# Original Paper

## Redox equilibria and constitution of polyvalent ions in oxide melts and glasses

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It is shown that redox equilibria of polyvalent ions in glass melts cannot usually be considered without complex-formation reactions and therefore without ligand formation and coordination behaviour. In principle, a distinction should be made between ligand numbers and coordination numbers, as well as between conditions at high temperatures and those at temperatures below $T_g$. The equations derived and some experiments in literature indicate that most transition metal ion pairs in melts show a stronger tendency to form complexes for the higher valency states than for the lower ones. In many cases this behaviour coincides with the ligand number of polyvalent cations in the corresponding glasses, viz. the higher valency state leads to a stronger complex formation with network-forming character and thus, to a lower coordination number than is the case with the lower valency state of a polyvalent ion. However, this behaviour often does not occur because of the very common tendency for coordination to change during cooling from the melt to the glassy state. Those differences between the stable melt at very high temperatures, the metastable melt at intermediate temperatures and the glassy state at room temperature need to be considered and are discussed.

**Redoxgleichgewichte und Konstitution polyvalenter Ionen in oxidischen Schmelzen und Gläsern**

Es wird gezeigt, daß Redoxgleichgewichte polyvalenter Ionen in Glasschmelzen nicht ohne Komplexbildungsreaktionen und damit nicht ohne Ligandenbildung und Koordinationsbestreben betrachtet werden können. Grundsätzlich sollte zwischen Liganden- und Koordinationszahl unterschieden werden, wie auch zwischen Zuständen bei hohen Temperaturen in der Schmelze einerseits und Temperaturen unterhalb $T_g$ andererseits. Die hier entwickelten Gleichungen und einige Experimente in der Literatur weisen darauf hin, daß die meisten Übergangsmetallionenpaare für den höheren Valenzzustand eine stärkere Tendenz zur Komplexbildung zeigen als für den niedrigeren. Dieses Verhalten stimmt in vielen Fällen mit der Ligandenzahl der polyvalenten Kationen in den entsprechenden Gläsern überein, d. h. der höhere Valenzzustand führt zu einer stärkeren Komplexbildung mit netzwerkbildendem Charakter und damit zu einer geringeren Koordinationszahl als es für den niederwertigen Zustand eines polyvalenten Ions der Fall ist. Allerdings trifft diese Übereinstimmung in vielen Fällen wegen des ganz allgemeinen Koordinationsbestrebens während der Abkühlung von der Schmelze in den glasigen Zustand nicht zu. Solche Unterschiede zwischen der stabilen Schmelze bei sehr hohen Temperaturen, der metastabilen Schmelze bei mittleren Temperaturen und dem Glaszustand bei Raumtemperatur sind zu berücksichtigen und werden diskutiert.

### 1. Introduction

Most investigations were made with respect to colour of glasses [1 and 2] but others were done in order to find out indicators for basicity [3]. Many redox equilibria in glass melts were investigated experimentally in an indirect manner by spectral and chemical analysis after quenching the melt to room temperature. Only a few papers have been published on redox equilibria between reduced and oxidized polyvalent ions directly within the melt at equilibrium temperatures. Some of these were evaluated directly by electrochemical methods at melt temperatures, by application of voltammetry and emf measurements [4 and 5]. The electrochemical series of TM (= Transition Metal) ions was proposed for some glass systems [4 to 7]. Effects of oxygen partial pressure, $P_{O_2}$, temperature and basicity on the redox equilibria were discussed by Paul [3]. These results, especially the effects of basicity, cannot be described only by the simple redox equilibrium such as

$$M^{n+} + m/4\ O_2 \rightleftharpoons M^{(n+m)+} + m/2\ O^{2-} \qquad (1)$$

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because if basicity (oxygen ion activity) is increased, the higher valency state is usually preferred and this contradicts equation (1). However, this decrepancy was argued into the formalistic conclusion that the variation of the equilibrium constant $K$

$$\frac{[M^{(n+m)+}]}{[M^{n+}]} = K\frac{(P_{O_2})^{m/4}}{(O^{2-})^{m/2}}$$

with composition may be the dominating controlling factor which determines the basicity dependence of the redox equilibrium. On the other hand, the proposal of complex formation in glass melts was made first by Dietzel et al. [8 and 9] (see also [10]) in the cases of iron and chromium as examples

$$2\ Fe^{2+} + 3\ O^{2-} + 1/2\ O_2 \rightleftharpoons 2\ FeO_2^-\ ,$$
$$2\ Cr^{3+} + 5\ O^{2-} + 3/2\ O_2 \rightleftharpoons 2\ CrO_4^{2-}$$

in which the effect of basicity is especially regarded.

The formation of complexes of polyvalent ions in glass melts was also suggested by several authors [11 to 15], and this idea was successfully applied to some

redox pairs, such as $Cr^{3+}/Cr^{6+}$, $Fe^{2+}/Fe^{3+}$, etc. However, most of the previously reported investigations have been done in a qualitative way because of the lack of sufficient data for oxygen ion activities of glass melts. On the other hand, various spectral analyses, such as optical absorption [16], ESR, Mössbauer etc., were applied to investigate the coordination states of TM ions [17] in glasses at room temperature.

In the present paper many experimental results previously reported are reviewed and the applicability of a combination of redox reactions leading to redox equilibria of polyvalent ions in glass melts are discussed from a more general point of view and a distinction will be made between ligand formation in the melts and change in coordination during cooling although both processes behave very similarly with temperature.

The following symbols will be used:

| | | |
|---|---|---|
| M | = | polyvalent cation |
| $n+$ | = | lower valency state |
| $(n+m)+$ | = | higher valency state |
| $x$ | = | coordination number of the polyvalent cation with the lower valency state |
| $y$ | = | coordination number of the polyvalent cation with the higher valency state |
| $P_{O_2}$ | = | oxygen partial pressure |
| $[O^{2-}]$ | = | oxygen activity (basicity) |
| $K_i$ | = | reaction constants |
| $R_{exp}$ | = | experimentally determined redox ratio |
| $R_{theor}$ | = | theoretical redox ratio (see equation (9)) |

## 2. Theoretical formalism

The simple redox reaction (equation (1)) is combined with the complex-formation reactions (equations (3 and 5)).

$$M^{n+} + m/4\ O_2 \rightleftharpoons M^{(n+m)+} + m/2\ O^{2-}\ , \tag{1}$$

$$K_1 = [M^{(n+m)+}]\,[O^{2-}]^{m/2} / ([M^{n+}]\,P_{O_2}^{m/4})\ , \tag{2}$$

$$M^{n+} + x\ O^{2-} \rightleftharpoons MO_x^{(2x-n)-}\ , \tag{3}$$

$$K_2 = [MO_x^{(2x-n)-}] / ([M^{n+}]\,[O^{2-}]^x)\ , \tag{4}$$

$$M^{(n+m)+} + y\ O^{2-} \rightleftharpoons MO_y^{(2y-m-n)-}, \tag{5}$$

$$K_3 = [MO_y^{(2y-m-n)-}] / ([M^{(n+m)+}]\,[O^{2-}]^y)\ . \tag{6}$$

The experimentally analysed concentrations of the reduced TM ions, $[M^{n+}]_{exp}$, and the oxidized cations, $[M^{(m+n)+}]_{exp}$, are as follows

$$[M^{n+}]_{exp} = [M^{n+}] + [MO_x^{(2x-n)-}]\ , \tag{7}$$

$$[M^{(m+n)+}]_{exp} = [M^{(m+n)+}] + [MO_y^{(2y-m-n)-}]\ , \tag{8}$$

where $x$ and $y$ mean the ligand numbers of the complexes formed. Therefore, the experimentally determined redox ratio in the usual way, $[M^{n+}]_{exp} / [M^{(m+n)+}]_{exp} = R_{exp}$, will be replaced here by

$$\frac{[M^{n+}]_{exp}}{[M^{(n+m)+}]_{exp}} = R_{exp} \triangleq \frac{[M^{n+}] + [MO_x^{(2x-n)-}]}{[M^{(n+m)+}] + [MO_y^{(2y-m-n)-}]} = R_{theor}\ . \tag{9}$$

From equations (1 to 9), $R_{exp}$ can be described with the equilibrium constants $K_1$, $K_2$ and $K_3$ by equation (10):

$$R = R_{theor} = \frac{[O^{2-}]^{m/2}}{K_1\,P_{O_2}^{m/4}} \cdot \frac{1 + K_2\,[O^{2-}]^x}{1 + K_3\,[O^{2-}]^y} \triangleq R_{exp}\ . \tag{10}$$

The redox ratio is expected to depend on $P_{O_2}^{m/4}$. The effect of basicity, $[O^{2-}]$, on the redox ratio depends on the oxygen activity and on the tendency of complex formation of the polyvalent ions, i.e. the equilibrium constants of equations (1, 3 and 5), i.e. $K_1$, $K_2$ and $K_3$, equations (2, 4 and 6).

