

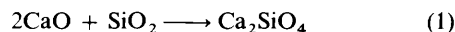
Analysis and Prediction of Acid–Base Reactions between Oxides and Oxysalts using the Optical Basicity Concept

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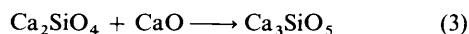
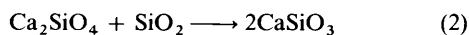
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The chemical reactions of (i) oxides with each other, *e.g.* CaO with SiO₂, (ii) oxides with oxysalts, *e.g.* CaO with CaSiO₃, and (iii) oxysalts with each other, *e.g.* Ca₂SiO₄ with Ca₃(PO₄)₂, have been considered from the point of view of acid–base theory. From known optical basicity values for alkali and alkaline-earth metal oxides and also for MgO, Al₂O₃, B₂O₃, SiO₂, P₂O₅, and SO₃, optical basicities were calculated for a large number of oxysalts. Examination of existing data on the reactions of these oxidic compounds at elevated temperatures, in the form of sub-solidus compatibility diagrams for ternary systems, has revealed that generally the optical basicity spanned by the products is less than that spanned by the reactants. This indicates that acid–base neutralisation is the major driving force behind the reaction; occasionally this principle is violated, as when other factors such as a stable network structure are of prime importance. It is shown how optical basicity analysis offers a method of constructing the tie-lines of sub-solidus compatibility diagrams, and it is suggested that this might be used as a guide for checking uncertainties in such diagrams.

When two oxides react it is often convenient to regard one as a base and the other as an acid, the product being an oxysalt. For example, in equation (1) CaO is usually considered as the base

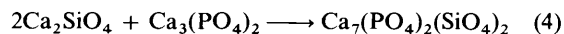


and SiO₂ as the acid.¹ Oxysalts may themselves undergo further acid–base reactions. For example, Ca₂SiO₄ reacts as a base in (2) and as an acid in (3). The three calcium silicates, CaSiO₃,



Ca₂SiO₄, and Ca₃SiO₅, increase in basicity with increasing ratio of basic oxide:acidic oxide.

In such reactions, the role of acid or base is readily assignable. However, in reactions between two oxysalts, such as that in equation (4), it is not immediately obvious which



reactant is the acid and which the base. Does the greater acidity of P₂O₅ over SiO₂ compensate for the higher proportion of base in the phosphate? Plainly we need some universal scale capable of ranking oxides and oxysalts in order of basicity or acidity.

In the past, experimentalists concerned with oxide systems, unable to exploit acid–base theory to any significant extent, have viewed the various phase equilibria² in terms of lattice energies or covalent network structures. Although these concepts can be made to work quite well, they tend to ignore variations in bonding; for example, in Group 2 the charge borne by the ions increases from MgO to BaO,³ but lattice-energy calculations imply charges of +2 and –2 in all four oxides. A quantitative acidity–basicity scale should be able to allow for changes in bonding, so that current theories for explaining phase equilibria might be improved or replaced. The present paper explores these possibilities.

Discussion

Optical Basicity.—Optical basicity^{4,5} is an acid–base concept particularly appropriate to oxide systems. It has been

successfully applied to the properties of glasses,^{5–9} the scavenging power of metallurgical slags,^{10–13} and the catalytic activity of solid oxide hosts.¹⁴ It also successfully explains the non-occurrence of a number of metal silicates.¹⁵

Optical basicity expresses the power that the oxide(–II) atoms or ions in the medium have for donating negative charge to an acidic probe. Ionic oxide(–II) has a very large electron-donor power, and oxides such as CaO or Na₂O are powerful bases. Covalent bonding tightens the orbitals and reduces the negative charge residing on the oxide(–II); the electron-donor power is then much less, and oxides such as Al₂O₃ or SiO₂ are only weakly basic.

