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# Effect of reaction temperature on the chlorination of a $Sm_2O_3$ -CeO<sub>2</sub>-C mixture

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# Abstract

The chlorination of a  $Sm_2O_3$ –CeO<sub>2</sub>–C mixture with gaseous chlorine was studied by thermogravimetry (TG). The effect of the reaction temperature between 400 and 950 °C on the reaction rate was analyzed. The reaction products were studied by X-ray diffraction (XRD) and energy dispersive spectroscopy (EDS). Compared to the results previously found in the individual systems, it was concluded that each oxide evolves as being an individual in the mixture. Combined with TG results along with observations done using scanning electron microscopy (SEM), the stoichiometries of the reactions involved were obtained. From these results, a two-stage separation method for both oxides was proposed.

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# 1. Introduction

The importance of both cerium and samarium compounds has increased markedly in the last decades. As pure oxides, both lanthanides are used in fuel cells [1,2]. Cerium oxide is used in catalysis [3,4] while samarium as either oxychloride, oxide or metal is used in permanent magnets and for unique optical materials [5,6]. The marked chemical similarities [7] between lanthanide oxides along with their high stability [8] make separation a difficult task. To overcome this problem, different separation methods have been proposed [9–11].

The chlorination and carbochlorination of  $Sm_2O_3$  and  $CeO_2$  and their mixture were previously studied [12–16]. Reaction products were identified and by TG analysis, the stoichiometry of these reactions was obtained [12–16].

 $CeO_2$  carbochlorination starts above 700 °C producing  $CeCl_3$  (s, l, g) [13] and  $Sm_2O_3$  carbochlorination starts over

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 $400 \,^{\circ}$ C [12] producing SmOCl (s) in one stage up to 650  $^{\circ}$ C and SmOCl (s) and SmCl<sub>3</sub> (s, l, g) in two successive stages from 650 to 950  $^{\circ}$ C [12].

These differences in reactivity towards C (s)+ $Cl_2$  (g) [12,13] suggest using this difference to separate these oxides. The chlorides and oxychlorides formed occur in different agregation states and have differences in their vapor pressures suggests separation by physical methods such as volatilization or fractional distillation.

# 2. Experimental

## 2.1. Materials and procedure

Ar 99.999% purity (AGA, Argentina), Cl<sub>2</sub> 99.8% (Indupa, Argentina) and raw  $Sm_2O_3$ , CeO<sub>2</sub> and C were the reactants used. These solids were previously characterized [12–16]. These reactants were weighed and mixed mechanically to obtain a CeO<sub>2</sub> (45 wt%)–Sm<sub>2</sub>O<sub>3</sub> (45 wt%)–C (10 wt%) mixture. The percentage of each oxide was determined using the Rietveld method [17] (see appendix for sample

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#### Nomenclature

а	cell parameter (Å)				
b	cell parameter (Å)				
с	cell parameter (Å)				
D	diffusion coefficient ( $m^2 s^{-1}$ )				
Ean	apparent activation energy (kI mol <sup><math>-1</math></sup> )				
-ap f	stoichiometric correction coefficient (dimen-				
5	sionless)				
FW	formula weight (kg mol <sup><math>-1</math></sup> )				
<i>q</i>	coefficient that relates $\Delta w$ to the mass change				
8	of carbon CeO <sub>2</sub> and $Sm_2O_2$ (dimensionless)				
L	characteristic dimension of the sample $(m)$				
$m_0$	initial mass sample (mg)				
$\Delta m$	mass variation (mg)				
$\Delta M$	balance mass variation (mg)				
Ν	molar flow of chlorine (mol $s^{-1}$ )				
NTP	normal pressure and temperature conditions				
r	reaction rate $(s^{-1})$				
R	reaction rate (mol $s^{-1}$ )				
t	time (s)				
Т	temperature (°C)				
z	adjustable parameter				
Greek s	ymbols				
α	cell angle (°)				
$\alpha_{\rm C,Sm_2C}$	$_{O_3}$ carbon, Sm <sub>2</sub> O <sub>3</sub> reaction degree (dimension-				
	less)				
β	cell angle (°)				
γ	cell angle (°)				
ν	kinematic viscosity ( $m^2 s^{-1}$ )				

parameters detail). Carbon percentage was determined by weighing it before and after burning the mixture at 950 °C [12,13,16].

