Original Paper

Redox chemistry of iron–manganese and iron–chromium interactions in soda lime silicate glass melts

Henry D. Schreiber, Lyle J. Peters, Joseph W. Beckman and Charlotte W. Schreiber
Center for Glass Chemistry, Virginia Military Insitute, Lexington, VA (USA)

Redox interactions between the $Fe^{2+}-Fe^{3+}$ and $Mn^{2+}-Mn^{3+}$ redox couples and the $Fe^{2+}-Fe^{3+}$ and $Cr^{6+}-Cr^{3+}$ redox couples were spectrophotometrically determined in soda lime silicate compositions quenched from different melting temperatures (1100 to 1400 °C) at air. Both Mn^{3+} and Cr^{6+} stoichiometrically oxidized Fe^{2+}. Thus, for example in the iron–manganese system, the color of the glass was determined by Fe^{3+} and Mn^{2+} along with either Fe^{2+} or Mn^{3+}, whichever one being in excess at that temperature. The electron exchange between the redox couples occurred during equilibration at melt temperature and not as an artifact of the quench. No evidence was obtained for a rapid internal re-equilibrium of redox states with decreasing temperature during the normal cooling of a melt to a glass. The degree of redox interaction of manganese or chromium with iron is independent of the manganese or chromium compound added, as long as the oxygen fugacity over the glass-forming melt is held constant externally.

Redoxchemie der Wechselwirkungen Eisen–Mangan und Eisen–Chrom in Kalk–Natronsilicatglasschmelzen

Die Redoxwechselwirkungen zwischen den Redoxpaaren $Fe^{2+}-Fe^{3+}$ und $Mn^{2+}-Mn^{3+}$ einerseits und $Fe^{2+}-Fe^{3+}$ und $Cr^{6+}-Cr^{3+}$ andererseits wurden spektrofotometrisch in Kalk–Natronsilicatzusammensetzungen untersucht, die in Luft von unterschiedlichen Schmelztemperaturen (1100 bis 1400 °C) abgeschreckt worden waren. Sowohl Mn^{3+} als auch Cr^{6+} oxidierten Fe^{2+} stöchiometrisch auf. So stellte sich z. B. im Eisen–Mangansystem die Farbe des Glases durch Fe^{3+} und Mn^{2+} in Verbindung mit Fe^{2+} oder Mn^{3+} ein, je nachdem, welches Ion bei der entsprechenden Temperatur im Überschuß vorlag. Der Elektronenaustausch zwischen den Redoxpaaren erfolgte während der Gleichgewichtseinstellung bei Schmelztemperatur und wurde nicht durch das Abschrecken hervorgerufen. Anzeichen für eine rasche erneute Einstellung des inneren Gleichgewichts der Redoxzustände mit sinkender Temperatur während der normalen Abkühlung der Schmelze zu einem Glas wurden nicht gefunden. Das Ausmaß der Redoxwechselwirkung von Mangan oder Chrom mit Eisen ist unabhängig von der zugesetzten Mangan- oder Chromverbindung, solange die Sauerstoffugazität über der glasbildenden Schmelze von außen konstant gehalten wird.

1. Introduction

1.1 Oxidation–reduction chemistry of multivalent elements

Most commercial glass compositions include multivalent elements, those that can exist in two or more redox states. These multivalent elements can be introduced into the composition either in the raw materials as impurities or in the batch to provide a glass with characteristic properties. Within a glass-forming melt, the redox states of a multivalent element exist in proportions defined by an equilibrium dependent primarily on the composition, temperature, and oxygen fugacity [1]. For example, when iron is dissolved in a soda lime silicate melt, the redox equilibrium between the ferric and ferrous ions can be expressed in simplified form as [2],

$$4Fe^{3+} + 2O^{2-} \leftrightarrow 4Fe^{2+} + O_2 \,. \qquad (1)$$

Oxygens from both the silicate melt network (as oxide ions) as well as from the melt atmosphere (as oxygen molecules) are direct participants in the establishment of the oxidation–reduction equilibrium of iron, in this case, in the glass-forming melt. Thus, the redox equilibrium of an individual multivalent element is always fixed with respect to the oxygen potential of the melt system – analogous to the role of hydrogen in aqueous solution. The control of the redox chemistry and in particular of the iron redox ratio (the relative concentrations of Fe^{2+} and Fe^{3+} ions) is of paramount importance for proper processing and color generation in commercial glass production [3]. For example, because Fe^{3+} and Fe^{2+} ions impart yellow and blue colors, respectively, to the glass, the hue of green in the final glass product depends on the ratio of the two redox ions of iron in the melt or glass.

Likewise, other multivalent elements establish their own redox equilibrium in glass-forming melts. Two such elements of commercial importance are manganese and chromium for which respective individual redox equilibria under relatively oxidizing conditions can be written as [1, 3 and 4];

$$4Mn^{3+} + 2O^{2-} \leftrightarrow 4Mn^{2+} + O_2 \,, \qquad (2)$$

$$4CrO_4^{2-} \leftrightarrow 4Cr^{3+} + 3O_2 + 10O^{2-} \qquad (3)$$

Received June 28, 1995, revised manuscript December 4, 1995.

where the chromate ion (CrO_4^{2-}) represents the form of the Cr^{6+} species in the melt or glass. As an illustration of a property of the glass controlled by the presence of individual redox ions, Mn^{3+} imparts a purple color while Mn^{2+} is colorless, and Cr^{6+} as chromate provides a yellow color while Cr^{3+} introduces a green color. Equations (2 and 3) stress once again that the positions of these redox equilibria are dependent on the composition (as reflected by the oxide ion activity, which is also a measure of the polymerization or basicity of the melt), temperature, and oxygen fugacity of the glass melt.

