

## Equilibrium constant – determination and influence on redox reactions in soda–lime–silica glass melts

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The iron, arsenic and chromium redox equilibrium in an oxide glass-forming melt has been studied quantitatively. The equilibrium constant  $K(T)$  and the thermodynamic standard values were determined for the redox reaction in the melt at temperatures between 1000 and 1450 °C. These values were compared with values from the literature. The equilibrium constant is dependent on the temperature and on the concentration of the polyvalent elements. This dependence applies to the polyvalent elements investigated. For each polyvalent element it is possible to find a step in the function  $\lg([R^y]/[R^x])$  versus  $R_aO_b$ . This seems to be explained by the concentration dependence of the equilibrium constant of the redox reaction. Possibilities to determine the equilibrium constants of the various polyvalent elements are described.

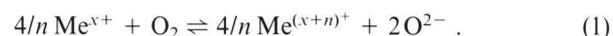
### Gleichgewichtskonstante – Bestimmung und Einfluß auf die Redoxreaktionen in Alkali–Erdkalisilicatglasschmelzen

Es wurden quantitative Untersuchungen zum Redoxgleichgewicht von Eisen, Arsen und Chrom in oxidischen Glasschmelzen durchgeführt. Die Gleichgewichtskonstante der entsprechenden Redoxreaktionen und die Werte der dazugehörigen thermodynamischen Funktionen wurden im Temperaturbereich von 1000 bis 1450 °C ermittelt. Die gewonnenen Werte wurden mit Angaben aus der Literatur verglichen. Die Gleichgewichtskonstante in Glasschmelzen ist abhängig von der Temperatur und der Konzentration der polyvalenten Elemente in der Schmelze. Dies gilt für die hier untersuchten polyvalenten Elemente. Für jedes untersuchte polyvalente Element findet sich in der Funktion  $\lg([R^y]/[R^x])$  versus  $R_aO_b$  eine Stufe. Dies läßt sich mit der Konzentrationsabhängigkeit der Gleichgewichtskonstanten der Redoxreaktionen erklären. Ferner werden die Methoden der Bestimmung der Gleichgewichtskonstanten für verschiedene polyvalente Elemente kurz beschrieben.

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## 1. Introduction

Polyvalent elements, like chromium, take different positions in the redox equilibrium. The behavior of the polyvalent elements is influenced by the chemical composition, the balance oxygen partial pressure (BOPP) and the temperature of the melt. Not only these parameters influence the melt and the final product, but also the kind and valency of the polyvalent element and the equilibrium constant of the redox reaction. The change of the redox condition of the glass melt containing one polyvalent element Me with the valencies  $x+$  and  $(x+n)+$  will be described by equation (1)



At temperatures above the transformation range ( $T_g$ ) it is possible to adjust the equilibrium. That means, the melt follows the Le Chatelier principle by changing the redox conditions. The ion ratio does not change in a finite time in the temperature range below  $T_g$ . It is possible to write the equilibrium relation in the following form

$$K \cdot p_{\text{O}_2} = [\text{Me}^{(x+n)+}] / ([\text{Me}^{x+}]^{4/n} \cdot [\text{O}^{2-}]^2) \quad (2)$$

After setting up the equilibrium between the melt and the gas atmosphere above the melt the BOPP is in direct relation to the ion ratio at constant temperature. If the concentration of  $\text{O}^{2-}$  is high enough, it is possible to include the oxygen ion activity in the equilibrium constant. Under this assumption the following can be seen:

- With changing temperature and constant gas atmosphere above the melt the ion ratio changes in the melt during the adjustment of the equilibrium due to the oxygen transfer between the melt and the gas atmosphere.
- With changing the gas atmosphere above the melt and constant temperature, the ion ratio changes in the melt during the adjustment of the equilibrium due to the oxygen transfer between the melt and the gas atmosphere.
- If the adjustment of the equilibrium between the melt and the gas atmosphere is not possible (small interphase, great depth of the tank, short duration), the ion ratio in the melt containing one polyvalent element does not change. Equation (2) then delivers a hypothetical BOPP. This is the oxygen partial pressure of that gas atmosphere with which the melt would be in equilibrium at this temperature. In the literature the notations “oxygen partial pressure” and “oxygen activity” are used as synonyms. This is not correct, because the value measured by the oxygen sensor is the BOPP mentioned above.