Ions such as Tl⁺ and Pb²⁺ have been used as acidic probes;⁴ the greater the negative charge donated to them, the more the positive nucleus is screened and the less the energy required to promote an outer *s* electron to the *p* level. These probe ions therefore respond to increasing basicity of the medium through a red shift relative to the free, unco-ordinated condition of their *s*–*p* electronic absorption bands. Studies of these spectroscopic shifts, principally the ¹S₀ → ³P₁ absorption maximum in the u.v. region, led to the concept of optical basicity.⁴ The optical basicity, Λ, of a medium is defined as the ratio of electron donation by the oxide(–II) species in that medium to that in an ionic oxide (CaO is chosen as the standard for practical reasons). Theories accounting for orbital expansion (nephelauxetic¹⁶) effects in spectroscopy indicate that this ratio equals the ratio of spectroscopic red shifts, and the data from different probe ions confirm this.⁴

Optical basicity measurements have been made for glass and molten salt systems of oxides of the alkali and alkaline-earth metals and the *p*-block oxides B₂O₃, Al₂O₃, SiO₂, P₂O₅, and SO₃. These data show that the optical basicity of a medium composed of various oxides AO_{*a*}, BO_{*b*}, . . ., *etc.* is given¹⁷ by equation (5) where X(AO_{*a*}), X(BO_{*b*}), . . ., *etc.* are the equivalent

$$\Lambda = X(\text{AO}_a)\Lambda(\text{AO}_a) + X(\text{BO}_b)\Lambda(\text{BO}_b) + \dots, \text{etc.} \quad (5)$$

fractions of the oxides with respect to the total number of oxide species, and Λ(AO_{*a*}), Λ(BO_{*b*}), . . ., *etc.* are their optical basicities. In this way, experimental values of optical basicity can be assigned to individual oxides (Table 1) and can be used to calculate the optical basicity of any compound formed from two or more of these oxides. For example, for Ca₇(PO₄)₂(SiO₄)₂ (*i.e.*

Table 1. Optical basicities, Λ , of oxides

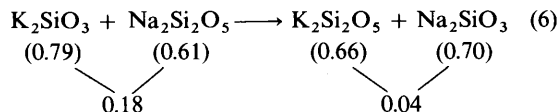
Oxide	Λ	Oxide	Λ
SO ₃	0.33	CaO	1.00
P ₂ O ₅	0.40	Li ₂ O	1.00
B ₂ O ₃	0.42	BaO	1.15
SiO ₂	0.48	Na ₂ O	1.15
Al ₂ O ₃	0.60	K ₂ O	1.4
MgO	0.78	Cs ₂ O	1.7

$$7\text{CaO}\cdot\text{P}_2\text{O}_5\cdot 2\text{SiO}_2: \Lambda = \frac{7}{16}\Lambda(\text{CaO}) + \frac{5}{16}\Lambda(\text{P}_2\text{O}_5) + \frac{4}{16}\Lambda(\text{SiO}_2) = 0.68.$$

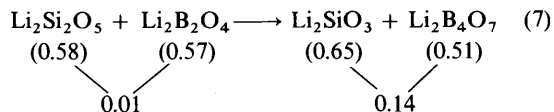
Acid-Base Reactions of Oxides.—In the formation of an oxysalt the more negatively charged oxide(–II) ions of the base and the less negatively charged oxide(–II) ions of the acid each achieve some intermediate negative charge. Since the extent of negative charge borne by the oxide(–II) atoms or ions governs the optical basicity of an oxidic material,¹⁸ the optical basicity also reaches an intermediate value. This is 'neutralisation' in terms of optical basicity. Although there is no particular Λ value that corresponds to 'neutrality,' Table 1 suggests that a value of $\Lambda \approx 0.6$ divides those oxides normally described as 'basic' from those described as 'acidic'; the Λ value of 0.6 for Al₂O₃ seems appropriate in view of its amphoteric behaviour. Large differences in optical basicity between two oxides should favour reaction to form an oxysalt.

