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Solubility of Cr₂O₃ and speciation of chromium in soda-limesilicate 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 (aO^{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 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⁻

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 O²⁻, 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:

$$M^{(m)+} \Leftrightarrow M^{(m+n)+} + ne^{-}$$

$$\frac{n}{4}O_{2} + ne^{-} \Leftrightarrow \frac{n}{2}O^{2-}$$

$$M^{(m)+} + \frac{n}{4}O_{2} \Leftrightarrow M^{(m+n)+} + \frac{n}{2}O^{2-}$$
Eq. 1

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 O²⁻ 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-acidbasicity, equilibrium described by Eq. 1 can be expressed by the equation:

$$MO_x^{(2x-m)-} + \frac{n}{4}O_2 + \left(y - x - \frac{n}{2}\right)O^{2-} \Leftrightarrow MO_y^{(2y-m-n)-}$$
 Eq. 2

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:

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

$$K(T) = \frac{\gamma_{M^{(m+n)+}} \cdot \left[MO_{y}^{(2y-m-n)-} \right] a \left(O^{2-} \right)^{(x-y+n/2)}}{\gamma_{M^{(m)+}} \cdot \left[MO_{x}^{(2x-m)-} \right] \left(fO_{2} \right)^{n/4}}$$
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:

$$K(T) = \frac{\left[MO_{y}^{(2y-m-n)-}\right]a\left(O^{2-}\right)^{(x-y+n/2)}}{\left[MO_{x}^{(2x-m)-}\right]\left(fO_{2}\right)^{n/4}}$$
Eq. 5

Consequently:

$$\Re = \frac{\left[MO_{y}^{(2y-m-n)-}\right]}{\left[MO_{x}^{(2x-m)-}\right]} = K(T) \cdot \left[a(O^{2-})\right]^{(x-y-n/2)} \cdot \left[fO_{2}\right]^{n/4}$$
Eq. 6

with \Re 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 (Cr₂O₃) 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 Na₂O-SiO₂ 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 fO_2 .

$$\frac{1}{2}Cr_2O_3(crystal) \Leftrightarrow Cr(III)O_x^{(2x-3)-}(melt) + \left(\frac{3}{2} - x\right)O^{2-}(melt)$$
 Eq. 7

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

$$Cr(III)O_x^{(2x-3)-}(melt) + \frac{3}{4}O_2(gas) \Leftrightarrow Cr(VI)O_y^{(2y-6)-}(melt) + \left(x - y + \frac{3}{2}\right)O^{2-}(melt)$$
 Eq. 8

$$Cr(III)O_x^{(2x-3)-}(melt) + \left(z - x + \frac{1}{2}\right)O^{2-} \Leftrightarrow Cr(VI)O_y^{(2y-6)-}(melt) + \frac{3}{4}O_2(gas)$$
 Eq. 9

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

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

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

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

where $a_i = \gamma_i X_i$ 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:

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

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

$$\log \frac{[Cr(II)]}{[Cr(III)]} = -\frac{1}{4} \log fO_2 + \left(z - x + \frac{1}{2}\right) \log a [O^{2-}] + \log K_{red}$$
 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 Cr_2O_3 solubility in the Na₂O-CaO-SiO₂ system.

2. Experimental

Sodium silicate and soda lime silicate glasses with the general composition of Na₂O-CaO- $xSiO_2$ (x=3, 4 and 7) were prepared from reagent-grade SiO₂ (Chempur 99.9 %), Na₂CO₃ (Chempur 99.5%) and CaCaO₃ (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.% Cr_2O_3 , 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 Cr_2O_3 grains in the glass network. A mixed Cr_2O_3 -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 (\emptyset^{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 (\emptyset^{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 $P_{total} < 10^{-6}$ 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 μ m 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 (Na₂O) by the oxide (CaO) on the chromia solubility, this one will be studied in the Na₂O-CaO-xSiO₂ 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 Na₂O-SiO₂ 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 :

$$Cr(tot) = Cr(II) + Cr(III) + Cr(VI)$$
 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 (fO_2) 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(III) and Cr(III). With these considerations, it can be written:

