*(O^{2-})$ in Fig. 5. In terms of polarizability, the increasing tendency for discarding electrons, as the negative charge on the oxide (-II) ions grows, leads to an increasing tendency for electron itinerancy. Both of these points of view (and also the fall in x_O in Fig. 3) lead us to expect that for oxides of highly electropositive metals, increasing ionicity is accompanied by an increasing approach to the onset of metallic bonding. This expectation seems very relevant to the recent preparation of metallic glasses in the rubidium–oxygen and cesium–oxygen systems (*29*) which have been shown to contain the oxide(-II) species and therefore might be regarded as Rb–Rb_2O or Cs–Cs_2O alloys.

It is very important to realize that the "mechanism" by which the increased tendency toward metallization is generated (through the highly negative charge on the oxide(-II) ion) distinguishes these oxides from other oxides (of less electropositive metals) where the charge on the oxide(-II) ion is much less and where some other "mechanism" operates. For example, in metallic transition metal oxides, electron itinerency arises from the overlapping of cation orbitals (*30, 31*) and therefore the magnitude of the charge on the oxide ions is of secondary importance. It should be noted that the plots of (i) x_O versus x_M, and (ii) $\chi^*(O^{2-})$ versus x_M (Figs. 3 and 5) distinguish these two types of oxide.

Classification of Oxides

Oxides with little tendency for metallization are insulators and can be regarded as having almost insignificant metallic character. Those oxides that are closer to the nonmetal/metal transition (e.g., as in Fig. 4) often exhibit properties which might be described as arising from cooperative behavior involving all, or a large proportion of, the ions in the solid. These properties include semiconduction, ferro-, and antiferromagnetism, intense coloration and ability to transfer (often reversibly) to a "mixed valency" oxide which, in turn, often has these properties in an enhanced form. Some practical examples are SnO_2 which is used as a transparent conductor in thin film form, yttrium-doped garnets which are used in magnetic bubble memories, and WO_3 which can be produced as a colorless film and can be electrolytically reduced to a highly colored "bronze" with much lower energy gap (formula: $M_x^{\mathrm{I}}W_x^{\mathrm{V}}W_{1-x}^{\mathrm{VI}}O_3$). Properties such as these are not normally possessed by oxides with little tendency for metallization.

Vitreous materials or solids with crystal defects often allow the attainment of specifically desired properties, and this is achieved through a knowledgeable selection of components which, in the case of an oxidic material, are oxides. For traditional materials, often the principles of acid–base chemistry can be successfully applied. However, for systems designed for exploitation of electro/optical/magnetic properties, the situation is much more complicated and no attempt has yet been made to systematize the chemical and physical properties of component oxides (or other compounds) with the properties of the final material. For tackling the problem, it would clearly be desirable to devise a classification which allows some form of charting of the component oxides according to their bonding characteristics.

In attempting such a classification we first of all consider the trend from covalent to ionic. Although generally for binary compounds, the Pauling electronegativity difference ($x_A - x_M$) can generally be used as an indication of ionic/covalent character, we have already seen that for oxides it is not possible to use this owing to the variation of x_O with x_M (see Fig. 3). However, it is apparent from the present discussion that the variation of x_O is a reflection of the extent to which the oxide(-II) species is negatively charged on going from one binary oxide to another. Thus, it seems reasonable to use x_O itself as a measure of ionicity. It is necessary to assign values to x_O denoting the covalent and ionic ends to the scale, and obviously the assignment of such limits must be arbitrary, but from trends in Fig. 3, the covalent end seems to be reached for x_O approximately 3.8. Imposing an "ionic" limit is more contentious, but bearing in mind the trends in Fig. 3, we choose this limit as $x_O = 2.0$.

We have already discussed how the tendency towards metallization can be thought of in terms of decreasing E or $(1 - R_m/V_m)$, with the nonmetal/metal transition occurring when these two quantities are zero. Bearing in mind their relationship with each other (Fig. 4), we shall adopt a scale of $\sqrt{E}$ or $(1 - R_m/V_m)$ using either absorption edge frequency or refractive index, depending on the availability of data for each metal oxide. A further advantage of using the square root of E rather than E itself is that it emphasizes the importance of small changes in E for oxides having very small band gaps. For example, a difference of 0.1 eV in E for compounds close to the onset of metallization would be very significant compared with compounds having E say, equal to 4 eV; plotting $\sqrt{E}$ values would locate the former compounds at a distance of 0.32 of a unit from the "metallic" region, whereas for the latter compounds, differences of 0.1 eV in E would hardly be registered. In choosing the limits for the two scales, it is obvious that the "metallic" limit is for $\sqrt{E} = (1 - R_m/V_m) = 0$; for the region where there is insignificant tendency towards metallization we take $\sqrt{E} = 3$ (and $(1 - R_m/V_m) = 0.7$), since this condition corresponds to highly insulating materials with no semiconducting properties.

