# Improvement of a Bulk Optical Basicity Table for Oxidic Systems

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**Optical basicity ($\Lambda$), defined by J. A. Duffy, can be an interesting parameter for the characterization of acid–base properties and the choice of solids used, for example, in glass working or heterogeneous mild oxidation catalysis. In this last field, the Lewis acid–base property of a catalyst is relevant. The purpose of the present work is to complete and improve an optical basicity table of ionic–covalent oxides and oxysalts, despite the lack of data for these solids. Values of optical basicity for most covalent transition metal oxides are indeed often missing or wrongly assessed. Furthermore, catalysts in mild oxidation of hydrocarbons mainly contain transition metal oxides with covalent bonds. To overcome these difficulties, attempts were made to correlate ICP (the ionic–covalent parameter defined by J. Portier) and $\Lambda$ of simple oxides. Four straight lines are observed depending on the electron configuration of the cations ($s$–$p$, $d^1$–$d^9$, $d^{10}$, $d^{10}s^2$). On the other hand, for highly covalent oxides ($d^0$ electron configuration), $\Lambda$ values were assumed based only on experimental logical considerations, thus giving a fifth correlation line. These results allow the calculation of $\Lambda$ values for any mixed oxide, depending on the valence and coordination numbers of each ion, and will help with the prediction of the Lewis acid–base and hence, the catalytic properties of the solids concerned.** © 1998 Academic Press

## INTRODUCTION

The acid–base character of ionic–covalent anhydrous oxides and oxysalts is a very important parameter that can affect their numerous properties. The problem of the classification of solids on a Lewis acid–base scale is well known in glass chemistry, but also concerns many fields of solid state chemistry and even heterogeneous catalysis. In this last case, the Lewis acid–base properties of the solids are known to be of major importance.

The acid–base characterization of solids is usually based on experimental measurements, such as the use of molecular probes or colored indicators, which at least allow *a posteriori* qualitative determinations and comparisons. For a long time authors have also tried to conceive and develop practical tools to represent and classify this character. However, the main works most often dealt with ions, either in aqueous solution or in the solid state, and the prediction of behavior phases has not been straightforward.

Recently, a new approach to the study of glasses and metallurgical slags, using the "Optical Basicity" concept, was investigated by Duffy *et al.* (1–3). Based at first on UV spectroscopy, the basicities of numerous simple oxides, from which the optical basicity of mixed oxides can be calculated, were determined. Among other things, this has the advantages of giving *a priori* evaluation of the properties of phases and allowing quantitative classification on a Lewis acid–base scale for many oxides and oxysalts.

The main limitation of this concept in the present state of the art concerns the behavior of certain transition metal oxides, namely the most covalent ones. In this case, classical means of measurement are not allowed.

Thus, the purpose of this study is to evaluate the missing values of optical basicity for the most covalent transition metal oxides by means of correlation with the so-called ionic–covalent parameter (ICP) defined by J. Portier (4). The application of the optical basicity concept to mild oxidation catalysis will be tackled. In this particular field, it is known that most of the performant catalysts involve highly covalent transition metal oxides.

## PREVIOUS STUDIES

### Hard and Soft Acids and Bases (HSAB)

Apart from classical studies on acidity (like Brønsted or Lewis theories), R. G. Pearson, in his theory of HSAB (5), introduced the notion of covalency and its effects on the acid properties of an ion. He classified ions as hard, soft, or borderline acids or bases and specified that a hard acid (A) will react with a hard base (B) and a soft acid with a soft base to give stable combinations according to the reaction

$$A(hard) + B(hard) \xrightleftharpoons{K} AB$$
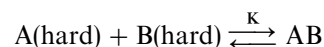
$$\log K = S_A S_B + \sigma_A \sigma_B, \qquad [1]$$

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where K represents the equilibrium constant and $S_i$ the acid/base strength and $\sigma_i$ is a covalency term. In an oxide, the cation will be the acid, as it can accept a partial negative charge, and the oxygen ion will be the base, as it can give a part of its negative charge. Pearson thus gives a table classifying different ions vs their acid (or basic) strength. Although this concept represents an important advance and is an extremely useful tool, this system of classification is still only qualitative.

## ICP

J. Portier *et al.* (4) have more recently tried to create a predictive concept, aiming to determine the properties of materials *a priori* through two simple tools: electronegativity and Lewis acid strength. By introducing moderating parameters, they defined a new approach to electronegativity ($\chi$, in Pauling-type unity), taking into consideration the valence and the coordination of the ions,

$$\chi = 0.274z - 0.15zr_i - 0.01r_i + 1 + \alpha, \qquad [2]$$

where $z$ is the charge number, $r_i$ is the ionic radius of the ion $i$ (Å) as proposed by Shannon for $R_{O^{2-}} = 1.40$ Å (7), and $\alpha$ is a correcting term, depending on each cation. From this, they proposed an ionic–covalent parameter (ICP), which represents the influence of ionic–covalent bonding in an oxide or oxysalt on the acid strength of cations,

$$ICP = \log(P) - 1.38\chi + 2.07, \qquad [3]$$

where $P$ is the polarizing power of the cation ($z/r_i^2$, with formal charge $z$ and Shannon ionic radius $r_i$) and $\chi$ the electronegativity as defined previously. The zero scale is set for $Au^+$ in coordination VI. ICP is a nondimensional number.

In their publications, Portier *et al.* present tables compiling the values of $r_i$, $\alpha$, $\chi$, and ICP for all the cations according to their valences and coordination numbers (4). These parameters represent a great advantage compared to Pearson's classification as they are *quantitative*. Unfortunately, these values concern only cations and thus may render difficult the prediction of phases with mixed thermodynamic properties.

## Optical Basicity

Another approach was investigated in the 1970s by Duffy (2) for the study of glasses. He defined the term "optical basicity" ($\Lambda$) as the electron-donating power of the oxygen in an oxidic glass. The basicity of the glass is a function of the alkali ion content, as alkali oxides are basic. Indeed, the basicity strongly depends on the polarizing power of the cations in the solid: if the solid is ionic (*i.e.*, contains cations with weak polarizing power), the charges are focused on

each ion and the oxygen will be able to give an important partial negative charge to a new cation. If the chemical bonds in the solid have an important covalent character, the negative charge will be shared by the cation and the anion and the oxygen will have a weak electron-donating power.

The first measurements of $\Lambda$ were performed by UV spectroscopy (3): the introduction of a probe ion (usually $Pb^{2+}$, $Tl^+$, or $Bi^{3+}$) into the investigated phase in a very weak quantity allows measurement of the shift of the probe's absorption peak maximum vs basicity. This leads to a linear correlation between the UV probe's peak shift and the basicity. This shift to lower frequencies is due to donation of negative charge from the oxygen to the probe ion. This can be explained by two covalency phenomena which lead to an expansion of the outer orbitals and hence a reduction of the interelectronic repulsion ("nephelauxetic effect"): (a) field effect, in which the extra negative charge is placed between the core and external orbitals of the cation, increasing the screening of peripheral electrons; and (b) symmetry effect, in which combining the orbitals of the oxygen and cation leads to the conversion of the cation orbitals into (larger) antibonding orbitals.

The experimental data can lead to values of $\Lambda_{exp}$ for all simple oxides except the transition metal oxides, which strongly absorb in the UV region (1, 3).

It is also possible to determine $\Lambda$ of the simple oxides by the use of the linear relationship between the Pauling electronegativity of the cation ($\chi_M$) and $\Lambda$ (1):

$$\Lambda = 0.75/(\chi_M - 0.25). \qquad [4]$$

However, Duffy clearly underscores that this relationship is only valid for certain nontransition metals.

