AN INTERPRETATION OF GLASS CHEMISTRY IN TERMS OF THE OPTICAL BASICITY CONCEPT

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The basicity of an oxide glass can be measured experimentally from the frequency shifts in the ultra-violet (UV) (s–p) spectra of probe ions such as Pb^{2+} and can be expressed on the numerical scale of *optical basicity* Λ (ideally Λ lies between zero and unity). It is possible to relate Λ with (i) the constitution, and (ii) the electronegativity of the cations (e.g. Na^+, Si^{4+}, etc.) of the glass, and the relationship allows *microscopic optical basicities* λ to be assigned to individual oxides and oxy-groups in the glass. These microscopic optical basicities are used for interpreting various aspects of the physics and chemistry of glass including refractivity, network coordination number changes, chemical durability, the glass electrode, UV transparency and the host behaviour of glass towards metal ions generally. Changes in glass basicity in going from one alkali metal oxide to another are also discussed. Finally, the concept of optical basicity, both as an experimentally obtained quantity and as a number calculated from glass constitution and electronegativity, is discussed in relation to the traditional approach to acid–base behaviour in glass.

1. Introduction

Commercially important glasses consist essentially of metal silicates, often with smaller quantities of phosphate, borate and other anions, and through the ability of the silicon, phosphorus and boron to form bridges with oxygen, these oxyanions exist largely as chains or networks. The formation of oxyanion glasses can be envisaged in terms of the reaction between a metal oxide (e.g. Na_2O, CaO, etc.) and an acidic oxide (e.g. SiO_2, B_2O_3, etc.), and because of the wide range of compositions attainable, products of varying degree of acidity and basicity can be obtained. The basic nature of the oxygen atoms is an important feature and has a profound bearing on the physics and chemistry of the glass. The measurement of basicity in a glass is not straightforward. Indeed, the term "basicity" is open to a number of interpretations, but in the context of this paper it refers to the "state" of the oxygen atoms and how they would react, for example, to the acid action of solute metal ions. According to this viewpoint, addition of a small concentration of a solute metal ion to a glass results in the oxygens of the glass donating some of their negative charge to the metal

ion. The oxygens behave as bases in the Lewis sense and correspondingly the metal ions behave as Lewis acids.

The ability of oxygen to donate negative charge is at a maximum when it exists as the "free" O^{2-} ion uninfluenced by surrounding cations; this situation is approached when the cations are almost non-polarizing, for example Na^+, K^+ or Ca^{2+}. When oxygen is attached to atoms such as silicon, as in terminal Si—O or bridging Si—O—Si units, its basicity is much less. A convenient way of regarding this lowering of the basicity is to envisage the oxygens in the Si—O or Si—O—Si units still as O^{2-} ions but influenced by their interaction with the highly polarizing Si^{4+} ion. In the terminal Si—O unit it is influenced by one Si^{4+} ion, while in the Si—O—Si unit it is influenced by two. The polarization of O^{2-} results in negative charge being drawn off the ion (i.e. covalent bond formation), and the oxygen is therefore less able to donate charge to a solute metal ion, i.e. it is less able to function as a Lewis base. The overall basicity of a glass containing both bridging and non-bridging oxides will depend upon the relative proportion of these two types of oxygen, and this will also determine the total electron donation to the solute metal ion.

Certain metal ions undergo observable changes (e.g. a colour change or a change of oxidation state) depending upon the degree of electron donation they receive from the oxygens, and therefore may be used as "probes" for basicity in glasses. One of the earliest studies of glass basicity using a metal probe ion was by Weyl and Thümen [1] in 1933 who exploited the Cr(III)/Cr(VI) equilibrium. Other examples of metal ion probes are the cobalt(II) ion (which undergoes an octahedral—tetrahedral change in stereochemistry at a critical basicity) and chromium(VI) (which changes from a dichromate species to CrO_4^{2-}) — see below.

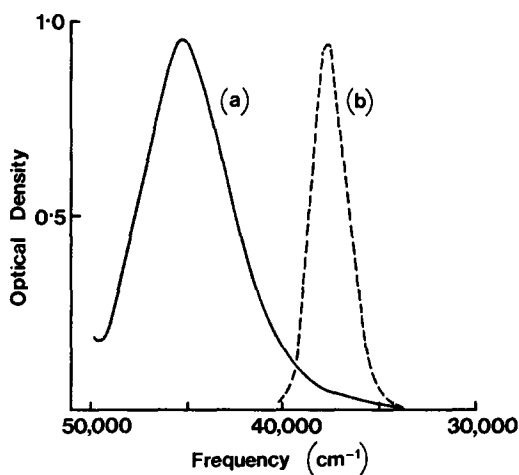All of these indicator ions suffer from the disadvantage that their use is necessar-

Fig. 1. (a) Absorption spectrum of Pb^{2+} in sodium borate (20% Na_2O) glass ($[Pb^{2+}]$ = 0.00113 M, path length 1.50 mm); spectrum (b) of Pb^{2+} in 11 M HCl is given for comparison.

ily limited to the one narrow region of basicity at which the critical change in the metal ion occurs. Their action is analogous to the colour change of, for example, methyl orange or litmus in aqueous acid—base equilibria. Furthermore, the way in which they signify a change in basicity is indirect and often depends upon specific conditions such as the O_2 partial pressure of the atmosphere in which the glass was melted. A more satisfactory type of probe ion is one which responds in a direct and, more importantly, a gradual manner to changes in glass basicity. Recently, it has become apparent that probe ions which respond in this way are p-block metal ions in oxidation states two units less than the number of the group to which they belong, e.g. Tl^+ (group III), Pb^{2+} (group IV), Bi^{3+} (group V). The electronic configurations of these metal ions is such that there is a pair of electrons in the outermost (6s) orbital, and when small concentrations of the ions are dissolved in glass, the 6s → 6p electronic transition gives rise to an intensely absorbing ultraviolet (UV) band, usually with a sharp maximum. A typical absorption spectrum is shown in fig. 1 for the Pb^{2+} ion in a borate glass and it can be compared with the corresponding spectrum for the chloro complex of lead(II) in hydrochloric acid. The absorption band is rather more broad in the glass, but in view of the enormous frequency shifts which changes in basicity can produce in these p-block metal ions, it is apparent that the probe ions tend to select closely similar sites rather than seek out a wide range of different sites *. Spectral measurements [4—7] of Tl^+, Pb^{2+} and Bi^{3+} in glasses have shown that the frequency of the absorption band is dramatically lowered by increased basicity of the glass, and the reason for this appears to be due to orbital expansion effects within the probe ion brought about by electron donation by the oxygens. This effect, known as the "nephelauxetic" effect, is well known in inorganic spectroscopy and is understood in sophisticated terms largely as a result of the pioneering studies of Jørgensen [8] during the 1950s and 1960s. Jørgensen's studies were concerned essentially with transition metal ions, but it has been shown that the nephelauxetic effect for p-block metal ions is fundamentally linked to that for transition metal ions [9,10].

To understand the spectroscopic shifts of p-block metal ions in their response to basicity and to appreciate how the orbital expansion comes about, it is necessary to view the interaction between the p-block metal ion and surrounding oxygens in terms of the molecular orbital theory. This has been discussed by the present authors in ref. [11]. (Incidentally, it is important to be aware that arguments based upon valence bond theory and orbital hybridization are inappropriate.) However, in simple terms, the decrease in frequency of the 6s → 6p transition can be thought of as a consequence of the covalency effect in which the electrons received from the oxygens are accommodated in σ and π bonding molecular orbitals [11]; some of this electron density is located between the inner electron core of the metal ion and its 6s orbital. This is shown schematically for the Pb^{2+} ion in fig. 2. One of the factors affecting the energy of the 6s → 6p process is the force of attraction that the 6s electron exper-

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* The converse sometimes occurs, as for instance in bromide—sulphate glasses [2] or in alkali borate glasses at elevated temperatures [3].
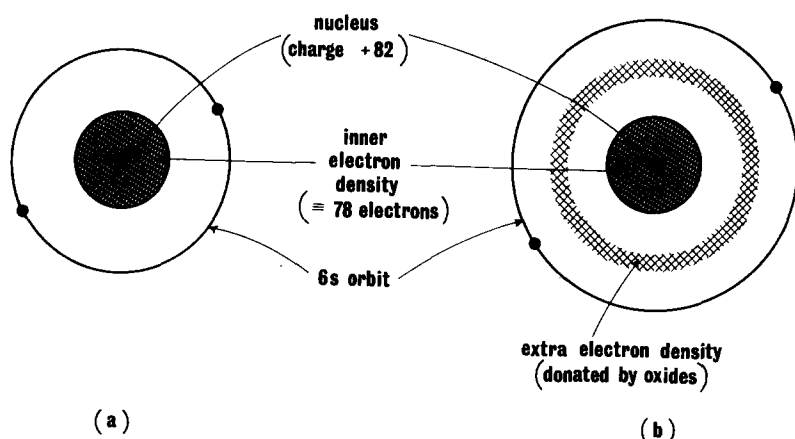
Fig. 2. Schematic diagram of (a) free Pb^{2+} ion, and (b) Pb^{2+} ion after receiving negative charge from neighbouring oxide ions.

iences from the nucleus. Much of the positive pull of the nucleus is screened by the inner electron core, but the electron density donated by the oxygens serves to increase this screening further and this in turn allows the 6s electron to escape more easily to the 6p level (even though the 6p level is also screened). Electron donation by the oxygens to the probe ion therefore brings about a reduction in the 6s − 6p energy difference, and therefore a reduction in frequency in the UV absorption band, compared with the free Pb^{2+} ion.

The question now arises as to what is meant by the free Pb^{2+} ion shown in fig. 2. The free Pb^{2+} ion is in fact only a hypothetical entity, but its properties may be calculated by extrapolation of the linear relationship between measured spectroscopic shifts and orbital expansion parameters for various ligand environments [9]. It is assumed that when the orbital expansion parameters of the ligands are extrapolated to zero, then the "electron donating ability" of the ligands is zero also; in effect they are able to provide an "unperturbing" environment for free Pb^{2+} ions. The extrapolated value of the $^1S_0 \rightarrow {}^3P_1$ transition (which represents the energy difference corresponding to the 6s → 6p process) for Pb^{2+} is found to be 60 700 cm^{-1}, and this will be referred to subsequently as $\nu_{\text{free ion}}$ [9]. It is worth noting that it is close to the experimentally determined value (64 390 cm^{-1}) for Pb^{2+} ions observed in gas discharges.

1.1. Optical basicity

The spectroscopic shifts observed in the $^1S_0 \rightarrow {}^3P_1$ bands of Tl^+, Pb^{2+} and Bi^{3+} have been used by us for setting up scales of basicity [5]. However, most data have been obtained for the Pb^{2+} ion and we shall centre our attention upon this ion. For Pb^{2+}, $\nu_{\text{free ion}}$ is 60 700 cm^{-1} (see above) and $\nu_{O^{2-}}$, the frequency of Pb^{2+} in an

"ionic" oxide, is 29 700 cm^{-1}. Thus on going from the unperturbed Pb^{2+} ion to the situation where the Pb^{2+} ion receives the electron density from free oxides, there is an enormous spectroscopic shift of 31 000 cm^{-1}. The frequency of 29 700 cm^{-1} is that for Pb^{2+} in CaO *, and no doubt if some other metal oxide, e.g. Na$_2$O or K$_2$O, were chosen for providing an environment of free oxides for Pb^{2+} a slightly different (and lower) frequency would be obtained, leading to a shift of even greater than 31 000 cm^{-1}. However, since an environment containing ideally ionic oxide ions certainly does not exist, the choice of metal oxide is necessarily arbitrary (see fig. 3).