Using these optical basicity values, Λ values may be calculated for the sulphates, phosphates, borates, silicates, and aluminates of Group 1 and 2 metals (Table 2). These oxysalts span a range of basicity (0.42–0.90); as expected, these values decrease with increasing acidity of the acidic oxide and with decreasing proportion of the basic oxide. We now see that in equation (4) above Ca₂SiO₄ ($\Lambda = 0.74$) is the base and Ca₃(PO₄)₂ ($\Lambda = 0.63$) is the acid.

Where reactions of oxysalts yield more than one product, *e.g.* equation (6), the acid–base driving force does not eliminate the



basicity difference, but merely reduces the optical basicity span (here, from 0.18 to 0.04). Moreover, the optical basicity span between the reactants is commonly much less than for reactions between acidic and basic oxides; *e.g.* for CaO and SiO₂, it is (1.00 – 0.48) = 0.52, whereas between oxysalts it is typically 0.2–0.3. It follows that the driving force for reaction between oxysalts is less than that for reaction between an acidic and a basic oxide. Indeed, acid–base 'neutralisation' is sometimes not the predominating factor. Consider equation (7). Here there is



actually an *increase* in the optical basicity span, and the driving force must derive from some other factor such as lattice energy. Such aberrations should involve only small increases in the optical basicity span.

Ternary Systems of Oxides.—Reactions involving oxides and oxysalts are usually studied at elevated temperatures, and the results summarised in the form of sub-solidus compatibility diagrams.² The equilibrium products of reaction are found on the appropriate ternary diagram; *e.g.* for equation (7), we would

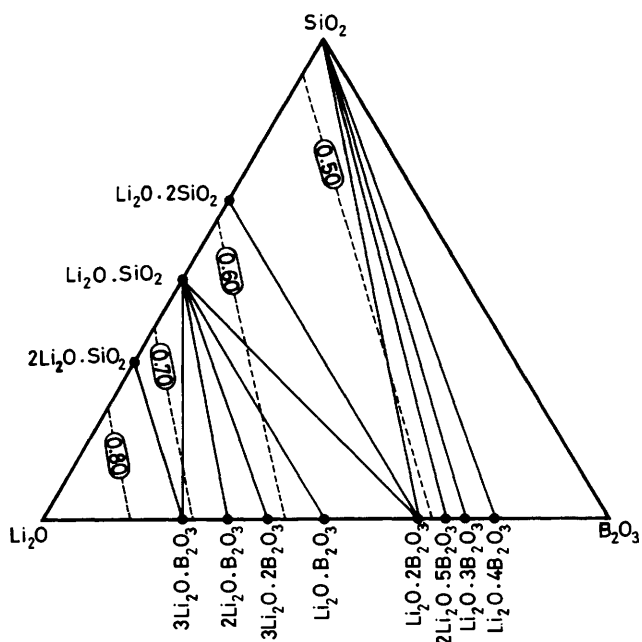


Figure 1. Sub-solidus compatibility diagram for the system Li₂O–B₂O₃–SiO₂. Isobasicity lines (shown broken) are labelled with their optical basicity value

consult the diagram¹⁹ for the system Li₂O–B₂O₃–SiO₂ (Figure 1). (Ternary diagrams frequently designate compounds in terms of stoichiometric ratios of the component oxides, *e.g.* Li₄SiO₄ ≡ 2Li₂O·SiO₂, a notation we adopt from now on.) The tie-lines connecting pairs of compounds signify compatibility, that is the compounds do not react with each other on heating. Compounds not so connected are incompatible and react; the equilibrium products are found on the diagram by referring to the corners of the triangle in which the overall composition of the mixture of reactants is located. For example, a large excess of Li₂O·2SiO₂ reacting with Li₂O·B₂O₃ [equation (7)] corresponds to a composition within the triangle with corners located at Li₂O·2SiO₂, Li₂O·SiO₂, and Li₂O·2B₂O₃, and these compounds would be the equilibrium products of reaction. With a large excess of Li₂O·B₂O₃ the composition lies in the triangle with corners at Li₂O·B₂O₃, Li₂O·2B₂O₃, and Li₂O·SiO₂, and a mixture of these would constitute the equilibrium product.