A thermogravimetric analyzer based on a Cahn 2000 electrobalance described elsewhere [18] was used to measure the chlorination rate. The mass change resolution of the system was  $\pm 10 \,\mu\text{g}$  under the experimental conditions [12,13,15]. Samples of Sm<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub>–C of 10 mg were placed inside a quartz crucible suspended by a quartz fiber inside a furnace. Isothermal and non-isothermal measurements were made under an overall pressure of 101.3 kPa and a total gas flow rate of 7.91h<sup>-1</sup> (NPT). In the isothermal experiments, samples were first heated for 1 h in Ar at the desired operation temperature, then Cl<sub>2</sub> was injected into the system reaching a pCl<sub>2</sub> = 30.3 kPa.

In the temperature scanning experiments, samples were heated from room temperature to 950 °C at 2.6 °C min<sup>-1</sup> at a pCl<sub>2</sub> = 30.3 kPa in flowing Ar–Cl<sub>2</sub>. In both cases, mass changes were measured and apparent mass changes were corrected as explained elsewhere [18]. Since the reaction products, SmCl<sub>3</sub> and CeCl<sub>3</sub>, are hygroscopic [19], samples

were treated and auxiliary measurements done in a globe box [12–15].

# 2.2. Expression of results

For non-isothermal runs, TG data are expressed as  $\Delta w$  versus *T*, where  $\Delta w$  and *T* are the mass change in milligrams and the temperature in °C, respectively. For isothermal runs, TG data are expressed as either the fractional carbon mass loss given by  $\alpha_{\rm C} = \Delta m({\rm C})/m_0({\rm C})$ , where  $\Delta m({\rm C})$  and  $m_0({\rm C})$  are the carbon mass change and carbon initial mass, respectively, or the fractional samarium oxide mass loss given by  $\alpha_{\rm Sm_2O_3} = \Delta m({\rm Sm_2O_3})/m_0({\rm Sm_2O_3})$ . Either Sm<sub>2</sub>O<sub>3</sub> or carbon consumption is related to the observed mass change by  $\Delta m({\rm C \, or \, Sm_2O_3}) = g \,\Delta w$ . *g* is a coefficient which relates the  $\Delta w$  to the mass change of carbon, CeO<sub>2</sub> and Sm<sub>2</sub>O<sub>3</sub>, and which depends on both the stoichiometry of the reaction and the aggregation state of reactants and products. Then, the reaction degree is transformed to:

$$\alpha_{\rm C,Sm_2O_3} = \frac{g \,\Delta m(\rm C,Sm_2O_3)}{m_{0(\rm C,Sm_2O_3)}} \tag{1}$$

where the parenthesis indicates that the symbol contained within the formula corresponds to either carbon or  $Sm_2O_3$ .The reaction rate (s<sup>-1</sup>) is:

$$r = -\frac{d\alpha_{C,Sm_2O_3}}{dt} = -\frac{g}{m_{0(C,Sm_2O_3)}}\frac{dm}{dt}$$
(2)

The reaction rate (mol  $Cl_2 s^{-1}$ ) is:

$$R = \frac{\mathrm{d}n_{\mathrm{Cl}_2}}{\mathrm{d}t} = \frac{fm_{0(\mathrm{C},\mathrm{Sm}_2\mathrm{O}_3)} \cdot r}{\mathrm{FW}(\mathrm{C},\mathrm{Sm}_2\mathrm{O}_3)} \tag{3}$$

where *n* is the moles of chlorine, *f* a coefficient that relates the stoichiometric consumption of moles of either carbon or  $Sm_2O_3$  to moles of chlorine and FW is the formula weight of either carbon or  $Sm_2O_3$ .

### 3. Results and discussion

# 3.1. Reactivity of the $CeO_2$ -Sm<sub>2</sub>O<sub>3</sub>-C system with chlorine and reaction products

Non-isothermal experiments were made to determine the main products of reaction from room temperature to 950 °C. The corrected TG curve is shown in curve (1) in Fig. 1. For comparison, the corrected TG curves of the individual carbochlorination of both CeO<sub>2</sub> (2) [13] and Sm<sub>2</sub>O<sub>3</sub> (3) [12] are also shown. In the CeO<sub>2</sub>–Sm<sub>2</sub>O<sub>3</sub>–Cl<sub>2</sub>–C system, the starting temperature of reaction (190 °C) is indicated by "A" in the curve. As temperature raises, the mass increases reaching a maximum at 350 °C where a flat zone corresponding to the formation of another condensed phase is observed up to 480 °C ("C"), followed by a flat zone. Above 650 °C, a further slow mass gain extends up to 700 °C ("D"). Between 700