In section 3.1. selection rules will be applied which can very easily be tested experimentally. If $R_{theor}$ increases with increasing basicity (oxygen activity $[O^{2-}]$) at constant oxygen partial pressure, $P_{O_2}$, redox pairs and corresponding equations belong to the reduced type, R-type; if $R_{theor}$ decreases with increasing basicity the oxidized type, O-type, is obtained.

### 2.1. The case $K_2\,[O^{2-}]$, $K_3\,[O^{2-}] \ll 1$

Equations (1 and 2) can be applied as approximations because $[M^{n+}] \gg [MO_x^{(2x-n)-}]$ and $[M^{(m+n)+} \gg [MO_y^{(2y-m-n)-}]$. $R_{theor}$ increases with increasing basicity (reduced type, or R-type). Examples are given in sections 3.1. and 3.5.4.

### 2.2. The case $K_2 \gg K_3$

The concentration of the complexes of the oxidized polyvalent ions can be neglected, and the redox reaction (equations (11 and 12)), which is a combination of reactions (equations (1 and 3)), can be applied:

$$MO_x^{(2x-n)-} + m/4\ O_2 \rightleftharpoons M^{(m+n)+} + (m/2 + x)\ O^{2-}\ , \tag{11}$$

$$K_4 = [M^{(m+n)+}]\,[O^{2-}]^{(m/2+x)} / ([MO_x^{(2x-n)-}]\,P_{O_2}^{m/4}) = K_1/K_2 \tag{12}$$

and therefore,

$$R_{theor} \approx \frac{1}{K_4}\,\frac{[O^{2-}]^{(m/2+x)}}{P_{O_2}^{m/4}}\ . \tag{13}$$

This means, that the redox ratio, $R_{theor}$, increases at $P_{O_2}$ = constant with increasing basicity (R-type),

because $m$ and $x$ are always positive. With increasing $P_{O_2}$ at constant basicity the redox ratio decreases, not only in this but also in all the other cases as is well-known also from experiments. An example is given in section 3.5.3.

### 2.3. The case $K_3 \gg K_2$

Only the complex formation of the oxidized TM ions will be discussed (equations (1 and 5)):

$$M^{n+} + m/4\ O_2 + (y - m/2)\ O^{2-} \rightleftharpoons MO_y^{(2y-m-n)-}, \tag{14}$$

$$K_5 = [MO_y^{(2y-m-n)-}]/([M^{n+}] P_{O_2}^{m/4} [O^{2-}]^{(y-m/2)}) = K_1 \cdot K_3 \tag{15}$$

and

$$R_{\text{theor}} \approx \frac{1}{K_5} \frac{1}{P_{O_2}^{m/4} [O^{2-}]^{(y-m/2)}}. \tag{16}$$

$R_{\text{theor}}$ decreases with increasing $[O^{2-}]$ if $(y - m/2) > 0$ (oxidized, or O-type), but increases if $(y - m/2) < 0$ (R-type). Examples are given in sections 3.5.1., 3.5.2., and 3.5.5.

It may be emphasized that a selection of the various possibilities for complex formations can be made by the decision or distinction between R- or O-type as follows:

$y > m/2$ or $y \geq (m + 1)/2$ for the O-type and
$y < m/2$ or $y \leq (m - 1)/2$ for the R-type. (14a)

### 2.4. The case $K_2 [O^{2-}]^x$, $K_3 [O^{2-}]^y \gg 1$

The equations (17 and 18) can be applied as approximations. The combination of equations (1, 3 and 5) results in the case where only complex formation is considered:

$$MO_x^{(2x-n)-} + m/4\ O_2 \rightleftharpoons MO_y^{(2y-m-n)-} + \\ + (m/2 - (y - x))\ O^{2-}, \tag{17}$$

$$K_6 = \frac{[MO_y^{(2y-m-n)-}]\,[O^{2-}]^{(m/2-(y-x))}}{[MO_x^{(2x-n)-}]\,P_{O_2}^{m/4}} = \frac{K_1 \cdot K_3}{K_2} \tag{18}$$

and

$$R_{\text{theor}} \approx \frac{[MO_x^{(2x-n)-}]}{[MO_y^{(2y-m-n)-}]} = \frac{[O^{2-}]^{(m/2-(y-x))}}{K_6\, P_{O_2}^{m/4}}. \tag{19}$$

$R_{\text{theor}}$ increases with increasing basicity, if $(m/2 - (y - x)) > 0$ (R-type), but decreases, if $(m/2 - (y - x)) < 0$ (O-type). Examples are given in sections 3.5.3., 3.5.4., and 3.5.7.

A selection of the various possibilities for complex formations can be made again by the distinction between R- or O-type with:

$y > x + m/2$ or $y \geq x + (m+1)/2$ for the O-type
and
$y < x + m/2$ or $y \leq x + (m-1)/2$ for the R-type. (17a)

## 3. Discussion

### 3.1. Selection rules and prerequisites

In addition to the selection rules mentioned in section 2., particularly expressed in equations (11, 14, 14a, 17 and 17a), some further principles should be regarded in the discussion of sections 3.3. to 3.5.:

First, distinctions should be made between ligand or complex formation which has a chance to exist in the melt at least over a certain period of lifetime and coordination which happens by accident with a very short lifetime (determined preferably by Brownian movement). Complex formation with real ligands around an ion is connected by stronger bonding and oriented forces with a relatively high portion of covalency; the common coordination tendency with a lower portion of covalency will be less stable than the complexes at comparable temperatures because of their higher portion of less directional ionic bonding.

Second, application of Weyl's screening theory should be made [18]. With respect to that three temperature regions may be distinguished: very high temperatures, $T_h$, corresponding to low viscosities or temperatures far above liquidus temperature; intermediate temperatures, $T_m$, corresponding to high viscosities or temperatures below liquidus temperature and low temperatures, $T_l$, corresponding to the glassy state which are below $T_g$. Complexes will behave in the following way. At $T_h$ they will be damaged partly by strong vibrations and intensive Brownian movements in the form of loosened or broken ligands, thus the ligand number will be lower than required for ideal complex formation when observed in a very short time interval in a statistic sense; in other words: lifetime of the complete complexes will be very short. At $T_m$ lifetime will be longer and additionally to the ligand number a coordination tendency might occur or not, depending on the size of the cation. Below $T_g$ a fixed condition is reached for which the coordination number can be identical with the ligand number or perhaps larger than that. In such a way an increase of both ligand numbers and also of coordination numbers, takes place with decreasing temperature. Also distortions of the normal symmetry can be introduced by the coordination of the surrounding network of the high viscosity melt and of the glass. On the other hand, coordinations which happen by accident behave in a similar manner according to Weyl's screening theory, but they are less stable at $T_h$ and $T_m$. Thus, there are differences possible between coordination numbers which are obtained from the melt and those from the

glassy state, if no distinction is made between coordination and ligand numbers. This will be regarded and implied in the discussion of sections 3.3. to 3.5. Field strength or coordination tendencies of the surrounding network and its influence on coordination or complex is not discussed here because it is of minor influence, although this also has an influence on colour shift [1].

