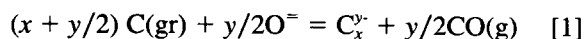


Communications

Carbon Solubility as Carbide in Calcium Silicate Melts

R.A. BERRYMAN and I.D. SOMMERVILLE

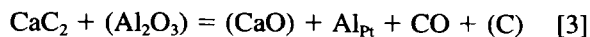
A number of workers have measured carbon solubility in calcium aluminates.^[1-4] Swisher^[1] also presented results showing carbon solubility across a range of liquids from $\text{CaO} \cdot \text{Al}_2\text{O}_3$ to $\text{CaO} \cdot \text{SiO}_2$, as shown in Figure 1. A sharp rise in measured carbon solubility occurs toward the silica-rich edge of the graph. Turkdogan^[5,6] noted that this trend did not agree with the accepted model for carbide dissolution discussed below, which involves consumption of free oxide ions. Another source of data for carbon solubility in liquid silicates is a study in the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ system by Ponomarenko and Kozlov.^[4] No compositions containing only CaO and SiO_2 were reported, but intermediate compositions close to those used by Swisher in Figure 1 were reported to have carbon solubilities even higher than those reported by Swisher. Also, their results for silica-free melts indicated solubilities up to 5 times higher than those for other work in calcium aluminates,^[1,2,3] suggesting that their data may not be reliable. Carbide capacity, C_c , is derived from the carbide dissolution reaction



If the activity of the carbide ion is proportional to its concentration, if the activity of graphite is unity, and if the value of y is 2, then carbide capacity can be defined as

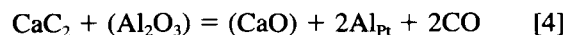
$$\begin{aligned} C_c &= (\text{Pct C}) (P_{\text{CO}}) \\ &= K_1(a_{\text{O}^{\ominus}})/(f_c) \end{aligned} \quad [2]$$

This parameter is an expression of the oxide ion availability but also includes the effect of the activity coefficient of carbide, f_c . In Reaction [1], the value of x is not specified. Although this is unimportant in the definition and use of carbide capacity, it would be useful to know its value to understand the dissolution chemistry more fully. Calcium carbide, which releases acetylene (C_2H_2) on contact with water, obviously contains the carbide ion C_2^{\ominus} . Swisher noted that calcium carbide had been observed^[7] to dissolve into CaCl_2 as C_2^{\ominus} , but felt that in the case of dissolution into melts in the lime-alumina-silica system, his results supported the existence of an ion containing a single carbon atom, C^{\ominus} . A reaction (unbalanced) of this type,



was observed when CaC_2 was added to $\text{CaO-Al}_2\text{O}_3$ melts in Pt crucibles. Less than 50 pct of the carbon added as

CaC_2 was recovered as dissolved carbon in any of the experiments. The supposed implication of this result was that the existence of such a reaction proved the C^{2-} ion had formed from the C_2^{2-} ion during dissolution. However, considering the highly reducing character of CaC_2 , it is also possible that the reaction which occurred was simply



and that the low recovery of carbon in the melt occurred because most of the calcium carbide reacted with the alumina. The C_2^{2-} ion is the form generally accepted by other workers, rather than a C^{2-} ion. Schwerdtfeger and Schubert^[8] noted that evidence also existed for the existence of a C^{4-} ion in aluminum oxycarbide.