1.2 Mutual interaction between multivalent elements

When both iron and manganese are introduced together into a glass-forming melt, mutual interaction of their redox ions may occur by an electron exchange reaction. Mn^{3+}, being a good oxidizing agent, reacts with the ferrous ion according to [5 and 6];

$$Fe^{2+} + Mn^{3+} \rightarrow Mn^{2+} + Fe^{3+} \ . \qquad (4)$$

This internal redox reaction has been used to chemically decolorize glass by adjusting the distribution of the iron redox ions [7]. A similar oxidation–reduction reaction occurs when iron and chromium are simultaneously present in the melt [8];

$$3Fe^{2+} + CrO_4^{2-} \rightarrow 3Fe^{3+} + Cr^{3+} + 4O^{2-} \ . \qquad (5)$$

Analogous redox reactions are well-established in aqueous chemistry, with the spontaneity of each reaction readily predicted from the sum of the standard oxidation and reduction potentials (E^0) of the two interacting redox couples. The thermodynamic driving force for such redox reactions follows the net reaction potential (E, where according to the Nernst equation, $E = E^0 + \{RT/F\} \ln \{Q\}$ with Q being the reaction quotient of product concentrations divided by reactant concentrations) going to zero at equilibrium. Thus, depending on the sign of E^0 for the reaction, the thermodynamics drives the reaction towards the products ($E^0 > 0$) or the reactants ($E^0 < 0$) in its approach to equilibrium. If the magnitude of E^0 is sufficiently positive, the equilibrium constant for the reaction becomes so large that the equilibrium lies heavily on the side of the products. In this case, the equation for the reaction is written as though it is stoichiometric; that is, it proceeds to completion. That such spontaneous electron exchange reactions occur in a soda lime silicate solvent system is likewise known, but the mechanism for the interaction is not. There are currently two opposing theories explaining "how and why" redox ions of one multivalent element interact with those of another redox couple [9 and 10] – one mechanism stresses kinetic processes [11] while the other emphasizes equilibrium considerations [12]. Exactly when the mutual interaction, or electron exchange, between the two redox pairs happens is the principal feature distinguishing the two schools of thought. The first theory believes the interaction occurs during cooling and the second believes it occurs in the melt [9].

This first mechanism, identified in this paper as the kinetic model, starts with each redox couple in equilibrium with the oxygen potential of the system ("open" with respect to oxygen) and with each other at the melt temperature. One version of this theory states that no interaction of the redox couples (for example, $Mn^{2+}-Mn^{3+}$ and $Fe^{2+}-Fe^{3+}$) occurs in the melt at the equilibration temperature. According to equations (1 and 2), the positions of the iron and manganese redox equilibria are fixed by the bulk composition, temperature, and oxygen fugacity; the presence of the second redox couple does not affect the position of the first and vice-versa [13]. Thus, the melt contains all four redox ions (Fe^{2+}, Fe^{3+}, Mn^{2+}, Mn^{3+}) co-existing under the processing conditions. However, as the glass-forming system cools during the quench, the system becomes "closed" with respect to oxygen because the diffusion of oxygen into or out of the melt and/or the glass cannot respond to the rapid decrease in temperature. Redox reactions in these solvent systems are still very fast at such temperatures, re-equilibrating rapidly with the decreasing temperature. Electron exchange then occurs because each individual redox couple possesses different thermal dependencies of its respective redox equilibrium [13 and 14]. The resulting redox ion distribution measured in the glass is therefore not equivalent to that present at melt temperature; it is controlled principally by the redox ions present at a much lower temperature where the ion concentrations are "frozen-in" as well as by the cooling rate from the equilibration temperature [5, 11 and 15].

The second mechanism, called the equilibrium model in this paper, interprets the mutual interaction of the two redox couples as occurring in the molten solvent, much like reactions take place in aqueous systems. Thus, one could employ the concept of redox potentials in the melt, analogous to those in water, to predict the direction and magnitude of the redox reaction [12]. One underlying ramification of this model is that short-range structural changes, for example the formation of $Fe^{n+}-O-Mn^{m+}$ complexes, must accompany such electron exchanges in the melt [12]. The quench, when the system is then closed with respect to oxygen, is sufficiently rapid to freeze-in the distribution of redox ions present at the melt temperature [8, 12, 16 and 17].

Araujo [9] has examined the two opposing theories on the chemical mechanism in detail and have concluded that indeed both have plausible thermodynamic bases. The electron exchange interaction between two redox couples in a glass-forming melt could be ascribed to a true interaction at melt temperature (equilibrium model) or to the system being transformed in response to a decrease in temperature into a closed system capable of rapid internal re-equilibrium of redox states (kinetic model). Although either mechanism is possible, energy considerations dictate that only one is likely correct for the soda lime silicate and comparable glass-forming systems. Both mechanistic models have their proponents, with experimental and theoretical evidence to support the contrasting views. It is especially difficult to design experiments to discern between the two possible mechanisms because the thermodynamic potentials for the ease of reduction of redox couples in the melt can be experimentally correlated with the thermal dependencies of the redox couples [18].

Most commercial glass compositions contain more than one multivalent element. In order to effectively control the redox state of a glass, one must understand the mechanism of the interacting redox couples, that is, whether one is controlling the thermodynamics of a process happening at melt temperature or whether one is controlling the kinetics of re-equilibration during the quench. This is not simply an academic exercise in the subtleties of chemical reactions but is information needed to design better redox control to achieve desired properties or processing. Oxidizing and reducing agents, for example, are often introduced to control the color of the glass or the refining of the melt.

