Giessner-Prettre, and Pullman,[30] computed different transition moment directions. In the zero-differential-overlap approximation, the "monopole" calculation in ref 3 is identical with the method used in ref 30. We have no explanation for this discrepancy. The experimental moments are compared in Table II with transition moments calculated by two different parameter choices, and it is evident that confidence in the theoretical moments is unwarranted. The discrepancies are particularly apparent for guanine and cytosine. The computed angle between the A and B guanine transitions is 74 or 66°, compared to the experimental 87°. In cytosine the angle between A and B is calculated as 71 or 51°. The experimental value is 2°. Even if we assume that the single-crystal results are unreliable and cannot be used to choose between the two alternatives presented by the cone analysis, the disagreement remains, since in both instances B and C are nearly perpendicular (87°), compared to the calculated difference, ≃40°.

Table II

Compound	Transitions	ϕ, deg Exptl	a	b
Adenine	A	-3	37	?
			52	94
	B	82 or 92	98	48
Uracil	A	-19	9	81
			9	133
	B	71	50	34
Cytosine	A	9	68	50
	B	7.5 10.5	-3	-1
		or		
	C	94 104	136	141
Guanine	A	ϕ^c	110	106
	B	$(\phi + 90)$	36	40
	C	$(\phi + 90)$	126	125

[a] Reference 30. [b] Reference 31. [c] The absolute directions in guanine are unknown.

Conclusion

Stretched-film spectra and fluorescence polarization measurements provide essentially the same qualitative information, and wherever fluorescence polarization information is available we have found essential agreement between the results of the two methods. It is easier to extract quantitative information about the relative transition moment directions from the stretched-film spectra. Higher resolution is also possible in absorption than in excitation spectra. Of course, in the absence of fluorescence, the fluorescence-polarization technique is inapplicable.

The calculation of transition moment directions by semiempirical procedures is fraught with uncertainty, and sufficient experimental information on the nucleic acid bases is not yet available to use in the calculations of interactions between the bases.

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Establishment of an Optical Scale for Lewis Basicity in Inorganic Oxyacids, Molten Salts, and Glasses

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Abstract: Nephelauxetic effects (measured from uv spectra) in the outer s and p orbitals of the probe ions Tl^+, Pb^{2+}, and Bi^{3+} are used for setting up scales of Lewis basicity for oxide systems. Values of Lewis basicity, expressed as "optical basicities," are assigned to a variety of oxide media including oxyanion glasses and oxyacids, thereby making it possible to compare the basicity of media for which comparisons based upon the Brønsted–Lowry or Lux–Flood concepts are not feasible. A critical evaluation of optical basicity is made in comparison with the conventional Lux–Flood approach to basicity in oxyanion media. The relevance of electronegativity to optical basicity is also considered. Scales for molten halides are also proposed, and from the optical basicities for the LiCl–KCl (41% KCl) melt and the $NaCl–AlCl_3$ (67% $AlCl_3$) melt, it is apparent that chloride is affected in a similar way to oxide by highly polarizing cations, but to a lesser extent.

The properties of solvent systems are often regarded in terms of acid–base behavior which, for protonic solvents, can be expressed quantitatively by referring to a scale such as pH or the Hammett acidity function.[1] For aprotic solvents, the expression of acidity or basicity in quantitative terms is less straightforward. One of the most general approaches to acid–base behavior is that due to Lewis,[2] although in the field of molten salt and glass chemistry, it has not proved very useful, and its application has been entirely qualitative.[3] The reason that it has not been applied quantitatively is that, until

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(1) L. P. Hammett, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1970, pp 267–272.

(2) G. N. Lewis, *J. Franklin Inst.*, **226**, 293 (1938).

(3) W. A. Weyl and E. G. Marboe, "The Constitution of Glasses," Vol. 1, Interscience, New York, N. Y., 1962, Chapter 5.

now, there has been no numerical scale of Lewis basicity. (This has been a fundamental criticism of the Lewis approach, having been commented upon previously.[4]) As a result of this situation, acid–base investigations in molten salts have been somewhat restricted and, for oxyanion melts and glasses, the Lux–Flood concept has been favored, since, in principle, it allows the establishment of scales of pO^{2-} analogous to pH.[5] Unfortunately, although this approach has been successfully applied to certain specific systems, usually it is not possible for acid–base comparisons to be made over a range of oxyanion systems owing to difficulties in defining thermodynamic oxide ion activities (see Results and Discussion) and also sometimes to the intervention of redox equilibria involving the formation of species such as superoxide.[6]

In applying the Lewis concept to solvent systems, one envisages the basicity of the solvent as its ability to share its electrons with an acidic solute. If a suitable metal ion is used as an acid probe for this effect, then through the effects of central-field and symmetry-restricted covalency there should be an expansion of the outer orbitals of the probe ion. This expansion is measured experimentally in the probe ions Tl^+, Pb^{2+}, and Bi^{3+} as the frequency of the $^3P_1 \leftarrow {}^1S_0$ transition and has been found[7] to be proportional to Jørgensen's *h* function,[8] a number (obtainable from the nephelauxetic parameter β) assignable to a ligand set and which, to some extent, can be taken to indicate the donor properties of the ligands. Thus by measuring the $^3P_1 \leftarrow {}^1S_0$ transition of the probe ion in the solvent system it is possible to assign a value of *h* which corresponds to the environment which the solvent provides for the probe ion.