A gas-liquid-solid equilibration technique was selected for the measurements. Premelted samples, 3 g in mass, were placed in crucibles (LECO* hydrogen de-

*LECO is a trademark of LECO Corporation, St. Louis, MI.

termination, high-purity graphite) having dimensions 10-mm ID and 30-mm high. Four such crucibles were placed inside a larger graphite crucible (32-mm ID and 76-mm high) with a lid. The thermocouple and gas inlet tube terminated between the smaller crucibles at the level of the liquid samples, as shown in Figure 2. The graphite container crucible was suspended inside a closed end alumina tube (48-mm ID) which was held in a larger vertical tube furnace. During the time taken (4 hours) for lowering the apparatus into the furnace, an Ar-5 pct H_2 gas mixture was passed through the apparatus. Once

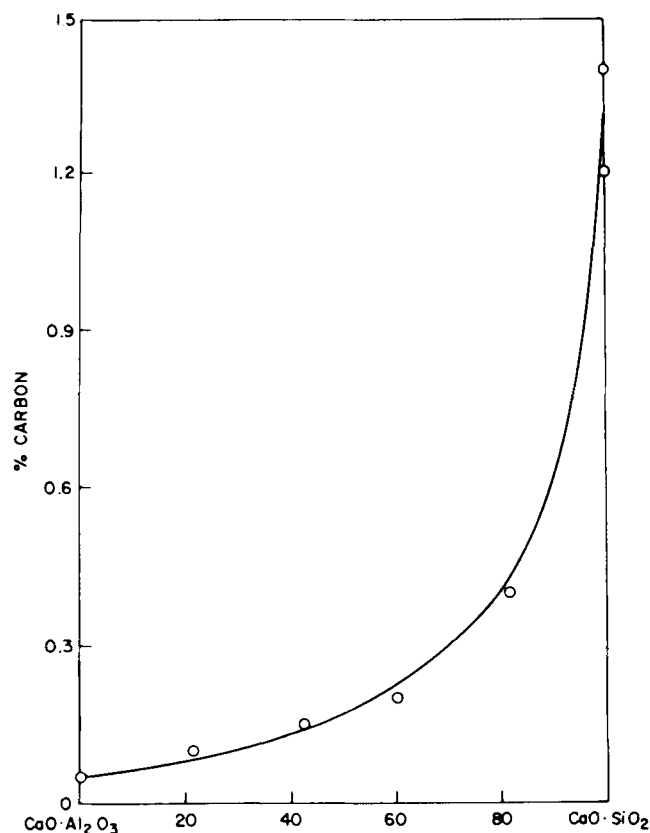


Fig. 1—Measured solubility of carbon in $\text{CaO-Al}_2\text{O}_3\text{-CaO-SiO}_2$ melts at 1883 K and 1 atm CO^1 .

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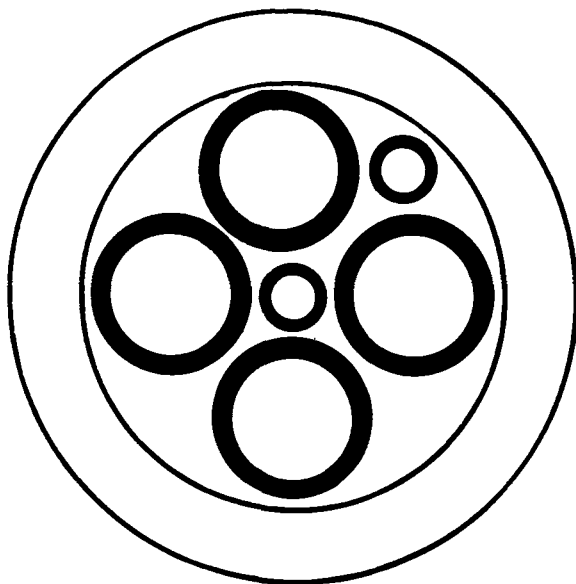
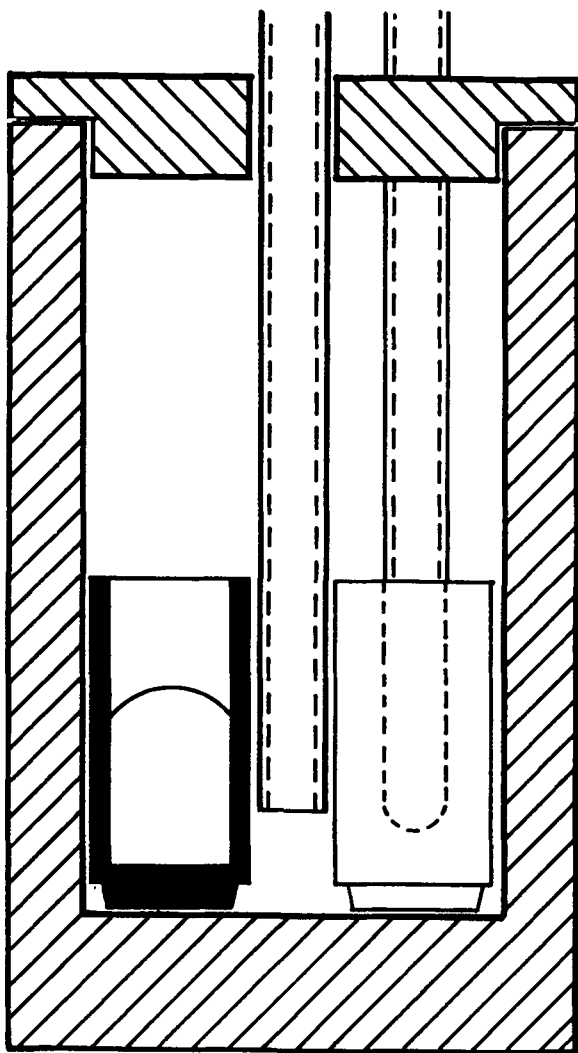