It is then possible to calculate the global basicity of a mixed oxide by combining the $\Lambda$ values for the simple oxides according to the part of the negative charge neutralized by each cation (2, 7, 8), as shown by the example

$$\Lambda_{th}(Mg_2V_2O_7) = 4/14\Lambda_{MgO} + 10/14\Lambda_{V_2O_5}, \qquad [5]$$

as $2Mg^{2+}$ neutralizes $2 \times (2/14)$ and $2V^{5+}$, $2 \times (5/14)$ negative charges.

The optical basicity thus obtained is a mean value without any theoretical justification (9), but is a useful tool in determining trends for the principal properties of glasses.

The great advantages of optical basicity compared to all the other concepts used in acidity–basicity are that $\Lambda$ is a *global parameter* (it concerns a *phase*) and that it permits *quantitative classification* of the phases and *calculation for mixed oxides*. This implies a predictive means to compare, *a priori*, the basicity of different oxides with no other experiments required.

The main limitations of the concept are that $\Lambda_{th}$ does not take into account the real structure of the materials, as it

was created for the study of glasses (even if Duffy noticed that differences between $\Lambda_{th}$ and $\Lambda_{emp}$ could arise from structural effects (10)), and, more important, that data for transition metal oxides are lacking.

### Electron Polarizability

When spectroscopy experiments could not be used, as in the case of transition metal ions which absorb intensely in the UV region, other methods were investigated to obtain $\Lambda$ values. These consist mainly of bonding energy measurements (by ESCA) (7, 11) or calculations based on the electronic polarizability of oxygen ($\alpha_O^{2-}$) vs the basicity of the material (3, 9). The first method was not properly investigated for $\Lambda$ calculations but seems to be a possibility, as the $E_B(O^{1s})$ is correlated to the charge carried by the oxygen (9), which is of course related to the basicity (12, 13). The second method has been more frequently used by Duffy (14, 15), who observed a linear correlation between $1/\alpha_O^{2-}$ and $\Lambda$ for a given structural family:

$$\Lambda = 1.67(1 - 1/\alpha_O^{2-}). \qquad [6]$$

$\alpha_O^{2-}$ is deduced from the molar electronic polarizability of the simple oxide ($\alpha_m$) by subtracting the contribution of the electronic polarizability of the cation, $\alpha_A$, (14) as given by the additivity rule (16)

$$\alpha_m(A_iB_j) = i\alpha_A + j\alpha_B, \qquad [7]$$

where $A$ is the cation, $B$ the anion, and $i$ and $j$ their respective proportions.

$\alpha_m$ can be calculated from the refractive index by the Lorentz–Lorenz (or Clausius–Mosotti) relationship (15,16)

$$\alpha_m = \frac{3V_m}{4\pi N}\frac{n^2-1}{n^2+2}, \qquad [8]$$

with $V_m$ the molecular volume, $N$ the Avogadro number, and $n$ the refractive index. Unfortunately, data for $n$, $\alpha_m$, and $\alpha_{cation}$ are scarce.

Duffy has determined the values of $\Lambda$ for only a few transition metal oxides (14,15) and has specified that the additivity of the electronic polarizabilities is normally only valid for the ionic compounds. The presence of a certain covalency introduces perturbations leading to a discrepancy in the linear correlation $1/\alpha_O^{2-}$ vs $\Lambda$. This would arise from the mutual overlapping of the $t_{2g}$ orbitals of the cations; in nontransition metal oxides, by contrast, the only overlapping would be of the orbitals of the cation with those of the oxygen. The values for many alkali metal and alkaline earth oxides and a few transition metal oxides found by Duffy are presented in Table 1.

**TABLE 1**
**Values of Optical Basicity for Simple Oxides from Various Authors**

| Phase | $\Lambda_a$ | $\Lambda_b$ | $\Lambda_c$ | Phase | $\Lambda_a$ | $\Lambda_b$ | $\Lambda_c$ |
|---|---|---|---|---|---|---|---|
| $Al_2O_3$ | 0.61 | 0.45 | | $MoO_3$ | | 1.07 | 1.07 |
| $B_2O_3$ | 0.42 | 0.43 | 0.42 | $Na_2O$ | 1.15 | | |
| BaO | 1.15 | 1.21 | 1.23 | $Nb_2O_5$ | | | 1.05 |
| $Bi_2O_3$ | | | 1.19 | NiO | | 0.91 | 0.92 |
| CaO | 1.00 | 1.00 | 0.95 | $P_2O_5$ | 0.33 | | |
| CdO | | 1.10 | 1.13 | PbO | 0.95 | 1.19 | 1.17 |
| $CeO_2$ | | | 1.01 | $Sb_2O_3$ | | 1.14 | 1.22 |
| CoO | | | 0.98 | $Sc_2O_3$ | | | 0.87 |
| $Cr_2O_3$ | 0.70 | | | $SiO_2$ | 0.48 | 0.48 | 0.52 |
| $Cs_2O$ | 1.70 | | | $SnO_2$ | | 0.79 | 0.91 |
| CuO | | 1.08 | 1.11 | $SO_3$ | 0.33 | | |
| $Fe_2O_3$ | 0.77 | 1.04 | 0.99 | SrO | 1.10 | 1.10 | 1.18 |
| FeO | 1.00 | | | $Ta_2O_3$ | | | 0.94 |
| $Ga_2O_3$ | | 0.71 | 0.80 | $TeO_2$ | | 0.99 | 0.96 |
| $GeO_2$ | 0.60 | 0.70 | 0.94 | $TiO_2$ (a) | | 1.02 | 0.98 |
| $H_2O$ | 0.40 | | | $TiO_2$ (r) | $0.75^a$ | 0.96 | 0.91 |
| $In_2O_3$ | | | 1.07 | $V_2O_5$ | | | 1.04 |
| $K_2O$ | 1.40 | | | $WO_3$ | | 1.05 | 1.04 |
| $Li_2O$ | 1.00 | 0.87 | | $Y_2O_3$ | | 0.99 | |
| MgO | 0.78 | 0.69 | 0.67 | ZnO | 0.95 | 1.03 | 1.13 |
| MnO | 0.98 | 0.94 | 0.96 | $ZrO_2$ | | 0.86 | 0.79 |

*Notes*: $\Lambda_a$: Duffy's values; $\Lambda_b$: Dimitrov's values, calculated using the refractive index; $\Lambda_c$: Dimitrov's values, calculated using the gap energies; a: anatase; r: rutile.

[a] Mean value.

More recently, Dimitrov and Sakka have tried to apply the correlation $1/\alpha_O^{2-} = f(\Lambda)$ to numerous transition metal oxides (17), since they have found a new means of determining the value of $\alpha_m$ for these oxides. When refractive indexes were not available, Dimitrov *et al.* used the gap energies of the oxides. The coincidence of the $\alpha_m$ values obtained by the two methods confirms the gap energy calculation as a valid method for $\alpha_m$ determination. A table is thus given in which most values of $\Lambda$ for nontransition metal oxides are in accordance with values given by Duffy (see Table 1).

It should be noted that Dimitrov and Duffy took for $\alpha_{cation}$ the value of the *free cation* and not the value of the *cation in the oxide*, which is only available for a very limited number of cations recently investigated.

### LIMITATIONS OF THE CLASSICAL METHODS

As we examine the results proposed by Dimitrov, we notice that some of the values of $\Lambda$ for the investigated solids are unjustified from the chemical properties point of view. In particular, all the transition metal oxides are found to have optical basicities very close to each other. The most covalent oxides ($V_2O_5$, $Nb_2O_5$, $WO_3$, $MoO_3\ldots$) are given as very basic, with $\Lambda$ close to 1, that is, as basic as CaO, which is

used as the reference for optical basicity. This seems very unlikely, as many authors consider those oxides to be acidic.