2. Experimental design

The objectives of this study are two-fold. One goal is to determine the direction and degree of interaction between iron and manganese as well as the iron and chromium redox couples in a soda lime silicate glass composition. The second goal is to ascertain unambiguously the mechanism for the electron exchange interaction of these redox couples in this solvent system.

Soda lime silicate compositions containing varying relative concentrations of iron and manganese (as well as of iron and chromium) were equilibrated at different melt temperatures. The content of manganese in the glass compositions was held constant while that of iron was varied, analogous to the concept of redox titrations in aqueous analytical chemistry. At a given temperature, the relative contents of the two redox components would define a system whereby excess Fe^{2+} was present in the high-iron composition while excess Mn^{3+} was present in the low-iron composition. At a lower melt temperature, the relative amount of Fe^{2+} decreased while that of Mn^{3+} increased so that the iron/manganese concentration ratio at which excess Mn^{3+} occurred was expected to change systematically with temperature. According to the equilibrium model for iron–manganese interaction, the redox ion distributions in the glass can be calculated when based on the initial ion concentrations representative of each individual element's equilibrium at the melt temperature (equations (1 and 2)) and assuming stoichiometric electron exchange by equation (4). Thus, the redox composition of the glass is defined only by reactions that occur at the melt temperature. If the interaction occurred during the quench as per the kinetic model, one would not expect a consistency of the experimental measurements of the redox ion distributions with such stoichiometric calculations. In fact, one interpretation of the kinetic model would indicate that the redox ion distribution would be fixed at some lower "freezing-in" temperature so that the measured redox ion distribution would be roughly independent of the melt temperature and more reflective of this lower temperature.

Table 1. Nominal weight percentages of added elements M (M = Fe, Mn, Cr) in soda lime silicate base compositions

sample code	concentration of added element in %		
	Fe	Mn	Cr
Fe	0.98	–	–
Mn	–	1.10	–
Cr	–	–	0.052
FeMn1	0.98	0.98	–
FeMn2	0.49	0.98	–
FeMn3	0.20	0.98	–
FeCr1	0.98	–	0.055
FeCr2	0.48	–	0.054
FeCr3	0.19	–	0.053
FeCr4	0.98	–	0.17
FeCr5	0.98	–	0.31

The equilibrium model assumes that the electron exchange interaction between the redox couples occurs at the melt temperature and remains unaffected by the quench. Soda lime silicate compositions containing both iron and manganese were equilibrated at a high temperature, then were dropped to a lower temperature still above the melting point. The samples remained at this new temperature for a period of time. The equilibrium model would require sufficient time at this new lower temperature for re-equilibration of the redox states to occur if the system is open with respect to oxygen. The exact time required for a measurable change in the observed redox ion distribution would be dependent on the sample size and configuration. However, because the kinetic model assumes rapid re-equilibration of the redox ion distributions during the quench, the temperature drop would, in a sense, simply reset the initial conditions of the melt. The measured redox ion distribution in the glass would be more reflective of the lower melt temperature, even if only held at that temperature for a relatively short period of time, than the higher melt temperature. This conclusion results from the assumption that the redox equilibrium is changing rapidly, keeping pace with the decreasing temperature during cooling.

3. Experimental procedures

3.1 Base compositions

The reference soda lime silicate composition contained (in mol%) 17 Na_2O, 11 CaO, and 72 SiO_2. The estimated melting temperature for this composition is 1000 °C with a glass transition point of 670 °C as an upper limit [19]. Additions of iron, manganese, and/or chromium were included in concentrations as indicated in table 1. The glass frits were prepared by mixing weighed quantities of ultrapure Na_2CO_3, CaO, and SiO_2 (as well as Fe_2O_3, MnO, and/or Cr_2O_3), melting in a platinum crucible for at least 18 h at 1400 °C in air, quenching rapidly, and then powdering with alumina mortar and pestle. Several reference compositions with (in wt%) about 1 Fe and 1 Mn were also prepared in which manganese was initally added as MnO_2 or $KMnO_4$ instead of as MnO.

3.2 Sample syntheses

Individual samples consisting of about 0.5 g of a base composition in a platinum capsule were synthesized by suspension in the hot zone of a high-temperature, controlled-atmosphere furnace. The samples were melted for at least 24 h, more than sufficient time for equilibrium to be attained for the sample configuration, at imposed temperatures of 1100, 1200, 1300 and 1400 °C. The atmosphere was air with an oxygen fugacity of $\approx 10^{-0.7}$ bar. Samples were quenched by removal from the furnace, which corresponded to a quench rate estimated at several hundred degrees per minute.

Another set of iron and manganese-containing samples was prepared with 24 h equilibration of the composition at 1400 °C and air. The furnace temperature was then dropped to 1200 °C at a rate of about 25 K/min. Synthesis conditions were then held constant at 1200 °C and air as a function of time (about 0.5 to 12 h) before quenching the sample by removal from the furnace.

3.3 Sample analyses

For glass compositions containing only iron as a multivalent element, the samples were analyzed for Fe^{2+} and total iron content via a colorimetric procedure [20]. A portion of the powdered glass was digested in acid under an inert atmosphere, complexed with o-phenanthroline at a buffered pH value, and analyzed colorimetrically to determine its Fe^{2+} concentration, then after addition of hydroquinone, re-analyzed colorimetrically to obtain its total iron concentration. Spectrophotometric analyses of a polished slab of the corresponding glass provided a semiquantitative calibration of the Fe^{2+} absorption peak in the near-infrared (at about 1100 nm) to the Fe^{2+} concentration in the glass [2].