### 3.2. Simple redox reaction

Equation (1) can be applied only to the redox pair $Cu^+/Cu^{2+}$. The redox ratio of $[Cu^+/Cu^{2+}]$ in lead silicate glass [19] and in alkali borate, silicate or germanate glass [20] is reported to increase with increasing basicity (R-type). However, this simple equation is not fulfilled for other redox pairs, because most of the redox equilibria are known to be of the O-type [12 to 15 and 21 to 27].

### 3.3. Both, reduced and oxidized cations form complex ions

Equation (17) could be applied to the $Cu^+/Cu^{2+}$ pair, if $Cu^+O_6$ and $Cu^{2+}O_6$ complexes are formed in glass melts. In this case, $(y - x)$ is less than $m/2$. Indeed, $Cu^{2+}$ ion in oxide glasses is known to be 6-fold coordinated [28 to 31] but this is not true for the $Cu^+$ ion. In the melt the complex formation of $Cu^+O_6$ is highly unrealistic, thus, equation (17) is regarded not to be valid in the melt. However, the 6-fold coordination may be realized in the glassy state, but then under non-equilibrium condition and by coordination which happens by accident. Further discussion on the $Cu^+/Cu^{2+}$ pair will be shown in section 3.5.4.

The ligand number of the oxidized TM ion, $y$, should be larger than $x$, if a redox equilibrium of the O-type is considered: $(y - x) > m/2$; e.g. if the coordinations are $Fe^{2+}O_4$ and $Fe^{3+}O_6$, respectively. However, the ligand number of the reduced TM ions is usually larger than that of the oxidized ones. Therefore, this condition, $(y - x) > m/2$, cannot usually be satisfied.

A special case are the iron ions, $Fe^{2+}$ and $Fe^{3+}$, because their coordination numbers in various glass systems are reported to be 4 and 6 for both of them [26 and 32 to 54]. Therefore, the redox ratio $[Fe^{2+}] / [Fe^{3+}]$ in glasses cannot be determined only by the reaction between $Fe^{2+}O_4$ and $Fe^{3+}O_6$ or $Fe^{2+}O_6$ and $Fe^{3+}O_4$, respectively, but also by others as will be shown in section 3.5.3.

### 3.4. The cases $K_2 \gg K_3$ and $K_3 \gg K_2$

Most of the redox equilibria of polyvalent ions are known to be of the O-type. Therefore, equations (11 to 13), which are an approximation to equation (10) on the basis of the condition $K_2 \gg K_3$ and $K_2 [O^{2-}] \gg 1$, are not suitable for most of the redox pairs.

On the other hand, the effect of basicity on redox equilibria of polyvalent ions, except $Cu^+/Cu^{2+}$, can be qualitatively described by equations (14 to 16) with the assumptions $K_3 \gg K_2$ and $(y - m/2) > 0$. That means, the oxidized ions have a stronger tendency to form complexes than the reduced ones and the ligand numbers of the oxidized species are usually larger than $m/2$ for redox reactions, even for one-electron reactions such as $Fe^{2+}/Fe^{3+}$ or $Ti^{3+}/Ti^{4+}$. This is easily understood, because the oxidized ions have the smaller ionic radii, the higher charges and therefore the larger cationic field strength. Thus, the application of equations (14 to 16) leads to

$$Ti^{3+} + 1/4\ O_2 + 7/2\ O^{2-} \leftrightharpoons TiO_4^{4-}\ , \tag{20}$$

$$Cr^{3+} + 3/4\ O_2 + 5/2\ O^{2-} \leftrightharpoons CrO_4^{2-}\ , \tag{21}$$

$$Fe^{2+} + 1/4\ O_2 + 7/2\ O^{2-} \leftrightharpoons FeO_4^{5-} \tag{22}$$

for intermediate temperatures, $T_m$, but for very high temperatures, $T_h$, the equations may also be valid:

$$Ti^{3+} + 1/4\ O_2 + 5/2\ O^{2-} \rightleftharpoons TiO_3^{2-}\ , \tag{20a}$$

$$Fe^{2+} + 1/4\ O_2 + 3/2\ O^{2-} \rightleftharpoons FeO_2^{-}\ , \tag{22a}$$

$$Fe^{2+} + 1/4\ O_2 + 5/2\ O^{2-} \rightleftharpoons FeO_3^{3-}\ . \tag{22b}$$

(For chromium see section 7.) Both formulations (equations (22a and 22b)) have been used and treated thermodynamically for high temperature silicate melts (1400 °C) by Karlsson [55 and 56] as a function of basicity (see also Cable [57]).

### 3.5. Comparison of coordination tendency of polyvalent ions in glass melts according to redox behaviour with known coordination numbers in glasses

It is often assumed that complex ions in glass melts will take part of the network when quenched to a glass. The coordination number of a network former is usually lower than that of a network modifier. Therefore, the valency of a polyvalent ion with lower ligand number in glass should have a higher tendency to form a complex in the melt and vice versa, as shown by various examples in what follows.

#### 3.5.1. $Ti^{3+}/Ti^{4+}$

The redox equilibrium of the $Ti^{3+}/Ti^{4+}$ ion pair is reported to be of O-type [13 and 22]. The redox reaction can be written according to equations (14, 20 and 20a). Therefore, $Ti^{4+}$ ion should have a stronger

tendency to form a complex than $Ti^{3+}$ ion. As a consequence, on cooling the coordination number of $Ti^{4+}$ ion in glass should be smaller than that of $Ti^{3+}$ ion, because the coordination of $Ti^{4+}$ ion is based on ligand formation and that of $Ti^{3+}$ ion more or less on accidental coordination. On the other hand, the coordination number of $Ti^{4+}$ ion in glass has been reported to be 4 or 6 [58 to 61], and that of $Ti^{3+}$ ion in glass has been reported as 6 [62 to 64]. These results suggest also the stronger tendency of $Ti^{4+}$ ion to be the dominant complex former of the two transition ions in glass melts.

### 3.5.2. $Cr^{3+}/Cr^{6+}$ and $Cr^{5+}$

The redox equilibrium of the $Cr^{3+}/Cr^{6+}$ pair in glass melts is known to be of O-type [21, 23 and 24], and the redox reaction has been suggested to be characterized by equation (21). $Cr^{6+}$ ion in oxide glasses has been reported to be 4-fold coordinated [8 to 10 and 65] and $Cr^{3+}$ ion to be 6-fold coordinated [15 and 66 to 68]. Thus, the known difference between the ligand number of $Cr^{6+}$ ion and the coordination number of $Cr^{3+}$ ion coincides well with the difference considered from the redox equilibrium of O-type and equations (14 to 16 and 21).

