

Relationship between Optical Basicity and Thermochemistry of Silicates

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The optical basicity treatment of oxidic network systems, for example silicates, has been successful in correlating a range of properties; since the method has the advantage of avoiding such problems as those associated with “single ion” activities, it allows comparisons between many different systems. However, several of the properties dealt with are traditionally viewed in terms of thermodynamics. It is therefore of significance that a link has now been discovered between optical basicity and thermochemistry, and is established through the quantitative relationship between optical basicity and electronegativity. This link shows that thermodynamic stability increases with increasing negative charge borne by the oxygen atoms and, in principle, should allow heats of formation, ΔH_f° , of silicate compounds to be predicted from their optical basicity values which, in turn, are calculated from chemical composition. This possibility is examined by making comparisons with experimentally obtained values of ΔH_f° , and it is shown that there is good agreement for silicates composed of the oxides CaO, MgO, Al_2O_3 , and SiO_2 .

1. Introduction

Fundamental research into oxide glasses is very much concerned with understanding how physical and chemical properties are related to chemical composition. Several approaches to this area of research have been made over the past hundred years, many of them invoking concepts such as oxide ion activity, network modification or electronic polarizability. In effect, these concepts are different aspects of acid–base theory. Recently, the use of thermodynamics for tackling these problems has been highlighted and, despite the paucity of thermochemical data available for oxidic glasses, much success has been achieved for modeling such properties as refractive index, durability, and redox equilibria (see, for example, refs 1,2).

A severe limitation of any thermodynamic approach to acid–base problems is the difficulty associated with “single ion” activities.³ Thus, in a sodium silicate melt system it is necessary to refer to Na_2O activities, whereas in a calcium silicate system reference must be made to CaO activities, and it is therefore impossible to make a quantitative comparison between the two systems. It is worth pointing out that although it is very convenient to refer to the oxide ion, O^{2-} , nevertheless the ion does not exist as such under normal chemical conditions owing to the very large negative electron affinity arising from the double negative charge. Several years ago, an approach to acid–base theory in oxidic systems was devised which circumvented these limitations.⁴ This was the optical basicity approach, which considers the electronic state of the oxygen atoms in terms of their electron donor power, in turn, reflecting the extent of negative charge borne. In effect, the optical basicity value of an oxidic medium quantifies the Lewis acid–base properties of the oxide(–II) species, and focuses very much on the interaction with metal ions which are, of course, Lewis acids.

In the molten state, one of the most important properties of glass is its role in determining the position of equilibrium for redox reactions involving the oxide(–II)–oxygen(0) couple. This is the type of problem that is well suited to the optical basicity approach. Traditionally, the oxide(–II)–oxygen(0)

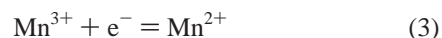
half reaction is expressed in the form



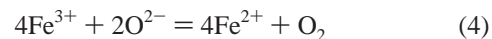
The equation can be combined with other half reactions, such as



or



yielding, for example,



Such equations must be used with care since they might be taken to imply that the reduction of Fe^{3+} to Fe^{2+} is effected actually by O^{2-} ions. However, it is much more realistic to think in terms of the oxide(–II) atoms of the silicate network and their tendency to participate, and that this tendency increases with the increasing negative charge that they bear. The optical basicity model adopts this approach and also considers the stabilization of the ions in terms of Lewis acid–base interaction. One of the most important advantages of the optical basicity approach is that it allows quantitative comparisons between glass systems regardless of whether they are comprised of Na_2O , CaO, or any other oxide. For example, to show the effect of alkali oxide concentration on an equilibrium, e.g., for $\text{Fe}^{2+}/\text{Fe}^{3+}$ (eq 4) in the three melts $\text{Li}_2\text{O}-\text{SiO}_2$, $\text{Na}_2\text{O}-\text{SiO}_2$, and $\text{K}_2\text{O}-\text{SiO}_2$, it was necessary at one time to make three separate plots. The use of optical basicity allows the effect to be presented as a united single trend.^{5,6}

This facility for switching between, and comparing, different systems has resulted in the successful application of optical basicity to technology. In particular, it is currently used for problems associated with glass science and extraction metallurgy.^{5–7} These problems are usually concerned with chemical equilibria