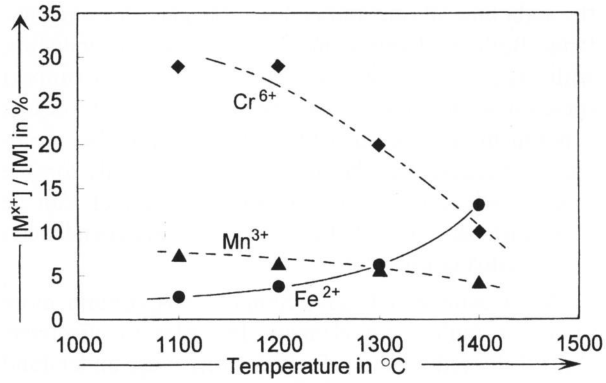

Figure 1. Temperature dependence of individual iron ($Fe^{2+}-Fe^{3+}$), manganese ($Mn^{2+}-Mn^{3+}$), and chromium ($Cr^{3+}-Cr^{6+}$) redox equilibria in the soda lime silicate glass composition. Equilibria are expressed as $[M^{x+}]/[M]$ in % with M = Fe, Mn, Cr.

For glass compositions containing only manganese as a multivalent element, the powdered samples were digested under an inert atmosphere in a solution of acids containing excess Fe^{2+}, then Fe^{2+} analyzed by redox titration with standard ceric sulfate. The molar quantity of Fe^{2+} that reacted during digestion of the glass sample was related to the amount of Mn^{3+} in the glass [21]. Polished sections of the glasses were analyzed spectrophotometrically from 2000 to 300 nm. The absorption peak at about 460 nm (with the baseline defined at 850 nm) is characteristic of Mn^{3+} in glass and was calibrated to the Mn^{3+} concentration (in wt%) [10]. For glasses normalized to 1 mm thickness, the calibration stated,

$$Mn^{3+} \text{ concentration} = 0.088 \cdot A \tag{6}$$

where A represents the peak minus baseline absorbance.

For glass compositions containing only chromium as a multivalent element, analogous redox titrations provided measures of the Cr^{6+} concentrations [21]. The spectral absorption at 360 nm characteristic of Cr^{6+} in the glass was similarly calibrated to the concentration (in wt%) of Cr^{6+} by equation (7) [10];

$$Cr^{6+} \text{ concentration} = 0.0066 \cdot A\,. \tag{7}$$

Spectral calibrations for both Mn^{3+} and Cr^{6+} are consistent with absorptivities measured in other glass systems, for example the sodium borosilicates [10].

Fe^{3+}, Mn^{2+}, and Cr^{3+} concentrations were determined in the respective glasses by difference of the analyzed Fe^{2+}, Mn^{3+}, and Cr^{6+} concentrations from the total content of each element. The analytical scheme provided a measurement of the total content of iron for iron-containing glasses; and the nominal concentrations were employed in the case of total manganese and total chromium.

For glasses simultaneously containing two multivalent elements (iron and manganese or iron and chromium), polished sections of the glasses were analyzed spectrophotometrically from 2000 to 300 nm. The concentrations of Mn^{3+} or Cr^{6+} were then obtained from the spectral calibrations of their characteristic absorption peaks, and the presence/absence of Fe^{2+} in the glass was determined by the presence/absence of the distinct absorption in the near-infrared region at 1100 nm.

4. Results

4.1 Compositions containing a single multivalent element

Figure 1 summarizes the experimental results for the temperature dependencies of the individual redox equi-

Table 2. Relative reduction potentials (E') of the manganese ($Mn^{3+} \rightarrow Mn^{2+}$), chromium ($Cr^{6+} \rightarrow Cr^{3+}$), and iron ($Fe^{3+} \rightarrow Fe^{2+}$) redox couples in various glass-forming systems

sample code	E' for					EFEL $Na_2Si_2O_5$ at 1085 °C, [24]	$E_{1/2}$ Na–Ca silicate at 1250 °C, [17]
	Na–Ca silicate at 1400 °C, results of this work	Na–Ca silicate at 1400 °C, [3]	Na–boro-silicate at 1150 °C, [10]	Na–Ca silicate at 1100 °C, [22]	$Na_2Si_2O_5$ at 1085 °C, [23]		
Mn	+1.2	+1.2	+0.8	–	+0.7	−0.1	−0.18
Cr	+0.4	+0.2	−0.3	−0.9	–	+0.05	−0.10
Fe	−1.0	−1.0	−1.7	−1.9	−2.1	+0.4	−0.47

Explanations: E' was calculated from the data of [22 and 23]. EFEL = electron-free level concept, defined with the opposite sign as E'. $E_{1/2}$ = half-wave potential in voltammetry, related to reduction potential.

libria of iron ($Fe^{2+}-Fe^{3+}$), manganese ($Mn^{2+}-Mn^{3+}$), and chromium ($Cr^{3+}-Cr^{6+}$) in the soda lime silicate composition at air. At all temperatures, the manganese-containing composition always had the largest percentage of its redox couple in the reduced state, while the iron-containing composition always had the largest percentage of its redox couple in the oxidized state. In other words, the progression is $Mn^{3+} > Cr^{6+} > Fe^{3+}$ in order of ease of reduction in the soda lime silicate composition.

To quantify the ease of reduction of the three redox couples in the reference soda lime silicate composition, the redox ratio of each at 1400 °C is used to determine its relative reduction potential at that temperature [12]. Such values are analogous to standard reduction potentials for redox couples in aqueous systems. Table 2 compiles the relative reduction potentials (E') of manganese, chromium, and iron in this solvent system as well as compares them to those in other analogous glass-forming melts. The ordering of the couples from $Mn^{3+}-Mn^{2+}$ to $Cr^{6+}-Cr^{3+}$ to $Fe^{3+}-Fe^{2+}$ from easiest to hardest to reduce is independent of the processing conditions; the absolute values of the relative reduction potentials reflect the composition, temperature, and oxygen fugacity, but the relative order of the values remains essentially invariant [25].