In the present paper, it is shown how thallium(I), lead(II), and bismuth(III) can be used as "spectroscopic indicators" for setting up scales of Lewis basicity which enable quantitative comparison to be made for a wide range of oxyanion media. The establishment of scales for other molten salt systems is also shown to be feasible.

Results and Discussion

A suitable system in which large changes in basicity can be effected is provided by the alkali metal borate glasses ($M_2O:B_2O_3$), the range of alkali metal oxide being from zero to approximately 35 mol %; also, in the $Na_2O:B_2O_3$ system, there is an additional glass-forming region at *ca.* 68% Na_2O.[9] These media can be regarded as an oxide system in which the donor properties of the oxides are greatly modified by polarizing boron(III) cations. In boric oxide glass all the boron(III) ions in the network are three-coordinate, but, as indicated by nmr studies,[10] the boron ions are progressively converted to four-coordination as alkali metal oxide is added. It is possible that this change does not fully correspond to the increased alkali metal oxide content, but that in addition there is some conversion of bridging oxides to terminal oxides.[11] Both of these effects should increase the Lewis basicity of the oxide ions in the glass, though the oxide ions undergoing greatest change in basicity will be the terminally converted ones. The least affected will be those oxides furthest from the terminal ones and furthest from four-coordinate borons.

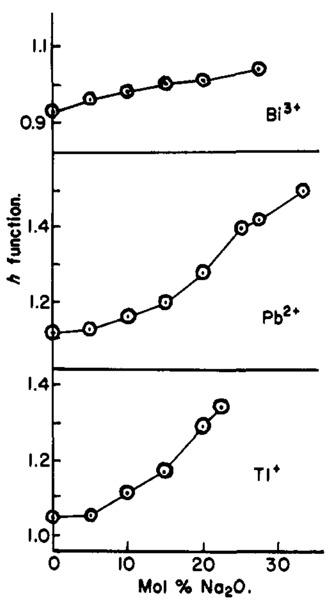

Figure 1. Plot of the *h* function, as determined using Tl^+, Pb^{2+}, and Bi^{3+} *vs.* Na_2O content in Na_2O–B_2O_3 glasses.

The uv spectra of Tl^+, Pb^{2+}, and Bi^{3+} in oxyanion glasses usually reveal a single absorption maximum which has been shown to be due to the transition $^3P_1 \leftarrow {}^1S_0$.[12] Spectral data of these three ions in the Na_2O–B_2O_3 glasses are given in Table I. (Data for Pb^{2+} agree well with spectra recently published by Paul.[13]) The *h* functions plotted in Figure 1 are calculated from the frequency ν of the $^3P_1 \leftarrow {}^1S_0$ transition using the rela-

Table I. Frequencies (ν_{max}, cm^{-1}) of the $^3P_1 \leftarrow {}^1S_0$ Transition for Thallium(I), Lead(II), and Bismuth(III) in Sodium Borate Glasses

Glass composition, % Na_2O	$Tl^{+\,a}$	Pb^{2+}	Bi^{3+}
0	48,500 46,300	47,100	44,100
5	48,400 46,400	46,800	43,800
10	48,200 45,800	46,400	43,600
15	47,700 45,300	46,100	43,400
20	46,900 44,400	45,000	43,200
22.5	46,500 44,000		
25		43,800	
27.5		43,500	42,800
33		42,500	

[a] Lower frequency estimated from band shape.

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(4) R. P. Bell, *Quart. Rev., Chem. Soc.*, **1**, 124 (1947); T. Moeller, "Inorganic Chemistry," Wiley, New York, N. Y., 1952, pp 328–329.

(5) H. Lux, *Z. Elektrochem.*, **45**, 303 (1934); H. Flood and T. Förland, *Acta Chem. Scand.*, **1**, 592 (1947).

(6) P. G. Zambonin and J. Jordan, *J. Amer. Chem. Soc.*, **91**, 2225 (1969).

(7) J. A. Duffy and M. D. Ingram, *J. Chem. Phys.*, **54**, 443 (1971).

(8) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, New York, N. Y., 1962, p 138.

(9) H. Rawson, "Inorganic Glass Forming Systems," Academic Press, New York, N. Y., 1967, pp 101–102.

(10) P. J. Bray and J. G. O'Keefe, *Phys. Chem. Glasses*, **4**, 37 (1963).

(11) H. de Waal, *ibid.*, **10**, 101 (1969).