Since the tie-lines connect compounds that do not react, it follows that they should span fairly narrow ranges of optical basicity, and when 'isobasicity' lines are superposed on the ternary diagram the tie-lines should run roughly parallel to them. Any tie-lines running more or less at right angles to the trends in optical basicity should be short. Figure 1 shows that this is true for the Li₂O–B₂O₃–SiO₂ system, and the expectations are borne out for all other systems for which adequate data are available.

Ternary diagrams can readily be analysed using the optical basicity values of the compounds in the appropriate binary systems. Again taking the Li₂O–B₂O₃–SiO₂ system as an example, the optical basicities for the compounds in the Li₂O–SiO₂ and Li₂O–B₂O₃ systems are displayed in Figure 2(a). Minimal spanning of optical basicity necessitates tie-lines emanating from SiO₂ rather than from B₂O₃; the span from SiO₂ to Li₂O·4B₂O₃ is approximately zero, whereas for B₂O₃ to the most appropriate compound in the Li₂O–SiO₂ system, Li₂O·2SiO₂, it is (0.58 – 0.42) = 0.16. Figure 2(b) shows the Li₂O–SiO₂ and Li₂O–B₂O₃ systems together with the tie-lines

Table 2. Optical basicities of some oxysalts

	Ratio*	Li ₂ O	Na ₂ O	K ₂ O	MgO	CaO	BaO	Al ₂ O ₃	B ₂ O ₃
SO ₃	1:3							0.40	
	1:2	0.42	0.44	0.48					
P ₂ O ₅	1:1	0.50	0.54	0.60	0.45	0.50	0.54		
	1:3							0.43	
	1:1	0.50	0.53	0.57	0.46	0.50	0.53	0.48	0.41
	2:1	0.57	0.61	0.51	0.57	0.61	0.48		
	3:1	0.63	0.68	0.78	0.54	0.63	0.68		
B ₂ O ₃	4:1					0.67			
	1:5			0.48					
	1:4	0.46	0.48	0.50		0.51	0.48		
	1:3	0.48	0.49	0.57					
	2:5	0.49							
	1:2	0.51	0.52	0.56		0.51	0.52		
	1:1	0.57	0.62	0.67	0.51	0.57	0.62		
	3:2	0.61							
	2:1	0.65	0.71		0.56	0.65		0.54	
	3:1	0.71		0.60	0.71	0.79			
SiO ₂	9:2							0.57	
	1:4			0.58					
	1:2	0.58	0.61	0.66					
	3:5						0.61		
	5:8						0.63		
	2:3						0.64		
	1:1	0.65	0.70	0.79	0.58	0.65	0.70		
	3:2					0.70		0.56	
	2:1	0.72	0.82		0.63	0.74		0.56	
	3:1					0.79			
Al ₂ O ₃	1:11		0.62	0.62					
	1:6					0.62	0.63		
	1:5	0.63							
	1:2					0.66			
	1:1	0.70	0.74	0.80	0.65	0.70	0.74		
	5:3					0.74			
	3:1					0.80	0.88		

* Basic oxide:acidic oxide. Thus the first entry relates to Li₂O:2SiO₂. The 1:1 ratios are given in bold for ease of comparison.

