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Solubility of Cr₂O₃ and speciation of chromium in soda-lime-silicate melts

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Abstract

Chromium oxide solubility was measured in soda-lime-silicate melts using a thermochemical reactor allowing an independent control of temperature, glass composition and oxygen fugacity in a closed system. This investigation performed ¹ in the ternary Na₂O-CaO-xSiO₂ (NCS) system showed that the physicochemical and thermochemical models used for chromium chemistry description in binary melts are applicable in the ternary system. The presence of Cr(II), Cr(III) and Cr(VI) has been evidenced and their respective contributions in the total chromium content dissolved in the melt were determined. A new approach based on optical basicity allowed the quantification of the basicity of the melt and consequently the free oxygen ions activity ($a_{O^{2-}}$). The treatment of the obtained results led to the determination of thermodynamical properties of the system. The standard enthalpies and entropies corresponding to the oxidation and reduction reactions were determined.

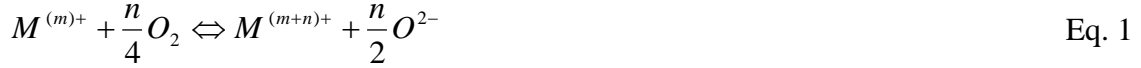
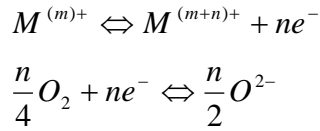
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1. Introduction

The dissolution processes of minerals and refractory materials in molten silicates are of major interest for geologists (relict grains, xenoliths, magma assimilation) and chemists (corrosion of ceramics by molten glasses). It has been shown that the solubility of elements in silicate melts strongly depends on glass basicity (alkaline oxides content), temperature and oxygen fugacity¹⁻⁴. This latter parameter influences the redox properties of the glass and yields to the stabilization of high or low oxidation states for the multivalent elements in the melt. Therefore, effects related to the action of both O^{2-} (basic effect) and O_2 (oxidizing effect) rule together the formation of the oxide polyhedron, the well known tetrahedra or octahedra, which stabilize the metallic or semi-metallic solute in the molten silicate liquid. Oxygen is one of the principal reactants in redox equilibria which occur in molten glasses. The equilibrium state of the glass strongly depends on its composition, which conditions the O^{2-} activity (i.e. the basicity). Thus, for glasses of fixed O^{2-} activity, the measurement of dissolved oxygen can be used to control some processes, such as the control of the properties of the melt (viscosity, quality of refining) or the final state of the material (colour, ageing...)⁵⁻⁸.

Melts containing one or more multivalent elements are in equilibrium when all the components taking part in the redox reactions assume a common value of the potential⁹. Reactions involving oxygen which are known to be generally slow around 25°C, are very fast at temperature higher than 1000°C. In this case, free oxygen ions O^{2-} , which are imposed by the glass composition⁹⁻¹¹, take part in redox reactions.

The redox reactions between oxygen and multivalent elements in the glass melt are often described as followed:

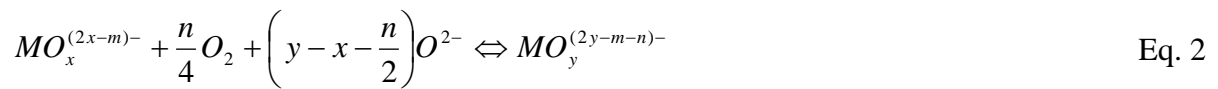


This reaction, in satisfying the equilibrium constant, allows the prediction of the influence of the state variables on this equilibrium:

- For constant temperature and glass composition (aO^{2-}), an increase in oxygen fugacity should increase the oxidized species ($M^{(m+n)+}$) content.
- For constant temperature and oxygen fugacity (fO_2), an increase in the O^{2-} activity should increase the concentration of the reduced species ($M^{(m)+}$).

Several studies confirm the first prediction¹²⁻¹⁴, but second was rejected by many others¹⁵⁻¹⁸. In this case, increasing basicity leads to an increase of the oxidized species concentration. This disagreement is explained by taking account of the oxyacid character of the cations which interact with the free oxygen ions. This leads to the formation of oxy-complexes which present different stabilities, charges, symmetries and coordination numbers¹⁹.

By taking into account the combined effect of the redox reaction and the oxy-acid-basicity, equilibrium described by Eq. 1 can be expressed by the equation:



In this equilibrium, the oxidized and reduced species are complexed by free oxygen ions, whereby the x and y indices are the coordination numbers of resulting oxo-complex species. If the value of the stoichiometric coefficient ($y-x-n/2$) related to (O^{2-}) is positive, an increase the basicity stabilizes the highest oxidation state. In the contrary case, the reverse occurs. The equilibrium constant of the reaction can be given by:

$$K(T) = \frac{a(MO_y^{(2y-m-n)-})a(O^{2-})^{(x-y+n/2)}}{a(MO_x^{(2x-m)-})(fO_2)^{n/4}} \quad \text{Eq. 3}$$

where a_i is the activity of the i element and fO_2 is the oxygen fugacity.

By replacing activities by the expression ($a_i = \gamma_i \cdot C_i$), the equilibrium constant can be written as:

$$K(T) = \frac{\gamma_{M^{(m+n)+}} \cdot [MO_y^{(2y-m-n)-}] a(O^{2-})^{(x-y+n/2)}}{\gamma_{M^{(m)+}} \cdot [MO_x^{(2x-m)-}] (fO_2)^{n/4}} \quad \text{Eq. 4}$$

with :

γ_i : activity coefficient of the i component in the melt

[i] : concentration of the i component in the melt

Since the concentrations of the multivalent ions in melts are generally low, applying Henry's law, their activities can be equated to their concentrations^{5,19}. Consequently, the equilibrium constant $K(T)$ expression can be evaluated, using only the concentrations of the multivalent elements, the oxygen fugacity and the activity of the free oxygen ions:

$$K(T) = \frac{[MO_y^{(2y-m-n)-}] a(O^{2-})^{(x-y+n/2)}}{[MO_x^{(2x-m)-}] (fO_2)^{n/4}} \quad \text{Eq. 5}$$

Consequently:

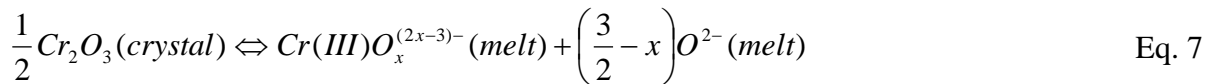
$$\mathfrak{R} = \frac{[MO_y^{(2y-m-n)-}]}{[MO_x^{(2x-m)-}]} = K(T) \cdot [a(O^{2-})]^{(x-y+n/2)} \cdot [fO_2]^{n/4} \quad \text{Eq. 6}$$

with \mathfrak{R} as the redox ratio

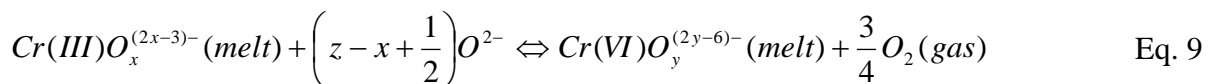
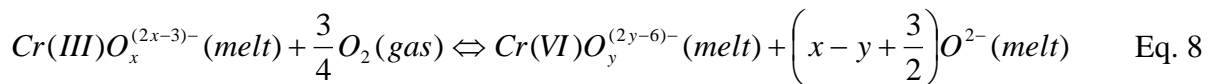
Chromium can exist in various oxidation states. It is often used in metallurgy for its properties of hardness and corrosion resistance. Much of the equipments used in the glass

industry involves superalloys containing up to 30% chromium. The ability of these alloys to resist corrosion is related to the chemical durability of the chromium oxide (Cr_2O_3) layer formed at the alloy/glass interface^{20,21}. In the ambient environments, chromium is primarily in the Cr(III) form, but also in the Cr(VI) form in some oxidizing environments close to the surface²². Nevertheless, several studies showed the existence of Cr(II) in silicates melted under reducing conditions²³⁻²⁷. The behavior of chromium in the silicate melts is of interest not only in glass manufacture²⁸, but also in many other areas such as nuclear waste immobilization²⁹, slag recycling²⁸ and geochemistry³⁰. However, a good description of the chemistry of chromium in silicate melts passes inevitably by a good comprehension of the chemical equilibria (acid-bases, redox) taking place between chromium and the melt.