TABLE 1: Heats of Formation,^a Electronegativity,^b and Optical Basicity^c Data

| | $-\Delta H_f^\circ$ kJ/mol | $x_O - x_M$ | x_M | x_O | γ_M | $\Lambda(M_dO_b)$ |
|--------------------------------|----------------------------|-------------|-------|-------|------------|-------------------|
| Li ₂ O | 597.9 | 1.91 | 1 | 2.91 | 1.0 | 1.0 |
| Na ₂ O | 414.2 | 1.65 | 0.9 | 2.55 | 0.87 | 1.15 |
| K ₂ O | 361.5 | 1.56 | 0.8 | 2.36 | 0.73 | 1.4 |
| Rb ₂ O | 339.0 | 1.52 | 0.75 | 2.27 | 0.67 | 1.55 |
| Cs ₂ O | 345.8 | 1.54 | 0.7 | 2.24 | 0.60 | 1.7 |
| MgO | 601.6 | 1.92 | 1.2 | 3.12 | 1.28 | 0.78 |
| CaO | 634.9 | 1.96 | 1 | 2.96 | 1.00 | 1.00 |
| SrO | 592.0 | 1.91 | 0.95 | 2.86 | 0.91 | 1.1 |
| BaO | 548.0 | 1.85 | 0.9 | 2.75 | 0.87 | 1.15 |
| Al ₂ O ₃ | 1675.7 | 1.86 | 1.5 | 3.36 | 1.66 | 0.60 |
| SiO ₂ | 910.7 | 1.71 | 1.8 | 3.51 | 2.08 | 0.48 |
| P ₄ O ₁₀ | 2979.0 | 1.15 | 2.1 | 3.25 | 3.0 | 0.33 |
| B ₂ O ₃ | 1273.5 | 1.66 | 2 | 3.66 | 2.36 | 0.42 |

^a ΔH_f° values from ref 21. ^b Electronegativity values are Pauling type.⁵ ^c Values of γ_M and Λ for oxides from ref 5.

and therefore have a thermodynamic basis. It is this aspect that has prompted the present investigation into discovering the nature of the link between optical basicity and thermodynamics.

2. Electronegativity and Thermochemistry of Simple Oxides

The (fractional) negative charge borne by an atom or ion arises from the unequal sharing of electrons in a compound. In terms of the valence bond theory, this is conceived as resonance between covalent and ionic structures. Pauling, in the 1930s, expressed this effect in terms of electronegativity values which he obtained from bond energies, taken as the heat of formation, Q (in electronvolts), divided by the number of bonds.⁸ Despite the many refinements that have been made for electronegativity since its conception, it is convenient to follow Pauling's treatment and to take $Q = -\Delta H_f^\circ/96.48$ where ΔH_f° is in kJ mol⁻¹. For present purposes, the data on heats of formation ($-\Delta H_f^\circ$) for several simple oxides (important for silicate science and technology) are taken from the literature, see Table 1.

For oxides (general formula: M_dO_b), Q requires the addition of 1.13 eV per oxygen owing to the double bond in the O₂ molecule, and the electronegativity difference between oxygen and the element with which it is combined is given by

$$x_O - x_M = \sqrt{\frac{Q + 1.13b}{2b}} \quad (5)$$

(The denominator, 2b, arises because it was taken by Pauling as the "number of bonds" in the oxide, e.g. two for CaO, four for SiO₂, etc.)

The electronegativity values assigned to most elements (in a given oxidation state) are fairly constant, but this is not so for oxygen.^{5,9} Unfortunately, the exceptional behavior of oxygen is not generally realized. Data show that for a series of oxides, M_dO_b , as the bonding becomes more ionic between M and O, the value of x_O decreases (Table 1). This is quite logical, because as the extent of negative charge borne by oxide(–II) increases, so its affinity for electron charge, that is, its electron attracting power, will decrease. Table 1 shows, for example, that the electronegativity difference for the Na–O bond is even less than for the Si–O bond, despite the difference in ionicity of the two bonds.