To confirm or disprove the values of $\Lambda$ given by Dimitrov and Sakka, it was necessary to examine in detail the calculation of $\alpha_O^{2-}$.

The additivity rule is, in fact, only approximately valid for ionic compounds (14, 16). In these solids, the polarizability of the cation can be assimilated, as a first approximation, to the polarizability of the free cation as given by Pauling (18). However, recent studies have shown that, as soon as the covalency in the solid increases, the additivity rule becomes incorrect and the electronic polarizability of the cation in the solid differs from that of the free ion (18, 19). As shown by Ishara et al. in the study of $TiO_2$ (20), the real electronic polarizability of the cation $Ti^{4+}$ in the crystal is higher than that calculated by classical methods (that is, that of the free ion). It has also been found that the structure has an influence on the polarizabilities: when the distortion increases, $\alpha_{Ti}^{4+}$ is reduced (thus $\alpha_O^{2-}$ is increased). Thus we can conclude that, even if we could still consider the additivity rule valid for this oxide, Dimitrov et al. would have overevaluated $\alpha_O^{2-}$ and $\Lambda$. This can explain the differences between the average $\Lambda$ values given by Duffy ($\Lambda_{TiO_2} = 0.75$) and Dimitrov ($\Lambda_{TiO_2} = 0.95$). Consequently the values of $\Lambda$ in Dimitrov's table appear improbable for the most covalent oxides.

The problem is thus to define a limit for the application of the additivity rule as a way of calculating the optical basicity. For this, we must use a parameter which will display the covalency of the bonds in solids. The graph $\chi$/ICP as given by Portier and completed by us (Fig. 1) can be of help given this aim. Figure 1 shows clearly the distribution of the cations according to their valence and coordination numbers in the areas "ionic–covalent" and "hard–soft acid". We can see on this graph that the cations with pronounced covalent character ($V^{5+}$, $W^{6+}$, $Mo^{6+}$ … ) are all located on the top left-hand side and set a limit for the application of the additivity rule, as well as for the correlation ($1/\alpha_O^{2-} - \Lambda$). From literature data, we know that $TiO_2$ possesses a covalent character that cannot be completely ignored (20). As Duffy gave experimental values for $TiO_2$ and $Fe_2O_3$ of about 0.75 and 0.78, respectively, compared with 0.98 and 0.99 given by Dimitrov, we will situate the limit of the additivity rule validity for an electronegativity located around the "$L_a$" line in Fig. 1. This limit approximately passes through the points representing $Ti^{4+}$ and $Fe^{3+}$ in coordinations 4 and 6, respectively. The calculation of $\Lambda$ from $\alpha_O^{2-}$ will be estimated as correct only for the cations situated under this limit on the $\chi$/ICP graph. That the ICP value can play a role must be taken into account, as the cations situated on the top right part of the graph have similar values of $\Lambda$ if determined experimentally (Duffy's values) or calculated from $\alpha_O^{2-}$ (Dimitrov's values), for example, for $SiO_2$ or $P_2O_5$.

We can thus assume the nonvalidity of the $1/\alpha_O^{2-}/\Lambda$ correlation, and thus Dimitrov's $\Lambda$ values, for all the cations situated on the top left part of the graph $\chi$/ICP ($\chi > 1.8$ and ICP $< 0.8$) .

## ESTABLISHMENT OF THE VALUES OF $\Lambda$ FOR COVALENT OXIDES

It now seems essential to estimate optical basicities for the most covalent transition metal oxides, but no data on these solids other than qualitative considerations are available. For instance, Goodenough (21) has highlighted the covalent character of certain oxides like $V_2O_5$, $WO_3$, and $MoO_3$. Ai (22) has also confirmed that if $TiO_2$ does possess a certain acidity, $V_2O_5$ and especially $MoO_3$ are much more acid. Lastly, Weng et al. (23) have established a scale for the donors and acceptors of "spillover" oxygen. According to these authors, acceptor solids have a pronounced tendency to covalency while donor solids usually give some polarized bonds (ionic solids). $MoO_3$ is given as the best acceptor, which implies the highest covalency. As ionic compounds have a strong optical basicity whereas covalent solids have a weak basicity (24), we can confirm that the $\Lambda$ values given by Dimitrov et al. for these last oxides are erroneous.

From all these considerations it can be concluded that the basicity must increase in the following order:

$$WO_3 = MoO_3 > V_2O_5 > TiO_2. \qquad [9]$$
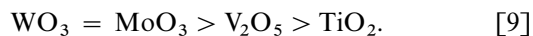
Referring to Fig. 1, it can be seen that the same order is observed in comparing tendencies to covalency (or electronegativity), taking into account the real coordination number in each solid: 6.

As no correct means of evaluation is known for these compounds, approximate values of $\Lambda$ have to be set up. For this purpose, the correlation ICP $= f(\Lambda)$ first established by Portier (4) for the $s$–$p$ configuration cations (comprising mostly alkali and alkali–earth cations) can be used. A linear correlation was observed for these oxides.

ICP/$\Lambda$ correlations could also be established for other cations. If we consider that the values given by Duffy or Dimitrov are true, except in the cases of the most covalent solids, and if we report them on this graph, a series of lines is obtained, depending on the electronic configuration of the cations (Fig. 2). We have used the $\Lambda$ data from Duffy as often as possible, and if necessary, the values from Dimitrov (mainly for weakly covalent transition metal oxides). Four straight lines are observed in Fig. 2, according to the electronic configuration of the cations involved ($sp$, $d^{10}$, $d^{10}s^2$, $d^1$–$d^9$). To know which value of $\Lambda$ was relevant, the real coordination of the cation in the simple oxide investigated has been checked.