Fig. 2—Apparatus for equilibrating melts with graphite and CO gas.

the hot zone temperature exceeded about 1600 K, the gas was changed to pure CO at a flow rate of 100 ml per minute and the temperature was rapidly raised to the desired value. After the required time had elapsed (4 to 20 hours), the furnace power was cut to allow the temperature to fall rapidly (10 to 20 minutes) to below the melting point of the liquid. The apparatus was then removed from the furnace under the argon-hydrogen mixture. The latter gas was used at the lower temperature in preference to carbon monoxide to prevent sooting.

At the conclusion of the experiment, the sample crucibles were reweighed, then carefully cut open to extract the solidified sample as a single pellet. Adhering graphite on the pellet surfaces was carefully ground away, after which the sample was ground to powder. A small number of samples were sectioned and polished to confirm the absence of suspended or precipitated carbon. Carbon analysis was performed using a LECO model 244 carbon/sulfur analyzer by heating a 0.25 g sample of the powder together with a metallic accelerator (a mixture of tungsten and iron chips) in a stream of flowing oxygen. Carbon dioxide released from the sample was measured by an infrared spectrometer. The blank reading for carbon was measured as 0.015 ± 0.005 pct.

Table I shows the compositions, temperatures, and times for which carbon solubility experiments were performed, along with the measured carbon contents after the experiments. The early trials over times ranging from 4 to 20 hours suggested that a time of 8 hours would be sufficient for equilibration to occur, as shown in Figure 3. Schubert and Schwerdtfeger,^[2] who conducted extensive experiments with CaO-Al₂O₃ liquids, found that over longer times (20 to 70 hours), reaction between the crucible and melt caused measurable changes in the melt composition. In the current work, with SiO₂ in the melt, this reaction would be more pronounced.

Figure 4 shows the results for carbon contents plotted as a function of composition for the CaO-SiO₂ melts at 1823 K (1550 °C). A considerable amount of variability in the results can be seen. This variability can be explained by considering that the blank was large (about 0.015 pct) and highly variable (± 0.005 pct) relative to the size of the concentrations being analyzed, introducing a considerable extra uncertainty into the results. However, all measurements fell between 0.02 and 0.05 mass pct C, and even considering the large error, it can be stated with reasonable confidence that the measured solubility of carbon in calcium oxide-silica melts at 1823 K under 1 atm CO is between 0.01 and 0.06 mass pct and appears to rise with calcium oxide concentration. Two types of experiments are in fact shown in Figure 4: open shapes represent melts prepared as described, and closed shapes represent samples into which 2 mass pct CaC₂ was mixed, as a powder, before melting. Since the latter samples contained carbon in the ionic carbide form, and hence no impediment to dissolution existed, these experiments represented an approach to equilibrium from the high-carbon side. The similarity of carbon contents of the melts in which equilibrium was approached from the high or low side is confirmation of the order of magnitude of the results.