The trend in x_O with increasing x_M is shown (Figure 1) for the oxides in Table 1. Other oxides, especially those where M has the inert gas configuration, also follow this trend which has previously been expressed (conveniently, but some-

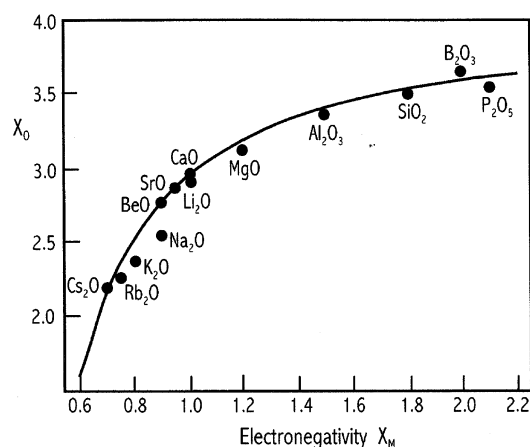


Figure 1. Values of oxygen electronegativity, x_O , in oxides, M_dO_b , versus electronegativity, x_M (Table 1); the curve is eq 6.

what approximately) in the form^{5,9}

$$x_O = A - \frac{B}{x_M - 0.25} \quad (6)$$

with $A = 4.1$ and $B = 0.86$ (continuous curve in Figure 1). It should be noted that, for reasons considered previously, transition metal ions with d electrons do not comply with this relationship.¹⁰

3. Optical Basicity and Heat of Formation of Simple Oxides

The optical basicity of an oxidic medium, such as a silicate melt, can be calculated from chemical composition using "basicity moderating parameters" assigned to cations on the basis of experimental optical basicity values.^{5,11} Originally, the optical basicity, Λ , of a medium was obtained by dissolving metal ion probes which were sensitive to the electron donation exercised by the oxide(–II) atoms.⁴ The method relies on antibonding effects which lead to decreased electron repulsion within the probe ion and to a corresponding red shift in the optical spectrum. Alternative methods have been developed based on, for example, far-infrared spectroscopy,¹² refractivity measurements,^{13,14} or O1s binding energy.¹⁵

Accumulated data indicate that the optical basicity of a material depends on the equivalent fraction, X , of each oxide, Na₂O, CaO, SiO₂ ... (that is, the proportion of oxide(–II) contributed), and a property of the Na⁺, Ca²⁺, Si⁴⁺ ... ions that they have for, what Weyl and Marboe¹⁶ aptly described as, a "tightening" of the electron charge clouds of the oxide(–II) atoms.^{5,11,17} It is this property that is represented by the basicity moderating parameter, γ , which can be thought of simply as a measure of the polarizing effect. Thus, for a medium comprised of the oxides $AO_{a/2}$, $BO_{b/2}$..., the following expression holds:

$$\Lambda = \frac{X(AO_{a/2})}{\gamma_A} + \frac{X(BO_{b/2})}{\gamma_B} + \dots \quad (7)$$

Values of γ for cations that are important for silicate science are given in Table 1. It is apparent from eq 7 that for a single oxide, M_dO_b , the optical basicity is simply $1/\gamma_M$.

In many respects, the idea associated with the basicity moderating parameter is similar to that for electronegativity. Both parameters are a measure of the attraction of electrons in chemical bonding and it follows that a relationship should exist. For the oxides in Table 1 it is a very simple one,

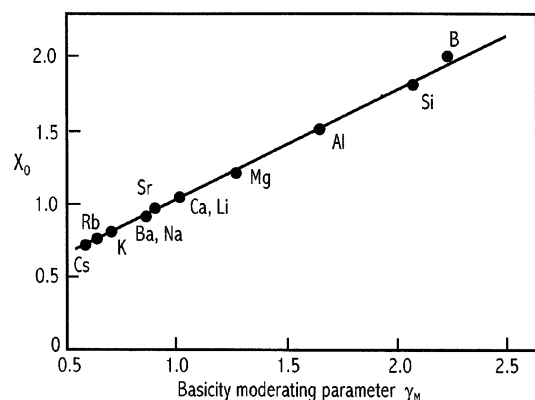


Figure 2. Plot of electronegativity, x_M , versus basicity moderating parameter, γ_M , relevant to oxides in Table 1; the line is eq 8.