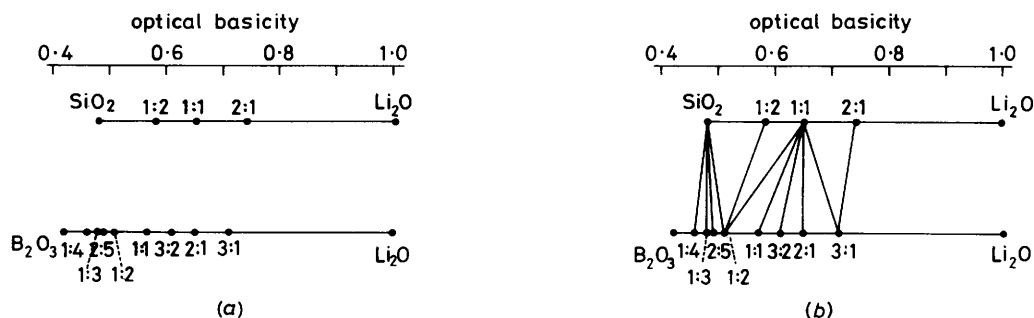
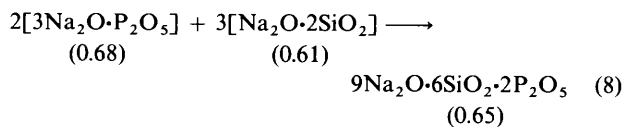


Figure 2. (a) Optical basicity values of compounds in the Li₂O–SiO₂ and Li₂O–B₂O₃ systems (the ratios indicate molar ratios of basic oxide:acidic oxide). (b) As (a), but with tie-lines transposed from the Li₂O–B₂O₃–SiO₂ sub-solidus compatibility diagram (Figure 1)

transposed from the ternary diagram of Figure 1, and indicates the magnitude of the optical basicity span associated with each. All tie-lines accord with optical basicity neutralisation except that between Li₂O·SiO₂ and Li₂O·2B₂O₃ [equation (7)].

Ternary sub-solidus diagrams often show compounds composed of all three oxides. For example, the Na₂O–SiO₂–P₂O₅ system [Figure 3(a)] shows that a compound of composition 9Na₂O·6SiO₂·2P₂O₅ results from the reaction (8).



In order to analyse this ternary diagram in terms of the optical basicity concept the intermediate compound must be included. It is located, with its Λ value, between the lines depicting the Na₂O–SiO₂ and Na₂O–P₂O₅ systems [Figure 3(b)]. The procedure is then as before and we expect tie-lines from SiO₂ to Na₂O·P₂O₅ and 2Na₂O·P₂O₅, but not from P₂O₅ to the sodium silicates. This is indeed found [Figure 3(a) and (b)], and all other tie-lines are as expected, except for that between SiO₂ and 9Na₂O·6SiO₂·2P₂O₅, where we might instead have expected one between Na₂O·2SiO₂ and 2Na₂O·SiO₂.

The Λ values of compounds composed of two and three oxides (Tables 2 and 3) allow optical basicity analyses of all the ternary systems in Table 3. In general, these systems can be