It has to be noticed that $\Lambda$ values for $d^{10}s^2$ are assumed to be all very close, as these cations are used as probes for
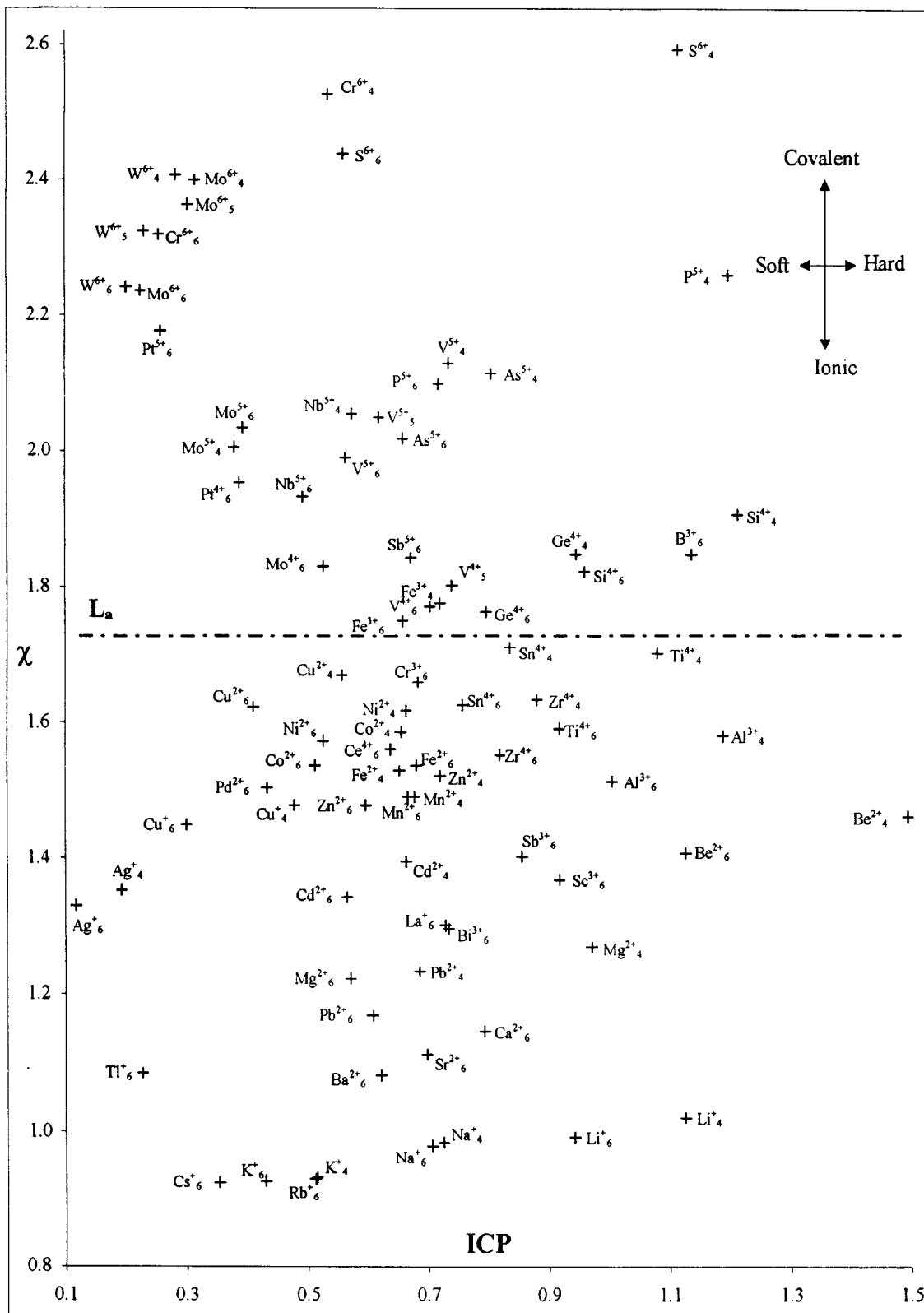
**FIG. 1.** Graph of $\chi = f(ICP)$. Symbol: $M_b^{a+}$ where $M$ is the cation and $a$ and $b$ are the oxidation and coordination numbers, respectively. Data after Ref. (4).
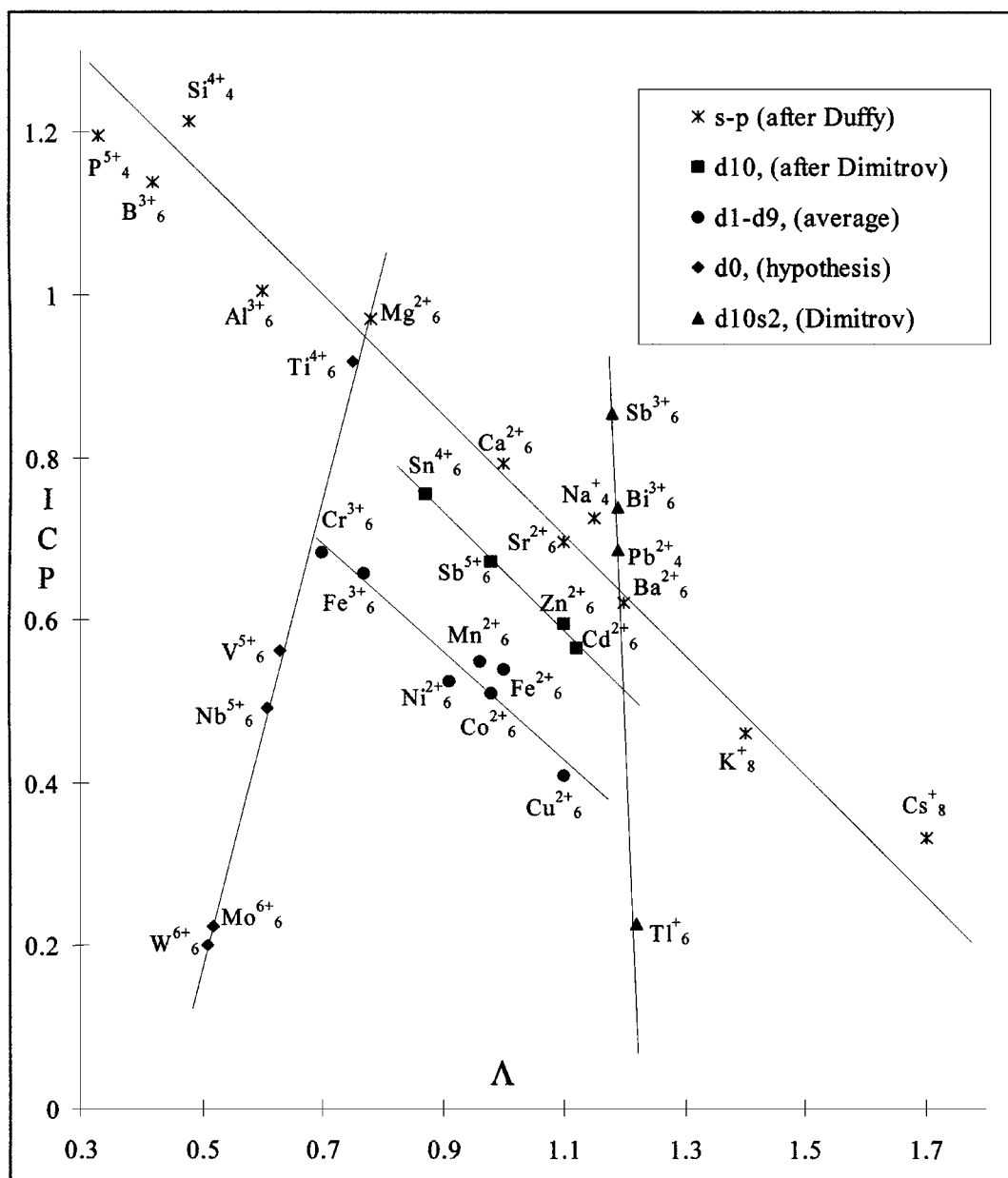
**FIG. 2.** Correlations of ICP/Λ for the various electronic configurations of the cations.

UV-Λ measurements. Thus, a certain invariability is expected as shown by the trend given by $Sb^{3+}$, $Bi^{3+}$, and $Pb^{2+}$ (vertical straight line). For $Tl^+$, Λ was assumed to be around 1.20. Ten iterations of the linear regression were made to adjust its value to 1.22.

The last line of the graph (ICP/Λ) concerns the most covalent transition metal oxides with electron configuration $d^0$ of the cations. This last correlation is assumed to be linear, like the four other lines, and is based on the $Λ(TiO_2)$ value given by Duffy and the qualitative considerations described earlier. The line was chosen to respect the order of

basicity described earlier by reporting the ICP values for the cations involved. The Λ values thus obtained are to be taken with caution, as they are only hypothetical, but even if some error in the absolute values is made, the optical basicities are relatively far away from the other values (except $P^{5+}$ and $Si^{4+}$), so the order of the global basicity of mixed oxides will be respected.