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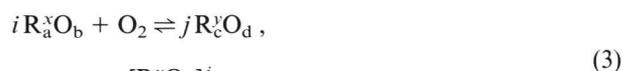
Table 1. Equilibration constant  $K$  as a function of temperature for arsenic calculated with equations (3 and 4)

temperature in °C	lg $K$ (equation (3))	lg $K$ (equation (4))
1000	-1.9	4.69
1450	-4.95	1.39

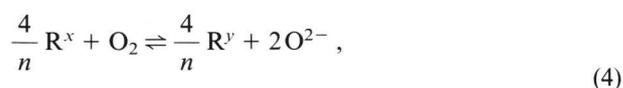
In order to model the relation between BOPP and the ion ratio, the values for the equilibrium constant are needed. For a melt containing different polyvalent elements it is necessary to know the equilibrium constant of each redox reaction in the melt. Since only in this way one can calculate the ion ratio after cooling the sample. An assumption therefore is that oxygen transfer through the interphase between melt and gas atmosphere does not take place during cooling. In this paper the authors tried to give a systematic survey of the ways of determining the equilibrium constant and present their primary investigations with simple soda–lime–silica glasses doped with different polyvalent elements.

## 2. Theory

The law of mass action describes the thermodynamic condition of the glass melt at equilibrium conditions, as that of other chemical systems, too. In glass melts this equilibrium condition lies at temperatures high above the transformation temperature. Thus, the redox process can be described as a reaction between molecules (equation (3)) and between ions (equation (4))



$$K \cdot p_{O_2} = \frac{[R_c^y O_d]^j}{[R_a^x O_b]^i} :$$

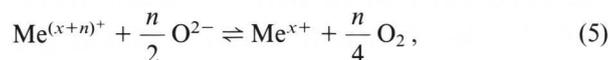


$$K \cdot p_{O_2} = \frac{[R^y]^{4/n} [O^{2-}]^2}{[R^x]^{4/n}} .$$

Therefore, the square of  $O^{2-}$  in equation (4) is included in the equilibrium constant, because it is very high or constant. If the redox equations (3 and 4) are both written for one mole oxygen, the dependences of the equilibrium constant on temperature are similar. On the other hand, both equations describe the same process, but the value of the equilibrium constant is different. The example of arsenic shows the great difference between the values of the equilibrium constant which were calculated from the thermodynamic data of the oxides and the values determined experimentally from the ion concentration (table 1).

Various authors [1 to 7] write the equilibrium constant of the redox reaction on the side of the high-valency ion. This is chemically correct, but it leads to a

change of the sign of lg equilibrium constant. Other authors [8 to 12] do not write the redox equation (6) for one mole oxygen, but give it in the following form:



$$K \cdot [O^{2-}]^{n/2} = \frac{[Me^{x+}]}{[Me^{(x+n)^+}]} \cdot [O_2]^{n/4}. \quad (6)$$

The different formulations of equation (5 and 6) show different results in the attempts of modeling the redox process in soda–lime–silica glass melts and also different results for the percentage of the oxygen physically dissolved in the melts. To minimize problems of understanding it is useful to decide in favor of one formulation. The authors use the form in equation (2) for their calculations. The equilibrium constant depends on the temperature.

$$K(T) = \exp(-\Delta G^0(T)/(RT)) \\ = \exp(-\Delta H^0/(RT)) \cdot \exp(\Delta S^0/R), \quad (7)$$

where  $\Delta G^0(T)$  is the change of the standard free enthalpy,  $\Delta H^0$  is the change of the standard reaction enthalpy, and  $\Delta S^0$  is the change of the standard entropy.