In a previous work¹, a chemical model describing chromium chemistry in the $\text{Na}_2\text{O-SiO}_2$ binary melts was developed. A description of the reactions occurring when chromium oxide is in contact with the glass melt is given in Figure 1. The first reaction (Eq. 7) is the direct dissolution of Cr_2O_3 into the melt as a Cr(III) oxo-complex. This is an acid-base reaction which is independent of the $f\text{O}_2$.



Cr(III) species can be oxidized to Cr(VI) species (Eq. 8), under oxidizing conditions, or reduced to Cr(II) species (Eq. 9), under reducing conditions



The equilibrium constants for the dissolution, oxidation, and reduction reactions can be written as:

$$K_d = a[O^{2-}]^{\left(\frac{3}{2}-x\right)}.a[Cr(III)] \quad \text{Eq. 10}$$

$$K_{ox} = \frac{a[Cr(VI)]a[O^{2-}]^{\left(x-y+\frac{3}{2}\right)}}{a[Cr(III)].fO_2^{\frac{3}{4}}} \quad \text{Eq. 11}$$

$$K_{red} = \frac{a[Cr(II)].fO_2^{\frac{1}{4}}}{a[Cr(III)].a[O^{2-}]^{\left(z-x+\frac{1}{2}\right)}} \quad \text{Eq. 12}$$

where $a_i = \gamma_i \cdot X_i$ and a_i is the activity, γ_i the activity coefficient and X_i the mole fraction of species i .

In glass melts, polyvalent ion contents are generally very low, and in conformity with Henry's law, the activity can be equated to the concentration, so that:

$$\log[Cr(III)] = \log K_{diss} + \left(x - \frac{3}{2}\right) \log a[O^{2-}] \quad \text{Eq. 13}$$

$$\log \frac{[Cr(VI)]}{[Cr(III)]} = \frac{3}{4} \log fO_2 - \left(x - y + \frac{3}{2}\right) \log a[O^{2-}] + \log K_{ox} \quad \text{Eq. 14}$$

$$\log \frac{[Cr(II)]}{[Cr(III)]} = -\frac{1}{4} \log fO_2 + \left(z - x + \frac{1}{2}\right) \log a[O^{2-}] + \log K_{red} \quad \text{Eq. 15}$$

The model developed in our previous works^{1,31} allows the determination of the redox ratio (Cr(II)/Cr(III) and Cr(VI)/Cr(III)). In this work, this model has been extended to a ternary system in order to study Cr₂O₃ solubility in the Na₂O-CaO-SiO₂ system.

2. Experimental

Sodium silicate and soda lime silicate glasses with the general composition of Na₂O-CaO-xSiO₂ (x=3, 4 and 7) were prepared from reagent-grade SiO₂ (Chempur 99.9 %), Na₂CO₃ (Chempur 99.5%) and CaCO₃ (Chempur 99%). Appropriate amounts of the reagent powders were weighed and mixed, introduced into a Pt-Au (95wt% of platinum and 5wt% of gold) crucible and heated in a muffle furnace. This type of crucible presents the advantage of a low

wetability with the glass, compared to a pure platinum crucible. In these conditions the glass does not adhere to the crucible walls.

To minimize the sodium losses by volatilization^{32,33}, not less than 200 grams of glass were melted and the following thermal cycle was used: 1200°C for 2h, 1400°C for 2h and then 1100°C for 24h. The melts were then quenched and finely crushed. Glass compositions were systematically checked by electron probe microanalysis: the intended and attained glass compositions are reported in Table 1. Ten grams of each resulting glass composition was mixed with 5 wt.% Cr₂O₃, finely grounded and melted at 1200°C for 5 minutes in a platinum crucible. The process was performed three times to ensure a regular distribution of the Cr₂O₃ grains in the glass network. A mixed Cr₂O₃-glass quantity (100 mg) was taken from the mixture, put in a carbon crucible, heated at 1200 °C for 1 minute and removed from the furnace to be quenched in air. Due to the poor wetability between the melt and the carbon crucible, the sample forms a glass ball.

The Cr₂O₃ solubility limit in the investigated melts was performed using the reactor described in our previous works^{1,31,34}. It allows the independent control of oxygen fugacity, temperature and alkali volatilization in the silicate melt. The cell is constituted by a sealed silica tube of around 25–30 cm³ ($\varnothing^{\text{ext}} = 22$ mm, $h \approx 120$ mm) containing several components that impose the thermochemical parameters of the system. The Na₂O partial vapor pressure is imposed by around 5 g of Na₂O–CaO–xSiO₂ source melt (with $1 < x < 7$) and located in a platinum crucible ($\varnothing^{\text{ext}} = 18$ mm, $h = 20$ mm), shut by a platinum lid. The studied glass balls (samples) are suspended in the reactor from the lid. The Pt crucible hosting the source and the sample constitute the reactor of the cell. The oxygen fugacity in the device is controlled by a solid M/M_xO_y buffer (M = Metallic element; Fe/FeO, FeO/Fe₃O₄, Co/CoO, Ni/NiO and Fe₃O₄/Fe₂O₃) incorporated below the reference reservoir either at the bottom of the silica tube or in an alumina crucible in order to prevent reactions with the silica tube and to avoid

alloying between the solid buffer and the platinum crucible. The silica tube is then evacuated and directly sealed under secondary vacuum. Direct measurements show that the residual pressures inside the thermochemical cell never exceed $P_{\text{total}} < 10^{-6}$ bar at room temperature.

When prepared, the silica tubes are introduced in a muffle furnace directly at the experimental temperature on an alumina support for a vertical maintain of the cell. After the heat treatment, the silica tubes are removed from the furnace and directly quenched into cold water. The presence of both metal and oxide phases in the solid buffer after each run is systematically checked by optical microscopy observation and X-ray diffraction.

Determinations of the total amount of dissolved chromium and of the final glass composition were performed using a CAMECA SX100 Electron Microprobe. The analyses conditions were normalized to an acceleration voltage of 25kV and a 6nA beam current. The electron beam was defocalized to a 15 μm diameter, to perform the analysis in a relatively large volume of the material, and to limit Na volatilization.

3. Results and discussions

To understand the effect of the partial substitution of alkaline oxide (Na_2O) by the oxide (CaO) on the chromia solubility, this one will be studied in the $\text{Na}_2\text{O-CaO-xSiO}_2$ system (noted NCS) for the three following melt compositions: $x=3, 4$ and 7 , as a function of temperature and oxygen fugacity. The liquidus temperatures in the NCS system are higher than in the $\text{Na}_2\text{O-SiO}_2$ system; therefore, the selected temperature range lay between 1200 and 1300°C .

Figure 2 shows three characteristic curves of chromium oxide solubility in the NCS system. These three curves show the variation of the dissolved total chromium content with the oxygen fugacity, and illustrate the influence of the three experimental parameters: oxygen fugacity, temperature and liquid composition. The obtained results show that:

- Regardless of oxygen fugacity, chromium oxide solubility increases with the temperature for a given liquid composition.
- Under oxidizing atmosphere, the solubility increases with the basicity (alkaline oxide content) of the glass.
- Under a reducing atmosphere, the solubility decreases when the basicity increases.
- Independently of the temperature or composition of the glass, the general shapes of the curves remain unchanged. They always comprise three distinct fields of solubility which are characteristic of the presence of the three chromium valences: Cr(II), Cr(III) and Cr(VI).