When the logarithm of the redox ratio of a certain multivalent element is plotted as a function of the reciprocal absolute temperature, the slope of the resulting linear relationship is employed to determine the enthalpy of reduction of that redox couple [13 and 18]. Table 3 compiles the enthalpies of reduction for these three multivalent elements in the soda lime silicate composition. As also shown on table 3, the experimental values compare favorably with those determined independently by others [10, 13, 22 and 23]. The ease of reduction of a given redox couple can be reflected by either the enthalpy of reduction or the relative reduction potential, as a strong correlation exists between the two values [18].

When the iron-containing composition was first equilibrated at 1400 °C, then dropped in temperature to 1200 °C before quenching, several hours were required to reestablish the iron redox equilibrium (equation (1)) at this lower temperature. In fact, about 8 h were needed to readjust the redox process to the half-way point. Before redox equilibrium is achieved, the oxygen potential of the melt needs to be reset to this new temperature, 1200 °C. The rate-limiting step for this process is the diffusion of molecular oxygen through the melt, a sluggish process at this lower temperature. This is consistent with the role of oxygen diffusion in redox kinetics as previously reported in other glass-forming systems with the same sample configuration [2, 26 and 27].

4.2 Compositions containing two multivalent elements

Table 4 summarizes the results for the iron–manganese mutual interaction study for soda lime silicate compositions equilibrated at a certain melt temperature before quenching. This table, which focuses on the concentrations of Fe^{2+} and Mn^{3+}, also compares these experimental measurements obtained from spectral analyses of the glasses with the redox ion distributions expected assuming no interaction between iron and manganese and with those predicted on the basis of stoichiometric mutual interaction according to equation (4). The former comparison is simply iron and manganese redox ion concentrations governed independently by equations (1 and 2), respectively, while the latter is a representation of the equilibrium model for the mechanism of the electron exchange reaction at melt temperature. The redox distributions in these soda lime silicate compositions possessed either Fe^{2+} or Mn^{3+} but not both, indicative of the occurrence of a stoichiometric redox reaction. Furthermore, the experimental results were consistent with the predictions of the equilibrium model in which the redox reaction goes to completion in the glass-forming solvent system. The consistency of the experiments with the predictions of the equilibrium model was striking, because even qualitatively the color of the glass was dependent on the equilibrium melt temperature as well as the nominal iron and manganese concentrations. Both variables played key roles in adjusting the Fe^{2+} and

Table 3. Enthalpies of reduction (ΔH_{red} in kJ/(mol M) with M = Fe, Mn, Cr) of the manganese ($Mn^{3+} \rightarrow Mn^{2+}$), chromium ($Cr^{6+} \rightarrow Cr^{3+}$), and iron ($Fe^{3+} \rightarrow Fe^{2+}$) redox couples in various glass-forming systems

sample code	ΔH_{red} in kJ/(mol M) for				
	Na–Ca silicate result of this work	Na–Ca silicate [22]	Na–Ca silicate [13]	Na–borosilicate [10]	$Na_2Si_2O_5$ [23]
Mn	36 ± 7	–	43 to 53	54 ± 13	59
Cr	79 ± 28	76	–	42 ± 13	–
Fe	107 ± 18	102	85 to 105	240 ± 100	117

Table 4. Iron-manganese-containing compositions equilibrated at melt temperature before quenching

sample code	concentration of added element in wt%		melt temperature in °C	ion concentration in wt%					
				as separate couples (without interaction)		predicted by stoichiometric reaction		experimentally determined in glass	
	Fe	Mn		Fe^{2+}	Mn^{3+}	Fe^{2+}	Mn^{3+}	Fe^{2+}	Mn^{3+}
FeMn1	0.98	0.98	1400	0.13	0.04	0.09	0	present	0
			1300	0.06	0.05	0.01	0	present	0
			1200	0.04	0.06	0	0.03	absent	0.03
			1100	0.025	0.07	0	0.045	absent	0.04
FeMn2	0.49	0.98	1400	0.065	0.04	0.02	0	present	0
			1300	0.03	0.05	0	0.025	absent	0.03
			1200	0.015	0.06	0	0.05	absent	0.05
			1100	0.01	0.07	0	0.06	absent	0.05
FeMn3	0.20	0.98	1400	0.025	0.04	0	0.015	absent	0.02
			1300	0.01	0.05	0	0.045	absent	0.04
			1200	0.008	0.06	0	0.05	absent	0.04
			1100	0.005	0.07	0	0.065	absent	0.06

Mn^{3+} concentrations to control which ion was in excess at that temperature. The relative proportion of Mn^{3+} available for reaction, for example, could be enhanced by simply increasing the manganese content at constant temperature, or by decreasing the equilibrium melt temperature at constant iron and manganese content.

For the soda lime silicate composition containing 0.98 wt% iron and 0.98 wt% manganese, the glass contains excess Fe^{2+} when equilibrated at 1400 °C but contains excess Mn^{3+} when equilibrated at 1100 °C. Consequently, the glass is colored yellow-green in the former case but purple in the latter, once again a dramatic example of the redox titration concept being illustrated by the equilibrium model. The final glass was colored accordingly (and with redox ion distributions as reported in table 4) independent of the compound in which the manganese was introduced in the composition, whether MnO, MnO_2, or $KMnO_4$. Equation (2) dictated the manganese redox ion distribution at that temperature (either 1400 or 1100 °C) which provided the same percentage of Mn^{3+}, no matter the source of manganese, to react with Fe^{2+} in the melt.

