THE EFFECT OF GLASS COMPOSITION
ON THE Fe^{2+}/Fe^{3+} EQUILIBRIUM

CHRISTIAN RÜSSEL, SANDRA GERLACH

Otto-Schott-Institut, Universität Jena, Fraunhoferstrasse 6, D-07743 Jena, Germany

Alkali-earth alkaline-silicate and -aluminosilicate glass melts of various compositions doped with 0.2 to 0.5 mol% Fe_2O_3 were studied using square-wave voltammetry. The increase in alkali content, as well as the increase in lime and alumina contents led to a shift in the redox equilibrium to the oxidized state. The oxidized state is also favoured if the type of alkali is varied from Li_2O to K_2O. Empirical correlations enabling the calculation of thermodynamic data from the melt composition are given.

INTRODUCTION

In the past decades, the thermodynamics of redox equilibria in glass have been intensively studied. The Fe^{2+}/Fe^{3+} equilibrium has been most frequently investigated, since iron is the most common impurity of raw materials and intentional addition which acts as polyvalent ion. Many physical properties of the melt and the final glass product are affected by the quantity and redox ratio of iron. The most important physical property is the light transmittance in a wavelength range from ultra violet to near infrared. In the past, redox equilibria were predominantly studied by equilibrating the melt with an atmosphere of well known oxygen partial pressure, quenching the sample and finally analyzing the glass using physical or chemical methods [1,2]. In the past few years, however, numerous studies on redox equilibria have also been carried out using electrochemical methods [3 - 8]. These methods allowing the determination of standard potentials are carried out directly in the glass melt at high temperatures. The equilibrium constant can be calculated from the standard potentials and if the temperature is varied during measurement, also the standard enthalpy and standard entropy of the redox reaction can be determined.

This paper studies the Fe^{2+}/Fe^{3+} redox equilibrium in various silicate glass melt com-positions. The effect of the type and quantity of alkali and earth alkaline as well as of the alumina concentration is reported.

THEORETICAL PART

At high temperatures, there is equilibrium between Fe^{2+}/Fe^{3+} and the physically dissolved oxygen.

$$4\ Fe^{3+} + 2\ O^{2-} \leftrightarrow 4\ Fe^{2+} + O_2 \qquad (1)$$
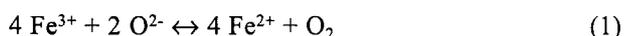
The attributed equilibrium constant, K, can be defined as follows:

$$K\ (T) = \frac{[Fe^{2+}]}{[Fe^{3+}]}\ P_{O_2}^{1/4} \qquad (2)$$

$K(T)$ depends on the temperature and the glass melt composition. It is correlated to the standard free enthalpy, $\Delta G°$, the standard enthalpy, $\Delta H°$, the standard entropy, $\Delta S°$, and the standard potential of the redox pair.

$$- RT\ \ln K(T) = \Delta G°\ (T) = \Delta H° - T\ \Delta S° = - zF\ E_0\ , \qquad (3)$$

where z is the number of electron transferred ($z = 1$ in the case of iron).

EXPERIMENTAL PART

The voltammetric measurements were carried out in an electrically heated furnace. A platinum crucible containing the melt was located in the middle of the furnace. Three electrodes were inserted from the top into the melt. Platinum wire and platinum plate were used as working and counter electrode, respectively. Zirconia probe flushed with air formed the reference electrode. The electronics were self constructed. The potentiostat was connected to a microcomputer controlling the potential time dependence and recording the current-potential curve. The method used was the square-wave voltammetry, a fast potentiostatic pulse method. The potential-time dependence supplied was formed by a staircase ramp with a superimposed rectangular wave of comparably short pulse time (1 to 100 ms) and high amplitude (100 mV). The current was measured at the end of every half-wave and then differentiated [3].

The measurements were carried out in alkali-lime-silicate, alkali-magnesia-silicate and alkali-lime-aluminosilicate melts doped with 0.2 to 0.5 mol% Fe_2O_3. The basic mol% compositions were: x R_2O, 10 CaO, (90-x) SiO_2; x R_2O, 10 MgO, (90-x) SiO_2, ($x = 10, 15, 20$ and 25, $R = Li, Na, K$); x Na_2O, (26-x) CaO, 74 SiO_2 ($x = 11$, $16, 21$ and 26) and 16 R_2O, 10 CaO, x Al_2O_3, (74-x) SiO_2 ($x = 0, 5, 10$ and 15, $R = Li, Na, K$).