The model developed in our previous works^{1,31} was applied to the experimental results obtained for the NCS system to determine the speciation of the chromium species as well as the redox parameters in the ternary system. When equilibrium is reached, the total chromium dissolved in the glass (Cr(tot)) is the sum of all chromium species :

$$\text{Cr(tot)} = \text{Cr(II)} + \text{Cr(III)} + \text{Cr(VI)} \quad \text{Eq. 16}$$

Using the same assumption as in the Na₂O-SiO₂ system, we consider that the Cr(III) content in the melt remains constant as a function of (*f*O₂) for a given temperature^{1,25}. The minimum of chromium content in the glass corresponds to the Cr(III) contribution. Therefore, under oxidizing conditions, Cr(II) content can be neglected compared to Cr(III) and Cr(VI). In the same way, under reducing conditions, Cr(VI) can be neglected compared to Cr(III) and Cr(II). With these considerations, it can be written:

Under oxidizing conditions

$$\text{Cr(tot)} = \text{Cr(III)} + \text{Cr(VI)} \quad \text{Eq. 17}$$

Under reducing conditions

$$\text{Cr}(\text{tot}) = \text{Cr}(\text{II}) + \text{Cr}(\text{III}) \quad \text{Eq. 18}$$

Using this formalism, $\log(\text{Cr}(\text{II})/\text{Cr}(\text{III}))$ and $\log(\text{Cr}(\text{VI})/\text{Cr}(\text{III}))$ were plotted as a function of $\log(f\text{O}_2)$ for the $\text{Na}_2\text{O}-\text{CaO}-3\text{SiO}_2$ system and reported on Figure 3. The obtained results show clearly that the two parameters are linearly dependent. The slope values obtained under reducing and oxidizing conditions are respectively -0.24 and 0.74. These are in good agreement with the theoretical values of the expected slopes (Eq. 14 and Eq. 15).

Variations of $\log(\text{Cr}(\text{II})/\text{Cr}(\text{III}))$ and $\log(\text{Cr}(\text{VI})/\text{Cr}(\text{III}))$ are reported as a function of $\log(f\text{O}_2)$ at $T=1250^\circ\text{C}$ for three different glass compositions (NC3S, NC4S and NC7S) in Figure 4. The results show that $\log(\text{Cr}(\text{II})/\text{Cr}(\text{III}))$ decreases with increasing basicity of the melt (Figure 4A), although this variation is weak. On the contrary, $\log(\text{Cr}(\text{VI})/\text{Cr}(\text{III}))$ increases with increasing melt basicity. Therefore, an increase in the basicity of the glass (alkaline oxides content) leads to stabilize the oxidized forms. This behavior is identical to that described in the $\text{Na}_2\text{O}-\text{SiO}_2$ system¹. These results are consistent with those obtained by other authors for various systems and various multivalent elements^{2,36,37}.

The influence of the temperature on the redox parameters was studied for the NC3S liquid composition. Values of $\log(\text{Cr}(\text{II})/\text{Cr}(\text{III}))$ and $\log(\text{Cr}(\text{VI})/\text{Cr}(\text{III}))$ are plotted as a function of $\log(f\text{O}_2)$ in Figure 5 for three different temperatures (1200, 1250 and 1300°C). The results reveal that whatever the imposed oxygen fugacity is, the redox ratio increases with increasing melt temperature. This same behavior was also observed in the $\text{Na}_2\text{O}-\text{SiO}_2$ system¹ and in several studies treating of the solubility of the multivalent species in silicate melts^{20,38,39}.

The treatment of the whole set of data should lead to the determination of formulas for chromium complexes formed in the NCS system, as well as the thermodynamic properties related to dissolution, oxidation and reduction processes of chromia. However, the determination of these properties cannot be realized without knowing the values of the $a\text{O}^{2-}$ in the given liquid. This parameter is essential for a complete and consistent exploitation of the

results. The following development permits a determination of the activity of the oxide ions $a_{O^{2-}}$.

In glass networks, the $a_{O^{2-}}$ was introduced as a basicity indicator^{40,41}. Nevertheless, no standard state can be defined for this ion. Moreover, this basicity depends on the bond strength between the alkali and oxygen ion. When the size of the alkali ion increases, the bond strength decreases. As a consequence the mobility of the oxide ions is higher^{5,42}. Furthermore, it is generally agreed, in binary melts, to equate the activity of the oxide ions ($a_{O^{2-}}$) to the activity of the sodium oxide (a_{Na_2O}).

In the case of binary melts (Na_2O-SiO_2 in this study), $a_{O^{2-}}$ is equated to the Na_2O activity⁴³⁻⁴⁵. In the case of ternary glasses, the situation is more complex. One of the key points is to establish where $a_{O^{2-}}$ can still be equated to Na_2O activity when adding another modifying oxide (CaO) to the Na_2O-SiO_2 network. In this case, there is competition between the two basic species Na_2O and CaO. From this, two assumptions can be proposed.

(i) If Na_2O is much more basic than CaO, the $a_{O^{2-}}$ could be equated to the Na_2O activity. Then the contribution of calcium oxide on the acid-base properties can be neglected. Several studies have determined the Na_2O activity in binary $Na_2O-xSiO_2$ and ternary NCS system⁴⁶⁻⁵¹. The values applied in this work are those measured by Neudorf *et al.*⁵⁰ and Abdelouhab *et al.*⁴⁶ (Table 2). In this case, basicity is given by the value of $\log[a_{Na_2O}]$. By comparing the two series of data, a_{Na_2O} values in NC3S and NC4S are the same as in the $Na_2O-2.5SiO_2$ and $Na_2O-3.5SiO_2$ melts, respectively (Table 2). Thus, these glasses have equivalent basicities. However, the NC7S composition does not have an equivalent in the binary melt.

(ii) If Na_2O and CaO basicities are close, $a_{O^{2-}}$ cannot be equated to the a_{Na_2O} . Initially, we propose, in the binary system, to equate the O^{2-} activity ($a_{O^{2-}}=a_{Na_2O}$ in binary system) to the calculated optical basicity. Optical basicity values (Table 3) were calculated according to

the Duffy and Ingram model⁵²⁻⁵⁴. The dependence of $\log[aO^{2-}]$ at $T=1250^{\circ}C$ on the optical basicity is plotted in Figure 6.

For comparison, the optical basicity values of the ternary melts (Table 3) are reported in Figure 6. This interpolation highlights that O^{2-} activities in ternary $Na_2O-CaO-x(3 \text{ and } 4)SiO_2$ glasses are comparable to O^{2-} activities in binary $Na_2O-x(1.7 \text{ and } 2.15)SiO_2$ glasses, respectively.

The oxide ions activities aO^{2-} obtained from the optical basicities interpolation are inconsistent with the Na_2O activities measured by Abdelouhad *et al.*⁴⁶ (Table 2). To validate one of these two assumptions, we compare results concerning chromia solubility in the two vitreous systems Na_2O-SiO_2 ³¹ and NCS. According to the equations Eq. 13, Eq. 14 and Eq. 15, redox ratios are expressed as a function of oxygen fugacity and O^{2-} activity. In these equations, for a given temperature and oxygen fugacity, only aO^{2-} has an effect on redox parameters. This means that for a given temperature and oxygen fugacity, the redox ratios should be the same for two glasses with the same aO^{2-} .

The comparison of $\log(Cr(VI)/Cr(III))$ vs $\log(fO_2)$ of the ternary glass NC3S with the redox ratio of various binary systems³¹ is plotted in Figure 7. This plot clearly shows that for given fO_2 and temperature, the redox ratio obtained in the ternary glass NC3S is closest to the characteristic redox ratio of N2.5S. In accordance with Eq. 6, it can thus be assumed that the basicities (i.e. O^{2-} activity) of NC3S and N2.5S are equivalent. In the same way, Figure 8 exhibits that the NC4S ternary glass presents a basicity which is close to the basicity of N3.5S and N3S binary glasses. It although seems to be a bit closer to the basicity of N3.5S glass. Regarding the results reported on Table 4, it can be considered that $aNa_2O = aO^{2-}$.

The determination of O^{2-} activities permit the characterization of the physico-chemical properties of chromium in the NCS system:

- the identification of chromium complexes formed in NCS system,
- the determination of the thermodynamic properties for dissolution, oxidation and reduction of the chromium species in NCS melts, according to the physico-chemical model suggested by our previous works^{1,31}.