Table 2 presents the values of both ICP and Λ for many simple oxides, taking into account the valence and coordination numbers of the cations in the solids, corresponding to Fig. 2. The values are classified according to electronic

**TABLE 2**
**Known Values of $\Lambda$ and ICP for Various Cations**

| Cation | Coordination | $\Lambda$ | ICP |
|---|---|---|---|
| El. config.[a]: sp | ICP $= -0.676^a \Lambda + 1.452$; $R^2 = 0.980$ | | |
| $Al^{3+}$ | 6 | 0.60 | 1.004 |
| $B^{3+}$ | 6 | 0.42 | 1.138 |
| $Ba^{2+}$ | 6 | 1.20 | 0.622 |
| $Ca^{2+}$ | 6 | 1.00 | 0.792 |
| $Cs^+$ | 8 | 1.70 | 0.333 |
| $K^+$ | 8 | 1.40 | 0.462 |
| $Mg^{2+}$ | 6 | 0.78 | 0.971 |
| $P^{5+}$ | 4 | 0.33 | 1.195 |
| $Si^{4+}$ | 4 | 0.48 | 1.214 |
| $Sr^{2+}$ | 6 | 1.10 | 0.696 |
| $Na^+$ | 4 | 1.15 | 0.726 |
| El. config.: $d^{10}s^2$ ICP $= -13.844^a \Lambda + 17.134$; $R^2 = 0.906$ after 10 iterations on $\Lambda_{T1+}$ | | | |
| $Bi^{3+}$ | 6 | 1.19 | 0.739 |
| $Pb^{2+}$ | 6 | 1.18 | 0.687 |
| $Sb^{3+}$ | 6 | 1.18 | 0.854 |
| $T1^+$ | 6 hypothesis on $\Lambda$ | 1.22 | 0.226 |
| El. config.: $d^0$ | ICP $= 3.007^a \Lambda - 1.336$; $R^2 = 0.999$ | | |
| $Mo^{6+}$ | 6 hypothesis on $\Lambda$ | 0.52 | 0.223 |
| $V^{5+}$ | 6 hypothesis on $\Lambda$ | 0.63 | 0.563 |
| $Ti^{4+}$ | 6 | 0.75 | 0.918 |
| $W^{6+}$ | 6 hypothesis on $\Lambda$ | 0.51 | 0.201 |
| El. config.: $d^1$–$d^9$ ICP $= -0.643^a \Lambda + 1.143$, $R^2 = 0.924$ | | | |
| $Co^{2+}$ | 6 $(d^7)$ | 0.98 | 0.510 |
| $Cr^{3+}$ | 6 $(d^2)$ | 0.70 | 0.684 |
| $Cu^{2+}$ | 6 $(d^9)$ | 1.10 | 0.410 |
| $Fe^{3+}$ | 6, LS $(d^5)$ | 0.77 | 0.657 |
| $Fe^{2+}$ | 6, HS $(d^6)$ | 1.00 | 0.540 |
| $Mn^{2+}$ | 6, HS $(d^5)$ | 0.96 | 0.549 |
| $Ni^{2+}$ | 6 $(d^8)$ | 0.91 | 0.525 |
| El. config.: $d^{10}$ | ICP $= -0.729^a \Lambda + 1.390$; $R^2 = 0.994$ | | |
| $Cd^{2+}$ | 6 | 1.12 | 0.566 |
| $Sb^{5+}$ | 6 | 0.98 | 0.672 |
| $Sn^{4+}$ | 6 | 0.87 | 0.756 |
| $Zn^{2+}$ | 6 | 1.10 | 0.596 |

*Notes*: LS: low spin; HS: high spin.
[a] Electronic configuration.

**TABLE 3**
**Calculated Values of $\Lambda$ for Various Coordinations and Valences Obtained from the Relation between ICP and $\Lambda$**

| Cation | Coordination | $\Lambda$ | ICP | Cation | Coordination | $\Lambda$ | ICP |
|---|---|---|---|---|---|---|---|
| El. config.: sp | | ICP $= -0.676^a \Lambda + 1.452$; $R^2 = 0.980$ | | | | | |
| $Ba^{2+}$ | 8 | 1.25 | 0.608 | $Mg^{2+}$ | 4 | 0.51 | 1.110 |
| $Be^{2+}$ | 6 | 0.48 | 1.125 | $Na^+$ | 6 | 1.10 | 0.705 |
| $Ca^{2+}$ | 8 | 1.05 | 0.745 | $Rb^+$ | 6 | 1.51 | 0.430 |
| $Li^+$ | 4 | 0.48 | 1.125 | $S^{6+}$ | 6 | 1.32 | 0.560 |
| El. config.: $d^{10}s^2$ | | ICP $= -13.844^a \Lambda + 17.134$, $R^2 = 0.906$ | | | | | |
| $Bi^{3+}$ | 8 | 1.18 | 0.712 | $Sb^{3+}$ | 4 | 1.17 | 0.854 |
| $Pb^{2+}$ | 4 | 1.19 | 0.687 | | | | |
| El. config.: $d^0$ | | ICP $= 3.007^a \Lambda - 1.336$; $R^2 = 0.999$ | | | | | |
| $Ce^{4+}$ | 6 | 0.66 | 0.637 | $V^{5+}$ | 5 | 0.65 | 0.618 |
| $La^{3+}$ | 8 | 0.68 | 0.708 | $W^{6+}$ | 4 | 0.54 | 0.284 |
| $Mo^{6+}$ | 4 | 0.55 | 0.313 | $W^{6+}$ | 5 | 0.52 | 0.229 |
| $Mo^{6+}$ | 5 | 0.53 | 0.254 | $Y^{3+}$ | 6 | 0.72 | 0.818 |
| $Nb^{5+}$ | 6 | 0.61 | 0.492 | $Zr^{4+}$ | 6 | 0.72 | 0.818 |
| $V^{5+}$ | 4 | 0.69 | 0.733 | $Zr^{4+}$ | 7 | 0.71 | 0.799 |
| El. config.: $d^1$–$d^9$ | | ICP $= -0.643^a \Lambda + 1.143$, $R^2 = 0.924$ | | | | | |
| $Ce^{3+}$ | 7 | 0.76 | 0.657 | $Ni^{2+}$ | 4 | 0.75 | 0.662 |
| $Co^{2+}$ | 4 | 0.77 | 0.650 | $Pd^{2+}$ | 4 | 0.85 | 0.594 |
| $Cu^{2+}$ | 4 | 0.91 | 0.557 | $Pd^{2+}$ | 6 | 1.11 | 0.431 |
| $Fe^{3+}$ | 4 | 0.66 | 0.719 | $Rh^{3+}$ | 6 | 0.92 | 0.551 |
| $Fe^{2+}$ | 4 | 0.76 | 0.652 | $Ti^{3+}$ | 6 | 0.23 | 0.998 |
| $Mn^{2+}$ | 4 | 0.72 | 0.677 | $U^{5+}$ | 6 | 0.94 | 0.541 |
| $Mn^{3+}$ | 6 | 0.81 | 0.620 | $V^{3+}$ | 6 | 0.55 | 0.789 |
| $Mn^{4+}$ | 6 | 0.88 | 0.574 | $V^{4+}$ | 5 | 0.63 | 0.740 |
| $Mo^{4+}$ | 6 | 0.96 | 0.526 | $V^{4+}$ | 6 | 0.68 | 0.704 |
| $Mo^{5+}$ | 6 | 1.17 | 0.392 | | | | |
| El. config.: $d^{10}$ | | ICP $= -0.729^a \Lambda + 1.390$; $R^2 = 0.994$ | | | | | |
| $Ag^+$ | 2 | 1.25 | 0.480 | $Ge^{4+}$ | 6 | 0.82 | 0.795 |
| $Cd^{2+}$ | 8 | 1.22 | 0.502 | $T1^{3+}$ | 6 | 1.03 | 0.636 |
| $Cu^+$ | 2 | 0.98 | 0.678 | $Zn^{2+}$ | 4 | 0.92 | 0.718 |

[a] Electronic configuration.

configuration. From the linear regressions of the correlations, the missing values of $\Lambda$ can be calculated for each valence and coordination as the ICP is known. Some of these values are given in Table 3.