Further data for carbon solubility in CaO-CaF₂-SiO₂ melts at 1723 K are shown in Table II and Figure 5.

Table I. Measured Carbon Solubilities in CaO-SiO₂ Melts

Melt Number	Pct CaO	Pct SiO ₂	Pct CaC ₂	Time (Hours)	T (K)	C _{mass} (Pct)
CS2	40	60	—	7:40	1833	0.030, 0.025
				14:30	1833	0.041, 0.031
CS2	39	59	2	20:00	1833	0.020, 0.021
CS3	45	55	—	7:40	1833	0.034, 0.031
CS3	44	54	2	20:00	1833	0.041, 0.040
CS5	37	63	—	14:30	1833	0.036, 0.041, 0.041
CS5	36	62	2	20:00	1833	0.027, 0.033
CS6	52	48	—	4:00	1833	0.049, 0.044
				7:40	1833	0.044
				14:30	1833	0.052, 0.048
				20:00	1833	0.051

These experiments were performed at a lower temperature to reduce the possibility of interference by SiO or SiC formation, and the lower temperature necessitated the addition of CaF₂ to reduce the melting points. In these experiments, no apparent effect of composition is seen. However, the experimental error is again sufficiently large relative to the quantity being measured as to mask any possible variation of carbon content with composition.

In this work, very low solubilities of carbon in calcium silicates at 1833 K (0.02 to 0.05 pct) and calcium fluorosilicates at 1723 (<0.03 pct) were measured. These results do not agree with those of Swisher.^[1] In that work, solubilities up to 1.5 mass pct were measured in CaO·SiO₂ liquid at 1883 K under 1 atm CO, as shown in Figure 1. The carbon solubility rapidly falls, as shown in the figure, as alumina is substituted for silica in the original calcium metasilicate composition. A silica-free CaO-Al₂O₃ composition was found to contain 0.06 pct C.

Results for the various studies of carbide capacity in calcium aluminate melts have been compared by Sommerville,^[9] as shown in Figure 6, using the concept of optical basicity. Since good agreement is evident between the different investigations, it was felt reasonable to extend this approach to permit comparison of carbide capacities in the calcium aluminate and silicate systems.

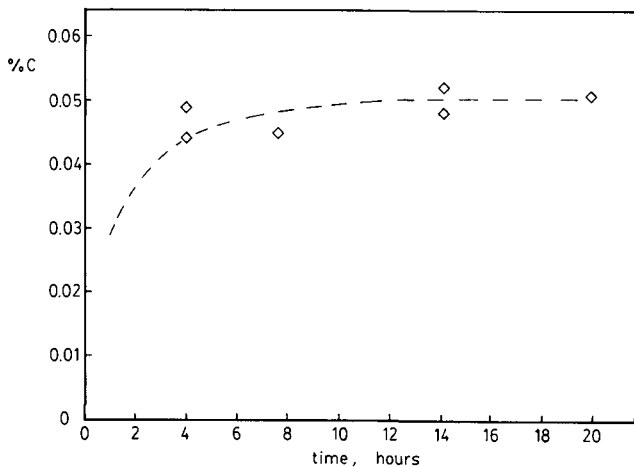


Fig. 3—Effect of time on carbon content in melt CS6, 52 pct CaO + 48 pct SiO₂.