The free enthalpy determines the direction of the reaction process according to reaction kinetics through value and sign. The equilibrium constant  $K$  determines the quantitative conversion of the chemical reaction. In the theory of chemical equilibrium there are two types of reactions. On the one hand, there is the so-called “homogeneous reaction”, which runs off in a closed system and is characterized by the same phases of basic and final material. This reaction always runs off to the equilibrium. The adjustment of the homogeneous equilibrium in a melt without mass transfer over the interphase to a gas phase above  $T_g$  is a spontaneous process. On the other hand, there is the so-called “heterogeneous reaction”. It is characterized by different phases of basic and final material. This reaction runs off only partly to the equilibrium only under certain conditions. The equilibrium constant  $K$  in a nonequilibrium reaction is only important for the speed and direction of the adjustment of the equilibrium of the redox process. Over the years, two methods for the measurement of the equilibrium constant have been developed. The first one is based on the investigation of the chemical condition of the system and on the calculation of  $K$ . For investigations of glass melts this means that the melt must be equilibrated with a determined gas atmosphere at a definite temperature. The sample has to be cooled quickly and then the glass has to be analyzed chemically or physically. At the same temperature it is necessary to measure the BOPP of the melt with an oxygen sensor. With the help of the BOPP and the analyzed ion ratio it is possible to calculate the value of the equilibrium constant with equation (6).

Thus, the concentration of polyvalent elements will be used in the calculation and not the activities of the polyvalent elements. That means the activity coefficients are set equal to unity. This can be accepted in a first approximation, because there are no values for the activity coefficients of polyvalent elements in glass melts and their determination is difficult.

The change of standard-free enthalpy, standard reaction enthalpy and standard entropy may be calculated with the following equations:

$$\Delta G^0(T) = -RT \ln K(T); \quad (8)$$

$$\Delta H^0 = RT^2 \frac{dK(T)}{dT}; \quad (9)$$

$$\Delta S^0 = \frac{-d\Delta G^0(T)}{dT}. \quad (10)$$

Prasad Singh et al. [13] found a possibility to calculate the equilibrium constant for various temperatures using the integrated form of the van't Hoff reaction isobare equation:

$$\lg K = -\frac{\Delta H^0}{4.567} \frac{1}{T} + \text{const.} \quad (11)$$

The thermodynamic functions are calculated using the following equations:

$$\Delta G = \Delta H - T\Delta S. \quad (12)$$

In the equilibrium  $(\Delta G)_{T_p} = 0$

$$\Delta S = \frac{\Delta H}{T} \quad (13)$$

applies [13].

This procedure is determined by a long melt cycle and is only possible for the investigation of melts containing one polyvalent element. In melts containing more than one polyvalent element there are interactions between the polyvalent elements during cooling. The reason is a different temperature dependence of each equilibrium constant of the redox reaction in a single-phase system like a glass melt. This leads to ion ratios which are dependent on temperature, i.e., they will change on cooling of the melts. Recently in-situ methods for investigations of ion ratios in glass melts have been developed. The theoretical background is that oxidic glasses are good ionic conductors and the electrochemical method for water solution can be used for glass melts with modifications. Voltammetry [1 and 8], chronopotentiometry [1] and potential sweep voltammetry [1] are generally used. These methods use the normal potential  $E_0$  of a redox reaction and the diffusion coefficient of the polyvalent element. The normal potential can be

measured with voltammetric methods against a zirconium-oxygen electrode.  $K$  and other thermodynamic functions, such as  $\Delta G^0$ ,  $\Delta H^0$ ,  $\Delta S^0$ , can be calculated with the normal potential measured using the following equations [1 and 11]:

$$\Delta G^0(T) = -nFE_0(T) = -RT \ln K(T); \quad (14)$$

$$\Delta S^0 = nF \left( \frac{\partial E_0(T)}{\partial T} \right); \quad (15)$$

$$\Delta H^0 = nF \left[ T \left( \frac{\partial E_0(T)}{\partial T} \right) - E_0(T) \right], \quad (16)$$

where  $n$  denotes the number of transferred electrons and  $F$  is the Faraday constant. An extensive description of these methods can be found in [1 and 11].

### 3. Experimental studies

For the investigations two kinds of glasses were used, first, a glass with the composition (in wt%): 70 SiO<sub>2</sub>, 20 Na<sub>2</sub>O, 10 CaO for melts containing iron or chromium; secondly, a glass with the composition 74 SiO<sub>2</sub>, 16 Na<sub>2</sub>O, 10 CaO for melts containing arsenic. 50 g of the batch were melted at a temperature of 1450 °C. The batch concentration of the various polyvalent elements was between 0.09 and 6 wt% and the oxides were used instead of silicon dioxide. The electromotive force (emf) was measured with an oxygen sensor. This was the basis for the calculation of the BOPP. The melts were kept at melting temperature until there were no bubbles in the melt. The heating rate was 10 K/min. The melts were cooled in air. Then ion ratios were determined by wet chemical or spectroscopic methods.