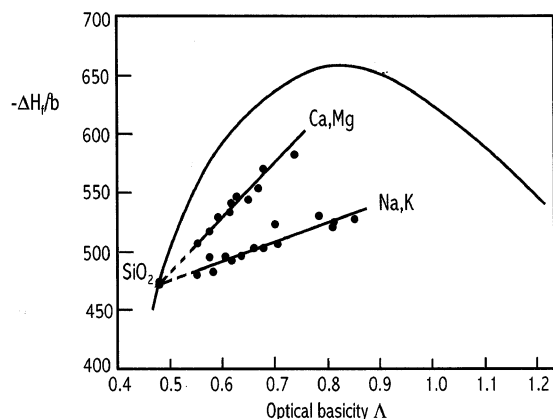


Figure 3. General relationship between the heat of formation per oxide(-II), $-\Delta H_f^0/b$ in kJ mol^{-1} , versus optical basicity, Λ , for binary oxides, expressed by eq 11 (continuous curve). The two straight lines are to guide the eye through the Ca/Mg set and the Na/K set of points calculated for the silicates and aluminosilicates in Table 2.

as shown in Figure 2, and is given by

$$x_M = 0.25 + 0.75\gamma_M \quad (8)$$

(Again, this relationship does not apply to transition metal ions.¹⁰) Using eq 8 to substitute for x_M in eq 6 (with $A = 4.1$ and $B = 0.86$, see previously), and bearing in mind that $1/\gamma_M = \Lambda(M_aO_b)$, yields

$$x_O = 4.1 - 1.16\Lambda(M_aO_b) \quad (9)$$

It follows from eq 5, together with eq 8, that

$$\sqrt{\frac{Q + 1.13b}{2b}} = 3.85 - 1.16\Lambda(M_aO_b) - 0.75/\Lambda(M_aO_b) \quad (10)$$

Hence, the heat of formation (in eV) per oxygen atom, is given by

$$Q/b = 2[3.85 - 1.16\Lambda(M_aO_b) - 0.75/\Lambda(M_aO_b)]^2 - 1.13 \quad (11)$$

For convenient numerical comparison with ΔH_f^0 data, Q/b must be converted from eV to kJ mol^{-1} through multiplication by -96.48 . It is shown in this form as the continuous curve in Figure 3.

TABLE 2: Heats of Formation^a and Optical Basicity^b Data for Silicates

| compound | $-\Delta H_f^0$ kJ mol^{-1} | number of O atoms | $-\Delta H_f^0$ kJ per O atom | Λ |
|---|---|----------------------|----------------------------------|-----------|
| $3\text{Na}_2\text{O} \cdot 8\text{SiO}_2$ | 9173 | 19 | 482.8 | 0.586 |
| $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ | 2473.6 | 5 | 494.7 | 0.611 |
| $\text{Na}_2\text{O} \cdot \text{SiO}_2$ | 1563.1 | 3 | 521.0 | 0.703 |
| $2\text{Na}_2\text{O} \cdot \text{SiO}_2$ | 2101.2 | 4 | 525.3 | 0.815 |
| $\text{K}_2\text{O} \cdot 4\text{SiO}_2$ | 4315.8 | 9 | 479.5 | 0.554 |
| $\text{K}_2\text{O} \cdot 2\text{SiO}_2$ | 2508.7 | 5 | 501.7 | 0.664 |
| $\text{K}_2\text{O} \cdot \text{SiO}_2$ | 1589.9 | 3 | 530.0 | 0.787 |
| $\text{MgO} \cdot \text{SiO}_2$ | 1548.5 | 3 | 516.2 | 0.580 |
| $2\text{MgO} \cdot \text{SiO}_2$ | 2176.9 | 4 | 544.2 | 0.630 |
| $\text{CaO} \cdot \text{SiO}_2$ | 1635.1 | 3 | 545.0 | 0.653 |
| $2\text{CaO} \cdot \text{SiO}_2$ | 2328.4 | 4 | 582.1 | 0.740 |
| $\text{Na}_2\text{O} \cdot \text{CaO} \cdot 5\text{SiO}_2$ | 5934 | 12 | 494.5 | 0.579 |
| $\text{Na}_2\text{O} \cdot 3\text{CaO} \cdot 6\text{SiO}_2$ | 8636.8 | 16 | 539.8 | 0.619 |
| $2\text{Na}_2\text{O} \cdot \text{CaO} \cdot 3\text{SiO}_2$ | 4763 | 9 | 519.6 | 0.687 |
| $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 3\text{SiO}_2$ | 4883.6 | 9 | 536.2 | 0.670 |
| $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ | 7841.2 | 16 | 490.1 | 0.622 |
| $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$ | 6039.6 | 12 | 503.3 | 0.679 |
| $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ | 4163.5 | 8 | 520.4 | 0.812 |
| $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ | 7914 | 16 | 494.6 | 0.640 |
| $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$ | 6068.9 | 12 | 505.7 | 0.704 |
| $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ | 4217.1 | 8 | 527.1 | 0.853 |
| $\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$ | 3202.3 | 6 | 533.7 | 0.617 |
| $2\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$ | 3876.9 | 7 | 553.8 | 0.671 |
| $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ | 4223.7 | 8 | 528.0 | 0.590 |
| $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ | 3989.4 | 7 | 569.9 | 0.680 |
| $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$ | 9113.2 | 18 | 506.3 | 0.553 |

^a From ref 1. ^b Λ calculated from eq 7.