Accordingly, the solubilities determined for carbon in the present work are plotted on the same graph, and the results of Swisher in the lime-silica system are also shown. The aluminate results, extrapolated to lower basicity, would have predicted a lower carbide capacity than that observed by a factor of about 5. Thus, the activity coefficient of carbide ion, f_c , may be about 5 times lower in the system CaO-SiO₂ than in CaO-Al₂O₃. It is proposed that the presence of silica in the melt lowers the activity of carbon in the melt relative to its activity in aluminate melts.

Given that there is some degree of accord between the

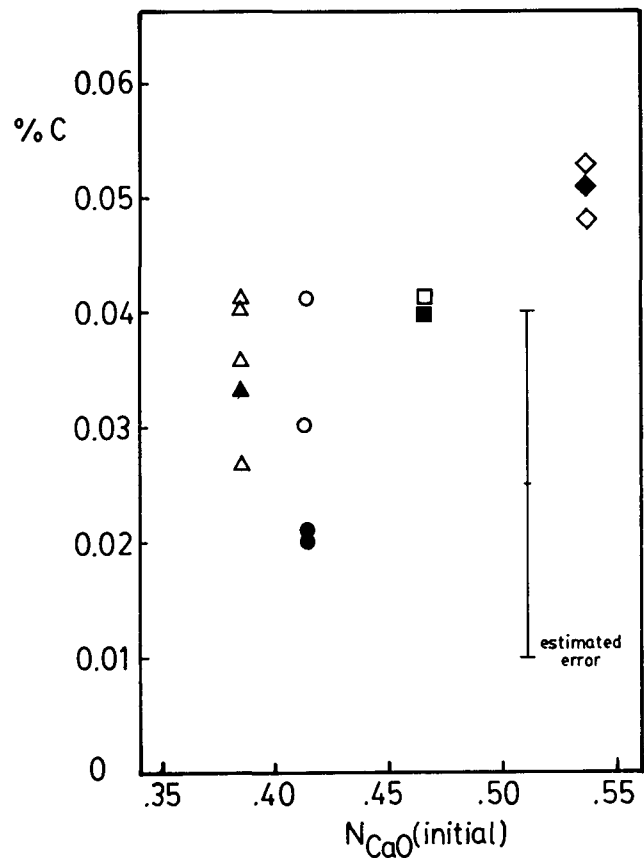


Fig. 4—Carbon content vs initial melt composition in CaO-SiO₂ melts. Open points: no initial carbon; closed points: 2 pct CaC₂ added.

Table II. Measured Carbon Solubilities in CaO-CaF₂-SiO₂ Melts

Melt Number	Pct CaO	Pct CaF ₂	Pct SiO ₂	Time (Hours)	T (K)	C _{mass} (Pct)
F1	52	3	44	8:00	1733	0.015
				17:15	1733	0.020, 0.023
				20:00	1733	0.033, 0.032, 0.034
F3	36	10	54	8:00	1733	0.017, 0.014
				17:15	1733	0.019, 0.026
				20:00	1733	0.035, 0.05
F6	50	10	40	8:00	1733	0.016, 0.020
				17:15	1733	0.022, 0.022
				20:00	1733	0.020, 0.019
F7	43	10	47	8:00	1733	0.016, 0.014
				17:15	1733	0.027, 0.022
				20:00	1733	0.013, 0.015