When the probe ion is influenced by the less basic oxides of a glass, the frequency shift is somewhat less. For example in CaO–P$_2$O$_5$ (1 : 1) glass the frequency of Pb^{2+} is 46 200 cm^{-1} while in Na$_2$O–SiO$_2$ (3 : 7) glass it is 42 200 cm^{-1}, corresponding to shifts of 14 500 and 18 500 cm^{-1}, resepctively. The spectroscopic shift represents the electron donor power of the oxides in the glass, and for comparing oxide glasses with each other it is convenient to express the basicity as the ratio of the electron donor power of oxides in the glass to the electron donor power of free oxide ions. This ratio is derived *entirely* from spectroscopic measurements and accordingly the glass basicity has been termed [5] "optical" basicity Λ. Using Pb^{2+} as the probe ion:

$$\Lambda_{Pb(II)} = \frac{\nu_{free\ ion} - \nu_{glass}}{\nu_{free\ ion} - \nu_{O^{2-}}} = \frac{\Delta\nu_{glass}}{\Delta\nu_{O^{2-}}} = \frac{\Delta\nu_{glass}}{31\ 000}, \tag{1}$$

where ν_{glass} is the frequency of the Pb^{2+} ion in the glass under investigation. By definition, $\Lambda_{Pb(II)}$(CaO) is unity.

In terms of specific examples, spectroscopic shifts ($\Delta\nu_{glass}$) yield optical basicities, $\Lambda_{Pb(II)}$ as follows: CaO $-$ P$_2$O$_5$ (1 : 1) glass, $\Delta\nu_{glass}$ = (60 700 $-$ 46 200) and $\Lambda_{Pb(II)}$ = 0.47; Na$_2$O $-$ SiO$_2$ (3 : 7) glass, $\Delta\nu_{glass}$ = (60 700 $-$ 42 200) and $\Lambda_{Pb(II)}$ = 0.60.

Although most optical basicity data have been obtained using Pb^{2+} as a probe ion, Tl$^+$ and Bi^{3+} have also been used, and the agreement between the values obtained using the three ions has been found to be good [5,12]. With these ions, the optical basicities are calculated as follows [5]:

$$\Lambda_{Tl(I)} = (55\ 300 - \nu_{glass})/18\ 300, \tag{2}$$

$$\Lambda_{Bi(III)} = (56\ 000 - \nu_{glass})/28\ 800. \tag{3}$$

1.2. Experimental

In the practical determination of optical basicity, the fragments of glass for spectroscopic examination need be only a few millimetres in cross-section; they are

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* The introduction of Pb^{2+} ions into an ionic metal oxide such as CaO may at first sight be expected to produce a lead—oxygen interaction which is predominantly ionic. However, such an expectation does not take account of the enormous polarizability of which the so-called "hard" oxide ion is capable.

mounted over a 3–4 mm dia. aperture of a mask that is placed in the light beam of the spectrophotometer (the reference beam being similarly attenuated). It is best to cast the glass with a path length of ≈ 1 mm (for which a probe ion concentration of $\approx 10^{-3}$ M is appropriate) to keep the absorbance of the glass as low as possible. If the glass itself absorbs significantly in the region of the probe ion absorption band, then it is necessary to correct the absorption using the spectrum of the undoped glass (of the same path length). The frequency of the absorption maximum can usually be determined to within ± 50 cm^{-1} (or sometimes better) and this corresponds to ± 0.001 unit of optical basicity. For obtaining the optical basicity of a number of glasses, the "platinum loop" technique of Easteal and Udy [7] is very useful.

At higher frequency than the $^1S_0 \rightarrow {}^3P_1$ band is also the $^1S_0 \rightarrow {}^1P_1$ band. The latter band is approximately five times more intense than the former and occasionally slight overlapping results in the requirement for a correction in frequency of the $^1S_0 \rightarrow {}^3P_1$ band; this correction is usually quite small (≈ 100 cm^{-1}).

1.3. Theoretical prediction of basicity values

Let us develop further the idea that the oxygen atoms in, say, CaO–P$_2$O$_5$ (1 : 1) glass are oxide ions influenced very strongly by the P^{5+} cations and less strongly by the Ca^{2+} cations in the glass. In this particular glass, the Ca^{2+} ions neutralize one-sixth of the negative charge of the oxide while the P^{5+} ions neutralize five-sixths. The lowering of the electron donor power of the oxides by the Ca^{2+} and P^{5+} ions [which corresponds to a frequency difference of (46 200–29 700) cm^{-1}, fig. 3] might be expected to be due to (i) the proportion of negative charge each cation neutralizes, and (ii) some polarizing or electron-attracting property of each cation. This latter property can be evaluated from experimental spectroscopic shifts and is known as the "basicity moderating power" γ [13,14]. This parameter appears to have fundamental significance, and indeed has been shown to be related to the Pauling electronegativity x by the equation $\gamma = 1.36 (x - 0.26)$.
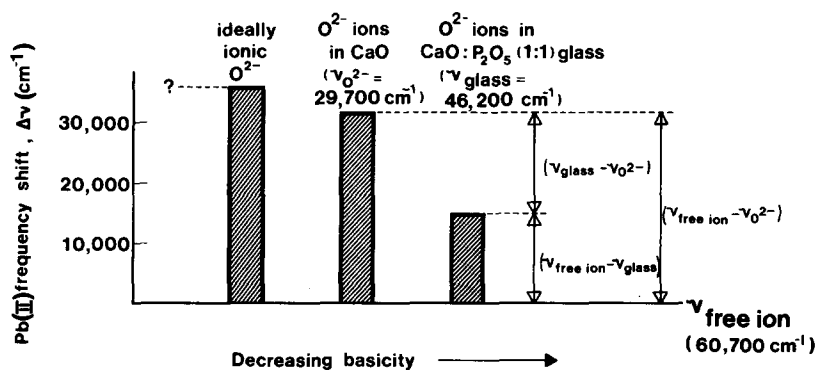

Fig. 3. Pictorial representation of electron donor power (height of shaded column = $\Delta\nu$) of oxide under various conditions. The frequencies are those registered by Pb^{2+} probe ions in sensing these basicities.

From the manner in which the basicity moderating parameters have been evaluated, it is possible to express the contribution to the lowering of the electron donor power of oxide in $CaO-P_2O_5$ (1 : 1) glass by

(a) calcium ions as $(\nu_{\text{free ion}} - \nu_{O^{2-}}) \cdot \frac{1}{6}(1 - 1/\gamma_{Ca})$;

(b) phosphorus ions as $(\nu_{\text{free ion}} - \nu_{O^{2-}}) \cdot \frac{5}{6}(1 - 1/\gamma_P)$.

Thus the total effect produced by both cations corresponds to the frequency difference of

$$(\nu_{\text{free ion}} - \nu_{O^{2-}})\{\tfrac{1}{6}(1 - 1/\gamma_{Ca}) + \tfrac{5}{6}(1 - 1/\gamma_P)\},$$

experimentally this is equal to $(46\ 200 - 29\ 700)\ cm^{-1}$. Since, as discussed above, the oxide ions in CaO are regarded as free oxide ions with the optical basicity of CaO as unity, γ_{Ca} must be unity; on the other hand the cation P^{5+} is expected to be highly polarizing and so γ_P is expected to be considerably greater than unity. (The value of γ_P is in fact 2.50; γ-values for other elements are in table 1.)

For oxide glasses generally, the lowering of the electron donor power of the oxides, expressed in terms of the frequency shift in going from CaO to the glass is given by

$$(\nu_{\text{glass}} - \nu_{O^{2-}}) = (\nu_{\text{free ion}} - \nu_{O^{2-}})\{(z_A r_A/2)(1 - 1/\gamma_A) + (z_B r_B/2)(1 - 1/\gamma_B) + ...\},$$

where z_A, z_B ... are the oxidation numbers of the cations A, B ... and r_A, r_B... are their ionic ratios with respect to the total number of oxides. Dividing the equation by $(\nu_{\text{free ion}} - \nu_{O^{2-}})$ and replacing $(\nu_{\text{glass}} - \nu_{O^{2-}})$ by $\{(\nu_{\text{free ion}} - \nu_{O^{2-}}) - (\nu_{\text{free ion}} -$

Table 1
Basicity moderating parameters, γ.

Element	γ
chlorine	3.73
nitrogen	3.73
sulphur	3.04
carbon	3.04
phosphorus	2.50
hydrogen	2.50
boron	2.36
silicon	2.09
zinc	1.82
aluminum	1.65
magnesium	1.28
calcium	1.00
lithium	1.00
sodium	0.87
potassium	0.73
rubidium	0.73
caesium	0.60

Table 2
Formulae for evaluating ideal optical basicity of borate, silicate and phosphate glasses containing $x\%$ of alkali oxide (M_2O).

Glass	Λ [a]
borate (xM_2O: $(100-x)B_2O_3$	$\dfrac{x}{\gamma_M(300-2x)} + \dfrac{3(100-x)}{2.36\,(300-2x)}$
silicate (xM_2O: $(100-x)SiO_2$)	$\dfrac{x}{\gamma_M(200-x)} + \dfrac{2(100-x)}{2.09(200-x)}$
phosphate (xM_2O: $(100-x)P_2O_5$	$\dfrac{x}{\gamma_M(500-4x)} + \dfrac{5(100-x)}{2.50(500-4x)}$

[a] Basicity moderating parameters γ_M for the alkali metals are given in table 1.

ν_{glass})} (see fig. 3) yields on rearrangement *

$$\Lambda = 1 - \{(z_A r_A/2)(1 - 1/\gamma_A) + (z_B r_B/2)(1 - 1/\gamma_B) + ...\}. \tag{4}$$

This formula allows Λ to be calculated for any oxide glass from its chemical constitution and from the basicity moderating parameters of the various cations, e.g. Na^+, Si^{4+}, B^{3+}, etc., present in the glass and good agreement is found with experimental Λ values [13,14].

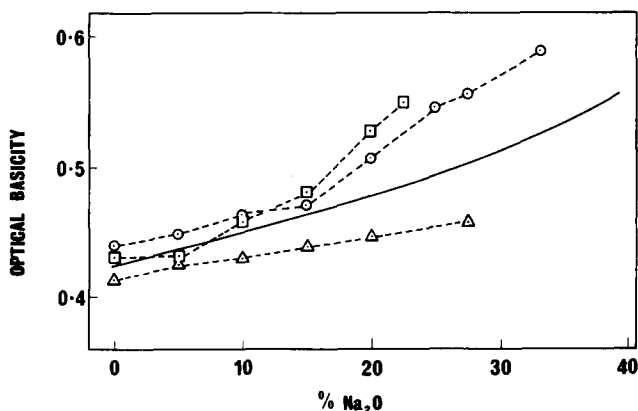The value of Λ obtained theoretically is an "ideal" optical basicity which is the

Fig. 4. Trend in ideal optical basicity in the $Na_2O-B_2O_3$ glass system (continuous line). Experimentally determined optical basicities are denoted: $\square$ Tl^+, $\odot$ Pb^{2+} and $\triangle$ Bi^{3+}.

* Equation (4) is presented rather than the simpler form [14]

$$\Lambda = (z_A r_A/2\gamma_A) + (z_B r_B/2\gamma_B) + ...$$

since the former is more versatile and enables the calculation of, for example, microscopic optical basicity values (see below).

average of all the oxides in the glass. It is possible to plot the trend in ideal optical basicity as the alkali content of a glass increases, and the appropriate formulae for borate, silicate and phosphate glasses are given in table 2 *. The trend for the $Na_2O-B_2O_3$ glass system is shown in fig. 4, together with experimental values of $\Lambda_{Tl(I)}$, $\Lambda_{Pb(II)}$ and $\Lambda_{Bi(III)}$. Up to about 16% Na_2O, agreement between experimental and ideal basicities is good, but with increasing Na_2O content there is increasing disagreement between the different experimental values. This unexpected effect has been discussed at length elsewhere [12,15,16]. We have suggested that the answer lies in the range of basicity values which is needed to characterize the sites present in a partially disrupted network glass, but phase separation may also be involved. It is interesting to note that $\Lambda_{Bi(III)}$ reflects most accurately the trend in ideal basicity.

1.4. Microscopic optical basicity, λ

As well as providing a means of calculating Λ for a bulk glass, eq. (4) makes it possible to calculate the *microscopic optical basicity* of individual oxygen atoms in any oxyanion unit.