In addition to the mentioned valency states, also the $Cr^{5+}$ ion has to be considered. Usually its concentration is very low, but easily detectable with ESR. The ability to form $[Cr^{5+}O_6]^{7-}$ or $CrO^{3+}$ complexes increases with the following increasing parameters: melting temperature, $P_{O_2}$, mean cooling rate, and tensile stress when quenched during fiber drawing process [69]. It seems that $Cr^{5+}$ ion is an intermediate and highly unstable state during the structural change from the octahedral symmetry of $Cr^{3+}$ ion to the tetrahedral symmetry of $Cr^{6+}$ ion and vice versa. $Cr^{5+}$ seems to be a suitable probe for the redox mechanism; e.g. the ESR intensity increases with increasing cooling rate. The redox equilibrium of chromium as a function of temperature may be written [69]:

$$[Cr^{6+}] / [Cr^{3+} + Cr^{5+}] = \exp(z\,\Delta\varepsilon/k\,T) \qquad (23)$$

with $z$ = number of electrons, $k$ = Boltzmann constant, $\Delta\varepsilon$ = free energy change for one-electron transition. According to the dependence on oxygen partial pressure and oxygen activity, equation (21) can be regarded as valid when $Cr^{6+}$ and $Cr^{5+}$ ions are combined:

$$Cr^{5+} + 1/4\ O_2 + 7/2\ O^{-2} \leftrightharpoons CrO_4^{2-} . \qquad (24)$$

### 3.5.3. $Fe^{2+}/Fe^{3+}$

The redox equilibrium of the $Fe^{2+}/Fe^{3+}$ pair is also known to be of the O-type when the total iron ion concentration (as $Fe_2O_3$ in the batch) is less than about 5 mol% [13, 14, 17, 24 and 25]. Therefore, the coordination number of $Fe^{3+}$ ion in oxide glasses is considered to be smaller than that of $Fe^{2+}$ ion. Many authors showed that $Fe^{3+}$ ions in glasses should be 4- and 6-fold coordinated, preferably 4-fold in silicate and borate glasses, particularly 6-fold in phosphate glasses [26 and 32 to 54]. $Fe^{2+}$ ions preferably should be 6-fold coordinated [26, 32 to 40, 42, 43, 45 to 48 and 50]. However, the coordination number of $Fe^{2+}$ ion has been reported also to be 4 when the total iron ion concentration is low [40, 48, 50 and 54]. 4- and 6-fold coordinated $Fe^{3+}$ and exclusively 6-fold coordinated $Fe^{2+}$ ions were detected in alkaline earth metaphosphate glasses from Mössbauer spectra [37]. Therefore, the $Fe^{3+}$ ion should usually have a stronger tendency to form a complex than the $Fe^{2+}$ ion, as predicted from the redox behaviour (equations (14 to 16, 22 and 22a)), from which a ligand number of 4 and at very high temperatures, $T_h$, a ligand number of 2 is stated for $Fe^{3+}$ (equation (22a)).

If, however, the total iron ion concentration (as $Fe_2O_3$ in the batch) exceeds 5 mol% in alkaline earth metaphosphate glasses, the redox equilibrium of the $Fe^{2+}/Fe^{3+}$ pair is of the R-type and the formation of $Fe^{2+}$ complex was suggested [14]. Similar results were obtained in barium–aluminophosphate glasses with high iron oxide concentrations [54]. Thus, equations (11 to 13 and 17 to 19) should be applied. This results in the following possible combinations of R-types, respectively, depending on concentration and glass composition:

$$FeO_4^{6-} + 1/4\ O_2 \leftrightharpoons Fe^{3+} + 9/2\ O^{2-} , \qquad (25)$$

$$FeO_4^{6-} + 1/4\ O_2 \leftrightharpoons FeO_4^{5-} + 1/2\ O^{2-} . \qquad (26)$$

### 3.5.4. $Cu^{+}/Cu^{2+}$

As mentioned in sections 3.2. and 3.3., equations (1 or 17) can be applied formalistically to the redox equilibrium between $Cu^{+}$ and $Cu^{2+}$ ions. The difference in tendency to form a complex in the melt should be small for the two copper ions. The $Cu^{+}$ ion should have spherical symmetry because of its $d^{10}$ configuration (noble gas like), and should be a free ion in glass melts. If so, only equation (1) should be applied for the $Cu^{+}/Cu^{2+}$ pair.

### 3.5.5. $V^{3+}/V^{4+}$ and $V^{4+}/V^{5+}$

The redox equilibria between $V^{3+}$ and $V^{4+}$, and between $V^{4+}$ and $V^{5+}$ ions are reported to be of O-type [12 and 54]. Therefore, the order of increasing tendency to form a complex is considered to be $V^{3+} < V^{4+} < V^{5+}$.

The coordination state of $V^{4+}$ ion in glass is known to be strongly tetragonal and, in some glasses,

also rhombohedrally distorted octahedron and that of $V^{5+}$ ion strongly distorted tetrahedral or octahedral [44, 54, 61 and 70 to 75]. The formation of vanadyl complex $VO^{2+}$ in glasses is also reported [54, 71 and 74]. Therefore, the redox reactions at intermediate temperatures, $T_m$, are considered to be as follows according to equations (14 to 16):

$$V^{4+} + 1/4\ O_2 + 7/2\ O^{2-} \leftrightharpoons VO_4^{3-}\ , \tag{27}$$

$$VO^{2+} + 1/4\ O_2 + 5/2\ O^{2-} \leftrightharpoons VO_4^{3-}\ , \tag{28}$$

and at very high temperatures, $T_h$:

$$V^{4+} + 1/4\ O_2 + 5/2\ O^{2-} \rightleftharpoons VO_3^{-} \tag{27a}$$

or possibly at low temperatures, $T_l$:

$$VO^{2+} + 1/4\ O_2 + 9/2\ O^{2-} \rightleftharpoons VO_6^{7-}\ . \tag{28a}$$

### 3.5.6. $Cr^{2+}/Cr^{3+}$

The equilibrium of $Cr^{2+}/Cr^{3+}$ pair is known to be of O-type [15]. Therefore, the tendency to form a complex of $Cr^{3+}$ ion should be stronger than that of $Cr^{2+}$ ion, and the coordination number of $Cr^{3+}$ should be lower than that of $Cr^{2+}$. However, the coordination states of $Cr^{2+}$ and $Cr^{3+}$ ions in alkaline earth metaphosphate glasses are both 6-fold [15, 34, 66 and 67]. Therefore, the tendency to form a complex in glass melts cannot be estimated only from the determination of coordination numbers of TM ions in glasses. For this case none of the given equations can be applied directly. However, the following formulation can be given with respect to [15] for the special case of strongly reduced phosphate glasses containing chromium:

$$CrO_l^{(2-2l)+} + 1/4\ O_2 + (h-l-1/2)\ O^{2-} \rightleftharpoons CrO_h^{(3-2h)+} \tag{29}$$

which follows from the redox reaction of chromium ions under strong reducing conditions. $h$ and $l$ are parameters related to the partially covalent nature of the chromium-oxygen bonds; they are no ligand numbers of chromium-oxy-acid complexes, but during cooling, a change of the coordination state of TM ions can occur as well as a change of redox ratio in the temperature range higher than the fictive temperature, as was suggested by Lenhart and Schaeffer [5 and 76]. Thus, complex-formation tendency is weak.

### 3.5.7. $Mn^{2+}/Mn^{3+}$

The redox equilibrium of the $Mn^{2+}/Mn^{3+}$ pair in borate [21] or silicate glasses [77] is known to be of O-type. Therefore, the coordination number of $Mn^{3+}$ ion is expected to be smaller than that of $Mn^{2+}$ ion. $Mn^{3+}$ ion is reported to be 6-fold coordinated in soda–lime–silica glass [16] and in silica glass [78]. However, Orgaz et al. [79] reported that the $Mn^{2+}$ ion is 4-fold and the $Mn^{3+}$ ion is 6-fold coordinated in silica glass coatings which were made through sol-gel process. $Mn^{2+}$ ion in borate glass is also reported to be 4-fold coordinated [80], but to be 6-fold coordinated in phosphate glass [81]. These results can be explained by equations (30 and 31) according to equations (3 and 17 to 19), respectively, which indicate that the $Mn^{2+}$ ion tends to form a complex in more basic glasses such as alkali borate glasses:

$$Mn^{2+} + 4\ O^{2-} \leftrightharpoons MnO_4^{6-}\ , \tag{30}$$

$$MnO_4^{6-} + 1/4\ O_2 + 3/2\ O^{2-} \leftrightharpoons MnO_6^{9-}\ . \tag{31}$$

The known coordination numbers of $Mn^{2+}$ and $Mn^{3+}$ ions in glasses by optical absorption spectroscopy [16 and 78 to 81] suggest that the $Mn^{2+}$ ion has stronger tendency to form a complex than the $Mn^{3+}$ ion, and that the redox equilibrium of the $Mn^{2+}/Mn^{3+}$ pair should be of R-type.