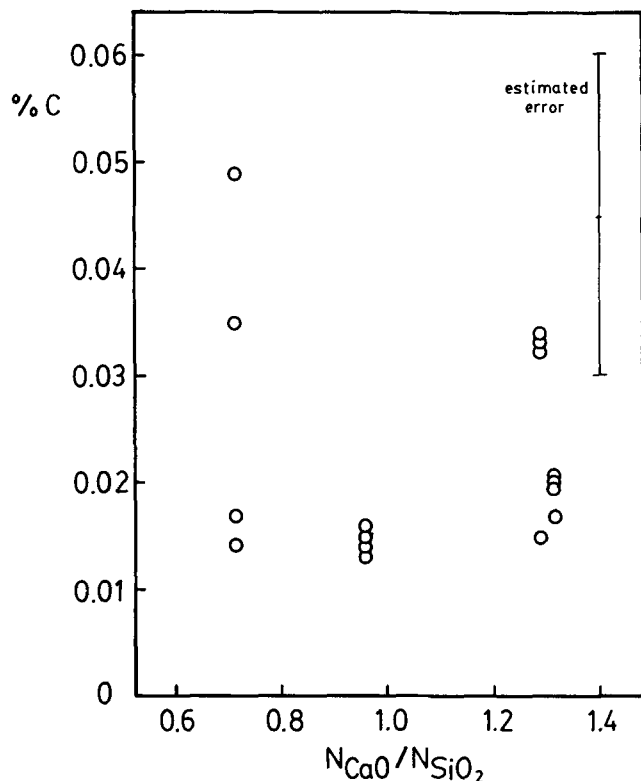


Fig. 5—Carbon content vs initial melt composition in CaO-CaF₂-SiO₂ melts.

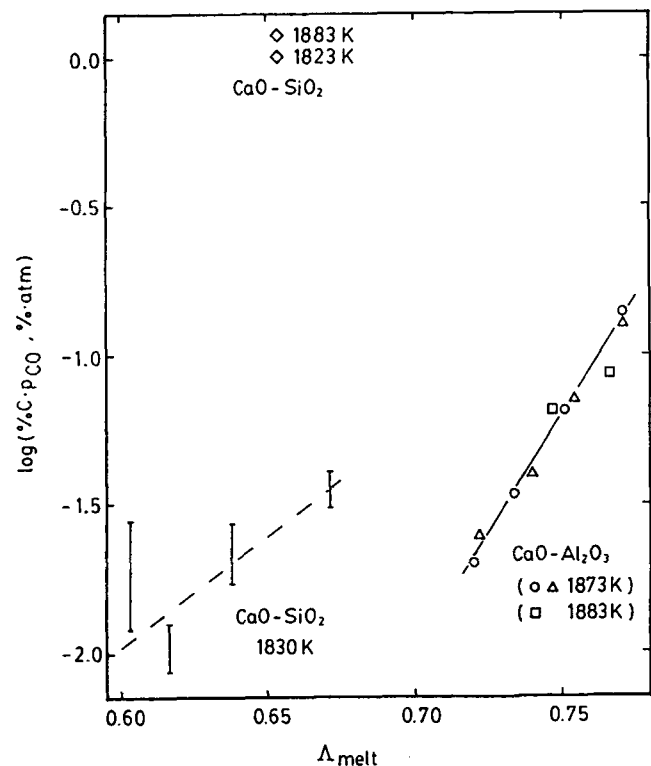


Fig. 6—Correlations of carbide capacity with optical basicity for CaO-Al₂O₃ and CaO-SiO₂ melts: \diamond , \square Swisher,⁽¹⁾ \circ Schubert and Schwerdtfeger,⁽²⁾ \triangle Schwerdtfeger and Schubert,⁽³⁾ and — present work.

results from this work and the work with calcium aluminates, how can Swisher's results in calcium metasilicate be rationalized? Two observations can be made regarding his work. First, the data used by Swisher for silicon carbide formation predicted a minimum temperature of 1908 ± 20 K (1635 ± 20 °C) for SiC formation. More recent data⁽¹⁰⁾ suggest a lower temperature, around 1795 ± 20 K (1522 °C) at unit activities and around 1860 K (1587 °C) at a silica activity of 0.4, corresponding⁽¹¹⁾ to the metasilicate composition. Thus, at 1883 K, the formation of silicon carbide appears to be thermodynamically likely. Second, an equilibration time of only 2 hours was used. Thus, silicon carbide may have precipitated in the melt but not yet acquired a particle size

sufficient to allow separation, so that most of the carbon found by analysis and assumed to be in solution in the slag was in fact present as silicon carbide. The present work was done at 1833 K, which should not cause SiC formation at an activity of silica less than 0.75.