Let us consider for example the oxygen atoms in the SiO_4^{4-} anion. We imagine first of all that there are no polarizing cations present other than the Si^{4+} ions, i.e. the other metal ions present are alkali or alkaline earth ions. Thus since there are four terminal oxides attached to each Si^{4+}, the Si : O ratio $r_{Si} = \frac{1}{4}$; therefore $z_{Si}r_{Si}/2 = (4 \times \frac{1}{4})/2 = \frac{1}{2}$. To distinguish microscopic basicity from bulk basicity, we replace Λ by λ, and eq. (4) yields $\lambda = 1 - \frac{1}{2}(1 - 1/\gamma)$. With $\gamma_{Si} = 2.09$ (see table 1), $\lambda = 0.74$.

If we now consider an oxide which, instead of being terminal, serves to bridge two silicons, the polarization effect on the oxide will be twice as great since it is being affected by two Si^{4+} ions. Eq. (4) now yields

$$\lambda = 1 - 2 \times \frac{1}{2}(1 - 1/\gamma_{Si})$$

and λ is therefore 0.48.

Now let us consider an oxide that bridges, say, a silicon and a (four-coordinated) aluminium. Again the oxide is affected by the Si^{4+} cation and r_{Si} equals $\frac{1}{4}$. However, the oxide is also affected by the Al^{3+} cation for which $r_{Al} = \frac{1}{4}$, $z_{Al} = 3$ and hence $z_{Al}r_{Al}/2 = \frac{3}{8}$. Thus, by eq. (5):

$$\lambda = 1 - \{\tfrac{1}{2}(1 - 1/\gamma_{Si}) + \tfrac{3}{8}(1 - 1/\gamma_{Al})\} ,$$

where $\gamma_{Si} = 2.09$ and $\gamma_{Al} = 1.65$ (table 1), and $\lambda = 0.59$. If the aluminium is six-co-ordinated instead of four-coordinated, $r_{Al} = \frac{1}{6}$, $z_{Al}r_{Al}/2 = \frac{1}{4}$, and $\lambda = 0.65$.

Table 3 gives values of λ for oxides in various bridging and non-bridging units encountered in oxide glasses. It should be noted that they were worked out on the as-

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* Strictly the values are for glasses in which the alkali is lithium; differences in basicity in going from one alkali metal to another are discussed later.

Table 3
Microscopic optical basicities (theoretical) λ for individual oxides in oxyanion networks, etc. [a].

Bridging or non-bridging oxide	Microscopic optical basicity λ [b]	
	three-coordinate boron	four-coordinate boron
B – O	0.71	0.78
B – O – B (3)	0.42	0.50
B – O – B (4)	0.50	0.57
B – O – Mg (6)	0.68	0.75
B – O – Al (4)	0.56	0.64
B – O – Al (6)	0.63	0.70
B – O – Si (4)	0.45	0.52
B – O – P (4)	0.34	0.41
B – O – H (1)	0.41	0.48
	four-coordinate silicon	
Si – O	0.74	
Si – O – Si (4)	0.48	
Si – O – B (3)	0.45	
Si – O – B (4)	0.52	
Si – O – Al (4)	0.59	
Si – O – Al (6)	0.65	
Si – O – P (4)	0.36	
Si – O – H (1)	0.44	
	four-coordinate phosphorus	
P – O	0.63	
P – O – P (4)	0.25	
P – O – Si (4)	0.36	
P – O – Al (4)	0.48	
P – O – Al (6)	0.54	
P – O – H (1)	0.32	
	four-coordinate aluminium	six-coordinate aluminium
Al – O	0.85	0.91
Al – O – Al (4)	0.70	0.77
Al – O – Al (6)	0.77	0.83
Al – O – H (1)	0.55	0.61

[a] Numbers in parentheses denote coordination numbers.
[b] It is assumed for the purpose of calculation that all coordination positions are similar (see text).

sumption that the basicity moderating parameter of the non-polarizing cations is unity. Owing to the necessity of having to choose calcium oxide as the environment providing free oxides for the Pb^{2+} probe ion (see above), the less electronegative alkali and alkaline earth ions will have basicity moderating parameters less than unity.

If these metal ions are present instead of Ca^{2+} or Li^+ ions, then many of the λ-values in table 3 will be increased. (This is usually not serious for Na^+, but might be for, say, Cs^+.) However, in this discussion we shall use λ-values mainly for comparing differences within one particular glass and not for comparing differences brought about by substituting one alkali or alkaline earth ion for another.

Easteal and Udy [7] have also recently proposed the assignment of λ-values to different groups in borate glasses. While acknowledging that their procedure for calculating these group basicities differs from ours, we feel it appropriate to use the symbol λ to cover all aspects of local basicity in glass.

1.5. Internal neutralization effects and group basicities

The optical basicity concept embodies the principle that reactions between acids and bases are those reactions which *tend towards the equalization of optical basicity.* Thus it follows that the reaction between $SiO_2(\Lambda = 0.48)$ and $Li_2O (\Lambda = 1.00)$ is a reaction between an acid and a base, because the product is a compound of intermediate basicity, e.g. $Li_4SiO_4 (\Lambda = 0.74)$.

Generally, it is not appropriate to regard a glass as a stoichiometric compound, and indeed the chemical and physical properties are greatly influenced by the variations in *microscopic* basicity. The principle of equalization of optical basicity still operates in favour of those chemical and physical processes which tend to smooth out variations in microscopic basicity. We are of the opinion that this principle is the key to an understanding of many aspects of glass chemistry (and will be useful even in glasses which are phase separated).

One immediate implication of the principle of equalization of microscopic basicity is that the crude microscopic basicities calculated in section 1.4 will have to be modified whenever more than one type of oxide is present in an oxyanion group. It is not clear to what extent the process of internal neutralization proceeds in such a "mixed" oxyanion, although the difference in bond lengths [17] in, for example, the SiO_4 unit of a metasilicate chain (fig. 5), where they are 1.68 and 1.57 Å for the bridging oxides and non-bridging oxides, respectively, suggest strongly that the extent of internal neutralization is only partial. For the isoelectronic series SiO_4^{4-}, PO_4^{3-}, SO_4^{2-}, ClO_4^-, the microscopic optical basicity appears to vary smoothly with bond length (fig. 6) and if one can use this relationship for estimating λ from bond
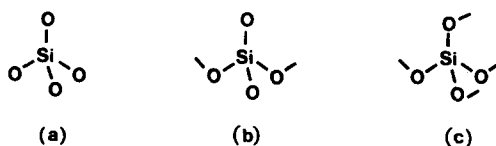

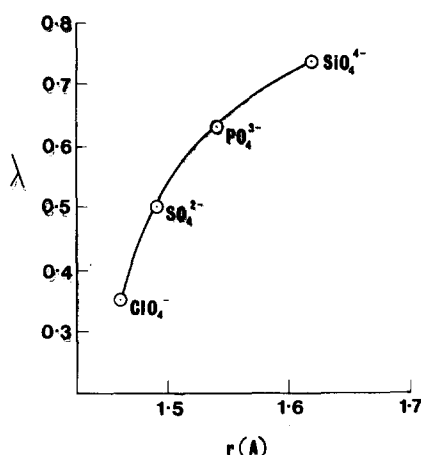Fig. 5. Groups representing the SiO_4 units of (a) orthosilicate ion, (b) metasilicate chain and (c) silica.

Fig. 6. Trend in microscopic optical basicity λ with bond length r, for an isoelectronic series of oxyanions. (Bond lengths from ref. [17].)

length, then, by interpolation, λ for a non-bridging oxide in metasilicate will be 0.68 (compared with 0.74 for non-bridging oxides in the orthosilicate anion). (Unfortunately, there are no data for the isoelectronic series SiO_2, PO_2^+, SO_2^{2+}, ClO_2^{3+}, and it is not possible to obtain λ for the bridging oxides in metasilicate.)

Thus it would seem that the microscopic basicity of an oxide in a mixed oxyanion unit lies between the value assigned on the basis of eq. (4) and the value if complete neutralization occurred within the oxyanion unit. This latter value is referred to as the *group basicity*, and is a very important parameter of a glass. As will be seen below, many properties can be explained by referring to the group basicity rather than the microscopic basicity of the individual oxides.

Group basicities can be evaluated using eq. (4) (we shall continue to distinguish from the bulk basicity, Λ, and to use the symbol λ for group basicity). Consider for example the tetrahedral SiO_4 units in fig. 5. For the group in fig. 5c, all four oxides are bridging, being attached to other silicon atoms. The central silicon, therefore, has a half share in four oxide ions and "owns" a total of two oxide ions; thus $r_{Si} = \frac{1}{2}$ and $z_{Si} r_{Si}/2 = 1$. Therefore $\lambda = [1 - 1(1 - 1/2.09)] = 0.48$. In the SiO_4 unit of fig. 5b two of the oxides are bridging and two are non-bridging, being terminal oxides. Thus the central silicon owns three oxide ions, and with $z_{Si} r_{Si}/2 = 2/3$, $\lambda = 0.65$. Similar considerations and the use of eq. (4) allow values of the group basicity to be calculated for other SiO_4 units (table 4). Table 4 also includes group basicity values for various PO_4, SO_4 and ClO_4 units, and the values that are in bold type in the table correspond to the unit that is present in the non-metal oxide, namely SiO_2, P_2O_5, SO_3 and Cl_2O_7. In phosphate and sulphate glasses, only those tetrahedral units having λ values to the right of those that are in bold type are normally encountered; for example, a PO_4 unit where all the oxides are bridging would only occur in a cationic PO_2^+ unit.
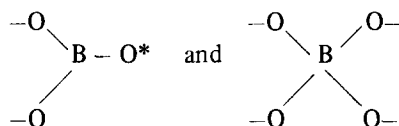
Table 4
Theoretical group basicities for tetrahedral oxy units [a].

	$\begin{matrix}-O\quad O-\\ \diagdown X \diagup \\ -O \diagup \diagdown O-\end{matrix}$	$\begin{matrix}-O\quad O*\\ \diagdown X \diagup \\ -O \diagup \diagdown O-\end{matrix}$	$\begin{matrix}-O\quad O*\\ \diagdown X \diagup \\ -O \diagup \diagdown O*\end{matrix}$	$\begin{matrix}*O\quad O*\\ \diagdown X \diagup \\ -O \diagup \diagdown O*\end{matrix}$	$\begin{matrix}*O\quad O*\\ \diagdown X \diagup \\ *O \diagup \diagdown O*\end{matrix}$
X = Si	**0.48** [b]	0.58	0.65	0.70	0.74
P	0.25	**0.40** [b]	0.50	0.57	0.63
S	0.00	0.19	**0.33** [b]	0.42	0.50
Cl	−0.28	−0.02	0.15	**0.27** [b]	0.36

[a] Bridging oxide denoted $-O'$ and terminal $-O*$.
[b] Numbers in bold type correspond to the neutral oxide; numbers to the right of these are for XO_4 units occurring in oxyanions, while those to the left are for XO_4 units occurring in (often imaginary) oxycations, e.g. PO_2^+.

Table 5 gives group λ-values for tetrahedral BO_4 units and trigonal BO_3 units. In the tetrahedral BO_4 units the assignment of the group basicity values is less straightforward. Thus it is surprising to see the same group basicity value $\lambda = 0.57$ being assigned to the

$$\begin{matrix} -O \\ \quad \diagdown \\ \qquad B - O* \quad \text{and} \quad \\ \diagup \\ -O \end{matrix} \qquad \begin{matrix} -O \qquad O- \\ \diagdown \quad \diagup \\ \quad B \\ \diagup \quad \diagdown \\ -O \qquad O- \end{matrix}$$

units, whereas chemical intuition suggests that the latter unit should be less basic than the former. The reason for this apparent anomaly is that in the terminally bonded oxygen all the "excess" negative charge is attached to one B^{3+} cation and the group is fairly well defined; in the tetrahedral boron atom, however, each *bridging* oxygen carries a formal charge of $-\frac{1}{4}$.

Table 5
Theoretical group basicities for three-coordinated and four-coordinated borate units [a].