However, the redox equilibrium was reported to be of O-type (see equations (30 and 31)). Further results for the coordination numbers of $Mn^{2+}$ and $Mn^{3+}$ ions should be obtained. Change in coordination numbers of manganese ions during quenching or by the mode of glass formation, e.g. melting at high temperature or sol-gel process, should be also discussed as well as in the case of $Cr^{2+}$ and $Cr^{3+}$ ions. At any rate the given equations describe the redox equilibrium correctly as O-type. However, the stronger complex formation of $Mn^{2+}$ ions as compared with $Mn^{3+}$ ions seems to be an anomaly within the series of transition metal ions.

### 3.5.8. $Sn^{2+}/Sn^{4+}$

The redox equilibrium of $Sn^{2+}/Sn^{4+}$ pair was reported to be of O-type [82]. The coordination numbers of $Sn^{2+}$ and $Sn^{4+}$ ions in glasses were determined by Mössbauer spectra to be 4 and 6 for the two valency states each. However, $Sn^{4+}$ ion has a stronger tendency to form a complex, i.e. a stronger tendency to 4-fold ligand formation in melts than $Sn^{2+}$ ion [83]. Therefore, equations (14 to 16) can be applied to the redox reaction in the melt between $Sn^{2+}$ and $Sn^{4+}$ ions in the following manner:

$$Sn^{2+} + 1/2\ O_2 + 3\ O^{2-} \rightleftharpoons SnO_4^{4-}\ , \tag{32}$$

$$K = [SnO_4^{4-}]/[Sn^{2+}]\ P_{O_2}^{1/2}\ [O^{2-}]^3\ , \tag{33}$$

or at very high temperatures, $T_h$:

$$Sn^{2+} + 1/2\ O_2 + 2\ O^{2-} \rightleftharpoons SnO_3^{2-}\ . \tag{32a}$$

### 3.5.9. $Ru^{3+}/Ru^{4+}/Ru^{6+}/Ru^{7+}$

Four oxidation states of ruthenium ions have been reported to exist in silicate and phosphate glasses [84]. With increasing $Na_2O$ content ruthenium is oxidized from $Ru^{3+}$ to $Ru^{6+}$ in silicate glasses, and from $Ru^{6+}$ to $Ru^{7+}$ in phosphate glasses of very high alkali oxide content (O-type). It was also reported that $Ru^{3+}$ and $Ru^{4+}$ ions are 6-fold and $Ru^{6+}$ and $Ru^{7+}$ ions 4-fold coordinated [84]. From these results the redox equilibrium between $Ru^{4+}$ and $Ru^{6+}$ ions may be described by equations (14 to 16) as the most stable complex-forming reaction among the various valency states of ruthenium:

$$Ru^{4+} + 1/2\ O_2 + 3\ O^{2-} \rightleftharpoons RuO_4^{2-}\ . \qquad (34)$$

The redox equilibrium of the $Ru^{3+}/Ru^{4+}$ pair may be analogous to that of $Cr^{2+}/Cr^{3+}$ pair (see section 3.5.6.). However, more quantitative investigations are required to elucidate these redox equilibria.

## 4. Remarks about conditions in the stable melt and in the glassy state

It is important to emphasize the remarkable difference between the complex formation in the melt and the development of coordination during cooling through the transition range to the glassy state as was mentioned in section 3.1. Usually the lower valency state of a polyvalent cation is preferred with increasing temperature. This indicates an R-type behaviour with respect to temperature and thus, a decrease of tendency to complex formation which is greater for the lower valence ions than for the higher. Therefore, for well-screened complex formations at all relatively low temperatures should be regarded but still those temperatures of the stable melt, viz. those temperatures just above but close to liquidus temperature. At those and higher temperatures there is no kinetic restraint for oxygen which will be needed for redox equilibration as was shown first by Lenhart and Schaeffer [5]. Therefore, the real redox equilibria will be obtained, even for those cases where more than one redox pair is present in the melt, if enough time is given for the diffusion process of oxygen between melt and furnace atmosphere. On cooling, however, the diffusion process between the gas atmosphere and the glass melt will be interrupted if the cooling rate is large enough ($\dot{T} \gtrapprox 7$ K/min) and the redox ratio will be frozen in. However, the diffusion process of oxygen between different polyvalent ions is not prevented (because the diffusion paths are very short) and in this way the complex formation of the polyvalent cations in the melt and their mutual interaction are not yet frozen in if more than one redox pair is present [5 to 7], because the whole network, which is still mobile, will also be changed only within the short-range and intermediate-range order. The complex formation around the polyvalent ions will be changed to distortions of complex symmetry and occasionally to additional coordination depending on the strength of the ligand field of the complex until the glass transition temperature is reached. In that way one may obtain another coordination arrangement in the glassy state at room temperature than in the melt. Therefore, it can be very doubtful that one can decide only from the coordination number, which has been determined from the glassy state to the complex formation in the melt and does not consider the given equations in section 2. and the selection rules in section 3.1. This will be demonstrated by some examples.

Copper was regarded in section 3.5.4. as a redox pair for which equation (1) is valid in the melt for two reasons: first, it is of R-type, second, $Cu^+$ ion exists as a mobile ion because of its noble gas-like configuration. Nevertheless, on cooling a certain agglomeration in form of a coordination takes place as is the case similar to that of $Na^+$ ions. In this way it is not surprising that a coordination number may be found in the glassy state. $Cu^{2+}$ may be regarded also as an ion, e.g. comparable with $Mg^{2+}$ ion in the melt, but coordinated 6-fold in the glassy state. Therefore, the formal equation

$$CuO_6^{11-} + 1/4\ O_2 \leftrightharpoons CuO_6^{10-} + 1/2\ O^{2-}$$

with respect to equations (17 to 19) for R-type is highly unrealistic in the melt although a 6-fold coordination is found in the solid glass caused by accidentally coordination tendency during cooling, but not as an equilibrium reaction equation of a complex formation.

For the chromium redox pairs equations (21, 24 and 29) have been considered to be valid for glass melts. The complex formation on the other hand with respect to equations (14 to 16), for example:

$$Cr^{2+} + 1/4\ O_2 + 11/2\ O^{2-} \leftrightharpoons CrO_6^{9-}$$

appears totally unrealistic in spite of the fact that this equation is of O-type as the experiments show and 6-fold coordination has been measured in glass. But this would be in contrast to equations (21 and 29) if $Cr^{3+}$ ion would form the complex $CrO_6^{9-}$ in the melt, because equations (17 to 19) must be applied then, which results in a R-type reaction between $Cr^{3+}$ and $Cr^{6+}$ ions

$$CrO_6^{9-} + 3/4\ O_2 \leftrightharpoons CrO_4^{2-} + 7/2\ O^{2-}$$

instead in an O-type one as experiments show. Even for the assumed complex $Cr^{6+}O_6^{6-}$ the application of equations (17 to 19) would result in a R- and not an O-type behaviour.

The case with iron redox pairs is relatively complicated because both the ferrous and ferric ions

can be coordinated with 4 and 6 oxygen atoms. Additionally they show O- and R-type behaviour depending on the total amount of iron oxide (section 3.5.3.). In spite of that behaviour resulting from room temperature measurements in the glassy state, only the equations (22, 25 and 26) with respect to the equations (11 to 13, 14 to 16 and 17 to 19) seem to be valid for O- and R-type behaviour, respectively.