(12) J. A. Duffy and M. D. Ingram, *J. Chem. Phys.*, **52**, 3752 (1970).

(13) A. Paul, *Phys. Chem. Glasses*, **11**, 46 (1970).

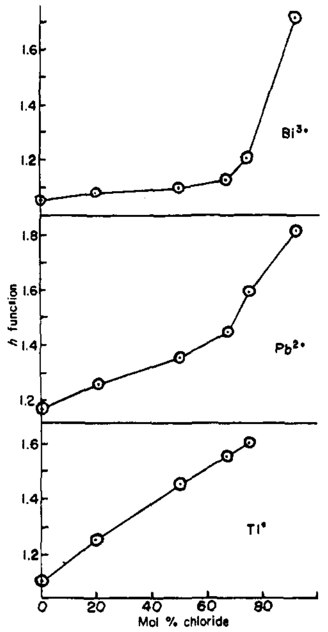

Figure 2. Plot of the *h* function, as determined using Tl^+, Pb^{2+}, and Bi^{3+} *vs.* sulfate–chloride composition in sulfate–chloride glasses. (Values of *h* are calculated using data from ref 12.)

tionship 1, ν_f being the (corrected) free-ion value of the

$$(1 - \nu/\nu_f) = hm \qquad (1)$$

transition and *m* being a parameter for each probe ion (Table II). For thallium(I), splitting of the $^3P_1 \leftarrow {}^1S_0$ band occurs in all the glasses. Such splitting has previously been observed in sulfate and bisulfate glasses[12,14] and may be due to Jahn–Teller splitting in the excited state[15] (which in a cubic field transforms as $^3T_1$). It is possible that the splitting is to the $^3B_2$ and ^3E terms, although, because this is not easy to prove, values of *h* were calculated from the equally weighted mean of the two frequencies.

Table II. Nephelauxetic Parameters for Thallium(I), Lead(II), and Bismuth(III)

Cation	ν_f, cm^{-1}	*m*
Thallium(I)	55,300	0.1356
Lead(II)	60,700	0.1992
Bismuth(III)	56,000	0.227

Figure 1 shows that the Lewis basicity, as measured by *h*, does indeed increase with increasing alkali metal oxide content, especially for Tl(I) and Pb(II). In the interpretation of these kinds of data, it is important to remember that if a medium is capable of offering a number of different sites for the probe ion, then all probe ions will not necessarily choose the same site. The different behavior observed for bismuth(III) compared with thallium(I) and lead(II) in the borate glasses (Figure 1) suggests that the Bi^{3+} ions are seeking out sites of lower *h* function. This might possibly be a general feature of the Bi^{3+} probe, since this behavior is also observed in sulfate–chloride glasses (Figure 2). Although addition of chloride to sulfate glass is shown by thallium(I) and lead(II) to markedly increase the *h* function of the glass, the changes shown by bismuth(III) are very much smaller; only at much higher chloride concentrations (beyond 70:30 chloride:sulfate mole ratio) does the entry of chloride into the coordination sphere of bismuth(III) become significant. The situation in the borate system is analogous to that in the sulfate–chloride system, as shown by the large value of *h* of bismuth(III) in the ultrahigh alkali borate glass (see later). Thus, it would appear that the probing properties of bismuth(III) are significantly different from those of thallium(I) and lead(II), probably because of its higher charge of 3+.

Optical Basicity. The greatest degree of electron donation by oxide to the probe cations is when there is complete absence of the polarizing boron(III), and all the oxygen is present as the unpolarized O^{2-} species. For this situation there will be the greatest red shift in the Rydberg bands, and the *h* function will reach a maximum. An environment closely approaching these conditions will be that provided in alkaline earth metal oxides, in which media frequencies of the $^3P_1 \leftarrow {}^1S_0$ transition have been reported for lead(II) (29,700 cm^{-1} in CaO) and bismuth(III) (27,200 cm^{-1} in SrO).[15] These frequencies correspond to *h* functions of the oxide ion having the values 2.56 based upon lead(II) data and 2.27 based upon bismuth(III) data. The difference in these values is too large to be accounted for by the difference in ionicity of CaO and SrO, and furthermore is in reverse direction to the effect expected. The most likely explanation for the difference is that for oxide coordination, separation of the *h* and *m* functions (eq 1) is much poorer than with, say, chloride coordination, and this in turn arises because oxide is a dinegative monatomic ion. (A similar—and possibly related—phenomenon is the wide variation in optical electronegativity which exists in oxide complexes.) It is likely that this discrepancy in *h* extends, but to a smaller degree, when the donor properties of oxide are modified by polarizing ions such as boron(III), sulfur(VI), etc.