Under oxidizing conditions

$$Cr(tot) = Cr(III) + Cr(VI)$$
 Eq. 17

Under reducing conditions

Using this formalism, $\log(Cr(II)/Cr(III))$ and $\log(Cr(VI)/Cr(III))$ were plotted as a function of $\log(fO_2)$ for the Na₂O-CaO-3SiO₂ 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(Cr(II)/Cr(III)) and log(Cr(VI)/Cr(III)) are reported as a function of log(fO_2) at T=1250°C for three different glass compositions (NC3S, NC4S and NC7S) in Figure 4. The results show that log(Cr(II)/Cr(III)) decreases with increasing basicity of the melt (Figure 4A), although this variation is weak. On the contrary, log(Cr(VI)/Cr(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 Na₂O-SiO₂ 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 $\log(Cr(II)/Cr(III))$ and $\log(Cr(VI)/Cr(III))$ are plotted as a function of $\log(fO_2)$ 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 Na₂O-SiO₂ 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 aO^{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 aO^{2-} .

In glass networks, the aO^{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 (aO^{2-}) to the activity of the sodium oxide (aNa_2O) .

In the case of binary melts (Na₂O-SiO₂ in this study), aO^{2-} is equated to the Na₂O activity⁴³⁻⁴⁵. In the case of ternary glasses, the situation is more complex. One of the key points is to establish where aO^{2-} can still be equated to Na₂O activity when adding another modifying oxide (CaO) to the Na₂O-SiO₂ network. In this case, there is competition between the two basic species Na₂O and CaO. From this, two assumptions can be proposed.

(i) If Na₂O is much more basic than CaO, the aO²⁻ could be equated to the Na₂O activity. Then the contribution of calcium oxide on the acid-base properties can be neglected. Several studies have determined the Na₂O activity in binary Na₂O-xSiO₂ 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[aNa₂O]. By comparing the two series of data, aNa₂O values in NC3S and NC4S are the same as in the Na₂O-2.5SiO₂ and Na₂O-3.5SiO₂ 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 Na₂O and CaO basicities are close, aO^{2-} cannot be equated to the aNa₂O. Initially, we propose, in the binary system, to equate the O²⁻ activity ($aO^{2-}=aNa_2O$ in binary system) to the calculated optical basicity. Optical basicity values (Table 3) were calculated according to

the Duffy and Ingram model⁵²⁻⁵⁴. The dependance of $\log[aO^{2-}]$ at T=1250°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 Na₂O-CaO-x(3 and 4)SiO₂ glasses are comparable to O^{2-} activities in binary Na₂O- x(1.7 and 2.15)SiO₂ glasses, respectively.

The oxide ions activities aO^{2-} obtained from the optical basicities interpolation are inconsistent with the Na₂O 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 Na₂O-SiO₂³¹ and NCS. According to the equations Eq. 13, Eq. 14 and Eq. 15, redox ratios are expressed as a function of oxygen fugacity and O²⁻ 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(fO₂) 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*(O₂)

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 (R²=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, (Cr₂O₇)²⁻ or (CrO₄)²⁻ respectively. Considering these two possible Cr(VI) formulas, Cr(III) formulas would be Cr₂O₃ or (CrO₂)⁻. However, the Cr₂O₃ formula for the Cr(III) complex cannot be considered: we assume that the Cr₂O₃ 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 Na₂O-CaO-SiO₂ 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}:

$$\frac{1}{2}Cr_2O_3 \stackrel{K_{Tdiss}}{\Leftrightarrow} Cr^{3+} + \frac{3}{2}O^{2-}$$
 Eq. 19

$$Cr^{3+} + \frac{1}{2}O^{2-} \Leftrightarrow^{K_{Tred}} Cr^{2+} + \frac{1}{4}O_2$$
 Eq. 20

$$Cr^{3+} + \frac{3}{4}O_2 \stackrel{K_{Tox}}{\Leftrightarrow} Cr^{6+} + \frac{3}{2}O^{2-}$$
 Eq. 21