Table 3. Optical basicities, Λ , of some three-oxide salts*

System	Salt composition	Λ	System	Salt composition	Λ
Li ₂ O–MgO–SiO ₂	1:1:1	0.69	K ₂ O–Al ₂ O ₃ –SiO ₂	1:1:6	0.56
Na ₂ O–MgO–SiO ₂	1:5:12	0.54		1:1:4	0.59
	1:2:6	0.56		1:1:2	0.64
	1:2:4	0.59	MgO–Al ₂ O ₃ –SiO ₂	1:1:1	0.59
	1:1:3	0.60		4:5:2	0.61
	2:3:5	0.63	CaO–Al ₂ O ₃ –SiO ₂	1:1:2	0.59
	2:1:3	0.66		2:1:1	0.68
	2:2:3	0.67	BaO–Al ₂ O ₃ –SiO ₂	1:1:2	0.61
Na ₂ O–CaO–SiO ₂	1:3:6	0.62	Na ₂ O–B ₂ O ₃ –SiO ₂	1:1:2	0.54
	1:2:3	0.67	CaO–B ₂ O ₃ –SiO ₂	1:1:1	0.54
	2:1:3	0.69		5:1:1	0.72
	1:2:2	0.72	BaO–B ₂ O ₃ –SiO ₂	3:3:2	0.57
	4:3:5	0.73	Na ₂ O–SiO ₂ –P ₂ O ₅	9:6:2	0.65
K ₂ O–MgO–SiO ₂	1:5:12	0.56	CaO–SiO ₂ –P ₂ O ₅	7:2:1	0.68
	1:1:5	0.58	CaO–SiO ₂ –SO ₃	5:2:1	0.66
	1:1:3	0.63	Li ₂ O–B ₂ O ₃ –P ₂ O ₅	2:3:1	0.49
	1:1:1	0.79		22:11:13	0.52
K ₂ O–CaO–SiO ₂	1:2:9	0.57	Na ₂ O–B ₂ O ₃ –P ₂ O ₅	5:4:3	0.52
	1:2:6	0.61		5:2:3	0.55
	2:1:6	0.64		2:1:1	0.56
	4:1:10	0.65		3:2:1	0.57
	2:1:3	0.74	CaO–MgO–P ₂ O ₅	1:1:1	0.54
	1:1:1	0.84		3:3:2	0.58
CaO–MgO–SiO ₂	1:1:2	0.62	BaO–MgO–P ₂ O ₅	2:1:2	0.54
	2:1:2	0.73		1:1:1	0.56
	1:1:1	0.69		1:2:1	0.59
	3:1:2	0.71		2:1:1	0.64
BaO–MgO–SiO ₂	1:1:3	0.60	Li ₂ O–Al ₂ O ₃ –B ₂ O ₃	2:2:3	0.55
	1:2:2	0.66		2:1:1	0.63
	2:1:2	0.71	Na ₂ O–CaO–Al ₂ O ₃	1:8:3	0.81
	1:1:1	0.72		2:3:5	0.72
	3:1:2	0.77	BaO–CaO–Al ₂ O ₃	1:2:4	0.69
BaO–CaO–SiO ₂	1:2:3	0.67			

* Systems are listed in the order: silicate, aluminosilicate, borosilicate, silicophosphate, and non-silicate.

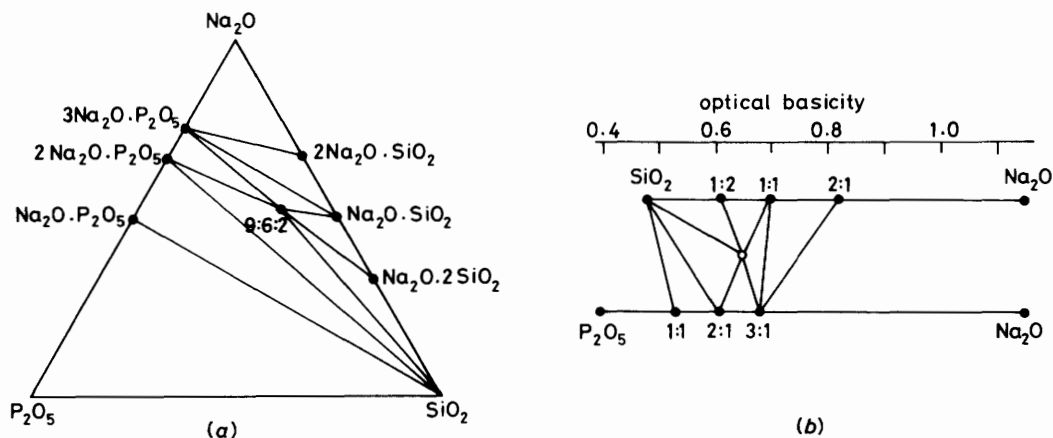


Figure 3. (a) Sub-solidus compatibility diagram for the Na₂O–SiO₂–P₂O₅ system showing the 9:6:2 compound 9Na₂O·6SiO₂·2P₂O₅. (b) Optical basicity values of compounds in the Na₂O–SiO₂ and Na₂O–P₂O₅ systems with tie-lines transposed from (a). Ratios as in Figure 2