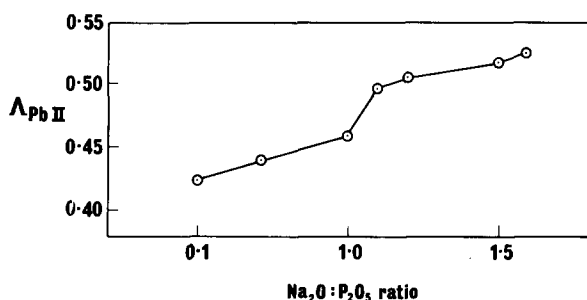| three-coordinated boron	$\begin{matrix}-O\\ \diagdown \\ \quad B-O \\ \diagup \\ -O\end{matrix}$	$\begin{matrix}-O\\ \diagdown \\ \quad B-O* \\ \diagup \\ -O\end{matrix}$	$\begin{matrix}*O\\ \diagdown \\ \quad B-O* \\ \diagup \\ -O\end{matrix}$	$\begin{matrix}*O\\ \diagdown \\ \quad B-O* \\ \diagup \\ *O\end{matrix}$	
	$\Lambda = 0.42$	0.57	0.65	0.71	
four-coordinated boron	$\begin{matrix}-O\quad O-\\ \diagdown B \diagup \\ -O \diagup \diagdown O-\end{matrix}$	$\begin{matrix}-O\quad O*\\ \diagdown B \diagup \\ -O \diagup \diagdown O-\end{matrix}$	$\begin{matrix}-O\quad O*\\ \diagdown B \diagup \\ -O \diagup \diagdown O*\end{matrix}$	$\begin{matrix}*O\quad O*\\ \diagdown B \diagup \\ -O \diagup \diagdown O*\end{matrix}$	$\begin{matrix}*O\quad O*\\ \diagdown B \diagup \\ *O \diagup \diagdown O*\end{matrix}$
	$\Lambda = 0.57$	0.65	0.71	0.75	0.78

[a] Bridging oxide denoted $-O'$ and terminal $-O*$.

Fig. 7. Plot of experimentally determined optical basicity, $\Lambda_{Pb(II)}$, versus $Na_2O : P_2O_5$ ratio in a sodium phosphate glass system.

As stated above, the amount of internal neutralization which actually occurs within the glass structure is difficult to quantify, but there are good grounds for thinking that the probe ions (e.g. Pb^{2+}) usually respond to group basicity rather than to microscopic basicity. This is seen for example in the $Na_2O-P_2O_5$ glass system where the basicity, as registered by Pb^{2+} ions, increases by 0.07 in the region of the metaphosphate (1 : 1) composition (fig. 7). Glasses more basic than $NaPO_3$ will contain a significant proportion of the terminal

$$
\begin{pmatrix}
& O^* & \\
& | & \\
-O - & P & - O^* \\
& | & \\
& O^* &
\end{pmatrix}
$$
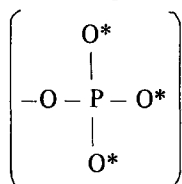
groups which will not be present in glasses less basic than $NaPO_3$. As can be seen from table 4, the introduction of these groups should introduce a jump in group basicity of 0.07 — in striking agreement with the measured rise in the experimental basicity.

2. Applications

2.1. Molar refractivity of O^{2-} ions

Reference must now be made to Weyl and Marboe's book [18] since a good deal of what follows is based on our reinterpretation of some of their ideas in terms of the optical basicity concept. Weyl and Marboe place great emphasis on the importance of the molar refractivity of the oxide ion $R_{O^{2-}}$ (usually expressed in $cm^3 \ mol^{-1}$). They attribute changes in the refractivity of oxide, which are caused by coordination of polarizing cations such as Al^{3+} and Si^{4+}, to a "tightening of its electron clouds". A close correlation between molar refractivity and optical basicity is therefore to be expected.
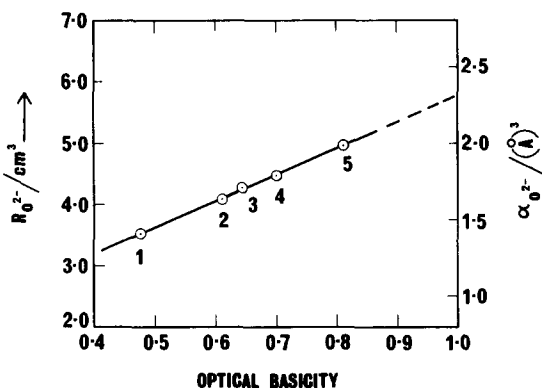
Fig. 8. Molar refractivity R and atomic polarizability α for various barium silicates (after Weyl and Marboe [18], p. 63) plotted against theoretical optical basicity [using eq. (4)] for: 1 SiO_2, 2 BaO : $2SiO_2$, 3 2BaO : $3SiO_2$, 4 BaO : SiO_2 and 5 2BaO : SiO_2.

Figure 8 shows molar refractivity data (from ref. [18], p.63) for a series of crystalline barium silicates plotted against values of Λ computed via eq. (4). The graph is a good straight line, and clearly an increase in $R_{O^{2-}}$ implies an increase in Λ. In terms of the data included in fig. 8

$$\Lambda = (R_{O^{2-}} - 1.5)/4.25 .\tag{5}$$

Weyl and Marboe emphasize that the molar refractivity values of the O^{2-} ions "are a summation over the responses of the electrons of all O^{2-} ions to an electrical field", and point out that "the molar refractivity cannot help us in structural problems that make it necessary to differentiate between the polarizabilities of individual O^{2-} ions". Furthermore, it was the opinion of the authors that there was no method for measuring the distribution of the values of $R_{O^{2-}}$ within a system. In order to overcome this limitation they visualized ([18], p. 342) a qualitative scheme such as that shown in fig. 9 which applies to a comparison of vitreous silica with
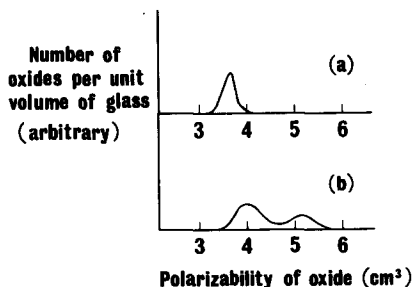

Fig. 9. Schematic diagram showing the polarizabilities of oxides in (a) vitreous silica, and (b) alkali silicate glass (after [18], p. 342).

vitreous alkali silicate. With such a scheme Weyl and Marboe were able to disregard the bulk molar refractivity of oxide in a glass and to account for various properties (e.g. chemical resistivity) in terms of distributions such as those in fig. 9b. Now with the relationship given by eq. (6), it is apparent that the qualitative scheme of Weyl and Marboe can be envisaged in terms of microscopic λ-values. The curve maximum in fig. 9a would correspond to a λ-value of 0.48. It should be observed that Weyl and Marboe anticipated a slight increase in $R_{O^{2-}}$ for the curve maximum of the bridging oxides in the system where terminal oxides were also present (fig. 9b) and this is in accordance with our anticipation of a slight increase in λ brought about by some degree of "internal neutralization" as argued earlier.

Through the Lorenz–Lorentz relationship between refractivity and polarizability, eq. (5) can be adapted to relate optical basicity to the polarizability of oxide ions in glass (or any other oxide-containing system). It is interesting that Tessman in his review [19] indicates a large spread of oxygen polarizability, and this is in accord with the correspondingly large spread of optical basicity. In principle, the polarizability of oxygen in a medium can be obtained from the optical basicity: often, polarizabilities are "guessed" (e.g. Dempsey's calculations on model zeolite crystals [20]).

2.2. Alkali metal oxyanion glasses

Changing from one alkali metal to another in a glass can produce a number of effects, and these are often accounted for in terms of the different polarizing actions of the different alkali metals. Weyl and Marboe for example state [18, p. 478] that the addition of Li_2O to molten SiO_2 introduces ions of "lower polarizability" than the addition of K_2O. In accounting for features in the Li_2O–SiO_2, Na_2O–SiO_2 and K_2O–SiO_2 systems such as (i) the greater tendency for compound formation by potassium (e.g. the existence of a stable potassium tetrasilicate but the non-existence of corresponding lithium and sodium compounds), and (ii) the (lower) eutectic temperature increasing K_2O–$SiO_2 <$ Na_2O–$SiO_2 <$ Li_2O–SiO_2, Weyl and Marboe argue that these effects are due to the polarizability differences between bridging and non-bridging oxides increasing from Li to Na to K.

Trends in optical basicity in the alkali metal group are in accordance with these

Table 6
Values of λ for alkali orthosilicate compared with λ for SiO_2.

Alkali metal	λ for oxide in M_4SiO_4	[λ (orthosilicate) $-$ λ (silica)] (i.e. $\delta\lambda$ between non-bridging Si–O and bridging Si–O–Si)
Li	0.74	0.26
Na	0.81	0.33
K, Rb	0.92	0.44
Cs	1.07	0.59

ideas. Table 6 shows how λ increases on going from the all-bridging situation in silica to the all-non-bridging situation in the alkali orthosilicate, and it is apparent that the difference in microscopic basicities λ increases significantly from Li to Cs. Of course, for an alkali silicate where the alkali oxide/SiO_2 ratio is less than 2 : 1, owing to internal neutralization effects (see above) in the SiO_4 units containing both bridging and non-bridging oxides, the value of $\delta\lambda$ will be less than the values indicated in table 6.

It is necessary to be circumspect before using differences in $\delta\lambda$ or λ that arise as a result of changing from one alkali metal to another. The reason for this is the possible unreliability of the alkali metal γ-values, which may arise because of the unrefined nature of Pauling electronegativity in this part (group I) of the Periodic Table Since Pauling [21] put forward his electronegativity values, several other electronegativity scales have been proposed. Some of these appear at first sight to yield more refined electronegativity values, and we now turn to one of the most popular, namely the Allred and Rochow [22] scale, as an alternative means of calculating basicity moderating parameters for the alkali metals. With the Allred and Rochow electronegativities the new basicity moderating parameter γ(A.R.)* is given by

$$\gamma(\text{A.R.}) = 1.29 \,[x(\text{A.R.}) - 0.27] \;.$$

Values of γ(A.R.) for the alkali metals, calculated from this equation, are given in table 7, and can be compared with the original γ-values based on Pauling electronegativity. We consider presently which set of γ-values is better in reflecting the polarizing action of the alkali metal ions in glass.

Weyl and Marboe give some emphasis to Dietzel's [23] use of the *field strength* (z/a^2) of a cation at distance a from the centre of an adjacent oxide, and they prefer this to the more conventional z/r^2 (r = cation radius). They state that z/a^2 can be

Table 7
Basicity moderating parameters γ, and field strengths z/a^2 of the alkali metal ions

Alkali metal	x(A.R.) [a]	γ (A.R.) [b]	γ (Pauling) [b]	z/a^2 [c]
Li	0.97	0.90	1.00	0.23
Na	1.01	0.95	0.87	0.17
K	0.91	0.83	0.73	0.13
Rb	0.89	0.80	0.73	0.12
Cs	0.86	0.76	0.60	0.10

[a] Electronegativity values are those of Allred and Rochow.

[b] Basicity moderating parameters γ (A.R.) calculated from Allred and Rochow electronegativity values (see text); γ-values obtained from Pauling electronegativities are given for comparison.

[c] Values of z/a^2 are those pertaining to the alkali metal monoxides.

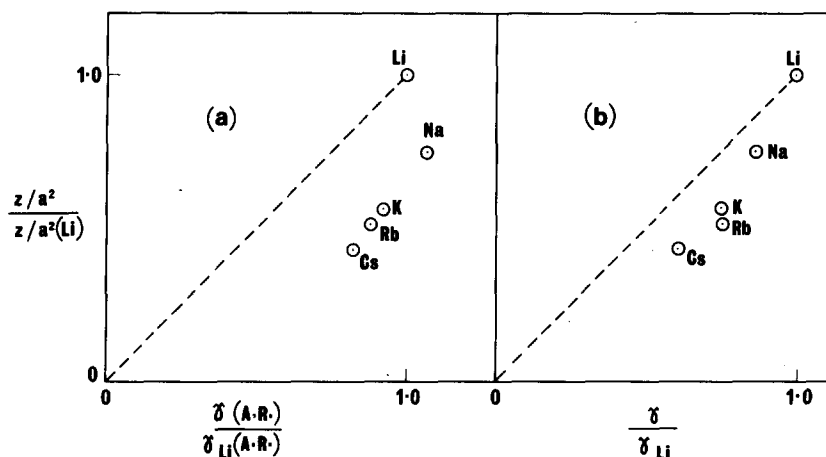* Based on values of x(A.R.) for Ca and H, see ref. [14] for details of calculations.