Although assignment of the frequencies of lead(II) and bismuth(III) in the alkaline earth metal oxide to the transition $^3P_1 \leftarrow {}^1S_0$ is probably correct,[16] it is not completely certain.[15] The validity of the assignments depends, in the present context, upon whether or not the above values for the *h* function of oxide are reasonable. Certainly for lead(II), the increasing trend in *h* for the borate glasses up to 33% alkali metal oxide would indicate that when the boron(III) composition was reduced to zero, *h* would rise to a value of approximately 2.5; this value is also indicated by the borate glasses doped with thallium(I). Furthermore, the data for the ultrahigh alkali borate glasses ($Na_2O:B_2O_3$, 67:33 mole ratio) also give this indication, not only for lead(II) (ν_{max} 39,600 cm^{-1}, h = 1.74), but also for bismuth(III) (ν_{max} 37,400 cm^{-1}, h = 1.53). Accepting the spectral assignments, therefore, we have a very wide frequency range for the $^3P_1 \leftarrow {}^1S_0$ transition, extending from its value when *h* is zero, and which corresponds to zero Lewis basicity (*i.e.*, 100% ionicity in the probe ion–oxygen interaction), to its value corresponding to the maximum Lewis basicity. For lead(II) this is a range

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[14] J. A. Duffy, S. M. Forbes, and M. D. Ingram, *J. Chem. Soc., A*, 451 (1970).

[15] D. S. McClure, *Solid State Phys.*, **9**, 518 (1959).

[16] J. Ewles, *Proc. Roy. Soc., Ser. A*, **167**, 34 (1938); W. A. Runciman, *Proc. Phys. Soc. London*, **68**, 647 (1955).

of 31,000 cm^{-1} and for bismuth(III), 28,800 cm^{-1}. To indicate which end of the scale a particular oxyanion solvent tends, and also to compensate for the discrepancies in h which are peculiar to oxide systems (see above), it is proposed that the solvent be assigned an "optical basicity," Λ, defined as

$$\Lambda_{\mathrm{Pb(II)}} = (60{,}700 - \nu)/31{,}000$$

and

$$\Lambda_{\mathrm{Bi(III)}} = (56{,}000 - \nu)/28{,}800$$

where ν is the $^3P_1 \leftarrow {}^1S_0$ frequency of lead(II) or of bismuth(III) in the solvent.

Values of optical basicity have been compiled from the spectral data of lead(II) and bismuth(III) in a number of oxyanion glasses and are presented in Table III.

Table III. Optical Basicities of a Variety of Oxyanion Glasses

Glass	Composition (mole ratio)	$\Lambda_{\mathrm{Pb(II)}}$	$\Lambda_{\mathrm{Bi(III)}}$	$\Lambda_{\mathrm{Tl(I)}}$
B_2O_3[a]		0.439	0.413	0.431
Li_2O–B_2O_3[b]	17.6:82.4	0.461		
	19.6:80.4	0.468		
	23.8:76.2	0.500		
	24.8:75.2	0.510		
	27.6:72.4	0.520		
Na_2O–B_2O_3[a]	5:95	0.448	0.424	0.431
	10:90	0.461	0.430	0.459
	15:85	0.471	0.438	0.480
	20:80	0.506	0.445	0.527
	22.5:77.5			0.549
	25:75	0.545		
	27.5:72.5	0.555	0.458	
	33:77	0.587		
K_2O–B_2O_3[b]	10.4:89.6	0.439		
	14.2:85.8	0.465		
	18.1:81.9	0.480		
	21.5:78.5	0.533		
	24.0:76.0	0.565		
	27.5:72.5	0.578		
	30.5:69.5	0.590		
Na_2O–B_2O_3[a]	67:33	0.680	0.673	
Na_2O–SiO_2[b]	30:70	0.597		
Na_2O–CaO–SiO_2[b]	20:10:70	0.574		
Na_2O–P_2O_5[c]	50:50	0.457	0.465	
K_2O–ZnO–SO_3[c]	20:30:50	0.455	0.465	
K_2O–Al_2O_3–B_2O_3[d]	15.4:15.4:69.2	0.491		

[a] Λ values are calculated from spectral data in the present work. [b] Λ values from data in ref 13. [c] Λ values from data in ref 12. [d] Λ values from data in A. K. Ghosh, *J. Chem. Phys.*, **42**, 2623 (1965); **44**, 535 (1966).

Although in systems where bismuth(III) can seek out local environments of low h functions there will be disagreement between the bismuth(III) and lead(II) scales, in systems where presumably there would be no choice, as for example in boric oxide glass or sulfate glass, it is gratifying to observe (Table III) that the two optical basicity values are similar. The closeness of $\Lambda_{\mathrm{Pb(II)}}$ and and $\Lambda_{\mathrm{Bi(III)}}$ for the 67% Na_2O–33% B_2O_3 glass is worthy of comment, expecially in view of the different h functions for this medium, and may be taken as further support for the validity of the spectral assignment in the alkaline earth metal oxides. Furthermore, this result emphasizes the usefulness of optical basicity rather than h for oxide systems. In contrast to the divergence of the optical basicity on the two scales in the 0–33% Na_2O range of borate glasses, it would appear that in the ultrahigh alkali borate glasses all the available sites are of similar basicity, probably because in the glasses there are only simple anions present (*i.e.*, $B_2O_5^{4-}$).