The related equilibrium constants are written as follows:

$$K_{Tdiss} = aCr^{3+} . (aO^{2-})^{\frac{3}{2}}$$
 Eq. 22

$$K_{Tred} = \frac{aCr^{2+}}{aCr^{3+} . (aO^{2-})^{\frac{1}{2}}} . (fO_2)^{\frac{1}{2}}$$
 Eq. 23

$$K_{Tox} = \frac{aCr^{6+}}{aCr^{3+}.(fO_2)^{\frac{3}{4}}}.(aO^{2-})^{\frac{3}{2}}$$
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:

$$K'_{Tdiss} = aCr^{3+}$$
 Eq. 22

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

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

with

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

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

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

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

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

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

$$\log \left[\frac{Cr^{6+}}{Cr^{3+}} \right] = \frac{3}{4} \log fO_2 + \log K'_{Tox}$$
 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 logK'_{Tred} and logK'_{Tox} values respectively (Eq. 29 and Eq. 30). Values of logK'_{Tdiss} 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 logK'_T is linearly correlated to (1/T), according to the following expression:

$$\log K = \alpha + \frac{\beta}{T}$$
 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:

$$\log K = -\frac{\Delta H^0}{2.3R} \left(\frac{1}{T}\right) + \frac{\Delta S^0}{2.3R}$$
 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:

$$\Delta S^0 = 2.3R\alpha$$
 Eq. 33

$$\Delta H_{diss}^0 = -2.3R\beta$$
 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 Na₂O-xSiO₂^{1,31} has been successfully applied to the ternary Na₂O-CaO-xSiO₂ system.
- The solubility of Cr₂O₃ has been determined as function of temperature, glass composition and oxygen fugacity.
- Cr₂O₃ 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[Cr(II)/Cr(III)] and log [Cr(VI)/Cr(III)] ratios vary with -1/4log(fO₂) and 3/4log(fO₂) respectively, independently of the melt composition and temperature.

- The (Δ H°diss, Δ S°diss), (Δ H°red, Δ S°red) and (Δ H°ox, Δ S°ox) have been estimated for Cr(III) \rightarrow Cr(VI) and Cr(III) \rightarrow Cr(II) redox reactions.

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Table Captions

Aimed glass Composition	Na ₂ CO ₃ wt.%	SiO ₂ wt.%	CaCO ₃ wt.%	Na (at.%) EPMA	Si (at.%) EPMA	Ca (at.%) EPMA	X
No. 0, 158:0	60.69	50.25		25.95	20.17		1.56
$Na_2O = 1.5SIO_2$	09.08	39.23	-	(0.40)	(0.19)	-	(0.04)
	59.10	65.07		21.91	22.38		2.04
$10a_2O - 251O_2$	38.19	03.97	-	(0.44)	(0.22)	-	(0.06)
N. O. 259'O	40.05	70.70		19.22	23.72		2.47
$Na_2O = 2.5SIO_2$	49.95	10.19	- (0.49)		(0.25)	-	(0.09)
N- 0, 20:0	12 75	74 41		16.34	25.16		3.08
INa2O-55IO2	45.75	/4.41	-	(0.22)	(0.11)	-	(0.06)
No. 0, 255:0	38.93	77.24 -		15.00	25.83		3.466
$10a_20-5.5510_2$			(0.33)	(0.17)	-	(0.10)	
Na ₂ O-CaO-	40.80	60.42	25 21	14.04	21.32	7.02	3.03
3SiO ₂	40.89	00.42	33.21	(0.25)	(0.15)	(0.09)	(0.06)
Na ₂ O-CaO-	24.04	(7.06	20.21	10.98	23.64	5.85	4.30
4SiO ₂	54.04	07.00	29.51	(0.16)	(0.12)	(0.10)	(0.08)
Na ₂ O-CaO-	22.64	79 09	10.50	7.57	26.82	3.70	7.09
$7SiO_2$	22.04	/0.08	19.30	(0.27)	(0.14)	(0.08)	(0.17)

Table 1: Composition of glasses used as started materials

Na2O-SiO	2 system ⁵⁰	Na2O-CaO-SiO2 (NCS) system ⁴⁶		
Composition	Log[aNa ₂ O]	Composition	Log[aNa ₂ O]	
Na ₂ O-1.5SiO ₂	-7.66	Na ₂ O-CaO-3SiO ₂	-8.78	
Na ₂ O-2SiO ₂	-8.24	Na ₂ O-CaO-4SiO ₂	-9.69	
Na ₂ O-2.5SiO ₂	-8.77	Na ₂ O-CaO-7SiO ₂	-10.28	
Na ₂ O-3SiO ₂	-9.35			
Na ₂ O-3.5SiO ₂	-9.62			
Na ₂ O-4SiO ₂	-9.43			

Table 2 : $log [aNa_2O]$ values in NCS and Na₂O-SiO₂ systems measured at $T=1250^{\circ} C$