As we have established correlations according to the cation's electronic configuration between ICP and $\Lambda$ and thus obtained, by using the corresponding linear regressions, the optical basicity value for each valence and coordination number in the oxides, we now have a tool *sensitive to the structure*. This allows the optical basicity to be calculated for any mixed oxides, taking into account the actual coordination of the component cations. For this purpose, the crystal structure of the solids has to be considered. Concerning the glasses, in which there is no long-range order structure, average values of $\Lambda$ can be used.

The following examples show how to calculate $\Lambda$ for crystallized compounds in which the valence of the cation is the same but the coordination number is not.

In $VOPO_4$ the coordination number of $V^{5+}$ is $6(\Lambda^{VI}_{V_2O_5} = 0.69)$ and that for $P^{5+}$ is $4(\Lambda^{IV}_{P_2O_5} = 0.33)$, whereas in $Mg_2V_2O_7$, $V^{5+}$ has a coordination number of 4 ($\Lambda^{IV}_{V_2O_5} = 0.63$) and $Mg^{2+}$ of 6 ($\Lambda^{VI}_{MgO} = 0.78$). We will then calculate $\Lambda_{solid}$ by

$$\Lambda_{VOPO_4} = \tfrac{5}{10} \times \mathbf{0.69} + \tfrac{5}{10} \times 0.33 = 0.48$$

$$\Lambda_{Mg_2V_2O_7} = \tfrac{4}{14} \times 0.78 + \tfrac{10}{14} \times \mathbf{0.63} = 0.72. \qquad [10]$$

The notation $\Lambda^{IV}_{V_2O_5}$ is informal, as the normal coordination of $V^{5+}$ in $V_2O_5$ is 6, but we will use this notation as a practical means for describing the calculation.

Table 4 gives a nonexhaustive list of mixed oxides with their calculated values of $\Lambda$.

**TABLE 4**
**Values of Optical Basicity for Many Simple and Mixed Oxides**

| Phase | Coordination | $\Lambda$ | Phase | Coordination | $\Lambda$ | Phase | Coordination | $\Lambda$ |
|---|---|---|---|---|---|---|---|---|
| $CO_2$ | | 0.30 | $CeO_2$ | $Ce_8^{4+}$ | 0.65 | $BiMoO_4$ | $Bi_6^{3+}, Mo_4^{5+}$ | 0.79 |
| $P_2O_5$ | $P_4^{5+}$ | 0.33 | $BiPO_4$ | $Bi_6^{3+}, P_4^{5+}$ | 0.65 | $CoMn_2O_4$ | $Co_4^{2+}, Mn_6^{3+}$ | 0.80 |
| $H_2O$ | | 0.40 | $CoMoO_4$ | $Co_6^{2+}, Mo_4^{6+}$ | 0.66 | $Cu_2V_2O_7$ | $Cu_6^{2+}, V_4^{5+}$ | 0.81 |
| $B_2O_3$ | $B_4^{3+}$ | 0.42 | $La_2O_3$ | $La_7^{3+}$ | 0.68 | $Zn_2V_2O_7$ | $Zn_6^{2+}, V_4^{5+}$ | 0.81 |
| $Mg_2P_2O_7$ | $Mg_6^{2+}, P_4^{5+}$ | 0.46 | $VO_2$ | $V_6^{4+}$ | 0.68 | $Mn_2O_3$ | $Mn_6^{3+}$ | 0.81 |
| $SiO_2$ | $Si^{4+}4$ | 0.48 | $V_6O_{13}$ | $4V_6^{4+}, 2V_6^{5+}$ | 0.68 | $CuFe_2O_4$ | $Cu_6^{2+}, Fe_{4/6}^{3+}$ | 0.81 |
| $Li_2O$ | $Li^+4$ | 0.48 | $Bi_2Mo_3O_{12}$ | $Bi_6^{3+}, Mo_6^{6+}$ | 0.69 | $BiVO_4/1.9\,MgO$ | | 0.81 |
| $BeO$ | $Be^{2+}6$ | 0.48 | $1V_2O_5/1TiO_2$ | $TiO_2$ rutile | 0.69 | $Zn_3V_2O_8$ | $Zn_6^{2+}, V_4^{5+}$ | 0.84 |
| $VOPO_4$ | $V_6^{5+}, P_4^{5+}$ | 0.48 | $CrVO_4$ | $Cr_3^{3+}, V_4^{5+}$ | 0.69 | $PdO$ | $Pd_4^{2+}$ p.c. | 0.85 |
| $VPO_{4.75}$ | $0.5V^{4+}\,0.5V^{5+}$ | 0.49 | $Cr_2O_3$ | $Cr_6^{3+}$ | 0.70 | $Bi_2MoO_6$ | $Bi_4^{3+}, Mo_6^{6+}$ | 0.86 |
| $(VO)_2P_2O_7$ | $V_6^{4+}, P_4^{5+}$ | 0.49 | $MgCr_2O_4$ | $Mg_4^{2+}, Cr_6^{3+}$ | 0.71 | $SnO_2$ | $Sn_6^{2+}$ | 0.87 |
| $FePO_4$ | $Fe_6^{3+}, P_4^{5+}$ | 0.50 | $MnCr_2O_4$ | $Mn_4^{2+}, Cr_6^{3+}$ | 0.71 | $BiVO_4$ | $Bi_6^{3+}, V_4^{5+}$ | 0.88 |
| $Ni_2P_2O_7$ | $Ni_6^{2+}, P_4^{5+}$ | 0.50 | $ZrO_2\,m$ | $Zr_8^{4+}$ | 0.71 | $MnO_2$ | $Mn_6^{4+}$ | 0.88 |
| $H_4PVMo_{11}O_{40}$ | $P_4^{5+}, V_6^{5+}, Mo_6^{6+}$ | 0.50 | $ZrO_2\,t$ | $Zr_7^{4+}$ | 0.71 | $FeSbO_4$ | $Fe_6^{3+}, Sb_6^{5+}$ | 0.90 |
| $Mn_2P_2O_7$ | $Mn_6^{2+}, P_4^{5+}$ | 0.51 | $Mg_2V_2O_7$ | $Mg_6^{2+}, V_4^{5+}$ | 0.72 | $Fe_4Bi_2O_9$ | $Bi_6^{3+}, Fe_6^{3+}$ | 0.91 |
| $WO_3$ | $W_6^{6+}$ | 0.51 | $CoCr_2O_4$ | $Co_4^{2+}, Cr_6^{3+}$ | 0.72 | $NiO$ | $Ni_6^{2+}$ | 0.91 |
| $Co_2P_2O_7$ | $Co_6^{2+}, P_4^{5+}$ | 0.52 | $Y_2O_3$ | $Y_6^{3+}$ | 0.72 | $ZnO$ (w) | $Zn_4^{2+}$ | 0.92 |
| $MoO_3$ | $Mo_6^{6+}$ | 0.52 | $Mg_3V_2O_8$ | $Mg_6^{2+}, V_4^{5+}$ | 0.72 | $MnO$ | $Mn_6^{2+}$ | 0.96 |
| $Fe_2P_2O_7$ | $Fe_6^{2+}, P_4^{5+}$ | 0.52 | $0.1V_2O_5 + 0.9TiO_2$ | | 0.74 | $Sb_2O_4 + SnO_2$ | | 0.96 |
| $GeO_2$ | $Ge_6^{4+}$ | 0.54 | $Bi_2Mo_2O_9$ | $Bi_6^{3+}, Mo_6^{6+}$ | 0.74 | $MoO_2$ | $Mo_6^{4+}$ | 0.96 |
| $Mo_{16}V_4Nb_2O_{63}$ | $Mo_6, V_6, Nb_6$ | 0.54 | $Mo_5O_{14}$ | $Mo_{6,7\,or\,8}^{6+}$ | 0.75 | $USb_3O_{10}$ | $U^{5+}, Sb^{5+}$ | 0.97 |
| $Cu_2P_2O_7$ | $Cu_6^{2+}, P_4^{5+}$ | 0.55 | $0.0234V_2O_5$ $+0.976TiO_2$ | | 0.75 | $Cu_2O$ | $Cu_2^+$ | 0.98 |
| $Zn_2P_2O_7$ | $Zn_6^{2+}, P_4^{5+}$ | 0.55 | $0.0234V_6O_{13}$ $+0.976TiO_2$ | | 0.75 | $Sb_2O_5$ | $Sb_6^{5+}$ | 0.98 |
| $CuO$ | $Cu_4^{2+}$ s.q | 0.56 | $TiO_2$ rutile[a] | $Ti_6^{4+}$ | 0.75 | $CoO$ | $Co_6^{2+}$ | 0.98 |
| $NiMoO_4 + MoO_3$ | $NiMoO_4$ l.t. | 0.57 | $CuCr_2O_4$ | $Cu_4^{2+}, Cr_6^{3+}$ | 0.75 | $CaO$ | $Ca_6^{2+}$ | 1.00 |
| $NiMoO_4 + MoO_3$ | $NiMoO_4$ h.t. | 0.58 | $Ni_2V_2O_7$ | $Ni_6^{2+}, V_4^{5+}$ | 0.75 | $FeO$ | $Fe_6^{2+}$ | 1.00 |
| $NiMoO_4 + 0.25\,MoO_3$ | $NiMoO_4$ l.t. | 0.60 | $Ce_2O_3$ | $Ce_6^{3+}$ | 0.76 | $Tl_2O_3 + \varepsilon Dy_2O_3$ | $Tl_6^{3+}$ [b] | 1.03 |
| $Al_2O_3$ | $Al_6^{3+}$ | 0.60 | $NiFe_2O_4$ | $Ni_6^{2+}, Fe_{4/6}^{3+}$ | 0.76 | $\alpha Sb_2O_4$ | $Sb_4^{3+}, Sb_6^{5+}$ | 1.05 |
| $Fe_2(MoO_4)_3$ | $Fe_6^{3+}, Mo_4^{6+}$ | 0.61 | $Mn_2V_2O_7$ | $Mn_6^{2+}, V_4^{5+}$ | 0.77 | $SrO$ | $Sr_6^{2+}$ | 1.10 |
| $Nb_2O_5$ | $Nb_6^{5+}$ | 0.61 | $Fe_2O_3$ | $Fe_6^{3+}$ | 0.77 | $CdO$ | $Cd_6^{2+}$ | 1.12 |
| $NiMoO_4 + 0.25\,MoO_3$ | $NiMoO_4$ h.t. | 0.62 | $Co_2V_2O_7$ | $Co_6^{2+}, V_4^{5+}$ | 0.77 | $Na_2O$ | $Na_4^+$ | 1.15 |
| $NiMoO_4$ b.t | $Ni_6^{2+}, Mo_4^{5+}$ | 0.62 | $RhVO_4$ | $Rh_3^{3+}, V_4^{5+}$ | 0.78 | $Bi_2O_3$ | $Bi_6^{3+}$ | 1.19 |
| $V_2O_5$ | $V_6^{5+}$ | 0.63 | $MgO$ | $Mg_6^{2+}$ | 0.78 | $BaO$ | $Ba_6^{2+}$ | 1.20 |
| $CoMoO_4$ | $Co_6^{2+}, Mo_6^{6+}$ | 0.64 | $CoFe_2O_4$ | $Co_6^{2+}, Fe_{4/6}^{3+}$ | 0.78 | $Ag_2O$ | $Ag_2^+$ | 1.25 |
| $NiMoO_4$ h.t | $Ni_6^{2+}, Mo_6^{6+}$ | 0.64 | $FeAsO_4$ | $Fe_6^{3+}, As_4^{5+}$ | 0.79 | $K_2O$ | $K_4^+$ | 1.40 |
| $Mo_2O_5/4MoO_3/$ $2V_2O_5/Nb_2O_5$ | $Mo_6^{5+}, Mo_6^{6+}$ $V_6^{4+}, Nb_6^{5+}$ | 0.64 | $La_2CuO_4$ | $La_8^{3+}, Cu_6^{2+}$ | 0.79 | $Rb_2O$ | $Rb_4^{+c}$ | <1.51 |
| $Mo_{18}O_{52}$ | $14Mo_6^{6+}, 4Mo_6^{5+}$ | 0.65 | $Fe_3O_4$ | $Fe_{4/6}^{3+}, 1Fe_6^{2+}$ | 0.79 | $Cs_2O$ | $Cs_3^{+c}$ | <1.70 |