Table 5 compiles the experimental and predicted results for the equilibrated compositions simultaneously containing iron and chromium. The glasses contained either Fe^{2+} or Cr^{6+} but not both, indicative of a stoichiometric redox reaction between the two redox couples at melt temperature as shown by equation (5). The stoichiometry of this electron exchange could also be written in simple form as,

$$3Fe^{2+} + Cr^{6+} \rightarrow Cr^{3+} + 3Fe^{3+} \tag{8}$$

to emphasize the 3:1 molar ratio of Fe^{2+} reacting with Cr^{6+} as the chromate ion. The experimental results reported in table 5 for the iron–chromium system are consistent with the equilibrium model as the mechanism for the electron exchange reaction at melt temperature.

Several iron–manganese as well as iron–chromium compositions were first equilibrated at 1400 °C in air, then dropped in temperature to 1200 °C before quenching. The compositions were chosen to provide samples in which Fe^{2+} was in excess at the higher temperature, but Mn^{3+} (or Cr^{6+}) was in excess at the lower temperature, so that a dramatic change in glass color should result depending on what temperature controlled the redox ion distribution of the final product. Establishment of the redox ion distribution defined by a stoichiometric reaction at the lower temperature was sluggish, taking many hours to reset from the stoichiometric reaction defined by the initial mutual interaction at the higher temperature. Thus, even after exposing the melt to 1200 °C

Table 5. Iron-chromium-containing compositions equilibrated at melt temperature before quenching

sample code	concentration of added element in wt%		melt temperature in °C	ion concentration in wt%					
				as separate couples (without interaction)		predicted by stoichiometric reaction		experimentally determined in glass	
	Fe	Cr		Fe^{2+}	Cr^{6+}	Fe^{2+}	Cr^{6+}	Fe^{2+}	Cr^{6+}
FeCr1	0.98	0.055	1400	0.13	0.006	0.04	0	present	0
			1300	0.06	0.011	0.01	0	present	0
			1200	0.04	0.016	0	0.003	absent	0.004
			1100	0.025	0.016	0	0.008	absent	0.009
FeCr2	0.48	0.054	1400	0.06	0.006	0.015	0	present	0
			1300	0.03	0.011	0	0	present	0
			1200	0.02	0.016	0	0.009	absent	0.009
			1100	0.01	0.016	0	0.012	absent	0.017
FeCr3	0.195	0.053	1400	0.025	0.006	0.002	0	present	0
			1300	0.01	0.011	0	0.007	absent	0.007
			1200	0.008	0.016	0	0.019	absent	0.015
			1100	0.005	0.016	0	0.014	absent	0.02
FeCr4	0.98	0.17	1400	0.13	0.017	0.03	0	present	0
			1300	0.06	0.035	0	0.015	absent	0.013
			1200	0.04	0.05	0	0.037	absent	0.04
			1100	0.025	0.05	0	0.04	absent	>0.03
FeCr5	0.98	0.31	1400	0.13	0.031	0.01	0	present	0
			1300	0.06	0.061	0	0.04	absent	>0.03
			1200	0.04	0.09	0	0.08	absent	>0.03
			1100	0.025	0.09	0	0.08	absent	>0.03

for many hours, the optical and redox properties of the final glass were controlled by the higher equilibration temperature of 1400 °C. These results are similar to the redox kinetics of the melt containing just the single multivalent element. In order to reset the mutual interaction at the lower temperature, the system had to become "open" with respect to oxygen. However, the melt is quite viscous at 1200 °C, so that the rate-determining step of this process is the sluggish diffusion of oxygen through the melt. That the purple color of Mn^{3+} was encroaching upon the bulk of the sample from the edges as a function of the time exposed to the lower temperature of 1200 °C is also qualitative evidence that oxygen diffusion in equilibrating with the atmosphere limits the rate at which the mutual interaction is reset. Nevertheless, in response to a decrease in temperature, the glass-forming melt was not transformed into a closed system capable of rapid internal re-equilibrium of the redox states as expounded by the kinetic model.

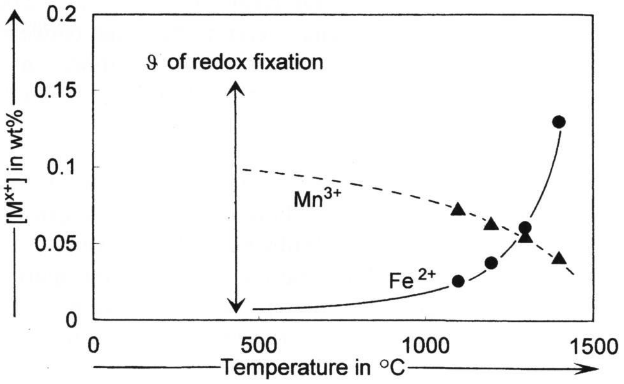

Figure 2. Temperature dependence of individual iron and manganese redox ion distribution in the soda lime silicate glass composition containing 0.98 wt% Fe and 0.98 wt% Mn (sample FeMn1). "ϑ of redox fixation" refers to the postulated temperature of the kinetic model at which the redox ion distributions become "frozen-in".

5. Discussion

By comparison of the experimental results with the predictions of the equilibrium model in tables 4 and 5, this study provides compelling evidence of internal electron exchange reactions occurring at melt temperature and not during the quench. Whether Fe^{2+} or Mn^{3+} (or Cr^{6+}) in iron–manganese (or iron–chromium) compositions is present in the quenched glass is determined solely by which ion is in excess at the equilibration or melt temperature. Similar calculations based on this equilibrium model for the mutual interactions of redox couples in glass-forming melts [12 and 28] have likewise shown consistency between the experiments and predictions. It is unnecessary to impose rapid re-equilibrations of the electron exchange reactions during the quench or cooling to explain the results.