Fig. 10. (a) Comparison of field strengths (z/a^2) with Allred and Rochow basicity moderating parameters [γ(A.R.)] of the alkali metals: plot of $(z/a^2)/(z/a^2)_{Li}$ versus γ(A.R.)/γ(A.R.)$_{Li}$. (The dashed line is of unit slope.) (b) Comparison of field strengths (z/a^2) with original (Pauling) basicity moderating parameters γ of the alkali metals: plot of $(z/a^2)/(z/a^2)_{Li}$ versus γ/γ_{Li}. (The dashed line is of unit slope.)

used for estimating the interaction between the cations and oxide ions "and with it the acidity or basicity of the oxide". This implies that the field strength of a cat-ion is effectively the same as the basicity moderating parameter (suitably scaled). However, because field strength involves the oxidation number z, it is only possible to compare values of z/a^2 with γ-values for unipositive ions.

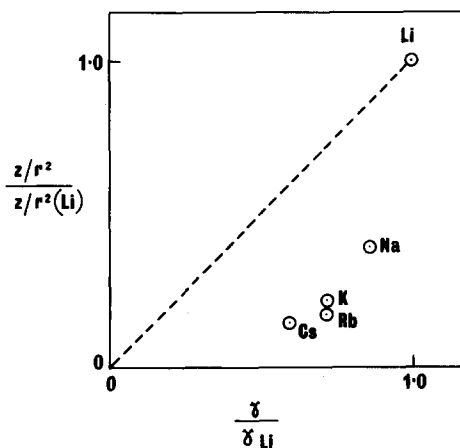When this comparison is made for the alkali metal ions (by normalizing all values

Fig. 11. Plot of $(z/r^2)/(z/r^2)_{Li}$ versus γ/γ_{Li} using original (Pauling) γ-values. (The dashed line is of unit slope.)

to unity for lithium), it is found that the basicity moderating parameters obtained from the Allred and Rochow electronegativities do not correlate at all well with the field strengths (fig. 10a). As can be seen from fig. 10b, a much better (linear) correlation is obtained using the original γ-values (obtained from Pauling electronegativities). (Incidentaly, it is interesting to note in relation to Weyl and Marboe's preference for z/a^2 over z/r^2 that the γ-values correlate very badly with values of z/r^2, see fig. 11.)

An area where the effects of different alkali metal ions on optical basicity have been investigated is in the alkali oxide $-$ B_2O_3 glass system, and as we shall see below, data for this system obtained by Easteal and Udy [7] correlate well with the original (Pauling) γ-values of the alkali metals. As discussed previously, owing to the tendencies of probing indicator ions to show slight site selectivity, experimental values of Λ do not tally exactly with the theoretical values. However, for a given indicator ion, it is possible that differences in optical basicity may become apparent, at a particular alkali oxide content, on changing from one alkali metal to another. At low alkali oxide compositions, differences in measured optical basicity are very small and are thus subject to uncertainties in the experimental determination of the $^1S_0 \rightarrow {}^3P_1$ frequency of the Pb^{2+} indicator ion. However, at higher alkali oxide contents, the optical basicity differences are larger and are therefore more reliable. The greatest difference in optical basicity, for a particular alkali oxide content, will be on going from the $Li_2O-B_2O_3$ glass to the $Cs_2O-B_2O_3$ glass. Table 8 compares the differences in experimentally determined optical basicity (for alkali oxide contents of 25%, 30% and 35%) with differences in theoretical Λ obtained from (i) the original γ-values, and (ii) γ-values derived from Allred and Rochow electronegativities. The two sets of theoretical Λ differences are quite distinct from each other, and comparison with experimental data indicates that the "Pauling" γ-values (table 1) for lithium and caesium express a numerical difference which accords with the experimental basicity difference between lithium borate and caesium borate glasses. In contrast, the γ-values derived from Allred and Rochow electronegativities predict a difference between lithium and caesium which is much too small.

Table 8
Differences in optical basicity between $Li_2O-B_2O_3$ glass and $Cs_2O-B_2O_3$ glass.

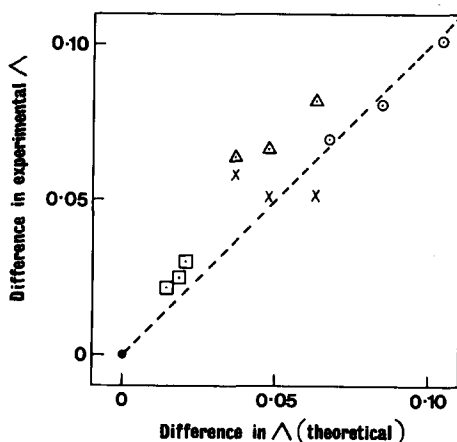| Glass composition	Optical basicity difference		
	Experimental [7]	calculated (Pauling)	calculated (Allred and Rochow)
25% alkali oxide	0.070	0.067	0.021
30% alkali oxide	0.081	0.085	0.025
35% alkali oxide	0.102	0.104	0.031

Fig. 12. Plot of experimental and theoretical differences in optical basicity for alkali oxide–B_2O_3 glasses (25%, 30% and 35% alkali oxide). Differences are between: Li–Cs ⊙, Li–Rb △, Li–K X, Li–Na ⊡ and Li–Li •. (The dashed line is of unit slope.)

To investigate how appropriate are the original γ-values of the other alkali metals, optical basicity differences between lithium and the alkali metals were calculated and the results compared with experimental differences. As seen from fig. 12, the original γ-values do express suitable numerical differences between all the alkali metals except for rubidium. Because potassium and rubidium have the same Pauling electronegativity they therefore have the same basicity moderating parameter, whereas the alkali borate glass data, and also the field strength data given in table 7, would indicate a γ-value for rubidium which is slightly below that for potassium.

2.3. Metal ions dissolved in glass

Many metal ions dissolve readily in molten silicates (borates, phosphates, etc.) and are held in solution when the melt is quenched to a glass. Many aspects of solute–solvent behaviour of these glasses can be studied if the metal ion is from the transition series, since the response of such ions to environment can be monitored by various spectroscopic techniques, the most obvious being absorption spectroscopy. It is usually quite a simple matter to establish (i) the oxidation state of the metal ion that is favoured by the glass, and (ii) the stereochemical environment that it provides for the metal ion. Both are affected profoundly by the optical basicity of the glass.

When a metal ion is dissolved in a glass, the oxide ions behave as donor atoms and impart some of their electron charge cloud density to the metal ion. In some glasses discrete complexes are produced. For example, it was shown [24] that in $KNO_3 - Ca(NO_3)_2$ glasses the Co^{2+} ion exists as the complex ion $[Co(NO_3)_4]^{2-}$. However, nitrate glasses may be regarded as "non-network" glasses [25] and hence

contain discrete anions which are free to enter the coordination sphere of a metal ion. In conventional network glasses, it is very difficult to define the coordination sphere and possibly it is best to regard the metal ion as occupying a site in the glass or as simply solvated by the glass.

If we have a metal ion capable of existing in two "medium" oxidation states, +2 and +3 say, then the +3 state will be favoured as the optical basicity of the glass is increased, since a high Λ-value means that the oxides are able to donate more negative charge, thereby stabilizing the metal ion. This phenomenon is observed for Fe^{2+}/Fe^{3+} and for Mn^{2+}/Mn^{3+} redox pairs in alkali borate glasses: as the alkali oxide content is increased [thus increasing Λ (fig. 4)] the upper/lower oxidation state ratio is also increased [26,27].

Some metals are more readily oxidized to what may be described as "high" (as opposed to medium) oxidation states, e.g. +5, +6. The oxidation of chromium(III) to chromium(VI) (by atmospheric oxygen) was studied as a function of alkali oxide content in the alkali borate glass system [28]. In fact the chromium(III) − chromium(VI) equilibrium was used as a basis for one of the earliest optical indicators [1, 29,30] for the degree of glass basicity. In the conversion of chromium(III) to chromium(VI), it is necessary that the oxides have sufficiently high optical basicity that at least some of them can detach themselves completely from the glass network. This part of the mechanism can be envisaged as follows:

$$\text{(chemical structure diagram)} \longrightarrow \text{(chemical structure diagram)} \quad + 3e \ . \tag{a}$$
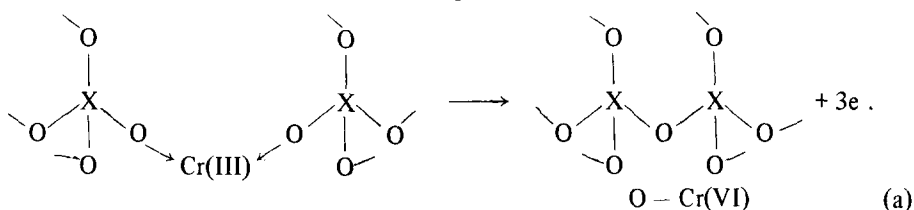
Since the redox half equation which balances the above reaction is

$$\tfrac{3}{4} O_2 + 3e \rightarrow \tfrac{3}{2} O^{2-} \tag{b}$$

it might appear (from Le Chatelier's principle) that the oxidation of chromium(III) to chromium(VI) would be favoured by a *decrease* in the alkali content of the glass. That this is not the case illustrates the overwhelming importance of glass basicity in providing the correct environment for stabilizing a particular oxidation state.

In eq. (a), only part of the coordination spheres of chromium(III) and chromium (VI) has been considered. As far as chromium(III) is concerned, it is probably best to envisage, as mentioned above, a solvation of the metal ion by the glass, and this would involve presumably both bridging (X−O−X) and non-bridging (X−O) oxides as donor atoms. However, in considering chromium(VI) (or any other metal ion in an "upper" oxidation state), the question arises as to whether the oxides, to which the metal ion is attached, are separate from the glass network (as eq. (a) implies) or whether one or more of the oxides are still attached to the glass network [thereby acting as a bridge between X and Cr(VI): X−O−Cr(VI)]. Spectroscopic studies of
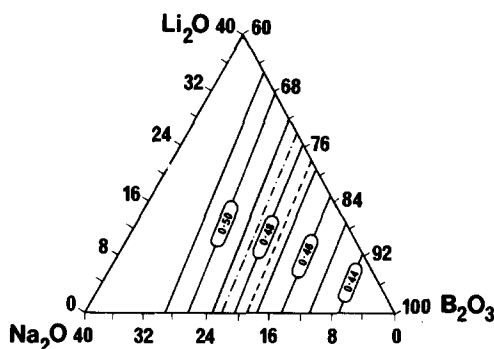
Fig. 13. Basicity contours (labelled according to Λ) in the glass system $Li_2O-Na_2O-B_2O_3$. Critical basicities are denoted $----$ for Co^{2+} and $-.-.-$ for Cr^{6+}. (After refs. [16, 31, 32].)

chromium(VI) in alkali borate glasses indicate that there is an equilibrium between these two coordinations [31,32] which depends upon the basicity of the glass. The equilibrium has been used for constructing "isobasicity" lines in various ternary systems such as $Li_2O-Na_2O-B_2O_3$, $Li_2O-K_2O-B_2O_3$ and $Na_2O-K_2O-B_2O_3$ [32]. These isobasicity lines follow closely the theoretical basicity contours which can be constructed for these systems using eq. (4) (e.g. see fig. 13).

In ultra-high alkali borate glass ($67Na_2O : 33B_2O_3$) and in sulphate glass ($40K_2SO_4 : 60ZnSO_4$) it appears that the chromium(VI) exists as the discrete chromate (CrO_4^{2-}) ion [33,34]. A similar situation seems to exist for vanadium(V) which is present as the discrete vanadate(V) ion in sulphate glass but not in bisulphate glass [34]. Thus, whereas the medium oxidation state metal ions enter into sites and are bonded into the network, it appears the upper oxidation state ions have the choice of existing either as the discrete oxyanion, or of being partly attached to the network by one (or perhaps more) oxides that serve as a bridge.