divided into those comprising (i) two basic oxides and one acidic, and (ii) one basic oxide and two acidic. Some of those containing Al₂O₃ may be classified in either group (i) or (ii), leading to a choice of constructions. For example, for the system Li₂O–Al₂O₃–B₂O₃ one might choose Al₂O₃–B₂O₃ and Li₂O–B₂O₃, with lithium aluminates located as intermediates, or Li₂O–Al₂O₃ and Al₂O₃–B₂O₃, with lithium borates as intermediates. The Al₂O₃–SiO₂–P₂O₅ system can be regarded as of type (ii), or as composed of three acidic oxides, again

leading to a choice in the analysis: either Al₂O₃–SiO₂ and Al₂O₃–P₂O₅, or SiO₂–P₂O₅ and Al₂O₃–P₂O₅.

We have examined all the systems listed in Table 3 to see how successful this method of analysis is in predicting the pattern of tie-lines. 'Predicted' sub-solidus compatibility diagrams were compared with the experimental ones from ref. 2. Figure 4 shows the process for the BaO–B₂O₃–SiO₂ system. Starting at SiO₂ in Figure 4(a), minimum optical basicity differences predict the following tie-lines: (i) from SiO₂ to the BaO–B₂O₃

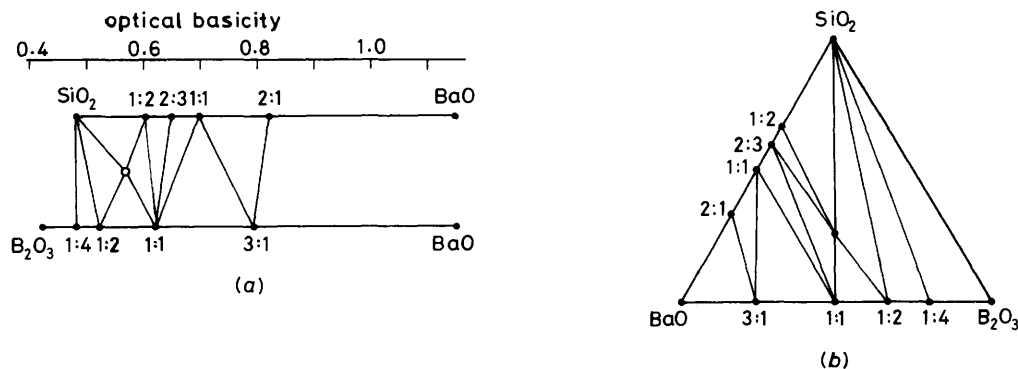


Figure 4. (a) Optical basicity values of compounds in the BaO-SiO₂ and BaO-B₂O₃ systems and of the intermediate compound 3BaO·3B₂O₃·2SiO₂ (open circle). Tie-lines have been drawn so that they span the minimum of optical basicity. (b) Predicted sub-solidus compatibility diagram for the system BaO-B₂O₃-SiO₂ obtained by transposing the tie-lines from (a)

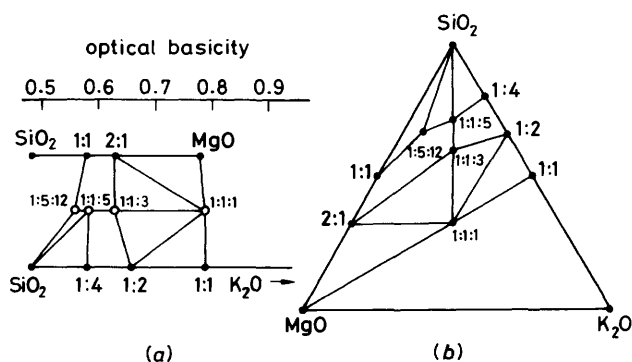


Figure 5. (a) Optical basicity values of compounds in the MgO-SiO₂ and K₂O-SiO₂ systems and the intermediates (open circles) K₂O·MgO·SiO₂, K₂O·MgO·3SiO₂, K₂O·MgO·5SiO₂, and K₂O·5MgO·12SiO₂. Tie-lines have been drawn so that they span the minimum of optical basicity. (b) Predicted (incomplete) sub-solidus compatibility diagram for the system K₂O-MgO-SiO₂ obtained by transposing the tie-lines from (a)