Determination of the chromium complexes formed in NCS systems at 1250 °C was achieved by plotting the logarithms of (Cr(III), Cr(II)/Cr(III) and Cr(VI)/Cr(III)) as a function of O^{2-} activities in the system (Figure 9). According to Eq. 13, Eq. 14 and Eq. 15, the slopes of the straight lines are directly correlated to the $(x-3/2)$, $(x-y+3/2)$ and $(z-x+1/2)$ parameters for a given temperature and $f(O_2)$

Results concerning $\log[Cr(III)]$ and $\log[Cr(II)/Cr(III)]$ variations, as a function aO^{2-} , cannot be directly exploited to calculate the x , y and z parameters necessary for the identification of the formulas for the chromium complexes. Indeed, the variation of $\log[Cr(III)]$ as well as $\log[Cr(II)/Cr(III)]$ present a very low variation with aO^{2-} . This makes impossible the determination of the $(3/2-x)$ and $(z-x+1/2)$ parameters. Nevertheless, results concerning $\log[Cr(VI)/Cr(III)]$ can be exploited. The slope of the obtained straight line is equal to 0,514 ($R^2=0,99$). This allows a calculation of the $(x-y)$ value which is equal to 2. Some of the most stable Cr(VI) formulas are dichromate or chromate³⁷, $(Cr_2O_7)^{2-}$ or $(CrO_4)^{2-}$ respectively. Considering these two possible Cr(VI) formulas, Cr(III) formulas would be Cr_2O_3 or $(CrO_2)^-$. However, the Cr_2O_3 formula for the Cr(III) complex cannot be considered: we assume that the Cr_2O_3 species is a solid precipitate in the melt.

At this stage, it is only possible to formulate assumptions concerning the nature of the chromium complexes formed in the $Na_2O-CaO-SiO_2$ system. The whole of the experimental data related to this system must be supplemented by complementary solubility measurements, covering a broader range of glass compositions.

The thermochemical model, developed in previous works^{1,31}, is based on the knowledge of the nature of the Cr(II), Cr(III) and Cr(VI) complexes through the determination of the values of the x, y and z parameters. As these latter parameters have not been obtained for this system, only an approximate calculation of the thermodynamic properties can be proposed. The development consists in simplified equations which do not take into account the nature of the chromium complexes^{38,55}:



The related equilibrium constants are written as follows:

$$K_{T_{diss}} = aCr^{3+} \cdot (aO^{2-})^{3/2} \quad \text{Eq. 22}$$

$$K_{T_{red}} = \frac{aCr^{2+}}{aCr^{3+} \cdot (aO^{2-})^{1/2}} \cdot (fO_2)^{1/4} \quad \text{Eq. 23}$$

$$K_{T_{tox}} = \frac{aCr^{6+}}{aCr^{3+} \cdot (fO_2)^{3/4}} \cdot (aO^{2-})^{3/2} \quad \text{Eq. 24}$$

As mentioned previously, the O^{2-} activity is related to the glass composition. The concentration of the multivalent element is considered to be relatively low compared to the concentration of the free oxygen ions, so that for a given temperature and glass composition, O^{2-} activity is not affected during a redox reaction and remains constant^{10,11}. It is thus advantageous to define equilibrium constants K_T' freed from the O^{2-} activity term as follows:

$$K'_{T_{diss}} = aCr^{3+} \quad \text{Eq. 22}$$

$$K'_{Tred} = \frac{aCr^{2+}}{aCr^{3+}} \cdot (fO_2)^{1/4} \quad \text{Eq. 23}$$

$$K'_{Tox} = \frac{aCr^{6+}}{aCr^{3+} \cdot (fO_2)^{3/4}} \quad \text{Eq. 24}$$

with

$$K'_{Tdis} = \frac{K_{Tdis}}{(aO^{2-})^{3/2}} \quad \text{Eq. 25}$$

$$K'_{Tred} = K_{Tred} \cdot (aO^{2-})^{1/2} \quad \text{Eq. 26}$$

$$K'_{Tred} = \frac{K_{Tred}}{(aO^{2-})^{3/2}} \quad \text{Eq. 27}$$

Logarithmic equations for the three constants can be proposed where the activity $a(Cr^{n+})$ has been replaced by the concentration $[Cr^{n+}]$

$$\log[Cr^{3+}] = \log K'_{Tdis} \quad \text{Eq. 28}$$

$$\log \left[\frac{Cr^{2+}}{Cr^{3+}} \right] = -\frac{1}{4} \log fO_2 + \log K'_{Tred} \quad \text{Eq. 29}$$

$$\log \left[\frac{Cr^{6+}}{Cr^{3+}} \right] = \frac{3}{4} \log fO_2 + \log K'_{Tox} \quad \text{Eq. 30}$$

The y-axis-intercept obtained by plotting $\log[Cr(II)/Cr(III)]$ and $\log[Cr(VI)/Cr(III)]$ vs. $\log fO_2$ for the different temperatures (Figure 5 A and B), correspond to $\log K'_{Tred}$ and $\log K'_{Tox}$ values respectively (Eq. 29 and Eq. 30). Values of $\log K'_{Tdis}$ are exactly equal to the $\log[Cr(III)]$ values. These three sets of data are reported on Figure 10 as a function of $(1/T)$. The results show that $\log K'_T$ is linearly correlated to $(1/T)$, according to the following expression:

$$\log K = \alpha + \frac{\beta}{T} \quad \text{Eq. 31}$$

The slopes and the Y-axis-intercepts of each straight line are related to the standard enthalpies and entropies for each reaction, in accordance with the following equation:

$$\log K = -\frac{\Delta H^0}{2.3R} \left(\frac{1}{T} \right) + \frac{\Delta S^0}{2.3R} \quad \text{Eq. 32}$$

By identification, the general formula expressing the standard entropies ΔS^0 and standard enthalpies ΔH^0 of the reactions can be written as:

$$\Delta S^0 = 2.3R\alpha \quad \text{Eq. 33}$$

$$\Delta H_{diss}^0 = -2.3R\beta \quad \text{Eq. 34}$$

The values concerning the standard enthalpies and entropies of dissolution, oxidation and reduction of the chromia in NC3S glass system are given in Table 5.

Conclusion

Several important points of the chemistry of chromium in the silicate melts have been highlighted in this study:

- The model previously developed for binary $\text{Na}_2\text{O-xSiO}_2$ ^{1,31} has been successfully applied to the ternary $\text{Na}_2\text{O-CaO-xSiO}_2$ system.
- The solubility of Cr_2O_3 has been determined as function of temperature, glass composition and oxygen fugacity.
- Cr_2O_3 is dissolved as Cr(II), Cr(III) and Cr(VI) species. The speciation of chromium ions has been determined as a function of oxygen fugacity and glass composition. The $\log[\text{Cr(II)/Cr(III)}]$ and $\log [\text{Cr(VI)/Cr(III)}]$ ratios vary with $-1/4\log(\text{fO}_2)$ and $3/4\log(\text{fO}_2)$ respectively, independently of the melt composition and temperature.

- The ($\Delta H^{\circ}\text{diss}$, $\Delta S^{\circ}\text{diss}$), ($\Delta H^{\circ}\text{red}$, $\Delta S^{\circ}\text{red}$) and ($\Delta H^{\circ}\text{ox}$, $\Delta S^{\circ}\text{ox}$) have been estimated for $\text{Cr(III)} \rightarrow \text{Cr(VI)}$ and $\text{Cr(III)} \rightarrow \text{Cr(II)}$ redox reactions.