### 4. Results and discussion

For the determination of the temperature dependence of the equilibrium constant the physicochemical relationship according to Schreiber [14 to 16] was used and the following equation formulated:

$$\lg \left( \frac{[\text{Me}^{(x+n)+}]}{[\text{Me}^{x+}]} \right) = \frac{n}{4} (\lg K(T) + \lg p_{\text{O}_2}). \quad (17)$$

Figures 1 and 2 show the measured values for BOPP and the ion ratio of the melts containing iron and chromium in a diagram  $\lg \left( \frac{[\text{Me}^{(x+n)+}]}{[\text{Me}^{x+}]} \right)$  versus  $\lg p_{\text{O}_2}$ . Thus, a straight line determined through the slope by  $n/4$  and the zero crossed by  $K(T)$  is obtained for each polyvalent element. Applying equation (17) and the diagram  $\lg \left( \frac{[\text{Me}^{(x+n)+}]}{[\text{Me}^{x+}]} \right)$  versus  $\lg p_{\text{O}_2}$  a value for  $p_{\text{O}_2}$  is determined for  $[\text{Me}^{(x+n)+}]/[\text{Me}^{x+}] = 1$ . With this value it is possible to solve the following simple equation:

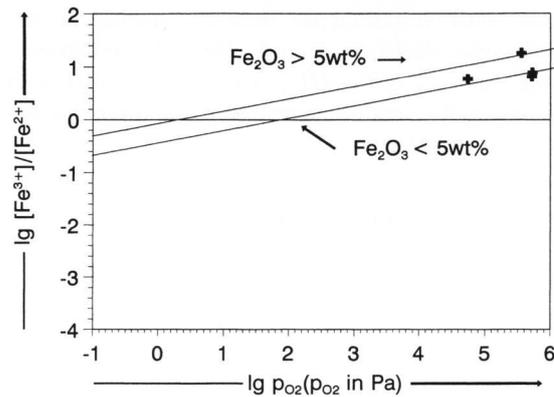


Figure 1. Determination of the iron equilibrium constant in silicate melts at 1450 °C.

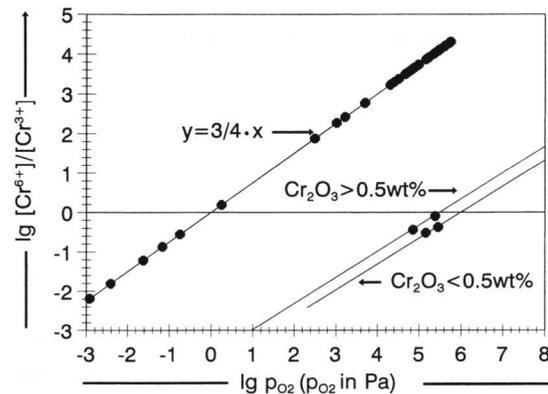


Figure 2. Determination of the chromium equilibrium constant in silicate melts at 1450 °C.

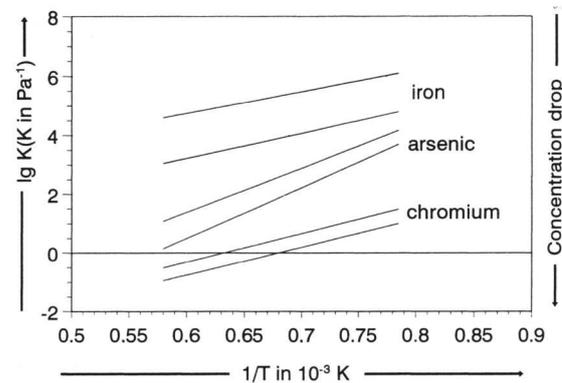


Figure 3. Equilibrium constant  $K$  as a function of the temperature according to the Arrhenius equation and concentration of chromium, arsenic and iron.

$$K(T) = \frac{1}{p_{O_2}} \quad (18)$$

In other words, with the crossing point in the diagram  $\lg ([Me^{(x+n)^+}]/[Me^{x+}])$  versus  $\lg p_{O_2}$  between the straight line with slope  $n/4$  and the horizontal line by

$\lg ([Me^{(x+n)^+}]/[Me^{x+}]) = 0$  and with the help of equation (18) it is possible to determine the equilibrium constant of the redox reaction in dependence on temperature. Table 2 shows the temperature effect on the equilibrium constants of arsenic, iron and chromium in a temperature range of 1000 to 1450 °C. A dependence of the equilibrium constant on the basic concentration of the polyvalent elements was found.