*Notes*: m: monoclinic; t: tetragonal; w: wurtzite; s.q.: square plane; l.t.: low temperature; h.t.: high temperature

[a] $TiO_2$ anatase; $Ti_6^{4+}$ distorted; $\Lambda$ slightly $< 0.75$.

[b] $Dy^{3+}$ neglected.

[c] ICP values known only for coordination 6. As ICP increases, $\Lambda$ decreases for alkali metal oxides. Thus we can state only that $\Lambda$ is lower than values calculated for the cations in coordination 6.

It should be noticed that changing only the valence or the coordination of one cation in a phase can modify greatly the global basicity value. For example, $\Lambda(Mo^{6+})^{VI} = 0.52$ but $\Lambda(Mo^{5+})^{VI} = 1.17$, and $\Lambda(Mg^{2+})^{VI} = 0.78$ but $\Lambda(Mg^{2+})^{IV} = 0.51$. Thus, the crystal structure of the solid can be very important, and structural modification can be characterized by $\Lambda$ calculations. For instance, this can explain reactivity evolutions of solids if structural modifications occur, by changing the global basicity of the investigated phase.

## APPLICATION OF OPTICAL BASICITY TO SELECTIVE OXIDATION

Many applications can be expected because $\Lambda_{th}$ can be correlated with various properties. Among others, $\Lambda$ can account for redox behavior, as the redox properties of a solid parallel its acid–base character (25, 26). These properties are involved in catalysis, and more particularly, in selective oxidation reactions, which proceed on oxides and mixed oxides.

In this particular field, the need for *predictive trends* of catalyst's behavior must be underscored. Indeed for more than a century, progress in catalysis, and particularly heterogeneous oxidation catalysis, has generally been based on numerous and sophisticated experiments required to determine and explain how a solid can catalyze, or not, a given reaction. Predictions are still difficult and are mostly based on empirical qualitative observations. To overcome this drawback, several authors have proposed theories like HSAB, Pearson's theory (5), or Wolkenstein's (28) and Krylov's (29) models for heterogeneous catalysis. But these concepts are not always easy to apply for predictions in mild oxidation.