compositions 1:4 and 1:2, and to the 3:3:2 intermediate; (ii) from the 3:3:2 intermediate to the BaO-B₂O₃ compositions 1:2 and 1:1 and to the BaO-SiO₂ composition 1:2; (iii) from BaO·B₂O₃ to the BaO-SiO₂ compositions 1:2, 2:3, and 1:1; and (iv) from 3BaO·B₂O₃ to the BaO-SiO₂ compositions 1:1 and 2:1. The ternary diagram, Figure 4(b), constructed in this way, is in accord with the experimental results.²⁰

In the above example, optical basicity analysis enables the complete sub-solidus compatibility diagram to be constructed. For some systems, although it is possible to build up a substantial part of the diagram, the choice of the final tie-lines may be ambiguous, leading to two or more possible diagrams. The diagrams differ only slightly, the ambiguity arising because of the small optical basicity spans involved. For the K₂O-MgO-SiO₂ system, for example, the optical basicity analysis shown in Figure 5(a) allows most of the sub-solidus compatibility diagram to be constructed [Figure 5(b)]. It cannot be completed because of the small optical basicity changes associated with the various alternatives remaining. These involve the tie-lines running as follows: (i) either (a) MgO·SiO₂ to K₂O·MgO·5SiO₂ and K₂O·MgO·3P₂O₅, (b) from 2MgO·SiO₂ to K₂O·5MgO·12SiO₂ and K₂O·MgO·5SiO₂, or (c) from K₂O·MgO·5SiO₂ to MgO·SiO₂ and 2MgO·SiO₂; (ii) (a) from K₂O·4SiO₂ to K₂O·MgO·3SiO₂ or (b) from K₂O·2SiO₂ to K₂O·MgO·5SiO₂.

Experimentally, it is found that the remaining tie-lines run as (i) (b) and (ii) (b).²¹

Even when it cannot be carried through to completion, this method of tie-line construction could be used as a guide for checking suspect sub-solidus compatibility diagrams.

Conclusions

For the oxides and oxysalts considered here, there is overwhelming evidence that acid-base neutralisation, as measured by optical basicity, is usually the major driving force in reaction. Although not infallible, optical basicity analysis can be used to construct substantial parts, if not all, of the sub-solidus compatibility diagrams for the ternary systems composed of any of the oxides listed in Table 1. The guiding principles of this analysis are as follows.

(1) Optical basicity ranks the oxides of the elements, increasing Λ designating increasing basicity. The value $\Lambda = 0.6$ appears to distinguish acidic from basic oxides.

(2) Acidic and basic oxides react to form oxysalts that have optical basicities intermediate between those of the parent oxides.

(3) The greater the optical basicity difference between the parent oxides, the greater is the tendency for reaction to occur.

(4) Oxysalts can behave as acids or bases, and react with oxides or other oxysalts.

(5) Oxysalts have optical basicities ranging from 0.42 to 0.90. Thus their reactions often involve a smaller optical basicity difference between the reactants than is the case for reaction between acidic and basic oxides.

(6) Reactions between oxysalts yield other oxysalts as products, lowering rather than eliminating the optical basicity span. Since the optical basicity differences may be quite small, neutralisation is a less important factor compared with reactions involving oxides, and the optical basicity span may even increase slightly.

(7) Optical basicities can be used with a fair degree of success to predict tie-lines in ternary diagrams, since compatible pairs of compounds should show minimum optical basicity differences.

(8) In systems containing two basic oxides, tie-lines emanate from the one of lower optical basicity; in systems containing two acidic oxides, they emanate from the acidic oxide of higher optical basicity.

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