The equilibrium constant follows the thermodynamic relation in equation (7).  $\Delta H^0$  and  $\Delta S^0$  are relatively independent of the temperature and they are used as constants. Equation (7) can be written in the following form, too:

$$\lg K = A + B/T, \quad (19)$$

where the temperature dependence follows the Arrhenius relation. The constants  $A$  and  $B$  can be calculated on the basis of the knowledge of two equilibrium constants and their temperature with the following equations:

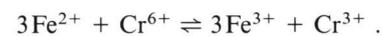
$$A = \frac{(T_1 \lg K_1 - T_2 \lg K_2)}{(T_1 - T_2)}, \quad (20)$$

$$B = \left( \frac{\lg (K_1/K_2)}{\frac{1}{T_1} - \frac{1}{T_2}} \right). \quad (21)$$

Figure 3 shows the dependence of the equilibrium constant on temperature according to the Arrhenius relation for the polyvalent elements iron, chromium and arsenic. Table 3 presents the calculated values of  $\Delta H^0$  for each polyvalent element.

If  $\Delta H^0$  is the potential of a redox pair for the reduction of another redox pair, then it is possible to establish a series similar to the standard potential series in wet chemistry. The good agreement of these values with those of Lenhart [19] and Weyl [20] is to be seen in table 4.

During cooling, the polyvalent element chromium can be reduced by iron as well as by arsenic. This follows from the series of polyvalent elements according to their values of  $\Delta H^0$ . It seems to be possible to reduce each amount of  $Cr^{6+}$  at melting temperature to  $Cr^{3+}$  due to a sufficient amount of  $Fe^{2+}$  in the cooling process. This assumption is expressed by the following equation,



The comparison of the equilibrium constant in this paper with constants in the literature is difficult. Until now, a definite determination of the equilibrium constant has not been used in literature, because of different handling of the equilibrium constant in the stoichiometric equation. Table 3 shows a comparison of the values of different experimental investigations. There are big differences between these experimental values. It is possible to indicate a value range for the thermodynamic

Table 2. Equilibrium constants for the redox equilibrium of arsenic, iron and chromium as a function of temperature and concentration in a soda–lime–silica glass

	arsenic		iron		chromium	
	<0.5 wt%	>0.5 wt%	<5 wt%	>5 wt%	<0.5 wt%	>0.5 wt%
$K(T)$ (in Pa <sup>-1</sup> ) at 1000 °C	$5.01 \cdot 10^4$	$1.48 \cdot 10^4$	$6.31 \cdot 10^4$	$1.26 \cdot 10^6$	10	$0.31 \cdot 10^2$
$K(T)$ (in Pa <sup>-1</sup> ) at 1450 °C	1.38	12.02	$1.12 \cdot 10^3$	$3.98 \cdot 10^4$	0.11	0.31

function  $\Delta H^0$  of each polyvalent element. These ranges depend on the concentration of the polyvalent element. Especially for iron and arsenic the following picture is given. For equal glass composition and equal dopant concentration of the polyvalent elements the  $\Delta H^0$  values determined by Rüssel et al. [1] are below those of the authors. The following reasons are responsible for these disagreements:

- different investigation methods with subjective influences;
- investigations of equilibrated and nonequilibrated melts;
- concentration dependence on the equilibrium constant.