The establishment of a scale based upon thallium(I) presents a difficulty in that there is lack of spectral data in metal oxides. However, if it is assumed that optical basicities based upon thallium(I) will also be consistent with those based upon lead(II) and bismuth(III) in the systems where no local variations in h function are to be expected, then extrapolated frequencies for thallium(I) in the all-oxide environment can be obtained. Taking the data of lead(II) and bismuth(III) in B_2O_3 glass and K_2SO_4–$ZnSO_4$ (2:3 mole ratio) glass, and of lead(II) in $NaHSO_4$–$KHSO_4$ (1:1 mole ratio) glass, the extrapolated frequencies for thallium(I) are found to lie in the range 36,600–37,300 cm^{-1}. The average value is 37,000 cm^{-1} (corresponding to h = 2.45, it should be noted). Optical basicity on the thallium(I) scale is thus given by

$$\Lambda_{\mathrm{Tl(I)}} = (55{,}300 - \nu)/18{,}300$$

ν being the $^3P_1 \leftarrow {}^1S_0$ frequency of thallium(I) in the medium. Using this relationship for the sodium borate glasses gives optical basicities very close to those obtained on the lead(II) scale (Table III).

Variation of Optical Basicity with Glass Composition. In the alkali metal borate glasses, it is possible to compare the optical basicities of glasses having a particular B_2O_3:M_2O ratio and thereby to observe the effect of changing from one alkali metal ion to another. Table III gives values of $\Lambda_{\mathrm{Pb(II)}}$ for lithium borate, sodium borate, and potassium borate glasses calculated from published data.[13] The effect of changing the alkali metal ion for a given ratio is almost negligible for alkali metal oxide content less than 20%. At higher compositions, however, a small effect is apparent, the rate of increase in $\Lambda_{\mathrm{Pb(II)}}$ being in the order $Li^+ < Na^+ < K^+$, which is a result compatible with the order of decreasing polarizing power.

Data for the potassium aluminoborate glass in Table III show the effect of substituting in potassium borate glass (i) some of the potassium ions and (ii) some of the boron(III) ions, with aluminum(III) ions. On going from K_2O–B_2O_3 (30.5:69.5) glass to K_2O–Al_2O_3–B_2O_3 (15.4:15.4:69.2) glass, there is a decrease in optical basicity (from 0.590 to 0.491), in accordance with the greater polarizing power of aluminum(III) ions compared with potassium ions. On the other hand, comparison of the potassium aluminoborate glass with K_2O–B_2O_3 (14.2:85.8) glass reveals an increase in optical basicity (from 0.465 to 0491) on replacing some of the boron(III) ions by aluminum(III) ions, a result which indicates that aluminum(III) is less effective in reducing the basicity of oxide than is boron(III).

Further data in Table III show how substituting calcium ions for sodium ions in a silicate glass brings about only a small decrease in optical basicity. In going from Na_2O–SiO_2 (30:70) glass to Na_2O–CaO–SiO_2 (20:10:70) glass, $\Lambda_{\mathrm{Pv(II)}}$ falls by 0.02 unit. Such a small decrease would be expected, since calcium ions bear very much more resemblance to alkali metal ions than they do to, say, aluminum(III) ions.

Optical Basicity and the Lux–Flood Concept. According to the Lux–Flood concept[5] of basicity, a base is defined as an oxide donor and an acid as an oxide acceptor. For example, the well-known basic properties of the carbonate ion are expressed by the equilibrium

$$\underset{\text{base}}{CO_3^{2-}} \rightleftharpoons \underset{\substack{\text{conjugate}\\ \text{acid}}}{CO_2} + O^{2-}$$

In the application of this concept, it has been customary to set up scales of pO^{2-} (*i.e.*, $-\log a_{O^{2-}}$) which replace the pH scale used in aqueous solution chemistry. This approach has had some success, but only in certain restricted situations. Thus, in molten alkali metal carbonates, an empirical scale of pO^{2-} was established[17] by assuming ideal dilute solution behavior and by equating $a_{O^{2-}}$ with the molarity of added alkali metal oxide. In the silicate systems of interest (*ca.* 25% alkali oxide), such an approach is not possible, since the solutions depart from ideality. It is necessary therefore to choose another standard state for the "oxide ion"; different workers have chosen[18] either pure alkali oxide or a sodium silicate reference glass. However, it was pointed out as long ago as 1929 by Guggenheim[19] that *single ion* activities cannot be defined as such, and therefore cannot be unambiguously measured. It is perhaps permissible to equate $a_{O^{2-}}$ with a_{Na_2O} in a simple binary system (*e.g.*, in Na_2O–SiO_2 or in Na_2O–B_2O_3), but the procedure is much less satisfactory in multicomponent mixtures. For example, in the Na_2O–CaO–SiO_2 system it is not possible to say whether "$a_{O^{2-}}$" should be taken as a_{Na_2O} or as ($a_{CaO} + a_{Na_2O}$), and indeed $a_{O^{2-}}$ has no real meaning. From these considerations, it is apparent that no universal scale of pO^{2-} can ever exist.