Charting the oxides presents the problem of whether to choose a triangular or some other scheme. Use of a triangular chart (with the three sides representing: covalent–ionic, ionic–metallic, and metallic–covalent trends) implies a strict three-way proportionality split in the bond character. However, we are making no attempt to assess the properties of ionic/metallic character of covalent/metallic character; indeed our approach would prevent these assessments from being made in a similar manner to the covalent/ionic character described above. Since oxides can approach the nonmetal/metal transition whether they are essentially covalent or essentially ionic, a sensible presentation would be to use a horizontal line for a covalent–ionic scale and the vertical to represent a growing tendency for the onset of metallization.

Oxides for which sufficient data are presently available are in Table II, and they are charted in Fig. 6. It can be seen how the acidic oxides, e.g., B_2O_3, P_2O_5, and SiO_2, are toward the covalent side, while the basic oxides, e.g., MgO and CaO, are to the right-hand (ionic) side of these. The highly basic oxides, such as BaO and Cs_2O, are even further to the right-hand side.

Figure 6 raises a number of interesting points and possible investigations for the future. For example, the series of oxides B_2O_3, P_2O_5, SiO_2, Al_2O_3, MgO, CaO, Li_2O, SrO, BaO, Na_2O, and Cs_2O have values of x_O which parallel their optical basicities, since Eqs. (3) and (4) yield the relationship

$$\Lambda(M_mO_n) = 0.87(4.1 - x_O). \qquad (10)$$

It would be instructive to discover whether the x_O values for the other oxides in Fig. 6 (mainly oxides of the transition metals) bear a similar relationship with optical ba-

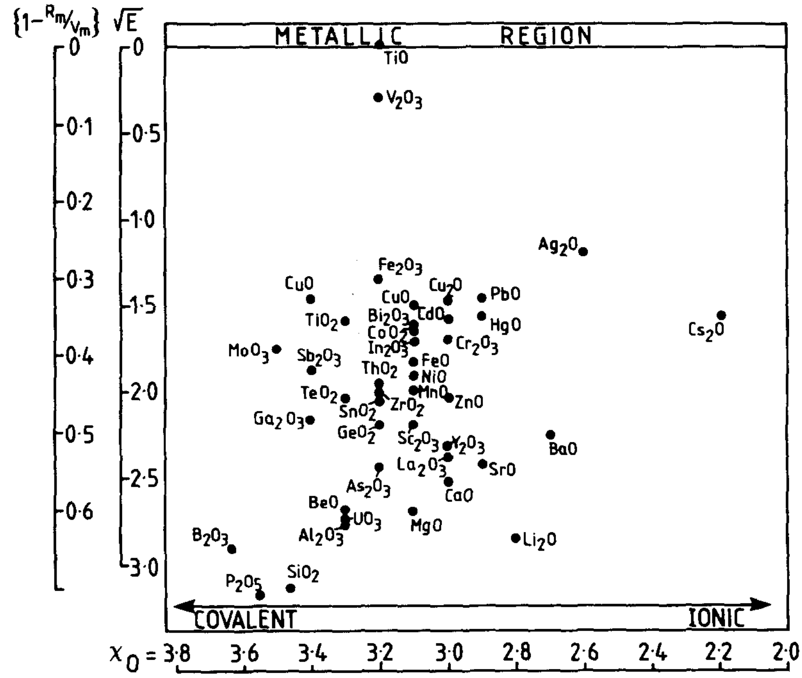

FIG. 6. Chart for oxides, M_mO_n. Covalent oxides are to the left and ionic oxides are to the right-hand side. The height above the covalent–ionic base line represents the proximity to the nonmetal/metal transition.

sicity. This would be especially important for studying the chemistry of metallurgical slags (*32–34*). Unfortunately, it is very difficult to make optical basicity measurements in systems containing transition metal ions owing to the severe impairment of ultraviolet transparency necessary for recording probe ion absorption spectra. However, "chemical" methods relying on equilibria such as

$$S_2 + O^{2-} \rightleftharpoons S^{2-} + O_2$$

show promise (*32*). Also the estimation of optical basicity using refractive index appears to be viable (*34, 35*).

A horizontal line could be drawn in Fig. 6 corresponding to $\sqrt{E} \approx 2.0$ ($(1 - R_m/V_m) = 0.45$) in order to create a very approximate division between semiconducting oxides (above the line) and insulating oxides (below). Reactions between acidic and basic oxides, that are both insulators, usually yield products (compounds or solid solutions) which are also insulators; if a semiconductor is produced, it indicates a significant change in oxidation number, structure or some other factor. If, in Fig. 6, another horizontal line were drawn for $\sqrt{E} = 1.7$ or $(1 - R_m/V_m) = 0.38$ (not shown), then oxides above this line are expected to be intensely colored since the absorption edge would be below 3 eV, that is, in the visible region of the spectrum.

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