In summary, the work of Swisher agrees with other results in the literature concerning carbon solubility in calcium aluminate melts. However, in calcium silicates, incorrect thermodynamic data and an equilibration time that was perhaps too short for the more viscous silicate melts appear to have caused a false interpretation of the results. In the present work, carbon solubilities in calcium silicates were found to be between 30 and 75 times lower than those reported by Swisher.

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Group Optical Basicities of Polymerized Anions in Slags

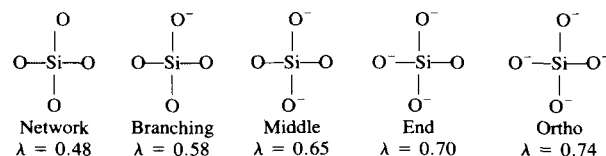
I.D. SOMMERVILLE and C.R. MASSON

Since its introduction to the metallurgical literature in 1978,^[1] the concept of optical basicity has been widely applied to rationalize and predict data on a range of chemical properties of slags and fluxes. The various correlations for slags have recently been reviewed elsewhere.^[2]

The macroscopic or average value of optical basicity of a slag of any given composition is governed by the cations and anions of which the slag is composed. Duffy and Ingram^[3] have shown how the microscopic optical basicities of individual oxygen "ions" and the group optical basicities of units such as SiO_4^{4-} may be calculated. The purpose of this short communication is to show how the optical basicities of these individual anions may also be calculated very simply using their approach.

In general, slags have been conceived as consisting of three types of oxygen ions, O^{2-} , O^- , and O^0 , referred to as free, terminal or nonbridging, and bridging oxy-

gens, respectively. The latter two are incorporated into the five basic structural entities in silicate melts:



where O represents a bridging oxygen and O^- a non-bridging oxygen.

Dron^[4,5] has shown that the equilibria between these groupings can be described in terms of four independent equilibrium constants, while Duffy and Ingram^[3] have calculated the group optical basicity, λ , of these units to have the values shown under each. These values were obtained using $\lambda = 0.74$ for nonbridging oxygens and $\lambda = 0.48$ for bridging oxygens. Taking the group called "middle" as an example, it has two nonbridging and two bridging oxygens, each of which is shared with one other silicon. Thus,

$$\lambda = \frac{2 \times 0.74 + 2 \times 0.5 \times 0.48}{2 + 2 \times 0.5} = 0.65$$

Generalizing this approach to any silicate ion with the formula $\text{Si}_n\text{O}_m^{x-}$, it is seen that there are χ nonbridging oxygens and $(m - \chi)$ bridging oxygens. Thus, by analogy with the formula used above, its optical basicity will be given by the expression

$$\lambda = \frac{0.74 + 0.24(m - \chi)}{\chi + 0.5(m - \chi)} \quad [1]$$

Although n does not appear explicitly in Eq. [1], it is nevertheless one of the factors governing the optical basicities of anions, since both χ and m are functions of n .

For linear chains, where $\chi = (2n + 2)$ and $m = (3n + 1)$, Eq. [1] reduces to

$$\lambda = \frac{0.74(2n + 2) + 0.24(n - 1)}{2.5n + 1.5} \quad [2]$$

and hence,

$$\lambda = \frac{1.72n + 1.24}{2.5n + 1.5} \quad [3]$$

Clearly, λ decreases with increasing chain length as non-bridging oxygens are replaced by bridging oxygens, as shown in Figure 1. Eventually, for an infinite linear chain,

$$\lambda = \frac{1.72}{2.5} = 0.688$$

For branched chains, the relation existing between n , m , and χ appears to be the same as for linear chains, and Eq. [2] may still be used.

For rings, where $m = (2n + 0.5\chi)$, Eq. [1] reduces to

$$\lambda = \frac{0.62\chi + 0.48n}{0.75\chi + n} \quad [4]$$

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