In order to evaluate the significance of a scale of basicity for oxyanion media, it is a prerequisite that the meaning of basicity should be defined. In most systems of practical interest, *e.g.*, silicate, phosphate, and borate slags and glasses, the dinegative oxide ion is not present as a discrete entity. To quote Flood and Förland,[5] " the characteristic process of acid–base reactions will then be the transfer of an oxygen ion from one state of polarization to another." Three examples of such reactions are given below.

$$CO_2(g) + O^{2-}(\text{solvated}) \rightleftharpoons CO_3^{2-}(\text{solvated}) \qquad (I)$$

$$\underset{\text{octahedral}}{Co^{2+}} + 4O^{2-}(\text{solvated}) \rightleftharpoons \underset{\text{tetrahedral}}{[CoO_4]^{6-}(\text{solvated})} \qquad (II)$$

$$\underset{\text{octahedral}}{Cr^{3+}(\text{solvated})} + 4O^{2-}(\text{solvated}) - 3e^- \rightleftharpoons [CrO_4]^{2-}(\text{solvated}) \qquad (III)$$

All of these reactions have previously been used to provide indicators of basicity in melts and glasses.[20] It is important to note that each reaction involves the transfer of polarizable oxide ions to the acidic solute with the formation of oxyanion species. This can be taken as the *operational criterion* of melt basicity.

The optical basicity measures the formation of covalent bonds between the probe ion and the "oxide" ions in the solvent, and hence is directly related to incipient oxyanion formation. Optical basicity is thus identical with the concept of basicity as it is generally understood, but, in contrast to pO^{2-} data, it provides, in principle, universal scales which enable quantitative comparisons to be made among all oxyanion systems. Nevertheless, it should be borne in mind that the optical basicity value is not an invariant property of the medium but can depend upon the acidity of the probe ion (as seen for bismuth(III) for example).

Optical Basicity and Protonic Systems. Concentrated sulfuric acid is such a powerful acid in the Brønsted–Lowry sense that its basic properties, in the Lewis sense, are often overlooked. The crystal-field and electron-transfer spectra of solutions of metal ions dissolved in concentrated sulfuric acid,[21,22] however, show that this medium does exhibit significant Lewis-base behavior. The optical basicity scale allows comparisons of Lewis basicity to be made with other oxyacids and also with neutral (Brønsted–Lowry sense) salts. The Lewis basicity of an oxyacid would be expected to be less than that of its "neutral" salts, provided that the cation constituent of the salt is less polarizing than the proton. Trends in optical basicity for the three sulfate media and the two phosphate media in Table IV indicate that this effect is indeed found.

Table IV. Optical Basicities of Protonic and Nonprotonic Oxyanion Media

Medium	Acidity function, H_0	Optical basicity[a] $\Lambda_{Pb(II)}$	$\Lambda_{Bi(III)}$	$\Lambda_{Tl(I)}$
K_2SO_4–$ZnSO_4$ (40:60) glass		0.455	0.465	0.46
$NaHSO_4$–$KHSO_4$ (50:50) glass	−1 to −2[b]	0.416	0.434	0.41
97% H_2SO_4	−10[c]	0.332	0.434	0.34
$NaPO_3$ glass		0.457	0.465	0.45
100% H_3PO_4	−5[d]	0.404	0.382	0.39

[a] Optical basicities are calculated from data in ref 12 and 14. [b] Values of H_0 are taken from M. D. Ingram, J. A. Duffy, and S. M. Forbes, *J. Appl. Electrochem.*, **1**, 53 (1971). [b] Values of H_0 from ref 1. [c] Values of H_0 from A. I. Gel'bshtein, G. C. Shcheglova, and M. I. Temkin, *Dokl. Akad. Nauk SSSR*, **107**, 108 (1956).

(The value on the bismuth(III) scale for sulfuric acid—and possibly for the $NaHSO_4$–$KHSO_4$ glass—probably again indicates some choice of site in the medium.)

Optical Basicity and Electronegativity. Optical basicity represents the extent of electron donation by a ligand in a coordinate bond, and therefore should be related in some way to the electronegativity difference between central atom and ligand. For halogeno complexes, this electronegativity difference, expressed in terms of optical electronegativity χ_{opt}, has been related to the frequency of the first Laporte-allowed electron-transfer band (which involves the transition of an electron from the halide ligand to the central atom) by the equation[23]

$$\nu_{\text{corrected}} = 30{,}000[\chi_{opt}(\text{ligand}) - \chi_{opt}(\text{central atom})]$$

where $\nu_{\text{corrected}}$ is the frequency of the band after cor-

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(23) C. K. Jørgensen, "Orbitals in Atoms and Molecules," Academic Press, New York, N. Y., 1962, p 95.

rection for spin-pairing or crystal-field effects. The proportionality factor of 30,000 was chosen so that χ_{opt} for each halide becomes the same numerically as the Pauling electronegativity. Values of χ_{opt} for halide and other ligands are given in Table V.