RESULTS

Figure 1 presents voltammograms recorded in a glass melt with the basic mol% composition of 16 Na_2O, 10 CaO, 5 Al_2O_3, 69 SiO_2 doped with 0.2 mol% Fe_2O_3. The pulse time was constant (20 ms), while the temperature was varied in the range from 1100 to 1300 °C. All voltammograms show a well pronounced peak caused by the reduction of Fe^{3+} to Fe^{2+}.

$$Fe^{3+} + e^- \leftrightarrow Fe^{2+} \tag{4}$$

At potentials below - 800 mV, the current increases again due to the decomposition of the glass matrix. This is also observed in melts without polyvalent elements. The peak potential being equal to the standard potential of the redox pair is shifted to lower values when decreasing the temperature. It should be mentioned that also the peak currents decrease with temperature. This is caused by decreasing self-diffusion coefficients of iron.

Figure 2. Standard potentials of the Fe^{2+}/Fe^{3+} equilibrium as a function of temperature in melts with the basic composition of 16 Na_2O, 10 CaO, x Al_2O_3, (74-x) SiO_2 mol%).
1 - x = 15; 2 - x = 10; 3 - x = 5; 4 - x = 0.

Figure 1. Square-wave voltammograms recorded in a glass melt with the composition 16 Na_2O, 10 CaO, 5 Al_2O_3, 69 SiO_2 mol% doped with 0.2 mol% Fe_2O_3.
1 - 1300 °C, 2 - 1200 °C, 3 -1100 °C (time step = 20 ms).
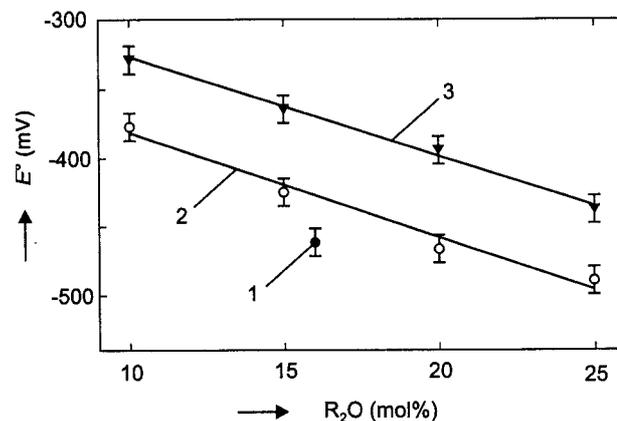
Figure 3. Standard potentials of the Fe^{2+}/Fe^{3+} equilibrium at 1300 °C as a function the R_2O content for alkali-magnesia-silicate glasses x R_2O, 10 MgO, (90-x) SiO_2 (mol%).
1- R = Li, 2 - R = Na, 3 - R = K.

Figure 2 shows the effect of temperature upon the standard potential in melts with the basic mol% composition of 16 Na_2O, 10 CaO, x Al_2O_3, (74-x) SiO_2 (x = 0, 5, 10 and 15) [8]. In all four melt compositions, a linear correlation is observed. The standard potential increases with increasing temperature. The same behaviour was observed in all melt compositions studied.

Concerning the effect of the alumina concentration, it can be stated that the standard potentials increase with increasing alumina content. Melts without alumina (see curve 4) exhibit lowest standard potentials, while those measured in the melt possessing an alumina content of 15 mol% are highest.

Figure 3 presents standard potentials measured in alkali-magnesia-aluminosilicate melts [5] at 1300 °C when varying the type and concentration of alkali. At

the same alkali concentration, K_2O containing glasses show the highest standard potential, while those of Na_2O containing melts are lower. The melt possessing a Li_2O content of 16 mol% has an even lower standard potential. The increase in the alkali concentration results in a decrease of the standard potentials. The same effect of type and concentration of alkali was also observed in the case of alkali-lime-silicate glasses [4].

Figure 4 presents standard potentials of the Fe^{2+}/Fe^{3+} equilibrium as a function of the Na_2O content for soda-lime-silicate glass melts (26-x) Na_2O, x CaO, 74 SiO_2 (mol%) at 1300 °C [6]. Within this series, the standard potential decreases with increasing CaO content, while the sum of molar Na_2O and CaO concentrations was kept constant.
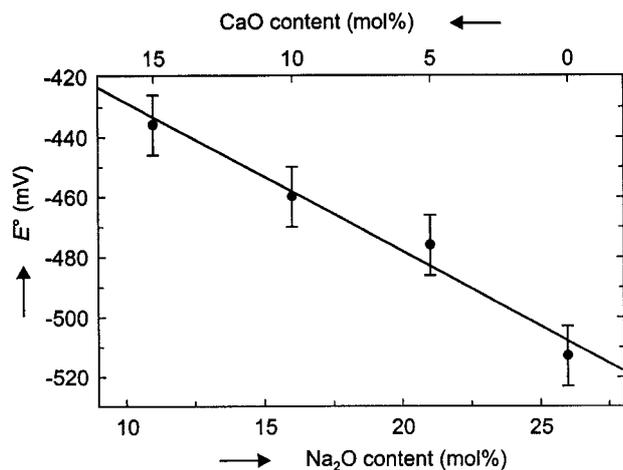
Figure 4. Standard potentials of the Fe^{2+}/Fe^{3+} equilibrium at 1300 °C as a function of the Na_2O content in glasses with the basic composition of $(26-x)$ Na_2O, x CaO, 74 SiO_2 (mol%) (s = 0, 5, 10 and 15).