Glasses with the highest optical basicity so far studied [2] are the ultra-high alkali borate glasses where the Na_2O content is in the range 66.5–71.5%. This composition range is very close to the composition corresponding to the stoichiometry of the pyroborate ion $B_2O_5^{4-}$, and indeed the behaviour of the Co^{2+} ion in this glass [33] appears similar to that in nitrate [24] and acetate [35] glass, indicating that probably the glass is of the non-network type. The glass with 68% Na_2O is found to have a Λ-value of 0.68. Not surprisingly, the upper oxidation states are very much favoured, vanadium existing as vanadate, chromium as chromate (see above) and manganese even existing as the blue manganate(V), MnO_4^{3-}, species [33] [and green manganate(VI), MnO_4^{2-}, in the melt [36]].

Although optical basicity is the main factor in determining the correct environment for a particular oxidation state, it is nevertheless possible to carry out redox reactions in the molten glass by controlling the atmosphere. In fact most glasses seem to impart a redox behaviour to metal ions which is very similar to that of

water (which has a Λ-value of 0.40): oxidation states that are difficult, but possible, to obtain in water are similarly so in glass, for example Ti^{3+}, V^{3+}.

Metal ions for which a change in stereochemistry is possible, also respond in an interesting way to the optical basicity of the glass. Cobalt(II), for example, in many glasses exists in the pink octahedral form. As the basicity of the glass increases, however, there is a gradual change to the blue tetrahedral form [37,38]. In terms of optical basicity, the explanation is straightforward in that as the microscopic λ-values of the oxides increase, so fewer are required to "neutralize" the Co^{2+} ion and the coordination number falls from six to four. As a rough guide, cobalt(II) is octahedral when $\Lambda < 0.5$, tetrahedral when > 0.5. It is worth pointing out in this connection that the colour of the glass is not always a good indication of whether cobalt(II) is octahedrally or tetrahedrally coordinated [39].

Now although glass basicity is a major factor in determining the coordination number of a dissolved metal ion, other variables such as temperature and pressure can be important also. Indeed, Angell [40] discussed the use of transition metal ions as probes for structural change in glasses and melts in relation to such thermodynamic concepts as free volume and configurational entropy.

The response of the vanadyl VO^{2+} ion to glass basicity is also interesting since this ion can register its sensitivity to the basicity of the environment through changes in the degree of covalent interaction in the V—O bond of the vanadyl group. This interaction is reflected in the frequency of the electronic transition of the single d-electron to the antibonding π^*-orbital associated with the V—O bond: as the V—O bond strength increases, the π bonding orbitals decrease in energy while the
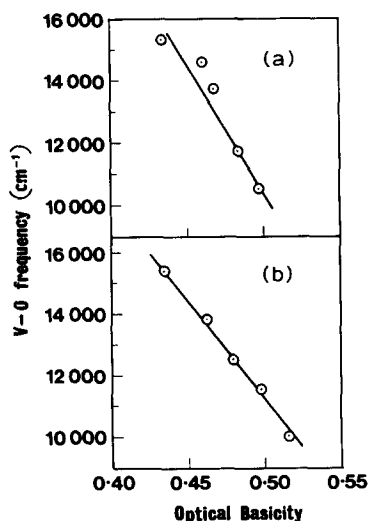

Fig. 14. Correlation between theoretical optical basicity (a) of $Li_2O-B_2O_3$ glass system and (b) of $Na_2O-B_2O_3$ with V—O frequency of VO^{2+} ion in these glasses. (The V—O frequency is that of the transition $^2B_2 \rightarrow {}^2E_\pi$).

corresponding antibonding π^* orbitals increase in energy, thereby increasing the energy separation between the latter orbitals and the orbital accommodating the d-electron. Therefore, as the donor power (Lewis basicity) of the environment decreases, the greater is the extent of donation by the oxygen to the vanadium in the V—O group. Lowering the basicity of the environment therefore brings about an increase in the separation between the d-electron and the antibonding π^*-orbitals and hence an increase in the frequency of the absorption band. This correlation was previously observed for the $H_2SO_4-H_2O$ system not only for VO^{2+} but for the analogous $(4d^1)$ MoO^{3+} species [41]. From the above reasoning it would be anticipated that for the alkali oxide—boric oxide system, the vanadyl ion would show an frequency decrease in this absorption band with increasing alkali oxide content. This has been observed [42], and it is interesting to plot the frequency shift against the optical basicity of the glass. For the $Li_2O-B_2O_3$ system and especially the $Na_2O-B_2O_3$ system the relationship between Λ and the V—O frequency is almost linear (fig. 14) [16]. The VO^{2+} ion appears in these two glass systems to be sensing Lewis basicity in a manner similar to that of a $d^{10}s^2$ probe ion such as Pb^{2+}, and is in fact giving a "better" experimental verification of the trend in theoretical optical basicity.

2.4. UV transparency

The UV transparency of a glass is usually impaired by even trace quantities of metal ion impurities. Most (coordinated) metal ions have strongly absorbing bands in the UV region, and it is the lower frequency edge of the first band which sets the frequency limit to which the glass is transparent. Metal ions can be divided into two types as far as the mechanism of UV absorption is concerned: (i) ions for which the electronic transition involves orbitals located essentially on the ion itself, and (ii) ions where the transition involves transference of an electron from oxide to the metal ion. When the mechanism is of the first type, the absorption band is usually influenced directly by the optical basicity of the glass, but for the second mechanism the relationship between band position and optical basicity is less straightforward.

Metal ions for which the first mechanism operates include some rare earth ions [43], but chiefly the p-block metal ions having oxidation numbers two units less than their group number, e.g. Pb^{2+} and Bi^{3+}. By virtue of the relationship between optical basicity and the frequency of the first absorption band, it is possible to estimate the extent of the red shift the absorption band will suffer as the optical basicity is increased. These shifts are given in table 9 for Tl^+, Pb^{2+} and Bi^{3+} [obtained using eqs. (1)–(3)], and for In^+, Sn^{2+} and Sb^{3+} (obtained using the equations applicable to these ions and derived from data in ref. [10]).

The second mechanism is much more common than the first. The energy of the electron transfer process (and hence the position of the absorption band) is determined by the electronegativity difference between the metal ion and the glass. The electronegativities are "optical electronegativities" χ, and the absorption maximum

Table 9

Frequency decrease of $^1S_0 \rightarrow {}^3P_1$ absorption band for an increase of 0.1 unit of optical basicity for p-block metal ions in glass.

metal ion	frequency decrease (cm^{-1})
In^+	1100
Tl^+	1800
Sn^{2+}	2300
Pb^{2+}	3100
Sb^{3+}	2500
Bi^{3+}	2900

ν (in cm^{-1}) * is given by [8]

$$\nu = 30\,000 \left\{ \chi \text{ (glass)} - \chi \text{ (metal ion)} \right\}. \tag{6}$$

χ (metal ion) and χ(glass) change on going from one metal ion to another or from one glass to another. Studies in borate, silicate and phosphate glasses have indicated, perhaps rather surprisingly, that altering the optical basicity of a glass does not necessarily bring about any corresponding change in the optical electronegativity of the glass; it appears rather that it is necessary for the basicity to correspond to some major change in glass structure for there to be any change in χ(glass) [44]. For example, the absorption band of Cu^{2+} in the $Na_2O-B_2O_3$ glass system undergoes little shift in the range 0–36% Na_2O, whereas in the $Na_2O-P_2O_5$ glass system, χ(glass) changes by nearly 0.1 unit around the 1 : 1 composition (where significant changes in structure are known to occur) and correspondingly the band shifts by approximately 3000 cm^{-1} [44].

The UV transparency of glasses free of trace metal ions improves as the alkali oxide content, and hence the basicity, is decreased. The tightening of the outer electrons of the oxides, which is manifested by the lower λ-values, results in increased binding energy and hence the absorption of light energy is shifted to higher frequencies.

Among the best glasses for UV transparency are the alkali and alkaline earth phosphate glasses. These glasses have low optical basicities [≈0.46 – cf. the less transparent Na_2O-SiO_2 (3 : 7) glass with $\Lambda = 0.60$] and when pure they have very little absorption even at the UV frequency limit of commercial spectrophotometers [just over 50 000 cm^{-1} (200 nm)]. However, since, as discussed above, the chief cause of impairment of UV transparency in the glass is the presence of metal ion impurities, it is important that the optical electronegativity difference [χ(glass) – χ(metal ion)] should be kept as great as possible so that the electron transfer bands absorb at the highest possible frequency [eq. (6)]. Thus the most important parameter, as far as common glasses are concerned, is the value of χ(glass) which should

* For certain ions, χ must be corrected for spin pairing and other effects.

be as high as possible. Phosphate glasses, with a value of ≈ 3.3 for $\chi(\text{glass})$ are there-fore superior in this respect compared with silicate and borate glasses which have values of $3.15-3.25$.

2.5. Changes in the network coordination number

The structures of silicate glasses are relatively simple in that silicon is always four-coordinate, and therefore the only groups which have to be considered are the various SiO_4 tetrahedra depicted in fig. 5. In these groups the number of bridging (and also terminal) oxides can vary from zero to four, and except in the case where all the oxides are either bridging or non-bridging there will be an imbalance in micro-scopic basicity $\delta\lambda$. This imbalance is only partially diminished by the internal neu-tralization, previously referred to, within the SiO_4 tetrahedron, but in other glasses variations in microscopic basicity can be reduced by changes in the coordination number of the network-forming cation.

This is the situation pertaining in glasses containing B^{3+}, Al^{3+} and Ge^{4+}, but we shall consider as examples only the alkali borate and alkali aluminosilicate glasses. We take as our working hypothesis that changes in coordination number occur, if by doing so the difference in microscopic basicities $\delta\lambda$ between O^{2-} ions attached to a common network-forming cation is thereby reduced (see above).

Because of the ability of boron to change between three- and fourfold coordina-tion, there are two possible reactions that can occur when alkali oxide is added to B_2O_3 (fig. 15). Retention of threefold coordination by the boron requires the for-mation of non-bridging oxides within the BO_3 units. However, if some borons change their coordination number to four, the added O^{2-} ions are incorporated as bridging oxides, and the creation of non-bridging oxides is avoided. In changing from a BO_3 to a BO_4 unit (fig. 15b), a bridging oxide undergoes an increase in λ

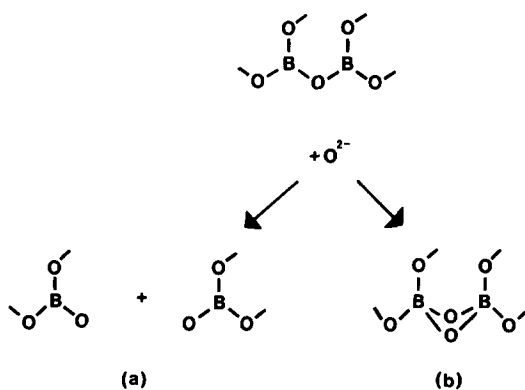(a)   (b)

Fig. 15. Addition of alkali oxide to B_2O_3 to produce (a) non-bridging oxides on BO_3 units, or (b) BO_4 units (but no non-bridging oxides).

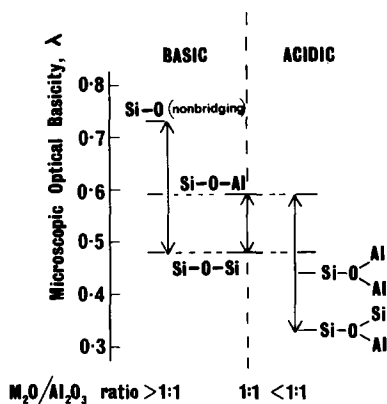Fig. 16. Spread in microscopic optical basicity, $\delta\lambda$ ($\equiv$ arrow length), for different Na_2O/Al_2O_3 ratios, in sodium aluminosilicate glasses. (Silicon and aluminium are both assumed to be four-coordinated.)

from 0.42 to 0.57 and $\delta\lambda$ is 0.15. If terminal oxides are produced (fig. 15a), λ increases from 0.42 to 0.71 and $\delta\lambda$ is 0.29. In accordance with our hypothesis, it is observed experimentally that addition of alkali to borate glasses does favour the production of four-coordinate boron rather than the formation of non-bridging oxides [45,46]. Furthermore, it would be expected that the reaction would not be as simple as that depicted in fig. 15b, but would yield not BO_4 units adjacent to each other but BO_4 units that were linked entirely to BO_3 units. As seen from table 2, an oxide bridging a four-coordinate boron to a three-coordinate boron has $\lambda = 0.50$ and $\delta\lambda$ is then only 0.08.