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Table Captions

Table 1 : *Composition of glasses used as started materials*

Aimed glass Composition	Na₂CO₃ wt.%	SiO₂ wt.%	CaCO₃ wt.%	Na (at.%) EPMA	Si (at.%) EPMA	Ca (at.%) EPMA	x
Na ₂ O–1.5SiO ₂	69.68	59.25	-	25.95 (0.40)	20.17 (0.19)	-	1.56 (0.04)
Na ₂ O–2SiO ₂	58.19	65.97	-	21.91 (0.44)	22.38 (0.22)	-	2.04 (0.06)
Na ₂ O–2.5SiO ₂	49.95	70.79	-	19.22 (0.49)	23.72 (0.25)	-	2.47 (0.09)
Na ₂ O–3SiO ₂	43.75	74.41	-	16.34 (0.22)	25.16 (0.11)	-	3.08 (0.06)
Na ₂ O–3.5SiO ₂	38.93	77.24	-	15.00 (0.33)	25.83 (0.17)	-	3.466 (0.10)
Na ₂ O-CaO-3SiO ₂	40.89	60.42	35.21	14.04 (0.25)	21.32 (0.15)	7.02 (0.09)	3.03 (0.06)
Na ₂ O-CaO-4SiO ₂	34.04	67.06	29.31	10.98 (0.16)	23.64 (0.12)	5.85 (0.10)	4.30 (0.08)
Na ₂ O-CaO-7SiO ₂	22.64	78.08	19.50	7.57 (0.27)	26.82 (0.14)	3.70 (0.08)	7.09 (0.17)

Table 2 : $\log [a_{\text{Na}_2\text{O}}]$ values in NCS and $\text{Na}_2\text{O-SiO}_2$ systems measured at $T=1250^\circ\text{C}$

$\text{Na}_2\text{O-SiO}_2$ system ⁵⁰		$\text{Na}_2\text{O-CaO-SiO}_2$ (NCS) system ⁴⁶	
Composition	$\text{Log}[a_{\text{Na}_2\text{O}}]$	Composition	$\text{Log}[a_{\text{Na}_2\text{O}}]$
$\text{Na}_2\text{O-1.5SiO}_2$	-7.66	$\text{Na}_2\text{O-CaO-3SiO}_2$	-8.78
$\text{Na}_2\text{O-2SiO}_2$	-8.24	$\text{Na}_2\text{O-CaO-4SiO}_2$	-9.69
$\text{Na}_2\text{O-2.5SiO}_2$	-8.77	$\text{Na}_2\text{O-CaO-7SiO}_2$	-10.28
$\text{Na}_2\text{O-3SiO}_2$	-9.35		
$\text{Na}_2\text{O-3.5SiO}_2$	-9.62		
$\text{Na}_2\text{O-4SiO}_2$	-9.43		

Table 3: Optical basicity values calculated for the binary end ternary systems according to Duffy and Ingram model ⁵²⁻⁵⁴

x (Na₂O-xSiO₂)	1.5	2	2.5	3
Optical Basicity	0.748	0.703	0.663	0.648
x(NC-xS)	3	4	7	
Optical Basicity	0.718	0.678	0.612	

Table 4 : $\log[aO^{2-}]$ as well as the composition of the binary equivalent with the ternary $Na_2O - CaO - xSiO_2$ for each studied case

Melt composition		$Na_2O-CaO-3SiO_2$	$Na_2O-CaO-4SiO_2$	$Na_2O-CaO-7SiO_2$
aNa_2O	Log[aNa_2O]	-8.75	-9,66	-10,42
	equivalent binary system	$Na_2O-2.5SiO_2$	$Na_2O-3.3SiO_2$	-
aO^{2-}	Log[aO^{2-}]	-7.97	-8.60	-10.24
	equivalent binary system	$Na_2O-1.7SiO_2$	$Na_2O-2.2SiO_2$	$Na_2O-4SiO_2$

Table 5 : *Thermodynamic data related to chromium oxide reactions in Na₂O – CaO - 3SiO₂ melt composition*

Dissolution		Oxidation		Reduction	
ΔH° (kJ.mol ⁻¹)	ΔS° (J.mol ⁻¹ .K ⁻¹)	ΔH° (kJ.mol ⁻¹)	ΔS° (J.mol ⁻¹ .K ⁻¹)	ΔH° (kJ.mol ⁻¹)	ΔS° (J.mol ⁻¹ .K ⁻¹)
33 ± 11	26 ± 9	50 ± 15	54 ± 16	172 ± 37	61 ± 16

Figure 1: Chemical reactions occurring when Cr_2O_3 crystals are in contact with the melt. The chromium oxide is dissolved to Cr(III) complexes following an acid-base reaction (Eq. 7). The obtained Cr(III) species can be oxidized to Cr(VI) (Eq. 8) or reduced to Cr(II) complexes (Eq. 9).

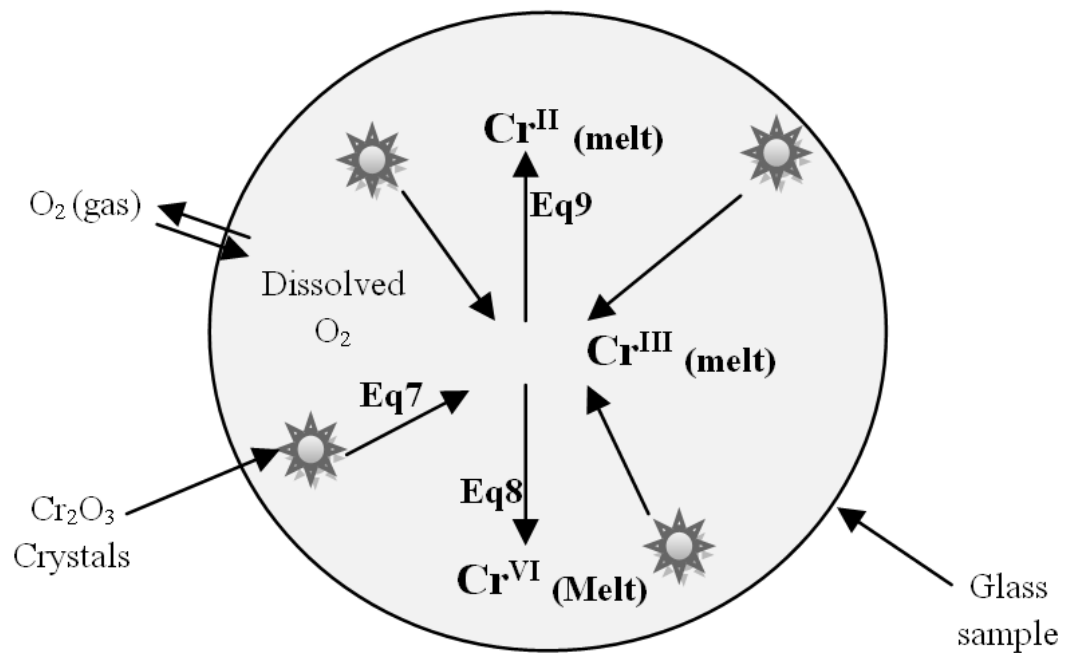


Figure 2 : Variation of Cr (at.%) content as function of $\log fO_2$:

(◆) $Na_2O-CaO-3SiO_2$ 1200°C

(▲) $Na_2O-CaO-3SiO_2$ 1250°C

(●) $Na_2O-CaO-7SiO_2$ 1250°C

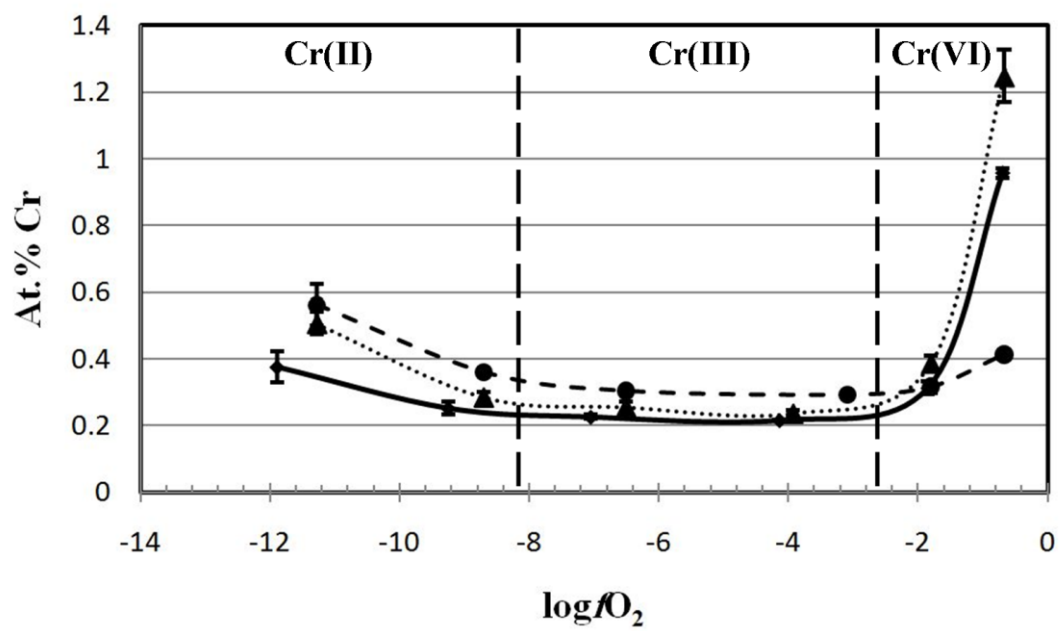


Figure 3 : Logarithmic plot of: (♦) $\log[\text{Cr(II)}/\text{Cr(III)}]$ and (▲) $\log[\text{Cr(VI)}/\text{Cr(III)}]$ as a function of $\log f\text{O}_2$ for $\text{Na}_2\text{O-CaO-3SiO}_2$ melt composition at 1250°C :

$$\log\left[\frac{\text{Cr(II)}}{\text{Cr(III)}}\right] = -0.248 \log f\text{O}_2 - 2.773 \quad (\text{R}^2 = 0.994)$$

$$\log\left[\frac{\text{Cr(VI)}}{\text{Cr(III)}}\right] = 0.747 \log f\text{O}_2 + 1.139 \quad (\text{R}^2 = 0.998)$$

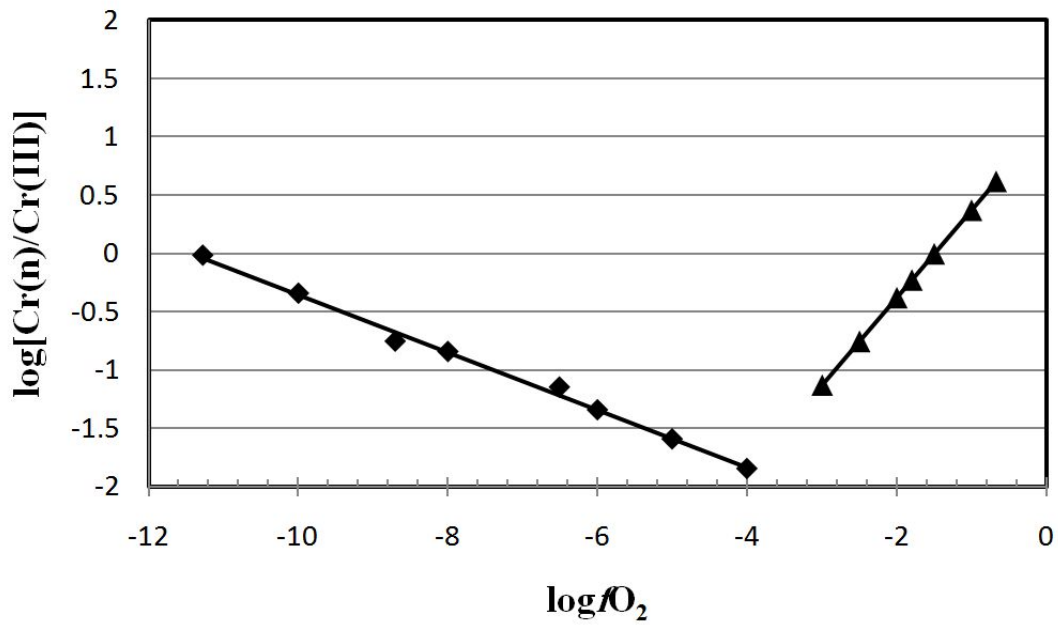


Figure 4 : Variation of $\log[\text{Cr(II)}/\text{Cr(III)}]$ (A) and $\log[\text{Cr(VI)}/\text{Cr(III)}]$ (B) Vs $\log(f\text{O}_2)$ for three compositions of glass of system $\text{Na}_2\text{O}-\text{CaO}-x\text{SiO}_2$ (noted NC_xS), $T=1250^\circ\text{C}$

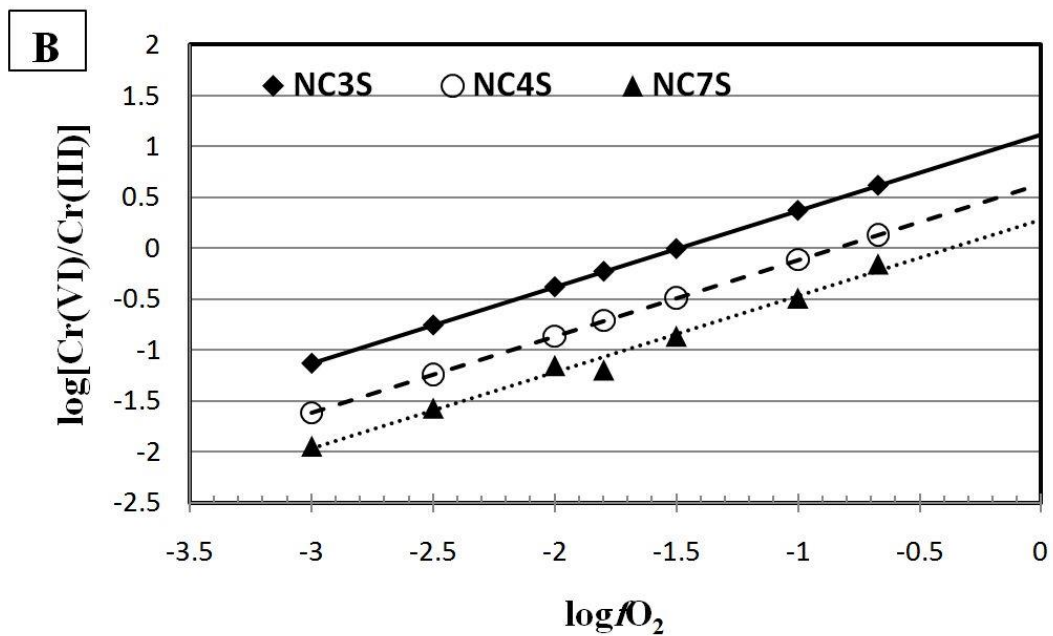
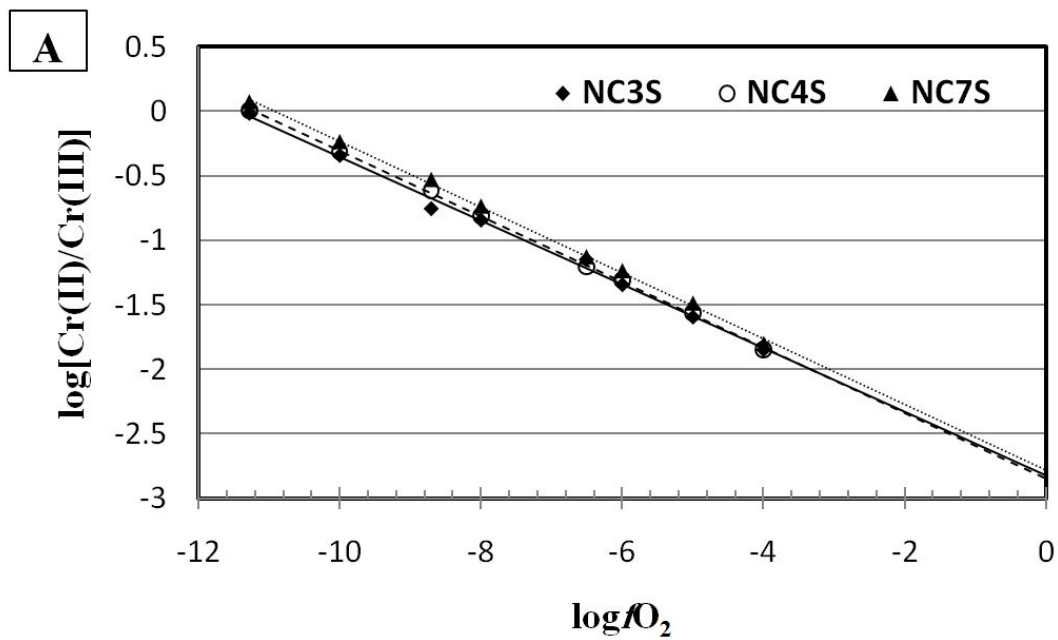