The specific use of $\Lambda$ in this aim can be understood if we consider the generally accepted Mars and van Krevelen mechanims (27), verified for most mild oxidation reactions. In this case, the surface lattice oxygens of the catalyst are inserted into the final oxidized product according to the general scheme

$$[R\text{–}CH] + KO \longrightarrow [R\text{–}C\text{–}O] + K \; (+ H_2O)$$

$$K + O_{(gas)} \longrightarrow KO, \qquad\qquad [11]$$
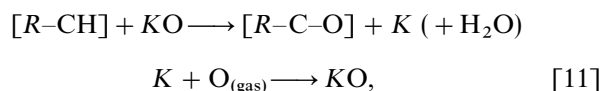
where $[R\text{–}CH]$ is a hydrocarbon (for example), $[R\text{–}C\text{–}O]$ the product, and KO and K the oxidized and reduced forms of the catalyst. In these reactions, both acid–base and redox properties are involved. It is generally accepted that the first and rate-limiting, step is the attack on a terminal C–H group by a surface lattice oxygen; the following step differs according to whether an olefin (formation of a $\pi$-allylic intermediate) or an alkane (mechanism still not well understood) is concerned. If lattice oxygen is electrophilic, it will lead to total combustion of an olefin or aromatic hydrocarbon, whereas if it is nucleophilic enough, a selective mild oxidation will result (30). For example, Mamedov *et al.* have shown the influence of the nucleophilic character of lattice oxygens on the catalytic properties of various mixed oxides in the propylene allylic oxidation (31).

This is why optical basicity, characterizing the capacity of oxygen to give a part of its negative charge, seems to be an interesting parameter and one which could predict the ability of an oxide to catalyze a given reaction. Table 4 presents values of $\Lambda_{th}$ for various solids, including a few known mild oxidation catalysts.

To apply the concept of optical basicity in practice to prediction in mild oxidation, the competition between the adsorption of the reactant and the desorption of the products must be taken into consideration. For instance, in oxidative dehydrogenation of propane to propene, the catalyst has to present "hard" acid surface sites (connected with a weak optical basicity of oxygen) to activate propane, which can be assimilated as a hard base because of the strong $\sigma$ bonds involved in the molecule. But the solid also has to present an overall basic character to allow the desorption of propene and avoid total oxidation. The best results are thus obtained for amphoteric catalysts with $\Lambda$ around 0.72 (for example $Mg_2V_2O_7$ (32, 33)). This illustrates that each mild oxidation reaction *requires a specific optical basicity zone* for the catalyst to be active and selective. It must be born in mind that $\Lambda$ will just be a preselective parameter, useful to *minimize*, if not avoid, the *number of required experiments* in the research of new catalysts. Catalytic tests and sophisticated characterization of solids would still be essential to complement and explain in detail the reaction mechanisms and observed performances.

Work is in progress to determine another scale for hydrocarbon molecules so that the optimum basicity zone for each reaction could be predicted. New catalyst formulations could then be investigated based on the estimation of the required $\Lambda$ value for a given reaction.

## CONCLUSION

Starting from the works carried out by Duffy and Portier and from experimental and calculated data we have drawn five linear correlations between the optical basicity, $\Lambda$, and the ionic–covalent parameter (ICP). These correlations are a function of the electron configuration of the related cation and allow $\Lambda_{th}$ to be calculated from the valence and coordination numbers of the componant cations. For the most covalent transition metal oxides, optical basicity cannot be calculated from the electronic polarizabilities of the oxygen ion. $\Lambda$ values were thus chosen on the basis of observations of the chemical properties for such oxides. These optical basicity values have to be regarded cautiously, as they are derived from logical considerations and chemical observations. In any case, the values of basicity found for these oxides by the correlation ICP/$\Lambda$ respect these experimental considerations and thus corroborate our predictions.

Therefore, we are able to calculate *a priori* the basicity and to classify them on a quantitative scale, of many mixed oxides, including covalent transition metal oxides, taking into account the actual coordination of each ion.

We have also proposed heterogeneous catalysis as one of the applications of this concept. But, as J. Portier has suggested for ICP (4), superconductivity could also probably be characterized by $\Lambda$. The specific application to mild oxidation catalysis will be further developed in a forthcoming publication.

## REFERENCES

1. J. A. Duffy, *J. Solid State Chem.* **62,** 145 (1986).
2. J. A. Duffy and M. D. Ingram, *J. Am. Chem. Soc.* 6448 (1971).
3. J. A. Duffy and M. D. Ingram, *J. Non-Cryst. Solids* **21,** 373 (1976).
4. J. Portier, G. Campet, J. Etourneau, M. C. R. Shastry and B. Tanguy, *J. Compounds Alloys* **209,** 59 (1994).
5. R. G. Pearson, "Hard and Soft Acids and Bases." Dowen, Hutchinson and Ros Inc., Stroudsburg, 1973; R. G. Pearson, *J. Am. Chem. Soc.* **85,** 3533 (1963).
6. R. D. Shannon, *Acta Crystallogr. Sect. A* **32,** 751 (1976).
7. J. A. Duffy and M. D. Ingram, *Metall. Slags*, 1410 (1977).
8. J. A. Duffy, M. D. Ingram, and I. D. Sommerville, *J. Chem. Soc., Faraday Trans. 1* **74,** 1410 (1978).
9. J. A. Duffy and M. D. Ingram, *J. Non-Cryst. Solids* **144,** 76 (1992).
10. J. A. Duffy, *J. Non-Cryst. Solids* **86,** 149 (1986).
11. T. A. Clarke, E. N. Rizkalla, *Chem. Phys. Lett.* **37,** 523 (1976).
12. J. A. Duffy, *Phys. Chem. Glasses* **36,** 53 (1995).
13. J. A. Duffy, *in* "Fundamentals of Glass Sciences and Technology, 3rd ESG Conference," *Glastech. Ber. Glass Sci. Technol* **68** (C1), 35 (1995).
14. J. A. Duffy, *Ironmak. Steelmak.* **16,** 426 (1989).
15. J. A. Duffy, *Geochim. Cosmochim. Acta* **57,** 3961 (1993).
16. J. R. Tessman, A. H. Kahn and W. Schockley, *Phys. Rev.* **92,** 890 (1953).
17. V. Dimitrov and S. Sakka, *J. Appl. Phys.* **79,** 1736 (1996).
18. N. C. Pyper, C. G. Pike, P. Popelier, and P. P. Edwards, *Mol. Phys.* **86,** 995 (1995).
19. P. W. Fowler and N. C. Pyper, *Proc. R. Soc. London Series A* **398,** 377 (1985).
20. S. Ishara and M. Tachiki, *Phys. Rev. B* **49,** 16123 (1994).
21. J. B. Goodenough, *Bull. Soc. Chim. Fr.* **4,** 1200 (1965).
22. M. Ai, *Bull. Chem. Soc. Jpn.* **49,** 1328 (1976).
23. L. T. Weng, P. Ruiz, and B. Delmon, *Stud. Surf. Sci. Catal.* **72,** 399 (1993).
24. J. H. Binks and J. A. Duffy, *J. Solid State Chem.* **87,** 195 (1990).
25. F. G. K. Baucke and J. A. Duffy, *Phys. Chem. Glasses* **34,** 158 (1993).
26. F. G. K. Baucke and J. A. Duffy, *Phys. Chem. Glasses* **35,** 17 (1994).
27. P. Mars and D. W. Van Krevelen, *Chem. Eng. Sci.* **3,** 41 (1954).
28. T. Wolkenstein, "Théorié electronique de la catalyse sur les semi-conducteurs," Masson, Paris, 1961.
29. O. V. Krylov, "Catalysis by Non-metals." Academic Press, New York, 1970.
30. J. Haber, *in* "Solid State Chemistry, in Catalysis" (R. K. Grasselli and J. F. Brazdil, Eds.), ACS Symposium Series, Vol. 279, Am. Chem-Soc., Washington, DC, 1985.
31. E. A. Mamedov, V. P. Vislovskii, R. M. Talyshinskii, and R. G. Rizayez, *Stud. Surf. Sci. Catal.* **72,** 379 (1992).
32. X. Gao, P. Ruiz, Q. Xin, X. Guo, and B. Delmon, *J. Catal.* **148,** 56 (1994).
33. M. A. Chaar, D. Patel, and H. H. Kung, *J. Catal.* **109,** 463 (1988).