4. Application to Alkali and Alkaline Earth Silicates

Equation 11 provides a link between thermochemistry and optical basicity. Its derivation relies on the relationship between oxygen electronegativity (in binary oxides) and the optical basicity values of those oxides. This is eq 9 which, in turn, relies on the relationship between the electronegativity of oxygen, x_O , for the oxides M_aO_b , and the electronegativity x_M . (The nonlinear form of this latter relationship, given by eq 6, is responsible for the curved nature of the continuous line in Figure 3; the chemical bonding implications have been discussed previously.¹⁸)

It is apparent in Figure 1 that although eq 6 is a fairly good fit for SiO_2 , MgO , and alkaline earth oxides, it is poor for Na_2O and K_2O . This observation is important when we consider the silicates of calcium, sodium, etc., to investigate how their heats of formation and optical basicities compare with the trends that might be expected from eq 11. To make this investigation, it is necessary to calculate for each compound (i) the heat of formation per oxygen atom, and (ii) the optical basicity. Data on heats of formation of some binary and ternary alkali and alkaline earth silicates are in Table 2. Taking $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ as an example, it is seen that with $\Delta H_f^0 = -4223.7 \text{ kJ mol}^{-1}$ (at 298 K), ΔH_f^0 per mole of oxide(-II) is one-eighth of -4223.7 kJ , i.e., -528.0 kJ ; Λ , by eq 7, is $((1/(8 \times 1.00)) + (3/(8 \times 1.65)) + (4/(8 \times 2.08))) = 0.590$.

The results of these calculations (which are in Table 2) are plotted in Figure 3 and divide into two sets: (i) for Na^+ or K^+ silicates and aluminosilicates, and (ii) for Mg^{2+} or Ca^{2+} silicates and aluminosilicates. It can be seen from Figure 3 that for both trends there is a numerical increase in $\Delta H_f^0/b$ with increasing optical basicity, and also it is possible to extrapolate almost to the data point for SiO_2 . However, the correlation for the Na/K set with eq 11 is very poor, but this is expected in view of the poor fit of Na_2O and K_2O in Figure 1 (as discussed above). On the other hand, the Ca/Mg set shows more promise.

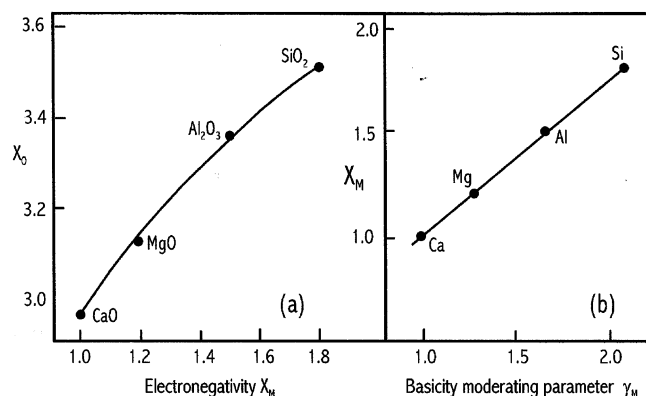


Figure 4. Plot of (a) electronegativities x_O versus x_M , and (b) x_M versus basicity moderating parameter, γ_M , for CaO, MgO, Al_2O_3 , and SiO_2 . The lines are eq 12 in (a) and 13 in (b).