Figure 2 compares schematically the two proposed theories for the mechanism of electron exchange between the iron and manganese redox couples in the soda lime silicate composition. At 1400 °C for this system, the concentration of Fe^{2+} is in excess of that of Mn^{3+} required for stoichiometric reaction by equation (4), while at 1200 °C, Mn^{3+} is in excess of Fe^{2+} for the mutual interaction. According to the equilibrium model for the reaction mechanism, the resulting glass should have excess Fe^{2+} if quenched from 1400 °C and excess Mn^{3+} if quenched from 1200 °C, two quite different glasses with dinstinct optical properties. This prediction is dramatically confirmed by the experimental results. Also in figure 2, the concentrations of Fe^{2+} and Mn^{3+} are extrapolated down to a temperature of about 450 °C, the temperature claimed to be where the redox ion distributions are frozen into the glass [5 and 11] according to the kinetic model. At this temperature, the concentration of Mn^{3+} is in great excess of that of Fe^{2+} in the iron and/or manganese-containing composition. Because the kinetic model for electron exchange assumes a rapid re-equilibrium of the redox states during the cooling of the melt to the glass [9], the final product should have excess Mn^{3+} no matter whether it was quenched from 1400 or 1200 °C. Clearly this prediction is incompatible with the experimental results. This illustration relies upon the interpretation of the kinetic model in which there is no initial interaction among the redox states at the equilibration temperature [13 and 15]. There is no need to impose properties of the redox system that are dependent on the temperature and cooling [13 to 15] in order to explain the experimental results of this study. The driving force for the internal electron exchange between two redox couples in a soda lime silicate composition is provided by the net reaction potential [9 and 12], analogous to that in other solvents like water.

Any manganese or chromium compound, when added to an iron-containing soda lime silicate composition in air, will act as an oxidizing agent towards the $Fe^{2+}-Fe^{3+}$ couple. For example, it does not matter whether chromium is added to the batch as metallic chromium, CrO, Cr_2O_3, or $KCrO_4$; all will behave as oxidizing agents as long as the oxygen fugacity over the melt is relatively oxidizing and externally controlled (an "open" system with respect to oxygen [9]). The chromium-containing melt will equilibrate to Cr^{6+} and Cr^{3+} contents as prescribed by equation (3) for that composition, temperature, and oxygen fugacity; with available Cr^{6+} oxidizing a stoichiometric amount of Fe^{2+} in the melt. This behavior is once again consistent with the redox reactions occurring in the melt as per the equilibrium model. It is surprising in one sense that Cr_2O_3 is an oxidizing agent in the melt even in the absence of the oxidized chromium (Cr^{6+}) in this compound; but once in the melt even Cr_2O_3 provides Cr^{6+} on the basis of the oxygen potential of the melt. Similarly, regardless of whether manganese is introduced into the system as oxidized or reduced manganese ions, processing conditions will define the manganese redox ion distribution and thus its interaction with iron in the melt. In order to control the redox states of the multivalent elements in the final glass, the crucial step is to be aware of the electron exchange reactions occurring in the melt, not during the cooling.

The temperature drop experiments display additional consistency with the electron exchange mechanism at melt temperature. This can be seen schematically in figure 2. The Fe^{2+} and Mn^{3+} concentrations in an iron and manganese-containing composition are a function of the temperature, but experiments show that once equilibrated at a certain melt temperature the concentrations do not change rapidly with falling temperature above the melting point of the system. In light of this observation, it is even more unlikely that these concentrations will further keep readjusting below the glass transition temperature to some final fixation temperature. Previous observations [13] have also indicated that the interaction between the manganese and iron redox couples becomes more sluggish with decreasing temperature due to viscosity changes of the soda lime silicate melt. One fundamental assumption in the kinetic model, that of rapid re-equilibration of the redox states during the quench [9], does not occur. However, some prior results [5, 29 and 30] are difficult to explain in the context of the equilibrium model for the mutual interaction of the redox couples.

6. Conclusions

Both manganese (as Mn^{3+}) and chromium (as Cr^{6+}) operate as oxidizing agents with respect to the iron redox couple in soda lime silicate compositions. The internal electron exchange reactions between Mn^{3+} and Fe^{2+} ions as well as between Cr^{6+} and Fe^{2+} ions are stoichiometric, in that both chemical equations occur to completion. These redox reactions occur in the melt at the equilibration or processing temperature, with the driving force for the interaction being the redox potentials of the reacting couples.

*

Support for this study was provided by the Industry-University Center for Glass Research sponsored by the National Science Foundation, the United States Glass Industry, and the New York State College of Ceramics at Alfred University. This project was part of an international scientific collaboration of the Industry-University Center for Glass Research with the Hüttentechnische Vereinigung der Deutschen Glasindustrie,

7. References

[1] Schreiber, H. D.: Redox processes in glass-forming melts. J. Non-Cryst. Solids **84** (1986) p. 129–141.

[2] Schreiber, H. D.; Kozak, S. J.; Merkel, R. C. et al.: Redox equilibria and kinetics of iron in a borosilicate glass-forming melt. J. Non-Cryst. Solids **84** (1986) p. 186–195.

[3] Schreiber, H. D.; Kochanowski, B. K.; Schreiber, C. W.: Compositional effects on the iron redox state in soda–lime–silica glasses. In: Schaeffer, H. A.; Pye, L. D. (eds.): Proc. 4th Int. Conf. Advances in Fusion and Processing of Glass, Würzburg (Germany) 1995. Glastech. Ber. Glass Sci. Technol. **68 C2** (1995) p. 233–240.