Certainly there are some more reasons for the influence of the determination of  $\Delta H^0$  and the determination of  $K$ . But the above-given ones should be sufficient to stimulate a discussion about the determination of  $K$  as well as a quantification of the redox conditions of the melt. For a standardized description of handling  $K$  it is necessary to decide in favor of description. The authors suggest using equation (2). In former discussions the concentration dependence of  $K$  was not represented. Schreiber [16] described and discussed the concentration dependence of the reaction enthalpy for the polyvalent element iron. Hayashi and Dorfled [2] reported on the same results for arsenic in a borosilicate glass, but the concentration dependence being not as strong as with iron. In the present investigation the same effects for all three polyvalent elements, regarding the concentration dependence, were found.

Figures 4 and 5 represent the dependence of the ion ratio on the basic concentration of the polyvalent element. Each element has a step in the curve at a definite concentration of the polyvalent element. The height of the step seems to depend on the amount of transferred electrons of each polyvalent element. It is the same as a valency change. The location of the step is influenced for each polyvalent element by the adjustment of oxygen linkage equilibrium in a soda–lime–silica glass described by the following equation:



Here ( $\text{O}^-$ ) denotes the kind of linkage as network modifier, ( $-\text{O}-$ ) the kind of linkage as network former, and ( $\text{O}^{2-}$ ) the freely moving oxygen ions [11]. If there are the

Table 3. Calculated values for  $\Delta H^0$  (in kJ/mol) by using equation (20) for each polyvalent element in comparison with values from literature for the same glass composition

arsenic	iron	chromium
288 to 332	139 to 163	107 to 138
230 [1]	102 [1]	227 [19]
401 [17]	338 [17]	
222 [16]	118 [16]	
	136 [18]	
	171 to 305 [14] <sup>1)</sup>	

<sup>1)</sup> Modified gross chemism.

Table 4. Series of  $\Delta H^0$  values of three kinds of polyvalent elements, similar to the standard potential series in wet chemistry

reaction element	$\Delta H^0$ in kJ/mol
arsenic	288 to 332
iron	139 to 163
chromium	107 to 138

same glass composition and the same linkage equilibrium in the melts the position of the step depends on the features of the polyvalent element, such as ion radius, coordination chemistry, equilibrium constant and the adjusted BOPP. An explanation of this effect has to include a connection of linkage and thermochemistry. The assembly of polyvalent ions in the network is possible either as covalent oxocomplex or as electrovalent coordination (coordination number CN = 6) [18 and 21 to 24]. Decision-makers are the ion radius, the ratio of cation to anion ( $\text{O}^{2-}$ ), the ligand field theory, and the electronegativity difference between an oxygen ion bonded to a silicon atom and a metal ion according to the following equation by Karlsson [25]

$$X_{\text{Me}} = 0.22q + 2 \ln z - 0.7 . \quad (23)$$

The  $\text{As}^{5+}$ ,  $\text{Cr}^{6+}$  and  $\text{Fe}^{3+}$  ions will be fitted in the glass structure as an oxocomplex with CN = 4 due to the electronegativity difference and the ratio of ion radii. Investigations by different authors [8, 19, 24 and 26 to 28] for arsenic, chromium and iron confirm this theory. The low valency forms of arsenic, chromium and iron are incorporated in the glass system, as a rule, in sixfold

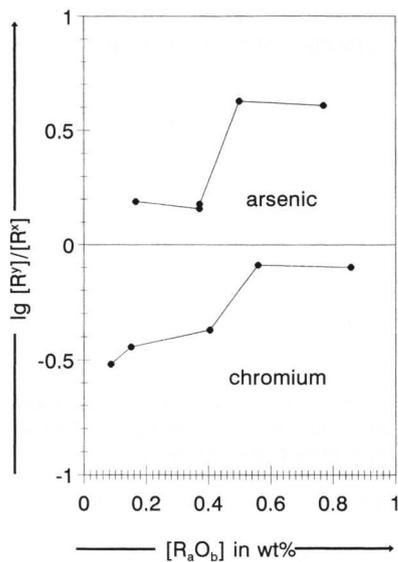


Figure 4. Ion ratio ( $\lg ([R^3]/[R^3])$ ) versus the concentration of the polyvalent elements arsenic and chromium at 1450°C.