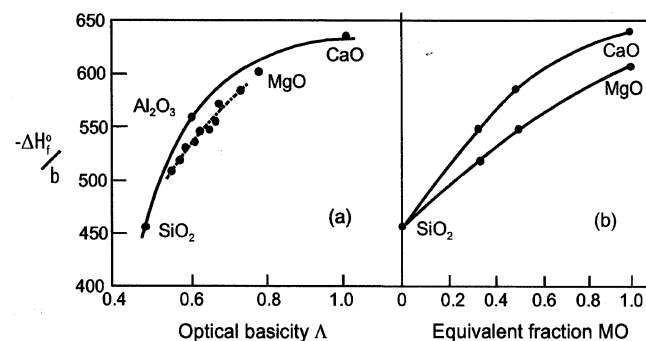


Figure 5. Plot of the heat of formation per oxide(-II), $-\Delta H_f^0/b$ in kJ mol⁻¹, of (a) calcium and magnesium silicates and aluminosilicates (Table 2) versus optical basicity, Λ , (the full curve is eq 14 with the right-hand side multiplied by -96.48 (see text), and the broken line is to guide the eye), and (b) of calcium and magnesium silicates versus an equivalent fraction of MO ($M = Ca$ or Mg) which is 0.33 for $MO \cdot SiO_2$ and 0.5 for $2MO \cdot SiO_2$.

It makes sense, at this point, to ignore the systems containing Na_2O or K_2O and to focus on those composed of the oxides CaO, MgO, Al_2O_3 , and SiO_2 . (It is worth pointing out that the latter systems have recently been the subject of a study linking activity coefficients with optical basicity.¹⁹) As previously, we consider relationships involving x_O , x_M , γ_M , and $\Lambda(M_aO_b)$, but restricted to these four oxides. Data are in Table 1 and are used to plot (i) electronegativities x_O versus x_M (Figure 4a), and (ii) x_M versus γ_M (Figure 4b). The relationships are now (Figure 4a)

$$x_O = 1.729 + 1.526x_M - 0.297x_M^2 \quad (12)$$

and (Figure 4b)

$$x_M = 0.743\gamma_M + 0.254 \quad (13)$$

Combining these two equations with eq 5 gives

$$Q/b = 2(1.844 + 0.279/\Lambda - 0.164/\Lambda^2)^2 - 1.13 \quad (14)$$

This relationship (with the right-hand side multiplied by -96.48 in order to convert from Q in eV to ΔH_f^0 in kJ mol⁻¹) is shown as the continuous line in Figure 5a.

The data points for calcium and magnesium silicates and aluminosilicates that were plotted in Figure 3 are now shown in Figure 5a. They are seen to lie close to the line that passes through the points for the four oxides (eq 14). The small discrepancy that can be seen for the silicates is such that the value for $-\Delta H_f^0/b$, predicted by eq 14, is greater by $25 (\pm 8)$ kJ mol⁻¹

compared with the experimental value. The reason for this small difference is not certain at present. An explanation might lie in the difference between the bonding in Al_2O_3 and in the silicates. In Al_2O_3 all of the oxide(-II) atoms (or ions) are involved in the same ionic-covalent interaction (with aluminum(III)), whereas in the (alumino)silicates the oxide(-II) atoms are bound both ionically (with Ca^{2+} or Mg^{2+} ions) and covalently to the silicon(IV). It should be noted that although Λ corresponds to the degree of negative charge borne by oxide(-II), for the silicates and aluminosilicates this is an average value.

5. Conclusions

The trends that have been identified here for silicate and aluminosilicate compounds of calcium and magnesium indicate the existence of an important and significant link between thermochemistry and optical basicity. First, the optical basicity values serve to rank the compounds in the exact order of increasing heat of formation per oxide(-II) atom. Second, since Λ represents the extent of (average) negative charge borne by the oxide(-II) atoms in an oxidic system, it is apparent that the increasing thermodynamic stability of silicates is associated with an increasing charge on the oxygen atoms. A third point is that we now have another example of the optical basicity approach serving to unite data into a single trend, thereby allowing comparisons to be made between different silicate systems. For example, there is no difficulty in comparing the CaO- Al_2O_3 - SiO_2 system with the CaO-MgO- SiO_2 system, and problems associated with "single ion" activities simply do not arise. To emphasize this point, Figure 5a should be contrasted with the necessity for showing two separate trends in Figure 5b, one for the calcium system and the other for the magnesium.

Previous studies have indicated fundamental links between optical basicity and such properties as oxide refractivity (that is, electronic polarizability),^{13,14} redox equilibria (e.g., as for Fe^{2+}/Fe^{3+} , eq 4),⁵⁻⁷ metal corrosion,²⁰ and infrared spectroscopy.¹² The relationship between these properties and heats of formation is now possible in the light of the optical basicity model, and might be worth future exploration. The extent to which eq 14 can be applied to other silicates for calculating ΔH_f^0 from chemical composition (by eq 7) should also be explored.

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