Figure 5 : Variation of $\log [\text{Cr(II)}/\text{Cr(III)}]$ (A) and $\log [\text{Cr(VI)}/\text{Cr(III)}]$ (B) Vs $\log(f\text{O}_2)$ for $\text{Na}_2\text{O}-\text{CaO}-3\text{SiO}_2$ at three different temperatures (1200, 1250 and 1300°C).

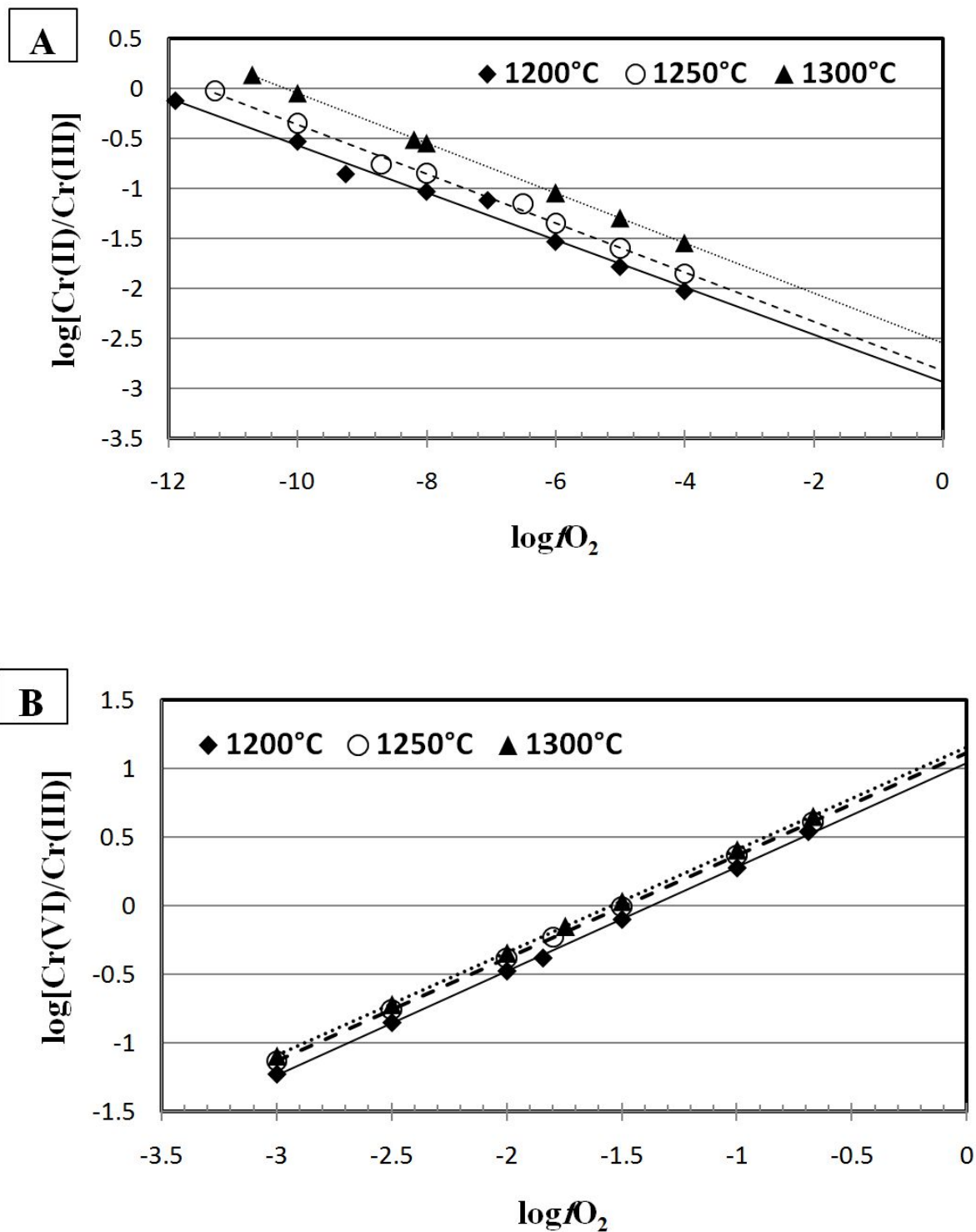


Figure 6 : $\log a(\text{O}^{2-})$ in binary melts at 1250°C as a function of calculated optical basicity. Dotted lines correspond to the extrapolation of $a(\text{O}^{2-})$ in ternary melts from their optical basicity values.

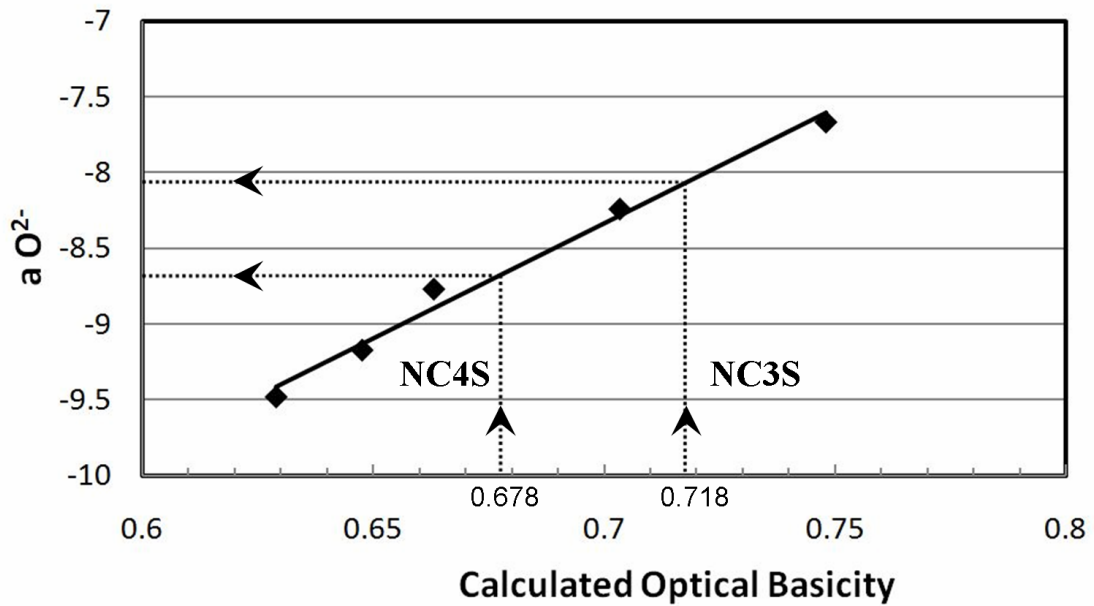


Figure 7: $\log[\text{Cr(VI)}/\text{Cr(III)}]$ as a function of $\log(f\text{O}_2)$ at $T=1250^\circ\text{C}$, in the ternary Na_2O - CaO - 3SiO_2 composition compared with different compositions of binary glasses.

