Short Communication

Covalent oxocomplexes and electrovalent coordination in glass

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The difference in electronegativity between an oxide ion bonded to silicon and a metal ion gives a hint whether an oxocomplex is expected or not. This has an implication for formulating correct stoichiometric reactions for transition metal ions in glass melts.

Kovalente Oxokomplexe und elektrovalente Koordination in Glas

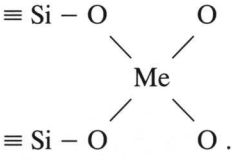
Der Elektronegativitätsunterschied zwischen einem an Silicium gebundenen Oxidion und einem Metallion zeigt an, ob die Bildung eines Oxokomplexes erwartet werden kann oder nicht. Dies hat Bedeutung für die Formulierung genauer stöchiometrischer Reaktionsgleichungen für Übergangsmetallionen in Glasschmelzen.

In a recent paper [1] about polyvalent ions in melts, an attempt is made to select the correct stoichiometric reaction among some twelve general alternatives. The main objection to this approach is that there is very little point in writing six reactions, each with two variables, for expressing some of the arithmetically correct alternatives, as long as no selection rules are at hand which definitely choose the one which is chemically relevant. Instead of the mathematical approach, in this case a chemical approach should be preferred, say, by either using chemical bonding concepts or chemical thermodynamics.

In the former, the difference in electronegativity gives a hint whether a covalent complex or an electrovalent coordination is to be expected. The electronegativity χ_O for oxide ions in silicate glasses is of the order of 3.3 on the Pauling scale, while the electronegativity of $3d$ ions in octahedral coordination is reasonably accurately described by

$$\chi_{Me} = 0.22\, q + 2 \ln z - 0.7\,, \tag{1}$$

where q is the number of d electrons and z is the formal oxidation number of the ion [2]. In tetrahedral coordination the electronegativity of the metal ion is some 0.25 units lower. When the difference $\chi_O - \chi_{Me}$ is about unity or less, a fairly covalent oxocomplex can be expected. It is interesting to note that this change to covalent dominance occurs when the radius ratio r_{Me}/r_O predicts preference for tetrahedral coordination. In other words, it gives the limit for network formers (or better, participators) in the Zachariasen approach. Thus, if a polyvalent ion forms an oxocomplex, it is probably also bonded to the silicate structure [3], like



The other approach (which in a way is the one attempted in [1]) is to note the response of a polyvalent ion to changes in the conditions of the solvent. Reactions are then either dependent on changes in the redox conditions only

$$Me^{n+} \rightleftharpoons Me^{n+1} + e^-\,, \tag{2}$$

in acidity only

$$Me^{n+1} + m\, O^{2-} \rightleftharpoons MeO_m^{n+1-2m}, \tag{3}$$

or in both simultaneously

$$Me^{n+} + m\, O^{2-} \rightleftharpoons MeO_m^{n+1-2m} + e^-. \tag{4}$$

If the equilibrium constants are known, the reactions (2 to 4) can be expressed graphically and the figure in [4] gives a good overview of the regions of dominance of each type of ion. It is, however, not possible to decide a priori which reaction actually describes the behaviour in the melt. This can be found only by experiments.

Nonetheless, there seems to be no need to consider the coordinated oxide ions in a reaction as long as they are mainly electrostatically attached to the metal ion, i.e. R-type reactions of the kind mentioned in [1] are extremely rare and exist only if the electronegativity of the lower valency ion is above 2.3, but then the electronegativity of the higher

Received 9 January 1989.

valency ion is still higher, i.e. also forms a covalent oxocomplex. One example would be the refining action of arsenic

$$AsO_2^- + 2\,O^{2-} \rightleftharpoons AsO_4^{3-} + 2\,e^- \,, \tag{5}$$

which shifts the reaction

$$O_2 + 4\,e^- \rightleftharpoons 2\,O^{2-} \tag{6}$$

to the right when the temperature is lowered. However, the electronegativity of the 3*d* ions Ti^{3+}, V^{3+}, Cr^{3+} and Mn^{3+} is probably too low to allow covalent complexes, in particular as there is also a ligand field stabilisation effect in preference for octahedral coordination. But still, theory only guides and experiments must decide whether this is true or not.

References

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