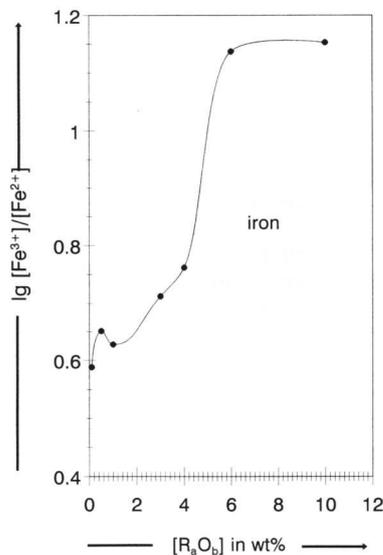


Figure 5. Ion ratio ( $\lg ([Fe^{3+}]/[Fe^{2+}])$ ) versus the concentration of the polyvalent element iron at 1450°C.

coordination with oxygen [11, 13, 24 and 28]. In form of oxocomplexes the high-valency ions function as network former, according to the Zachariasen theory, and strengthen the glass structure; while the low-valency forms expand the glass structure. The assembly of metal ions in their oxidic form is restricted by the laws of thermochemistry, represented in the value of the equilibrium constant. In the high-temperature range at 1450°C only the equilibrium constant of iron stimulates the stability of the ion form, which will be built in as a network former into the glass structure. This could be a reason for much more assembling of iron ions than arsenic or chromium ions in the glass melt, as seen in figure 2, where the dependence of the equilibrium constant on the

concentration and the temperature is described in the Arrhenius diagram. The influence of temperature on the equilibrium constant for each polyvalent element is valid for the investigated glass composition and is not transferable to another glass composition.

## 5. Conclusion

There are many factors influencing the redox condition of the melt, but it is difficult to separate each factor. For a long time, the dependences of the redox equilibrium on oxygen activity, glass composition, basicity and of equilibrium constant of the redox reaction have been known. All of these features depend on the glass composition and the experimental conditions. Investigations were carried out to establish these dependences of the equilibrium constant under definite conditions and of the gross chemism. The values for the equilibrium constant of each polyvalent element are comparable with the values from literature. A comparison between the different values represents the influence by different measurement methods and is of relevance. It could be shown that the equilibrium constant derived from the thermodynamic data and the equilibrium constant determined experimentally have different values. The thermodynamic values from the oxides can not be used for thermodynamic calculations for glass melts, because the polyvalent ion is built in as a simple or complex ionic form in the glass melt. With increasing importance of the equilibrium constant for regulation of the redox process in glass melts, it is necessary to discuss about the handling of the equilibrium constant of redox reactions. At first, a uniform treatment of the equilibrium constant in equations has to be observed. Some dependences of the equilibrium constant for the polyvalent elements arsenic, chromium and iron were detected. In a melt containing one of these polyvalent elements, the equilibrium constant of the redox reaction is dependent on the glass composition, the temperature and on the basic concentration of the polyvalent element. Thus, increasing basic concentration leads to increasing values of the equilibrium constant for each polyvalent element. A possible explanation leads to a relation between linkage and thermochemistry. The calculated and experimentally determined values for this glass composition are open for discussion, but they are not transferable to another glass composition.

## 6. Nomenclature

$A, B$	constants
$E_0$	normal potential
$F$	Faraday constant ( $= 9.64 \cdot 10^4 \text{ C/mol}$ )
$\Delta G^0$	change of standard free enthalpy in J/mol
$\Delta G_{Tp}$	change of standard free enthalpy depending on temperature and pressure in J/mol
$\Delta H^0$	change of standard reaction enthalpy in J/mol
$i, j$	molar quantity of substance in mol
$K$	equilibrium constant in $\text{Pa}^{-1}$
$Me^{x+}$	low-valency polyvalent element

$\text{Me}^{(x+n)+}$	high-valency polyvalent element
$n$	number of transferred electrons
$p_{\text{O}_2}$	balance oxygen partial pressure in Pa
$q$	number of d-electrons
$R$	gas constant (= 8.3143 J/(K mol))
$\text{R}^x$	low-valency polyvalent oxide
$\text{R}^y$	high-valency polyvalent oxide
$\text{R}_a\text{O}_b$	low-valency oxide
$\text{R}_c\text{O}_d$	high-valency oxide
$\Delta S^0$	change of standard entropy in J/mol
$T$	temperature in K
$X_{\text{Me}}$	electronegativity of the metal ion
$z$	formal oxidation number of the ion

\*

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