The formal combinations, for example,

$$FeO_4^{6-} + 1/4\ O_2 + 3/2\ O^2 \rightleftharpoons FeO_6^{9-},$$

O-type, in accordance with equations (17 to 19),

$$FeO_6^{10-} + 1/4\ O_2 \rightleftharpoons FeO_4^{5-} + 5/2\ O^{2-},$$

R-type, in accordance with equations (17 to 19), appear highly unrealistic in the melt because in the case of O-type (low iron oxide concentrations) the $Fe^{3+}$ ion is predominantly 4-fold and the $Fe^{2+}$ ion 6-fold coordinated even in the glass. The ligand and/or coordination number in the melt cannot be higher than that in the glassy state. In the case of R-type at high iron oxide contents the second equation has also to be excluded because the complex $Fe^{2+}O_6^{10-}$ is unstable in the melt, especially as a network modifier, and the situation of equation (26) is more probable for that reason.

In general, the high-charged complex formations seem to have a very low probability in the melt as compared to the low-charged ones, predominantly those with network-modifying character, a statement which agrees with section 3.1.

## 5. Conclusions

Redox equilibria of polyvalent ions in glass melts can be described with combinations of simple redox and complex formation reactions of polyvalent ions, if some selection rules are considered such as the R- or O-type of a redox pair and Weyl's screening tendency with respect to ionic radii and temperature.

Further discussions based on more quantitative data of oxygen activities in glass melts as functions of temperature, composition and basicity than are available today will be needed to confirm the effect of complex formation on the redox equilibria.

The tendency of polyvalent ions to form a complex in glass melts predicted from the change in redox ratio with increasing basicity agrees with the tendency, which is suggested from the coordination numbers of polyvalent ions, determined in the glassy state by spectroscopic methods in many but not in all cases. This is explained by the tendency of coordination during cooling below the glass transition temperature, thus, in some cases larger coordination numbers are found in the glassy state than ligand numbers in the stable melt as is demonstrated for the ion pairs $Cu^+/Cu^{2+}$, $Cr^{2+}/Cr^{3+}$, $Mn^{2+}/Mn^{3+}$ and $Fe^{2+}/Fe^{3+}$ as examples.

## 6. References


[1] Weyl, W. A.: Coloured glasses. Sheffield: Soc. Glass Technol. 1951.

[2] Bamford, C. R.: Colour generation and control in glass. Amsterdam: Elsevier 1977.

[3] Paul, A.: Chemistry of glasses. London: Chapman and Hall 1982.

[4] Takahashi, K.; Miura, Y.: Electrochemical studies on diffusion and redox behaviour of various metal ions in some molten glasses. J. Non-Cryst. Solids **38 & 39** (1980) p. 527–532.

[5] Lenhart, A.; Schaeffer, H. A.: The determination of oxidation state and redox behaviour of glass melts using electrochemical sensors. In: XIV International Congress on Glass. New Delhi 1986. Coll. Papers. Vol. 1, p. 147–154.

[6] Brückner, R.: Redox ratio shifts and electrical transport properties in redox pairs containing glasses. J. Non-Cryst. Solids **71** (1985) no. 1–3, p. 49–57.

[7] Lee, J.-H.; Brückner, R.: The electrochemical series of the 3d transition metal ions in alkali borate glasses. Glastech. Ber. **59** (1986) no. 9, p. 233–251.

[8] Csaki, P.; Dietzel, A.: Elektrochemische Messung des Sauerstoffpartialdruckes in Glasschmelzen. Untersuchungen von Oxydationsgleichgewichten. T. I u. II. Glastech. Ber. **18** (1940) no. 2, p. 33–45; no. 3, p. 65–69.

[9] Stegmaier, W.; Dietzel, A.: Die Bedeutung der Basizität von Glasschmelzen und Versuche zu deren Messung. T. I u. II. Glastech. Ber. **18** (1940) no. 11, p. 297–308; no. 12, p. 353–362.

[10] Franz, H.: Oxygen ion activity and reaction equilibria in glass melts. J. Can. Ceram. Soc. **38** (1969) p. 89–93.

[11] Budd, S. M.: Redox equilibrium in glasses. A comment on the papers by Douglas et al. Phys. Chem. Glasses **7** (1966) no. 6, p. 210–213.

[12] Nagano, M.; Kato, A.; Mochida, I. et al.: The effect of acid-base properties on the redox equilibrium of vanadium in molten $V_2O_5$–$M_2O$ and $V_2O_5$–$MPO_3$ (M: alkali metal). J. Ceram. Soc. Jpn. **78** (1970) no. 12, p. 401–410.

[13] Yoshida, T.; Arai, K.; Hashimoto, T. et al.: Redox equilibria of glass melts with gas phase and specific resistivities of quenched glasses in the systems $Fe_2O_3$–$RP_2O_6$ and $TiO_2$–$RP_2O_6$ (R = Mg, Ca, Ba). J. Ceram. Soc. Jpn. **81** (1973) no. 4, p. 139–148.

[14] Yoshida, T.; Okada, Y.; Hirashima, H.: The effect of iron oxide concentration on redox equilibrium of the melts of FeO–$Fe_2O_3$–$RP_2O_6$ system (R = Mg, Ca, Ba) with gas phase. J. Ceram. Soc. Jpn. **81** (1973) no. 7, p. 281–289.

[15] Hirashima, H.; Toyoda, H.; Yoshida, T.: Redox equilibria of chromium ions in glass melts, $RP_2O_6$ (R = Mg, Ca, Ba), with gas phase. J. Ceram. Soc. Jpn. **82** (1974) no. 6, p. 309–317.

[16] Bates, T.: Ligand field theory and absorption spectra of transition-metal ions in glasses. In: Mackenzie, J. D. (ed.): Modern aspects of the vitreous state. Vol. 2. London: Butterworths 1962. p. 195–254.

[17] Wong, J.; Angell, C. A.: Glass//Structure by spectroscopy. New York, Basel: Dekker 1976.

[18] Weyl, W. A.; Chostner Marboe, E.: The constitution of glasses. A dynamic interpretation. Vol. 1//Fundamentals of the structure of inorganic liquids and solids. Vol. 2//Constitution and properties of some representative glasses. Pt. 1 and 2. New York, London: Interscience 1962–1967.

[19] Edwards, R. J.; Paul, A.; Douglas, R. W.: Spectroscopy and oxidation-reduction of iron and copper in $Na_2O$–PbO–$SiO_2$ glasses. Phys. Chem. Glasses **13** (1972) no. 5, p. 131–136.

[20] Lee, J.-H.; Brückner, R.: Redoxgleichgewicht von Kupferoxid in Alkaliborat-, -germanat- und -silicatgläsern. Ein Beitrag zum Indikatorverhalten polyvalenter Kationen. Glastech. Ber. **55** (1982) no. 11, p. 219–227.

[21] Lee, J.-H.; Brückner, R.: Zum Redoxgleichgewicht Chrom–Mangan in Silicat- und Boratgläsern. Glastech. Ber. **57** (1984) no. 1, p. 7–11.

[22] Schreiber, H. D.; Thanyasiri, T.; Lach, J. J. et al.: Redox equilibria of Ti, Cr, and Eu in silicate melts: reduction potentials and mutual interactions. Phys. Chem. Glasses **19** (1978) no. 6, p. 126–139.

[23] Nath, P.; Douglas, R. W.: $Cr^{3+}$–$Cr^{6+}$ equilibrium in binary alkali silicate glasses. Phys. Chem. Glasses **6** (1965) no. 6, p. 197–202.

[24] Nath, P.; Paul, A.; Douglas, R. W.: Physical and chemical estimation of trivalent and hexavalent chromium in glasses. Phys. Chem. Glasses **6** (1965) no. 6, p. 203–206.

[25] Paul, A.; Douglas, R. W.: Ferrous–ferric equilibrium in binary alkali silicate glasses. Phys. Chem. Glasses **6** (1965) no. 6, p. 207–211.