Table V. Pauling Electronegativities and Jørgensen Optical Electronegativities of Some Common Ligands

Ligand	Optical electronegativity	Pauling electronegativity
Fluoride	4.0	4.0
Oxide	3.4–3.6[a]	3.5
Phosphate	3.3[b]	
Sulfate	3.1	
Chloride	3.0	3.0
Bromide	2.8	2.8
Iodide	2.5	2.5

[a] Based on data for first-row transitional elements taken from ref 23. [b] J. A. Duffy, unpublished results.

The assumption that the interaction between ligands and a given metal ion becomes less ionic and more covalent as the optical electronegativity of the ligand decreases may hold for the halides, but as a general principle it is false. For example, we have seen how the pressence of sulfur(VI) reduces markedly the extent of electron donation of oxide (the optical basicity falls from unity to 0.46 in K_2SO_4–$ZnSO_4$ glass), and yet the optical electronegativity of sulfate is considerably lower than that of oxide (χ_{opt} = 3.1 and 3.5, respectively). Furthermore, in comparing sulfate with chloride, although their optical electronegativities are close (3.1 and 3.0, respectively), it has been shown[14] that the environment provided by sulfate ligands is significantly more ionic than that provided by chloride. At the "ionic end" of the ionic–covalent interaction scale, it would seem that spectral measurements which can be related to spectral data for the free metal ion (as for Tl^+, Pb^{2+}, and Bi^{3+}, for example) are a more reliable guide for indicating the degree of covalent character than are data based upon electron-transfer spectra.

Nevertheless, some electron-transfer data can be rationalized by referring to optical basicity. Many metal ions in oxyanion glasses exhibit strongly absorbing bands in the uv, and the first Laport-allowed transition usually involves electron transfer from the oxyanion of the glass to the metal ion. This has been shown for di- and tripositive transition metal ions in sulfate and phosphate glasses, for example.[22] On the other hand, if the oxidation state of the metal ion is high, as in chromium(VI), for example, electron transfer to the metal ion will be from oxide rather than from the oxyanion of the glass, since only oxide ligands will be present in the coordination sphere. These two electron-transfer processes depend not only upon the oxidation state of the metal ion, but also upon the Lewis basicity of the medium, since a high Lewis basicity will favor oxyanion formation for the probe metal ion. The situation is exemplified by vanadium(V), which, in $NaHSO_4$–$KHSO_4$ glass, has the first Laport-allowed band at 28,400 cm^{-1}, but in K_2SO_4–$ZnSO_4$ glass, has it at 37,200 cm^{-1}.[22] Arguments based upon optical electronegativity indicate that in the former glass there are sulfate ligands in the coordination sphere of the vanadium, but in the latter glass, which has a greater optical basicity (Table IV), all the ligands in the coordination sphere are oxide.

Scales for Other Systems. The concept of Lewis basicity has wide applicability, and the study of its variation within a given system extends to systems other than the oxide media considered above. For example, in molten alkali metal chlorides the basicity can be reduced by adding polarizing cations such as aluminum(III). This has been demonstrated in a qualitative manner by following the change from tetrahedral to octahedral coordination of Co^{2+} and Ni^{2+} (detected from d–d spectra) as the concentration of polarizing cation is increased.[24] The effects of these polarizing cations on the Lewis basicity of the chloride ions in the melt are analogous to the polarizing effects just discussed for the oxide system, and it is possible to express them quantitatively in terms of optical basicity.

In setting up the optical basicity scale for molten chlorides, the optical range for the $^3P_1 \leftarrow {}^1S_0$ transition of the probe ion will extend from the (corrected) free ion frequency (ν_f in Table II) to the frequency where the probe ion experiences the maximum Lewis basicity of the chloride environment. This environment may be chosen as the one provided by sites in alkali metal chloride crystals, though since we are considering the molten state, it is more realistic to refer to a molten alkali metal chloride eutectic, such as the LiCl–KCl (41 mol % KCl) melt at 440°, spectral data for which are given in Table VI. (Spectral data for the crystalline state[25] and for the melt differ only slightly.) The optical basicity of a chloride melt of a particular composition is then defined as

$$\Lambda_{Pb(II)}(\text{chloride}) = (60{,}700 - \nu)/24{,}500$$

$$\Lambda_{Bi(III)}(\text{chloride}) = (56{,}000 - \nu)/25{,}800$$

$$\Lambda_{Tl(I)}(\text{chloride}) = (55{,}300 - \nu)/14{,}800$$

where ν is the frequency of the $^3P_1 \leftarrow {}^1S_0$ transition for the probe ion in the melt. Scales for fluoride, bromide, and iodide melts could similarly be established.