In table 1, standard potentials of the Fe^{2+}/Fe^{3+} equilibrium at 1300 °C are summarized for various glass compositions.

DISCUSSION

The standard potentials of all glasses studied were shifted to lower values when decreasing the temperature (see also figure 2). This effect has often been described in the literature and was observed in all studies on the thermodynamics of iron (see e.g. references [1, 4]). The decrease of the standard potentials with decreasing temperature are attributed to a shift in the equilibrium according to equation (1) to the left, i. e. the oxidized state, Fe^{3+} is favoured at decreasing temperatures. The linear dependence of E_0 upon the temperature as shown in figure 2, enables the calculation of standard enthalpies, $\Delta H°$, and standard entropies, $\Delta S°$. In all glass systems studied, higher alkali contents led to lower standard potentials. In melts containing different types of alkali, lowest standard potentials were observed in the case of lithium containing melts, highest in those containing K_2O. As shown in table 1, the standard potentials of iron were notably higher in magnesia containing melts than in those containing the same molar quantity of CaO.

The effect of glass composition on the Fe^{2+}/Fe^{3+} equilibrium has often been interpreted as an effect of basicity. For this purpose, an optical basicity of a glass melt has been defined, which in principle can be measured spectroscopically, but usually is calculated from the chemical composition using empirical correlations. Two effects reported in this paper can be qualitatively explained by the basicity concept. First, the decrease in the standard potentials with increasing alkali content and, furthermore, the effect of the type of alkali. K_2O-containing glasses possess higher basicities than those

Table 1. Standard potentials (at 1300 °C) of the Fe^{2+}/Fe^{3+} equilibrium of various glass composition.

Glass composition (mol%)				$E°$ (mV)	
				measured	calculated
74 SiO_2	16 Li_2O	10 MgO		- 461	-
80 SiO_2	10 Na_2O	10 MgO		- 377	- 375
75 SiO_2	15 Na_2O	10 MgO		- 425	- 420
70 SiO_2	20 Na_2O	10 MgO		- 466	- 465
65 SiO_2	25 Na_2O	10 MgO		- 489	- 510
80 SiO_2	10 K_2O	10 MgO		- 328	- 340
75 SiO_2	15 K_2O	10 MgO		- 364	- 367
70 SiO_2	20 K_2O	10 MgO		- 394	- 395
65 SiO_2	25 K_2O	10 MgO		- 434	- 423
80 SiO_2	10 Na_2O	10 CaO		- 410	- 425
74 SiO_2	16 Na_2O	10 CaO		- 460	- 452
70 SiO_2	20 Na_2O	10 CaO		- 463	- 470
80 SiO_2	10 K_2O	10 CaO		- 430	- 420
75 SiO_2	15 K_2O	10 CaO		- 440	- 440
70 SiO_2	20 K_2O	10 CaO		- 461	- 460
65 SiO_2	25 K_2O	10 CaO		- 478	- 480
74 SiO_2	16 Cs_2O	10 CaO		- 407	-
80 SiO_2	10 Na_2O	10 CaO		- 410	- 425
80 SiO_2	20 Na_2O			- 488	- 490
70 SiO_2	20 Na_2O	10 CaO		- 463	- 470
74 SiO_2	11 Na_2O	15 CaO		- 436	- 420
74 SiO_2	21 Na_2O	5 CaO		- 476	- 485
74 SiO_2	26 Na_2O			- 517	- 513
74 SiO_2	16 Li_2O	10 CaO	10 Al_2O_3	- 427	-
69 SiO_2	16 Na_2O	10 CaO	5 Al_2O_3	- 417	- 402
64 SiO_2	16 Na_2O	10 CaO	10 Al_2O_3	- 347	- 352
59 SiO_2	16 Na_2O	10 CaO	15 Al_2O_3	- 298	- 302
69 SiO_2	16 K_2O	10 CaO	5 Al_2O_3	- 398	- 394
62.7 SiO_2	31.8 Na_2O	5.5 Al_2O_3		- 470	- 486