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	

Table 4 : $log[aO^{2^{-}}]$ as well as the composition of the binary equivalent with the ternary Na₂O $- CaO - xSiO_2$ for each studied case

Melt composition		Na ₂ O-CaO-3SiO ₂	Na ₂ O-CaO-4SiO ₂	Na ₂ O-CaO-7SiO ₂	
aNa2O	Log[aNa2O]	-8.75	-9,66	-10,42	
	equivalent binary system	Na ₂ O-2.5SiO ₂	Na ₂ O-3.3SiO ₂	-	
aO ²	Log[aO ²⁻]	-7.97	-8.60	-10.24	
	equivalent binary system	Na ₂ O-1.7SiO ₂	Na ₂ O-2.2SiO ₂	Na ₂ O-4SiO ₂	

Table 5 : Thermodynamic data related to chromium oxide reactions in $Na_2O - CaO - 3SiO_2$ melt composition

Dissolution		Oxida	tion	Reduction		
$\Delta H^{\circ} (kJ.mol^{-1})$	$\Delta S^{\circ} (J.mo1^{l-}.K^{-1})$	$\Delta H^{\circ} (kJ.mol^{-1})$	$\Delta S^{\circ} (J.mo1^{l-}.K^{-1})$	$\Delta H^{\circ} (kJ.mol^{-1})$	$\Delta S^{\circ} (J.mol^{-1}.K^{-1})$	
33 ± 11	26 ± 9	50 ± 15	54 ± 16	172 ± 37	61 ± 16	

Figure 1: Chemical reactions occurring when Cr₂O₃ 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 $\log fO_2$:

(♦) Na₂O-CaO-3SiO₂ 1200°C

(▲)Na2O-CaO-3SiO₂ 1250°C

(•)Na2O-CaO-7SiO2 1250°C



Figure 3 : Logarithmic plot of: (\blacklozenge) log[Cr(II)/Cr(III]) and (\blacktriangle) log[Cr(VI)/Cr(III]) as a function of log *f*O₂ for Na₂O-CaO-3SiO₂ melt composition at 1250°C:

$$\log\left[\frac{Cr(II)}{Cr(III)}\right] = -0.248 \log fO_2 - 2.773 \qquad (R^2 = 0.994)$$
$$\log\left[\frac{Cr(VI)}{Cr(III)}\right] = 0.747 \log fO_2 + 1.139 \qquad (R^2 = 0.998)$$



Figure 4 : Variation of $\log[Cr(II)/Cr(III)]$ (A) and $\log[Cr(VI)/Cr(III)]$ (B) Vs log (fO_2) for three compositions of glass of system Na₂O-CaO-xSiO₂ (noted NCxS), T=1250°C





Figure 5 : Variation of log [Cr(II)/Cr(III)] (A) and log [Cr(VI)/C (III)] (B) Vs $log(fO_2)$ for Na₂O-CaO-3SiO₂ at three different temperatures (1200, 1250 and 1300°C).





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



Figure 7: $\log[Cr(VI)/Cr(III)]$ as a function of $\log(fO_2)$ at T=1250°C, in the ternary Na₂O-CaO-3SiO₂ composition compared with different compositions of binary glasses.



Figure 8: $\log[Cr(VI)/Cr(III)]$ as a function of $\log(fO_2)$ at T=1250°C, in the ternary Na₂O-CaO-4SiO₂ composition compared with different compositions of binary glasses.



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

- (•) log[Cr(III)]=-0.03log[a(Na₂O)]-0,89 (R²=0.95)
- (•) log [Cr(II)/Cr(III)]=-0.07log[a(Na₂O)]-0,92 (R²=0.95)
- (**•**) log[Cr(VI)/Cr(III)]=0.5 log[a(Na₂O)]+4,86 (R²=0.99)



Figure 10 : Representation of $\log(K'_{Tdiss})$, $\log(K'_{Tred})$ and $\log(K'_{Tox})$ as a function of (1/T) for glass NC3S:

(•)
$$\log K'_{Tdiss} = 1.381 - \frac{1724}{T}$$
 (R²=0.980)

(•)
$$\log K'_{Tred} = 3.138 - \frac{8989}{T}$$
 (R²=0.934)

(
$$\diamond$$
) log $K'_{Tox} = 2.828 - \frac{2619}{T}$ (R²=0.973)