Spectral data for Tl^+, Pb^{2+}, and Bi^{3+} in molten metal halides are at present very sparse, but sufficient exist for examining the effect of aluminum(III) ions in chloride melts (Table VI). On going from the LiCl–KCl (41 % KCl) melt to the NaCl–$AlCl_3$ (67 % $AlCl_3$) melt, the optical basicity falls from unity to 0.87 (the lead(II) and bismuth(III) values agree well; unfortunately, there are no data available for thallium(I)). This result indicates, by comparison with optical basicity data in the oxide system (Table III), that the chloride ion is much less polarizable than the (dinegative) oxide ion. The effect of increasing temperature on basicity can also be observed (Table VI) and is seen to result in only a small increase in Λ values. Whether this increase in Λ is brought about by an increase in covalency in the bonding between chloride and probe ion or results from increased ionicity in the interaction between the alkali metal cations and halide anions is difficult to decide on the basis of the present data. The changes in ionic–covalent character of chemical bonding brought about by temperature are very much open to discussion among molten salts chemists;[26] it would seem a worthwhile ex-

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Table VI. Optical Basicity Data in Molten Chloride Systems[a]

System		Pb^{2+}		Bi^{3+}		Tl^{+}	
		ν	$\Lambda_{Pb(II)}$	ν	$\Lambda_{Bi(III)}$	ν	$\Lambda_{Tl(I)}$
LiCl-KCl (41% KCl)	440° [b]	36,200	1.000	30,200	1.000	40,500	1.000
	640° [b]	35,800	1.018	29,800	1.017	40,100	1.028
NaCl-$AlCl_3$ (67% $AlCl_3$)	250° [c]	39,500	0.865	33,600	0.867		

[a] Frequencies in cm^{-1}. [b] Frequencies of the $^3P_1 \leftarrow {}^1S_0$ transition (ν) are taken from ref 27. [c] Frequencies of the $^3P_1 \leftarrow {}^1S_0$ transition are from G. P. Smith and C. R. Boston, personal communication.

periment to choose a melt where changes in ionic–covalent interaction are monitored not only by the probe cation but also by the bulk cation (manganese(II) is an obvious example).

The comparison in Lewis basicity between one halide melt and another (*e.g.*, a chloride melt and a bromide melt) cannot be made on the basis of optical basicity. From the definitions of Λ given above, it is apparent that in terms of Jørgensen's *h* function, the optical basicity of the medium is given by h'/h, where h and h' refer to a *single* monatomic anion in its unpolarized and polarized states, respectively. Whether Lewis basicity is truly represented by the *h* function when the latter is measured for media having no common anion is not certain.

In this discussion no consideration has been given to possible changes in stereochemistry of the probe ion. It is well known that in halide melts and in oxyanion melts and glasses, certain metal ions undergo major changes in stereochemistry as the composition of the medium is altered, for example, Co^{2+} and Ni^{2+} mentioned above. Changes in the stereochemistry of Tl^+, Pb^{2+}, and Bi^{3+} are difficult to detect from optical spectroscopy[27] (though severe departure from cubic symmetry would usually split the $^3P_1 \leftarrow {}^1S_0$ band), and it is not possible to say whether the probe ions undergo marked changes in stereochemistry in any of the systems studied here. An investigation of the effect of stereochemical changes on the probing properties of $d^{10}s^2$ cations might be possible with tin(II) and antimony(III) in conjunction with Mössbauer spectroscopy. However, it is doubtful if the effect of basicity change can ever adequately be separated from changes in coordination number. Thus, coordination number is known to be very dependent on basicity (see above), and it is very difficult to interpret shifts in s–p spectra so as to distinguish between the effect of stereochemical change and the effect of changing basicity which is synergic with it.

The development of new spectroscopic techniques to extend the data on ionic interactions in glasses and melts could provide a useful extension to the optical basicity scales. Thus, preliminary experiments using esca have been performed and appear to be promising.

Experimental Section

Sodium borate glasses were prepared from mixtures of AnalaR anhydrous sodium carbonate and boric acid or borax. They were doped by adding to the mixture aqueous solutions of Tl_2CO_3, $Pb(NO_3)_2$, and $Bi(NO_3)_3$. The batches were heated at 900° in a platinum crucible for 2 hr and quenched to a glass (water cooling.) The ultrahigh alkali borate glasses were heated in alumina crucibles for 0.75 hr; buttons of the melt, obtained by pouring on to a brass block, were pressed to give glass plates of thickness 0.3–0.5 mm. Spectra were recorded on a Unicam SP700C instrument.

Acknowledgment. The authors are grateful to Drs. G. P. Smith and C. R. Boston for communicating their hitherto unpublished spectral data in molten NaCl–$AlCl_3$.

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