containing Na_2O or Li_2O and also show smaller standard potentials. By contrast, if Na_2O is replaced by equimolar quantities of CaO, the basicity remains almost constant, however, the standard potentials increase by around 100 mV within the range of 0 to 15 mol% CaO. By analogy, also the effects observed while replacing CaO by MgO or SiO_2 by Al_2O_3 cannot simply be explained as an effect of basicity. The optical basicities are average values for the medium present and do not take into account specific interactions of various components. Hence, the local basicity, i. e. that in the coordination sphere, may differ notably from the average ones. The data presented in table 1 column 2 can be empirically described for lime-containing melts using the following correlation [8]:

$$E_0 \text{ (at 1300 °C)} = a + b \text{ [Na}_2\text{O]} + c \text{ [K}_2\text{O]} + d \text{ [CaO]} + e \text{ [Al}_2\text{O}_3] \tag{5}$$

with a = - 400 mV, b = - 4.5 mV, c = - 4 mV, d = 2 mV and e = 10 mV (all concentrations in mol%).

For magnesia containing melts [5], another empirical correlation can be given:

$$E_0 \text{ (at 1300 °C)} = a + b \text{ [Na}_2\text{O]} + c \text{ [K}_2\text{O]} + d \text{ [MgO]}$$

$$(6)$$

with a = -400 mV, b = -9 mV, c = -5.5 mV and d = 11.5 mV.

Table 1, column 2 summarizes E_0 values calculated using the empirical formulae given above. In the most cases, they agree within the error limit ($\pm$ 10 mV) with the experimental E_0 values. The largest deviation observed is 21 mV. Fe^{3+} occurs in glasses predominantly in a four fold coordination. The Fe^{3+}-tetrahedron hence possesses a negative charge compensated by an alkali ion. According to EPR-studies [9], this results in a C_{2v}-symmetry, i. e. a distorted tetrahedron. Due to smaller cation size, Li^+ stabilizes this complex more effectively, while with larger alkali cations, the Coulomb forces are weaker. Thus, both small alkali cations as well as larger alkali concentrations stabilizes the C_{2v}-complex and hence the oxidized state, Fe^{3+}. Using this model, the effect of type and concentration of alkali can be explained. The introduction of Al_2O_3 into the glass network is achieved, at the composition range studied, also by negatively charged AlO_4-tetrahedra. Thus, the number of alkali ions coordinated with non-bridging oxygen decreases with increasing alumina content. Those alkali ions contributing to the charge compensation of the AlO_4-tetrahedra are no longer available to stabilize the Fe^{3+}-C_{2v}-complex, and hence an increase in the alumina concentration has the same effect as a decrease in the alkali content.

CONCLUSIONS

An increase in the alkali content, a decrease in the size of the alkali cation, a decrease in the Al_2O_3, the CaO and the MgO content of the silicate melts studied led to a decrease in the standard potentials, i. e. favoured the oxidized state, Fe^{3+}. This was described using empirical formulae allowing the calculation of standard potentials of the redox pair Fe^{2+}/Fe^{3+}. The cal- culated values were in good agreement with those determined by square-wave voltammetry. This can be explained using a structural model for the incorporation of Fe^{3+}.

References

1. Paul A.: J. Non-Cryst. Solids *71*, 269 (1985).
2. Schreiber H.D., Kozak S.I., Merkel R.C., Balazs G.B., Jones P.W.: J. Non-Cryst. Solids *84*, 186 (1986).
3. Freude E., Rüssel C.: Glastechn. Ber. *60*, 202 (1987).
4. Rüssel C.: Glastechn. Ber. *66*, 93 (1993).
5. Gerlach S., Claußen O., Rüssel C.: J. Non-Cryst. Solids *238*, 75(1998).
6. Claußen O., Rüssel C.: Phys. Chem. Glasses *39*, 200 (1998).
7. Takahashi K., Miura Y.: J. Non-Cryst. Solids *80*, 11 (1986).
8. Gerlach S., Claußen O., Rüssel C.: J. Non-Cryst. Solids *248*, 92 (1999).
9. Rüssel C.: Glastechn. Ber. *66*, 68 (1993).

Submitted in English by the authors.

VLIV SLOŽENÍ SKLA NA ROVNOVÁHU Fe^{2+}/Fe^{3+}

CHRISTIAN RÜSSEL, SANDRA GERLACH

Otto-Schott-Institut,
Universität Jena,
Fraunhoferstrasse 6, D-07743 Jena, Germany

Alaklicko křemičitá a alkalicko-vápenato(hořečnato)-hlinito-křemičitá skla s přídavkem 0.2-0.5 mol.% Fe_2O_3 byla studována diferenční pulsní voltametriií. Růst obsahu alkálií stejně jako růst obsahu CaO a MgO vedly k posunu rovnováhy směrem k oxidovanému stavu. Oxidovaný stav byl také preferován při změně alaklického oxidu v řadě Li_2O – K_2O. Jsou uvedeny empirické vztahy umožňující výpočet termodynamických dat ze složení taveniny.