It is a generally accepted principle [47] (see also ref. [18, p.510]) that the proportion of non-bridging oxide in sodium aluminosilicate glasses decreases with increasing Al_2O_3 : Na_2O ratio, and that when this ratio is unity all the oxygens are in bridging positions. The $[AlO_4]^-$ groups are thus the characteristic structural entities in these glasses. However, when the Al_2O_3 : Na_2O ratio is greater than unity then the coordination number of oxygen must rise, and there has been some discussion in the literature as to existence of AlO_6 octahedra [48,49] and AlO_4 triclusters [50,51].

The spread in the microscopic basicity λ in sodium aluminosilicate glasses for different Al_2O_3 : Na_2O ratios and assuming retention of fourfold coordination is shown schematically in fig. 16. (The values are taken from tables 3 and 10 which strictly refer to Li-containing glasses, but in view of the internal neutralization effects it is hardly worth calculating new values here for each alkali metal ion.) The main feature in this diagram is that the range in microscopic basicities $\delta\lambda$ goes through a minimum at the Al_2O_3 : Na_2O ratio of 1 : 1. This is in accord with the notion that this composition marks some kind of "neutralization point" and has an important bearing on the ease of workability and resistance towards devitrification of glasses around this composition.

Table 10
λ-values of three-coordinate oxides in aluminosilicate networks.

|	four-coordinate Al	six-coordinate Al
Si | O Si / \ Al	0.33	0.38
Si | O Al / \ Al	0.44	0.54
Al | O Al / \ Al	0.55	0.70

Values of λ for various types of three-coordinate oxygen in aluminosilicate glasses are given in table 10. This list is not exhaustive, but it shows that by making suitable permutations among the possible arrangements of Si and Al it is possible to obtain O^{2-} ions of almost any desired basicity. This is perhaps the clue as to why the chemistry of aluminosilicates is so complex, and may ultimately explain some of the puzzling changes in Al-coordination number which have been proposed [52]. In $LiAlSiO_4$ glass it is believed [18, p. 514] that Al^{3+} ions are present in sixfold coordination.

2.6. Chemical durability and acid–base equilibria at the glass/water interface

Concerning the technology of glass this is obviously a topic of paramount importance. Studies into the chemistry and physics of glass would lose much of their point if glasses were not available to stand service in window panes, glass containers and in precision optical instruments. The literature on this subject is extensive and frequently in apparent conflict (the situation for metallic corrosion is similar), and it is fortunate that Weyl and Marboe [18, pp. 1010 et seq.] have provided a comprehensive and lucid review of the field. It appears that glass durability depends on many factors including glass composition, thermal history, pH of the corroding medium and the presence of various catalysts and inhibitors. For silicate glasses, the production of a surface layer of hydrated silicic acid has also been shown to be very much involved in the mechanism of glass dissolution.

A full treatment of surface durability is obviously outside the scope of this paper. However, two factors which can be singled out as contributing to a decrease in durability are: (i) increase in the number of non-bridging oxides in the glass, and (ii) increase in pH of the dissolving medium. The possible link between these two factors may well be the Lewis basicity of the oxides in (i) the glass, and (ii) the aqueous medium, and we therefore examine this problem in quantitative terms.

To tackle the problem of proton exchange between glasses and aqueous solutions, we found it best to start with the well-documented behaviour of oxyanions in solution. In the context of the Bronsted—Lowry theory, all oxyanions may be regarded as the conjugate bases of their parent acids, regardless of whether the acids are weak or strong. Thus, for example, the NO_3^- ion is the conjugate base of HNO_3, and *in principle* equilibria can always be written of the type

$$NO_3^- + H_3O^+ \rightleftharpoons HNO_3 + H_2O \; ;$$
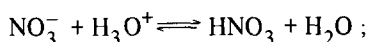
For this equilibrium,

$$K' = \{a_{(HNO_3)} \, a_{(H_2O)}\}/\{a_{(NO_3^-)} \, a_{(H_3O^+)}\}$$

and log K' is obviously the pK of the conjugate acid (HNO_3) (pK data for inorganic acids are readily available in a standard reference text [53]). If proton affinity is
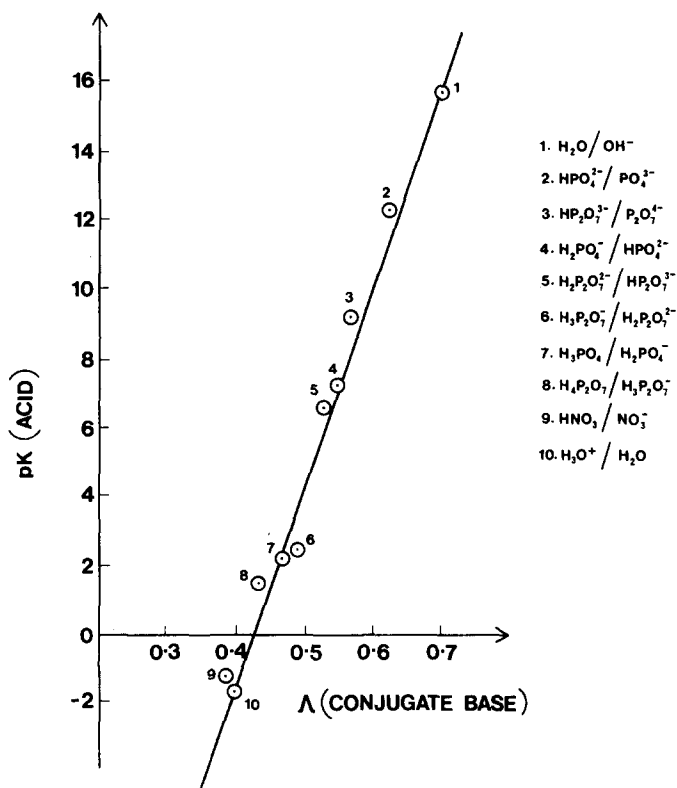

1. H_2O/OH^-
2. HPO_4^{2-}/PO_4^{3-}
3. $HP_2O_7^{3-}/P_2O_7^{4-}$
4. $H_2PO_4^-/HPO_4^{2-}$
5. $H_2P_2O_7^{2-}/HP_2O_7^{3-}$
6. $H_3P_2O_7^-/H_2P_2O_7^{2-}$
7. $H_3PO_4/H_2PO_4^-$
8. $H_4P_2O_7/H_3P_2O_7^-$
9. HNO_3/NO_3^-
10. H_3O^+/H_2O

Fig. 17. Plot of pK (oxyacid) versus the optical basicity of the conjugate base. (N.B. Λ for NO_3^- is 0.39 and not 0.50 as stated in ref [14].) It should be noted that the pK-values of the H_3O^+/H_2O and H_2O/OH^- acid—base couples are set to −1.74 and +15.74, respectively, and not to zero and +14, since in aqueous solution the concentration of water is 55 M.

determined by optical basicity, we shall expect to find a correlation between optical basicity of the anion and the pK of the conjugate acid.

Of the principal glass-forming cations (Si^{4+}, B^{3+} and P^{5+}), the oxyacids of silicon and boron provide very meagre data as far as their acid strengths in water are concerned (the equilibrium constant is complicated for boric acid because of the change in coordination number: $B(OH)_3 + H_2O \rightleftharpoons H^+ + [B(OH)_4]^-$ and for silicic acid because of condensation reactions). However phosphorus(V) forms, in addition to orthophosphoric acid, H_3PO_4, several condensed oxyacids containing both bridging and non-bridging oxides (this last feature makes them particularly attractive for the present purposes) and among these is pyrophosphoric acid $H_4P_2O_7$ for which all four dissociation constants have been obtained. In fig. 17, pK (conjugate acid) values for the various phosphate species are plotted against the optical basicity Λ and for the "bases" which are always present in water, namely H_2O and OH^-. The salient feature of this graph is the linearity between pK and Λ. If the "best" straight line is taken to be that which passes through the data points relating to the self-ionization of water, then it follows that

$$pK + 1.74 = 58.3 \ [\Lambda - 0.40] \ . \tag{7}$$

In simple terms, an anion will attract protons, and hence the conjugate acid will be weak, if its optical basicity is greater than that of water ($\Lambda = 0.40$). Incidentally, it is found that the above relationship holds quite well for a much wider range of oxyacids which involve elements other than phosphorus [54], and the equation is therefore important in that it establishes for the first time a quantitative link between the Bronsted theory of acidity for protonic systems and a theory of basicity which has been developed entirely within the context of oxyanion melts and glasses. It cannot be emphasized too strongly that the numerical values of pK and Λ used to establish this correlation are *entirely independent of each other.*

As far as the surface chemistry of glass is concerned two points may be noted. First, the pK value of an acid depends only on Λ and is independent of the charge carried by the conjugate base. This is a useful simplification. Second, the λ-values of the oxyanions are group basicities rather than microscopic basicities. The surface of an oxyanion glass, wetted by an aqueous medium, can be regarded as a particular "condition" of a hydrated anion. For the purposes of considering the protonation at a glass/water interface, we can apply the same principles as for the oxyanion/water interface. From this, it follows that the extent of protonation of a glass surface can be estimated by calculating λ-values corresponding to the "groups" which are present in the surface layers, and obtaining pK values from eq. (7) or fig. 17 for these groups.

In table 11 are the group basicities λ for several structural units likely to be present in glass surfaces together with the predicted values of pK. For a SiO_4 tetrahedron containing one non-bridging oxide, it is apparent that this oxide ion should have a $>50\%$ chance of existing in a protonated condition at all pH values below about 9. Above this pH-value non-bridging oxides will become progressively deprotonated, and it is significant to note that experimentally the "alkaline attack" on glass manifests itself in this pH region.

Table 11

Theoretical group basicities λ, and pK values for units in aluminosilicate glasses.

Group [a]	λ	pK [b]
(Si)–O O* Si (Si)–O O–(Si)	0.58 [c]	8.8
(Si)–O O* Si (Si)–O O*	0.65 [c]	12.8
(Si)–O O–(Si) Al {aluminosilicate (Si)–O O–(Si) group (A)}	0.59 [d]	9.3
"Al $(SiO_4)_4$" {aluminosilicate group (B)}	0.52	5.2

[a] Bridging oxides denoted –O´ and terminal –O* .

[b] pK values obtained from λ using eq. (7).

[c] Values also given in table 4.

[d] Same as Si–O–Al (4) values in table 3.

Dissolution of a silicate glass (in alkaline solutions) must involve some breaking up of the network structure, and this process must be preceded by hydration of the glass surface. It is reasonable to assume that the areas that are most heavily hydrated (i.e. those having the greatest affinity for water molecules) will be most prone to break away from the network structure and go into solution. Such "hot spots" will exist in regions where the oxides have significantly higher microscopic optical basicity than average since a high optical basicity goes hand in hand with a high electron density on the oxide, and it is this concentration of negative charge which serves to attract the positive ends of the water molecules. Removal of a proton from a non-bridging oxide (which occurs for pH >9, see above) leads to the formation of one of these hot spots, and the situation can be envisaged as shown in fig. 18.
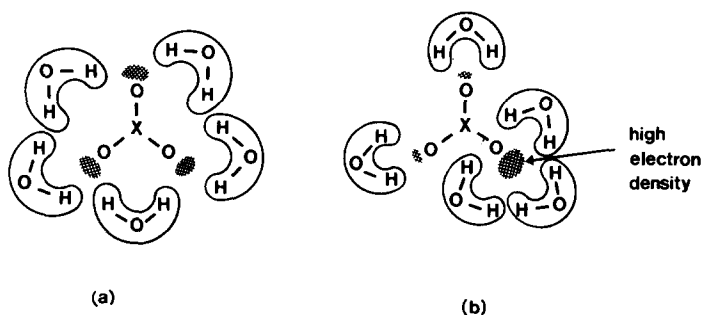

Fig. 18. Pictorial representation of the hydration of an oxyanion unit at the surface of a glass (drawn flat for clarity) when (a) δλ is zero leading to uniform hydration, and (b) δλ is large leading to a hydration "hot spot". (Charge density represented schematically by hatching.)