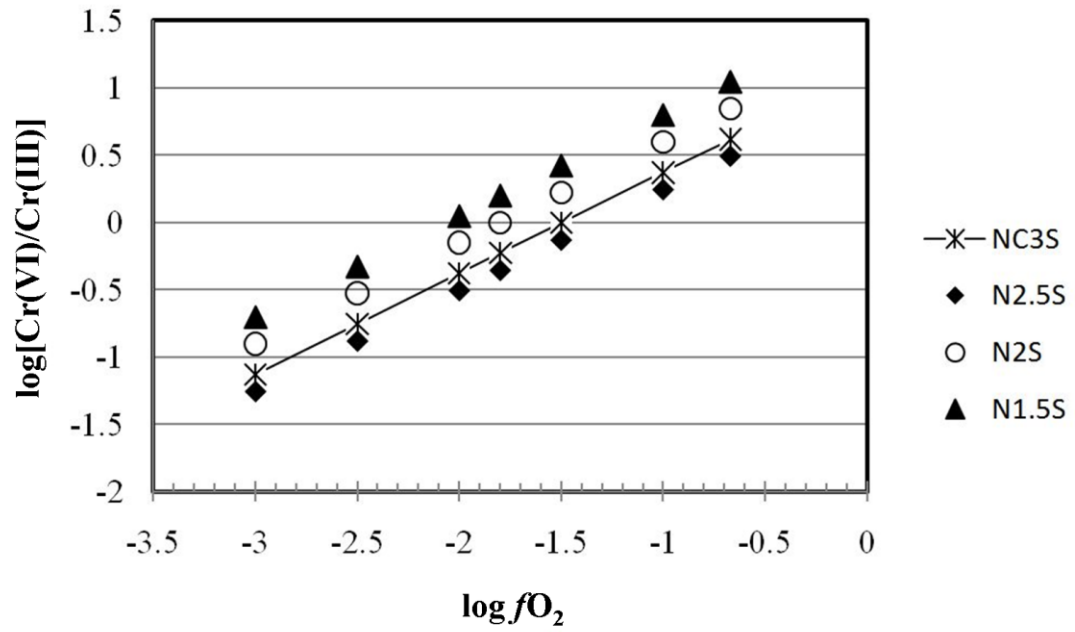


Figure 8: $\log[\text{Cr(VI)}/\text{Cr(III)}]$ as a function of $\log(f\text{O}_2)$ at $T=1250^\circ\text{C}$, in the ternary Na_2O - CaO - 4SiO_2 composition compared with different compositions of binary glasses.

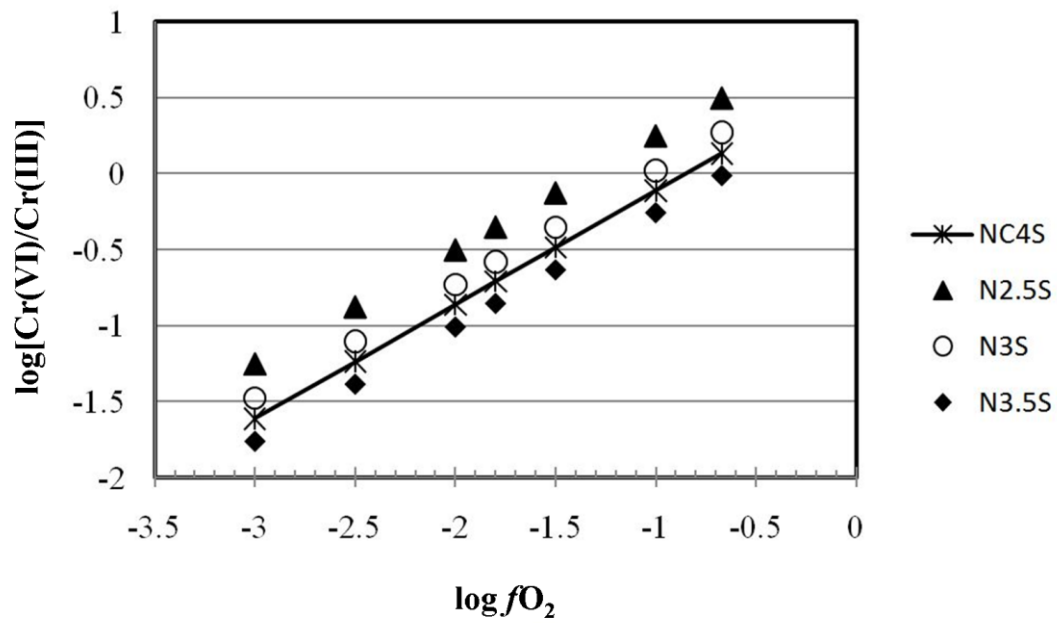


Figure 9 : Variation as a function of $\log[a(O^{2-})]$ at $T=1250^{\circ}C$ of:

- (◆) $\log[Cr(III)]=-0.03\log[a(Na_2O)]-0,89$ ($R^2=0.95$)
- (◆) $\log [Cr(II)/Cr(III)]=-0.07\log[a(Na_2O)]-0,92$ ($R^2=0.95$)
- (◆) $\log[Cr(VI)/Cr(III)]=0.5 \log[a(Na_2O)]+4,86$ ($R^2=0.99$)

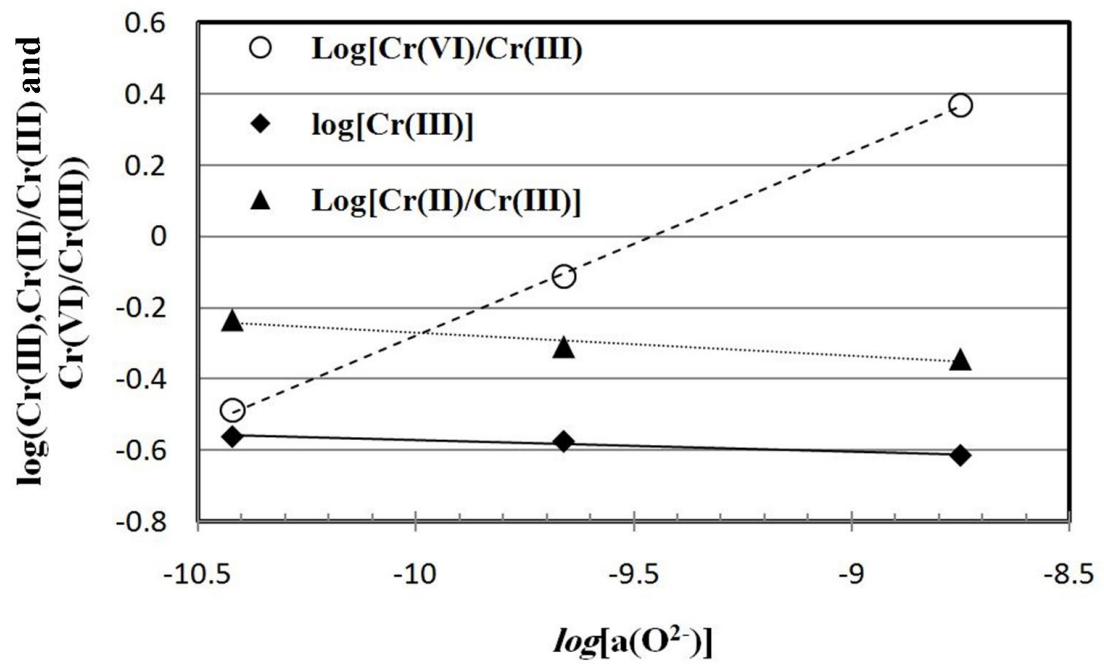


Figure 10 : Representation of $\log(K'_{T_{diss}})$, $\log(K'_{T_{red}})$ and $\log(K'_{T_{tox}})$ as a function of $(1/T)$ for glass NC3S:

$$(\blacklozenge) \log K'_{T_{diss}} = 1.381 - \frac{1724}{T} \quad (R^2=0.980)$$

$$(\blacklozenge) \log K'_{T_{red}} = 3.138 - \frac{8989}{T} \quad (R^2=0.934)$$

$$(\blacklozenge) \log K'_{T_{tox}} = 2.828 - \frac{2619}{T} \quad (R^2=0.973)$$