[26] Steele, F. N.; Douglas, R. W.: Some observations on the absorption of iron in silicate and borate glasses. Phys. Chem. Glasses **6** (1965) no. 6, p. 246–252.

[27] Paul, A.; Douglas, R. W.: Cerous–ceric equilibrium in binary alkali borate and alkali silicate glasses. Phys. Chem. Glasses **6** (1965) no. 6, p. 212–215.

[28] Hecht, H. G.: Study of copper in soda-boric oxide glasses. Phys. Chem. Glasses **9** (1968) no. 6, p. 179–183.

[29] Paul, A.: Optical absorption of copper ions in $Na_2O$–$NaCl$–$B_2O_3$ glasses. Phys. Chem. Glasses **11** (1970) no. 5, p. 159–167.

[30] Kordes, E.; Navarrete, J.: Optische Untersuchungen zur Aufklärung des Molekularbaus der Zinkphosphatgläser und des Kupfer(II)-Metaphosphatglases. Glastech. Ber. **46** (1973) no. 6, p. 113–119.

[31] Ahmed, A. A.; Ashour, G. M.; El-Shamy, T. M.: Absorption spectra of $Cu^{2+}$ ions in some lead glasses. In: Frischat, G. H. (ed.): The Physics of Non-Crystalline Solids. Aedermannsdorf: Trans Tech Pub. 1977. p. 330–335.

[32] Bamford, C. R.: A study of the magnetic properties of iron in relation to its colouring action in glass. Pt. 1//Iron in sodium borate glasses melted under oxidizing conditions. Phys. Chem. Glasses **1** (1960) no. 5, p. 159–164.

[33] Bamford, C. R.: A study of the magnetic properties of iron in relation to its colouring action in glass. Pt. 2//Iron in sodium borate glasses melted under reducing conditions. Phys. Chem. Glasses **1** (1960) no. 5, p. 165–169.

[34] Bamford, C. R.: A study of the magnetic properties of iron in relation to its colouring action in glass. Pt. 3//Iron in sodium silicate glasses; and the sulphur-amber coloration. Phys. Chem. Glasses **2** (1961) no. 5, p. 163–168.

[35] Bamford, C. R.: A study of the magnetic properties of iron in relation to its colouring action in glass. Pt. 4//Iron in sodium phosphate glasses. Phys. Chem. Glasses **3** (1962) no. 2, p. 54–57.

[36] Kurkjian, C. R.; Buchanan, D. N. E.: Mössbauer absorption of $Fe^{57}$ in inorganic glasses. Phys. Chem. Glasses **5** (1964) no. 3, p. 63–70.

[37] Hirayama, C.; Castle, J. G. jr.; Kuriayma, M.: Spectra of iron in alkaline earth phosphate glasses. Phys. Chem. Glasses **9** (1968) no. 4, p. 109–114.

[38] Kurkjian, C. R.; Sigety, E. A.: Co-ordination of $Fe^{3+}$ in glass. Phys. Chem. Glasses **9** (1968) no. 3, p. 73–83.

[39] Castner, T.; Newell, G. S.; Holten, W. C. et al.: Note of the paramagnetic resonance of iron in glass. J. Chem. Phys. **32** (1960) no. 3, p. 668–673.

[40] Bishay, A. M.; Makar, L.: Role of iron in calcium phosphate glasses. J. Am. Ceram. Soc. **52** (1969) no. 11, p. 605–609.

[41] Loveridge, D.; Parke, S.: Electron spin resonance of $Fe^{3+}$, $Mn^{2+}$, and $Cr^{3+}$ in glasses. Phys. Chem. Glasses **12** (1971) no. 1, p. 19–27.

[42] Pargamin, L.; Lupis, C. H. P.; Flinn, P. A.: Mössbauer analysis of distribution of iron cations in silicate slags. Metall. Trans. **3** (1972) no. 8, p. 2093–2105.

[43] Taragin, M. F.; Eisenstein, J. C.; Haller, W.: Mössbauer study of $Fe^{57}$ in an aluminophosphate glass. Phys. Chem. Glasses **13** (1972) no. 5, p. 149–152.

[44] Grunin, V. S.; Ioffe, V. A.; Zonn, Z. N.: EPR study in the $SiO_2$ system. J. Non-Cryst. Solids **11** (1973) no. 4, p. 341–349.

[45] Morinaga, K.; Suginohara, Y.; Yanagase, T.: Oxygen coordination number of Fe ions in $CaO$–$SiO_2$ and $Na_2O$–$SiO_2$ systems. (Orig. Jpn.) J. Jpn. Inst. Met. **40** (1976) no. 5, p. 480–486.

[46] Morinaga, K.; Suginohara, Y.; Yanagase, T.: Infrared absorption spectra of silicate glasses containing $Fe_2O_3$. (Orig. Jpn.) J. Jpn. Inst. Met. **40** (1976) no. 8, p. 775–780.

[47] Fernandez Navarro, J. M.; Brückner, R.: Zum strukturellen Einbau des Eisens in oxidische Gläser. Glastech. Ber. **49** (1976) no. 4, p. 82–94.

[48] Levy, R. A.; Lupis, C. H. P.; Flinn, P. A.: Mössbauer analysis of the valence and coordination of iron cations in $SiO_2$–$Na_2O$–$CaO$ glasses. Phys. Chem. Glasses **17** (1976) no. 4, p. 94–103.

[49] Camara, B.: Einbau von Eisen in Glas. Glastech. Ber. **51** (1978) no. 5, p. 87–95.

[50] Burzo, E.; Ardelean, I.: Mössbauer effect study of iron cations in lead borate glasses. Phys. Chem. Glasses **20** (1979) no. 1, p. 15–20.

[51] Momo, F.; Ranieri, G. A.; Sotgiu, A.: High temperature ESR study of Fe(III) in various vitreous matrices. J. Non-Cryst. Solids **46** (1981) p. 115–118.

[52] Baiocchi, E.; Montenero, A.; Bettinelli, M. et al.: Optical and magnetic properties of first-row transition metal ions in lead-silicate glass. J. Non-Cryst. Solids **46** (1981) p. 203–215.

[53] Park, J. W.; Chen, H.: The coordination of $Fe^{3+}$ in sodium disilicate glass. Phys. Chem. Glasses **23** (1982) no. 3, p. 107–109.

[54] Zirkelbach, K.; Brückner, R.: Spectroscopic investigations of barium aluminophosphate glasses containing vanadium, iron and manganese oxides. Glastech. Ber. **60** (1987) no. 9, p. 312–323.

[55] Karlsson, K. H.: Synpunkter på jonjämvikter i glas. Glastek. Tidskr. **32** (1977) no. 1, p. 6–10.

[56] Karlsson, K. H.: Comments on "Equilibrium studies of Fe in alkali phosphate glasses". J. Am. Ceram. Soc. **58** (1975) no. 11–12, p. 524.

[57] Cable, M.: Glasses. In: Lovering, D. G. (ed.): Molten salt technology. New York: Plenum Press 1982. p. 223–264.

[58] Janakirama Rao, B. V.: The dual rôle of titanium in the system $K_2O \cdot SiO_2 \cdot TiO_2$. Phys. Chem. Glasses **4** (1963) no. 1, p. 22–34.

[59] Janakirama Rao, B. V.: Properties and structure of glasses in the binary systems alkali–$TiO_2$. J. Am. Ceram. Soc. **47** (1964) no. 9, p. 455–463.

[60] Kurkjian, C. R.; Peterson, G. E.: An EPR study of $Ti^{3+}$–$Ti^{4+}$ in $TiO_2$–$SiO_2$ glasses. Phys. Chem. Glasses **15** (1974) no. 1, p. 12–17.