[4] Schreiber, H. D.; Kochanowski, B. K.; Schreiber, C. W. et al.: Compositional dependence of redox equilibria in sodium silicate glasses. J. Non-Cryst. Solids **177** (1994) p. 340–346.
[5] Gravanis, G.; Rüssel, C.: Redox reactions in Fe_2O_3, As_2O_5 and Mn_2O_3 doped soda–lime–silica glasses during cooling – A high-temperature ESR investigation. Glastech. Ber. **62** (1989) no. 10, p. 345–350.
[6] Schreiber, H. D.; Minnix, L. M.; Balazs, G. B. et al.: The chemistry of uranium in borosilicate glasses. Pt. 4. The ferric–ferrous couple as a potential redox buffer for the uranium redox state distribution against oxidising agents in a borosilicate melt. Phys. Chem. Glasses **25** (1984) no. 1, p. 1–10.
[7] Volf, M. B.: Chemical approach to glass. Amsterdam (et al.): Elsevier 1984. (Glass Science and Technology. Vol. 7.)
[8] Paul, A.; Douglas, R. W.: Mutual interaction of different redox pairs in glass. Phys. Chem. Glasses **7** (1966) no. 1, p. 1–13.
[9] Araujo, R.: Interactions among polyvalent ions in a melt. High Temper Sci. **32** (1991) p. 51–57.
[10] Schreiber, H. D.; Riethmiller, M. W.; Downey, J. S.: A model for redox interactions in glass melts: The chromium-manganese electron exchange. In: 2nd Int. Conf. Advances in the Fusion and Processing of Glass, Düsseldorf (Germany) 1990. Glastech. Ber. **63K** (1990) p. 212–221.
[11] Rüssel, C.: Redox reactions during cooling of glass melts. – A theoretical consideration. Glastech. Ber. **62** (1989) no. 6, p. 199–203.
[12] Schreiber, H. D.: Mutual interactions of redox couples via electron exchange in silicate melts: Models for geochemical melt systems. J. Geophys. Res. **B9** (1987) p. 9233–9245.
[13] Lenhart, A.; Schaeffer, H. A.: Redox behavior of glass melts. Diffusion Defect Data **53–54** (1987) p. 335–344.
[14] 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.
[15] Paul, A.: Chemistry of glasses. 2nd ed. London: Chapman & Hall 1990.
[16] Schreiber, H. D.; Balazs, G. B.: An electromotive force series for redox couples in a borosilicate melt: The basis for electron exchange interactions of the redox couples. J. Non-Cryst. Solids **71** (1985) p. 59–67.
[17] Takahashi, K.; Miura, Y.: Electrochemical studies on diffusion and redox behavior of various metal ions in some molten glasses. J. Non-Cryst. Solids **38–39** (1980) p. 527–532.
[18] Schreiber, H. D.; Schreiber, C. W.; Riethmiller, M. W. et al.: The effect of temperature on the redox constraints for the processing of high-level nuclear waste into a glass waste form. In: Oversby, V. M.; Brown, P. W. (eds.): Scientific Basis for Nuclear Waste Management, Conference Boston, MA (USA) 1989. **XIII** (1990) p. 419–426.
[19] Kingery, W. D.; Bowen, H. K.; Uhlmann, D. R.: Introduction to ceramics. 2nd ed. New York (et al.): Wiley 1976.
[20] Jones, D. R.; Janskeski, W. C.; Goldman, D. S.: Spectrophotometric determination of reduced and total iron in glass with o-phenanthroline. Anal. Chem. **53** (1981) p. 923–924.
[21] Close, W. P.; Tillman, J. F.: Chemical analysis of some elements in oxidation–reduction equilibria in silicate glasses. Glass Technol. **10** (1969) no. 3, p. 134–146.
[22] Rüssel, C.: Online measurements of redox properties in glass forming melts. Glass Researcher **3** (1993), no. 1, p. 4–5.
[23] Johnston, W. D.: Oxidation-reduction equilibria in molten $Na_2O \cdot 2SiO_2$ glass. J. Am. Ceram. Soc. **48** (1965) no. 4, p. 184–190.
[24] Wong, J.; Angell, C. A.: Glass, structure by spectroscopy. New York, Basel: Dekker 1976.
[25] Schreiber, H. D.; Coolbaugh, M. T.: Solvations of redox ions in glass-forming silicate melts. J. Non-Cryst. Solids **181** (1995) p. 225–230.
[26] Schreiber, H. D.; Kozak, S. J.; Fritchman, A. L. et al.: Redox kinetics and oxygen diffusion in a borosilicate melt. Phys. Chem. Glasses **27** (1986) no. 4, p. 152–177.
[27] Schreiber, H. D.; Kozak, S. J.; Trandel, B. D. et al.: Oxygen diffusion in SRL waste glass melts. Ceram. Trans. **20** (1986) p. 125–132.
[28] Schreiber, H. D.; Hockman, A. L.: Redox chemistry in candidate glasses for nuclear waste immobilization. J. Am. Ceram. Soc. **70** (1987) no. 8, p. 591–594.
[29] Rüssel, C.; Freude, E.: Voltammetric studies in a soda–lime–silica glass melt containing two different polyvalent ions. Glastech. Ber. **63** (1990) no. 6, p. 149–153.
[30] Blair, J. A.; Duffy, J. A.: Sites for hosted metal ions in glasses and melts. Phys. Chem. Glasses **36** (1995) no. 1, p. 12–16.

0996P001

Address of the authors:
H. D. Schreiber, L. J. Peters, J. W. Beckman, C. W. Schreiber
Virginia Military Institute
Department of Chemistry
Lexington, VA 24450-0304 (USA)