It is interesting to relate this theory of glass dissolution to the following situation cited by Weyl and Marboe [18, p. 64] to illustrate the uselessness of bulk $R_{O^{2-}}$ values and the necessity of being able to "differentiate between the polarizabilities of individual O^{2-} ions" (which the assignment of microscopic optical basicities λ enables us to do). Weyl and Marboe state that it is possible to lower the molar refractivity of a sodium silicate glass by adding either silica or alumina, but that "the effects of the two additions upon the chemical resistance of the resulting glasses are very different and do not parallel the molar refractivity". In considering this problem, and in accounting for the greater chemical resistance (i.e. lower chemical activity) of the aluminosilicate glass, particularly under alkaline solutions, compare an aluminosilicate glass of composition $Na_2O-Al_2O_3-SiO_2$ (1 : 1 : 6) with the sodium silicate glass Na_2O-SiO_2 (1 : 7). Both glasses have the same Na_2O content and their theoretical optical basicities are very close (0.54 and 0.52, respectively). With a Na_2O : Al_2O_3 ratio of 1 : 1, assuming fourfold coordination for the aluminium (see above) the $Na_2O-Al_2O_3-SiO_2$ (1 : 1 : 6) glass will contain no non-bridging oxides. Disregarding any Al—O—Al groups (if they are present at all, their concentration would be very small), oxides of highest basicity will be those in the Al—O—Si group which have $\lambda = 0.59$ (table 2). This compares with the oxides of highest basicity in the Na_2O-SiO_2 (1 : 7) glass, which will be the non-bridging oxides having $\lambda = 0.74$. The majority of oxides in both glasses will be oxides bridging two silicons, for which $\lambda = 0.48$, and it therefore follows that for the aluminosilicate glass $\delta\lambda$ is only 0.11 compared with 0.25 for the sodium silicate glass. Therefore, in the latter glass there is a greater electrical imbalance between the oxides of the oxyanion units with the production of hydration "hot-spots" and ensuing decomposition of the glass.

2.7. The glass electrode

The properties of H^+-selective glass electrodes have been discussed in monographs [55,56] and in recent publications [57,58]. It has been established that protons from solution invade the glass structure (followed by water molecules) leading to the formation of a leached layer of hydrated silica gel which is effectively dealkalized. The pH response is governed in part by the mobility of H^+ ions in the bulk of the glass membrane, but more significantly by equilibria at the gel/solution interphase. Thus Baucke [57] has drawn attention to the importance of acid—base equilibria of the type

$$SiOH_{gel} + H_2O_{solution} \rightleftharpoons SiO^-_{gel} + H_3O^+_{solution} .$$
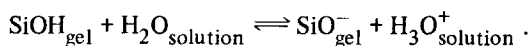
From the data in table 11, it can be seen that a SiO_4 group containing one non-bridging oxide is assigned a pK value of 8.8, which means that at a pH of 8.8, the tendency of this SiO_4 group for existing in the protonated form is the same as in unprotonated form. Therefore, at pH values greater than 8.8, the tendency for the group to exist in the unprotonated form will progressively increase. Referring to the actual performance of glass electrodes, it is indeed noteworthy that Corning 015

glass ($Na_2O : CaO : SiO_2 = 26 : 6 : 72$) performs perfectly satisfactorily when pH <9, but in solutions of higher pH shows the well-known "alkaline error".

From about 1940 [59,60], electrode glasses containing Li_2O as the principal alkali became available for H^+-ion measurement. These glasses have certain advantages over the Corning 015 composition used previously, in particular their response to Na^+ ions is much reduced. This is in part due to the existence of a mixed-alkali effect which reduces the Na^+ mobility in the bulk of the glass membrane. However, it is interesting to note that the "best" pH glasses are multicomponent mixtures [59,60] including a few mol% of an "oxygen modifier" such as La_2O_3 "to provide a high ratio of oxygen to silicon". Such glasses contain only about 63% mol% SiO_2, and therefore some of the SiO_4 structural units must contain more than one non-bridging oxide. From table 11, it is seen that such groups have a pK value ≈ 12, and should therefore show a pH response over an increased range. Recent studies of pH glass electrodes by Baucke [61,62] using ion-sputtering techniques [63,64] indicate a pK value of -10.3, and it is interesting to note that this is midway between our calculated values in table 11.

The presence of Al_2O_3 in glass markedly enhances the alkaline error and leads to a diminished range of pH response. Indeed, Al_2O_3 has been added deliberately to glass compositions to render the glasses insensitive to pH so that instead they can be used as *cation-selective* glass electrodes. The question naturally arises as to whether or not this effect can be deduced from changes in the optical basicity of structural entities in the glass surface. As stated above, the characteristic "structure" of aluminosilicate glasses envisages AlO_4 tetrahedra fitted into the network of SiO_4 tetrahedra. However the assignment of a "group basicity" to the AlO_4 units is not straightforward.

In table 11, two different versions of the AlO_4 group, as it exists in aluminosilicate glasses, are given. In the first (group A), the group comprises only those four oxides directly bound to the central Al^{3+}. The group basicity λ is the same as the *microscopic* basicity for each oxide in a Si—O—Al (4) unit (0.59). Further reference to table 11 shows that this value of λ is actually *greater* than the basicity of the

$$- O - \underset{\underset{O_{\searrow}}{|}}{\overset{\overset{O^{\nearrow}}{|}}{Si}} - O*$$
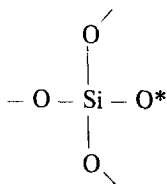
group (0.58) and it is difficult to see why pH response should be impaired. However, this version, group A (table 11), makes no allowance for internal neutralization within the four SiO_4 tetrahedra linked by the Al^{3+} ion. In other words, the AlO_4 unit (group A in table 11) should be considered not on its own but as part of a larger group which incorporates the whole of the four SiO_4 units surrounding the Al^{3+}

(group B in table 11). The group basicity is now 0.52 and pK = 5.2. According to this figure, glass electrodes containing significant amounts of Al_2O_3 should fail to respond to H^+ ions at pH > 5. In fact, departure from pH response begins when pH > 3, but in view of the difficulty of identifying all the entities present in alumino-silicate glass (see above) this disagreement is not too discouraging.

3. Conclusions

3.1. Theories of acid–base behaviour

Theories of acid–base behaviour in glasses fall conveniently into three main classes. These are as follows: (i) Lux–Flood approach [65,66]; (ii) self-ionization theories [67]; (iii) optical (Lewis) basicity concept [5].

According to the Lux–Flood theory, the characteristic acid–base reaction involves exchange of O^{2-} ions, and we can write: base $\rightleftharpoons O^{2-}$ + conjugate acid.

It is true to say that this theory has won general acceptance in the treatment of acid–base equilibria in molten salts and slags, as well as in glasses. Indeed, following on from the classic paper of Flood and Forland [66] it has become almost axiomatic that the correct expression for the *basicity* of an oxyanion system is in terms of an *oxide ion activity*, $a_{O^{2-}}$, and various attempts have been made to set up pO^{2-} scales analogous to the pH scale applicable in aqueous solutions. However, this procedure is not free from ambiguity. Thus from the standpoint of rigorous thermodynamics various authors [68,69] have cited Guggenheim [70] as to the indefinability of *single* ion activities. Attempts to use the concept of oxide ion activity have led to at least two controversies in the glass literature in recent years [68,69,71–73].

In view of the popularity of the $a_{O^{2-}}$ concept, it is easy to forget that the O^{2-} ion has no *independent* existence. Thus, the free O^{2-} ion in the gas phase, if it existed, would have zero ionization energy and infinite polarizability [74]. In chemical environments, O^{2-} is stabilized only by interaction with acidic cations such as Ca^{2+} or H^+. Its polarizability is thereby reduced and becomes comparable with those of other anions. If this is borne in mind, then there is no difficulty in accepting the finding of Zambonin and Jordan [75] that addition of Na_2O to molten alkali nitrates leads to the formation of O_2^{2-} and O_2^- ions and very little O^{2-}. It is now obvious that the controversy which surrounded these important results for several years was largely due to the general acceptance of the notion of oxide ion activity.

It remains to be asked whether or not the Lux–Flood theory can be modified so that its application to glass chemistry becomes more fruitful. Flood and Forland [66] define an acid–base reaction as one in which "an oxide ion changes from one state of polarization to another". It is our opinion that this is a correct and entirely definitive statement of the problem, but that their assumption that this "state of polarization" can be expressed in terms of oxide ion activity is not valid, and cer-

tainly does not apply to oxides in glass networks *. Following the arguments set forth earlier in this paper, it is possible to unify both the Lux–Flood and Lewis theories by regarding the state of polarization of oxide ions in terms of optical basicity. Thus we restate the Lux–Flood concept as it should be applied in glass chemistry as follows: "An acid-base reaction in an oxyanion glass is one in which oxide ions change from one state of (optical) basicity to another". It will be recalled, as previously discussed, that equilibria involving glass surfaces and anions in solution can also be treated in terms of optical basicity changes; therefore this statement holds for both protonic and non-protonic systems.

Self-dissociation theories are usually thought of as elaborations of the Lux–Flood concept in that the basicity of a particular glass is measured in terms of some specified O^{2-} exchange reaction. Thus Paul [67] has argued that basicity in borate glasses depends on equilibria of the type

$$- \overset{|}{\underset{|}{B}} - O - B\hspace{-0.3em}\diagdown \;\; \rightleftharpoons \; - \overset{|}{\underset{|}{B}} + {}^{*}O - B\hspace{-0.3em}\diagdown \; .$$
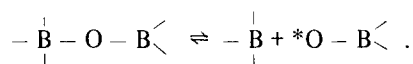
However, it is apparent that free oxide ions do not have to be present in the glass or melt for acid–base reactions of this type to occur. This approach is attractive in that it gives a *structural* interpretation of acid–base behaviour, but it seems more satisfactory to base the quantitative treatment not on oxide ion activities but on group or microscopic basicities.

In view of the above discussion the important question arises as to why so little attention has been given to applying the Lewis concept of acid–base behaviour in glasses and related systems. In the past there seem to have been two major difficulties. First, the concept of Lewis acid–base interaction has been envisaged in terms of reactions involving completion of the Lewis octet [18, p. 55] and generally Lewis acids and bases are thought of in terms of species such as BF_3 and NH_3. Second, with the Lewis approach there was the lack of a quantitative scale of acid or base strength [76].

The concept of optical basicity removes these difficulties by recognizing that the interaction between a probe metal ion and the oxides in a glass system is a Lewis acid–base interaction and that the degree of electron donation can be measured by UV spectroscopy. With the increased understanding of ionic interactions which have been obtained recently, it is now possible to use probe ions to detect and measure the donor abilities of O^{2-} ions in any glass network. This is

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* These comments should not be taken to imply the general uselessness of oxide ion activity data. In certain molten salts containing discrete oxyanions, e.g. carbonates and nitrates, oxide can be added to form solutions containing well-defined solute species such as O^{2-}, OH^- and O_2^-. In these cases, a full description of acid–base behaviour requires a combination of the optical basicity concept with the more traditional equilibrium constant approach as discussed elsewhere [14].

the logical foundation of the optical basicity concept, which appears to us to be a "natural" approach to glass chemistry, and one moreover to which other workers are making important contributions [7,77,78]. It is, however, the correlation between optical basicity and Pauling electronegativity which is especially useful. The correlation has made possible the calculation of microscopic and group basicities which are used extensively in this paper. As well as providing a scale of basicity for systematizing the behaviour of various indicator ions in glass, optical basicity provides a convenient framework for the quantitative application of electronegativity to a wide range of chemical problems.

Acknowledgement

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