[61] Duffy, J. A.: Coordinating behaviour of ultra high alkali borate glass (68 % $Na_2O$) towards transition metal ions. Phys. Chem. Glasses **16** (1975) no. 1, p. 22–26.

[62] Böhm, H.; Bayer, G.: ESR-spectra of sodium-titanium-silicate glasses and of titanium-containing oxide compounds. J. Phys. Chem. Solids **31** (1970) p. 2125–2137.

[63] Paul, A.: Optical and ESR spectra of titanium(III) in $Na_2O$–$B_2O_3$ and $Na_2O$–$P_2O_5$ glasses. J. Mater. Sci. **10** (1975) p. 692–696.

[64] Iwamoto, N.; Hidaka, H.; Makino, Y.: State of $Ti^{3+}$ ion and $Ti^{3+}$–$Ti^{4+}$ redox reaction in reduced sodium silicate glasses. J. Non-Cryst. Solids **58** (1983) p. 131–141.

[65] Paul, A.; Douglas, R. W.: Ultra-violet absorption of chromium(VI) in binary alkali borate glasses. Phys. Chem. Glasses **8** (1967) no. 4, p. 151–159.

[66] Bates, T.; Douglas, R. W.: The absorption bands of $Cr^{3+}$ ions in solutions, crystals and glasses. J. Soc. Glass Technol. **43** (1959) no. 213, p. 289T–307T.
[67] Sakaino, T.; Moriya, T.: A study of the color of chromium-containing glasses. (Orig. Jpn.) J. Ceram. Soc. Jpn. **70** (1962) no. 1, p. 1–8.
[68] Landry, R. J.; Fournier, J. T.; Young, C. G.: Electron spin resonance and optical absorption studies of $Cr^{3+}$ in a phosphate glass. J. Phys. Chem. **46** (1967) no. 4, p. 1285–1290.
[69] Brückner, R.; Sammet, M.; Stockhorst, H.: Evidence of structural anisotropies in silicate glass fibres by ESR. J. Non-Cryst. Solids **40** (1980) p. 273–289.
[70] Johnston, W. D.: Optical spectra of the various valence states of vanadium in $Na_2O \cdot 2\,SiO_2$ glass. J. Am. Ceram. Soc. **48** (1965) no. 12, p. 608–611.
[71] Kakabadse, G. J.; Vassiliou, E.: The isolation of vanadium oxides in glasses. Phys. Chem. Glasses **6** (1965) no. 2, p. 33–37.
[72] Nagiev, V. M.: An investigation of vanadium phosphate glasses by electron paramagnetic resonance. Sov. Phys. Solid State **7** (1966) no. 9, p. 2204–2206.
[73] Nagano, M.; Mochida, I.; Kato, A. et al.: Study on the structure of vanadium in $V_2O_5$–sodium phosphate glasses by ESR. J. Ceram. Soc. Jpn. **79** (1971) no. 8, p. 270–273.
[74] Toyuki, H.; Akagi, S.: EPR and optical spectra of $VO^{2+}$ ion in x KF-(1-x) $B_2O_3$ glasses. Phys. Chem. Glasses **15** (1974) no. 1, p. 1–5.
[75] Nassar, A. M. A.; Ghoneim, N. A.: Vanadium contribution in different glasses in view of the ligand field theory. J. Non-Cryst. Solids **46** (1981) p. 181–195.
[76] Lenhart, A.: Untersuchung des Redoxverhaltens polyvalenter Elemente in Glasschmelzen unter Einsatz elektrochemischer Meßverfahren. Univ. Erlangen-Nürnberg, Tech. Fak., PhD thesis 1984.
[77] Bamford, C. R.: The application of the ligand field theory to coloured glasses. Phys. Chem. Glasses **3** (1962) no. 6, p. 189–202.
[78] Schultz, P. C.: Optical absorption of the transition elements in vitreous silica. J. Am. Ceram. Soc. **57** (1974) no. 7, p. 309–313.
[79] Orgaz, F.; Rawson, H.: Coloured coatings prepared by the sol-gel process. J. Non-Cryst. Solids **82** (1986) p. 378–390.
[80] Ghoneim, N. A.; El Batal, H. A.: The effect of different alkali ions on the optical and magnetic properties of $R_2O$–$B_2O_3$ + $MnO_2$ glasses. J. Non-Cryst. Solids **12** (1973) p. 189–198.
[81] Konstants, Z.; Vaivada, M.: Phosphate glasses containing major proportions of transition metal oxides. J. Non-Cryst. Solids **45** (1981) p. 105–114.
[82] Pyare, R.; Nath, P.: Stannous-stannic equilibrium in molten binary alkali silicate and ternary silicate glasses. J. Am. Ceram. Soc. **65** (1982) no. 11, p. 549–554.
[83] Dannheim, H.; Oel, H. J.; Tomandl, G.: Mössbauer-Effekt an Zinn in Silicatgläsern. Glastech. Ber. **49** (1976) no. 7, p. 170–175.
[84] Mukerji, J.; Biswas, S. R.: Oxidation states of ruthenium in glasses. Glass Technol. **12** (1971) no. 4, p. 107–111.

## 7. Appendix

It will be shown very briefly how to find out the most probable complex formations in a glass melt using the theoretical formalism in connection with the selection rules given in the present paper; the example is chromium, $Cr^{3+}/Cr^{6+}$ ($m = 3$).

First selection: The reaction equation is of O-type. This means, equation (11) with its formalistic possibilities is eliminated. Equation (14) may be applied with the second selection: $x = 0$, $y \leq m/2 - 1/2$. Equation (17) may be applied also, but with the exception, viz. with the third selection: $y \leq x + (m - 1)/2$.

The following other formal combinations have to be taken into consideration from high temperatures of the melt down to lower temperatures from which further selection is easily made by Weyl's screening principle and partly with coordination numbers measured in the glassy state:

| | | |
|---|---|---|
| $x = 0$ | $y = 2$: $Cr^{3+} + 3/4\ O_2 + 1/2\ O^{2-} \rightleftharpoons CrO_2^{2+}$ | highly improbable |
| | $y = 3$: $Cr^{3+} + 3/4\ O_2 + 3/2\ O^{2-} \rightleftharpoons CrO_3$ | may be probable at very high temperatures and low $[O^{2-}]$ |
| | $y = 4$: $Cr^{3+} + 3/4\ O_2 + 5/2\ O^{2-} \rightleftharpoons CrO_4^{2-}$ | most probable |
| | $y = 5$: $Cr^{3+} + 3/4\ O_2 + 7/2\ O^{2-} \rightleftharpoons CrO_5^{4-}$ | highly improbable |
| | $y = 6$: $Cr^{3+} + 3/4\ O_2 + 9/2\ O^{2-} \rightleftharpoons CrO_6^{6-}$ | |
| $x = 2$ | $y = 4$: $CrO_2^- + 3/4\ O_2 + 1/2\ O^{2-} \rightleftharpoons CrO_4^{2-}$ | may be probable at lower temperatures and high $[O^{2-}]$ |
| | $y = 5$: $CrO_2^- + 3/4\ O_2 + 3/2\ O^{2-} \rightleftharpoons CrO_5^{4-}$ | |
| | $y = 6$: $CrO_2^- + 3/4\ O_2 + 5/2\ O^{2-} \rightleftharpoons CrO_6^{6-}$ | |
| $x = 3$ | $y = 5$: $CrO_3^{3-} + 3/4\ O_2 + 1/2\ O^{2-} \rightleftharpoons CrO_5^{4-}$ | highly improbable |
| | $y = 6$: $CrO_3^{3-} + 3/4\ O_2 + 3/2\ O^{2-} \rightleftharpoons CrO_6^{6-}$ | |
| $x = 4$ | $y = 6$: $CrO_4^{5-} + 3/4\ O_2 + 1/2\ O^{2-} \rightleftharpoons CrO_6^{6-}$ | |

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