Fig. 1. (1) Non-isothermal curve of the chlorination of  $Sm_2O_3$ –CeO<sub>2</sub>–C. XRD, EDS and SEM observations are indicated by full circles, hollow circles and full squares, respectively. (2) Non-isothermal curve of the chlorination of CeO<sub>2</sub>–C [13]. (3) Non-isothermal curve of the chlorination of Sm<sub>2</sub>O<sub>3</sub>–C [12]. Reaction products [12,13] are labeled in the figure.

and 800 °C ("E"), a marked mass gain occurs. Above 800 °C, an increasing rate of mass loss is observed up to 950 °C. This mass loss is attributed to vaporization of the reaction products. This curve resembles the curves for the individual carbochlorination of  $Sm_2O_3$  [12] and  $CeO_2$  [13] suggesting formation of similar products. Differences in mass gain between the mixture and the individual oxide in each temperature range are attributed to the differences in the C content in the initial mixtures [12,13]. The identity of phases formed in each of the individual systems [12,13] are labeled in Fig. 1.

To identify the reaction products, isothermal experiments were done at selected temperatures and the reaction products were characterized by XRD, EDS and SEM at the points on the TG curve of Fig. 1 indicated by full circles, hollow circles and full squares, respectively. With the aid of mass balances, the stoichiometries of the reactions involved were assessed.

# 3.2. Stoichiometries and reaction products between 400 and $625 \,^{\circ}C$

Four hundred and 550 °C were selected as representative temperatures in this range. The diffraction patterns of the reaction products at 3 min (a), 20 min (b) and 40 min (c) at 550 °C along with the reference patterns of CeO<sub>2</sub> [20] (d) Sm<sub>2</sub>O<sub>3</sub> [21] (e) and SmOCl [22] (f) are displayed in Fig. 2. SmOCl diffraction lines increase with time as the ones of Sm<sub>2</sub>O<sub>3</sub> decreases. No Ce compound other than CeO<sub>2</sub> is observed. No product of interaction between Sm and Ce is observed in the diffraction patterns. SEM images of reaction products at 400 °C show chemical attack in the shape of pits on the carbon indicating it is involved in the reaction [12,13]. These results along with mass balances at various temperatures lead to the conclusion that in this temperature range



Fig. 2. Diffraction patterns of the reaction products at 550 °C.

only Sm<sub>2</sub>O<sub>3</sub> reacts with the stoichiometry,

$$2Sm_2O_3(s) + 2Cl_2(g) + C(s) = 4SmOCl(s) + CO_2(g)$$
(4)

XRD and SEM analysis performed at temperatures lower than 400 °C indicated that only direct chlorination of  $Sm_2O_3$  occurs [12,14]. Like the individual CeO<sub>2</sub>-Cl<sub>2</sub> system [15], no chlorination of the CeO<sub>2</sub> present in the  $Sm_2O_3$ -CeO<sub>2</sub>-C mixture is observed.

# 3.3. Stoichiometries and reaction products between 650 and 700 $^{\circ}\mathrm{C}$

Six hundred and fifty and 700  $^{\circ}$ C were selected for analysis of the reaction products. The diffraction patterns obtained at various times at both temperatures are shown in Fig. 3. At



Fig. 3. Diffraction patterns of the reaction products at 650 and 700 °C.



Fig. 4. Diffraction patterns of the reaction products at 750, 800 and 900  $^\circ\text{C}$  [20–24].

shorter times at both temperatures (Fig. 3a and d), the formation of SmOCl is detected. At longer times, the further carbochlorination of this oxychloride leads to the formation of SmCl<sub>3</sub>. This product is incompletely obtained at 650 °C (Fig. 3c). At 700 °C, the successive formation of both compounds is observed but no SmOCl is detected at longer times (Fig. 3e). No products of the carbochlorination of CeO<sub>2</sub> are observed in this temperature range (Fig. 3a–e). These results are in agreement with those obtained from the individual carbochlorination of each oxide [12,13]. A SEM image of the reaction products at 650 °C analyzed by EDS shows SmCl<sub>3</sub> particles that were vaporized during the preparation of the sample. These results along with mass balances led to the conclusion that only Sm<sub>2</sub>O<sub>3</sub> reacts in two steps, the first one defined by Eq. (4) and the second one,

$$2Sm_2O_3(s) + 3C(s) + 6Cl_2(g) = 4SmCl_3 + 3CO_2(g)$$
(5)

which is the same as the individual carbochlorination of  $Sm_2O_3$  [12].

# 3.4. Stoichiometries and reaction products between 700 and $950 \,^{\circ}C$

Seven hundred and fifty, 800 and 900 °C were selected as the representative temperatures in this range. The reaction products obtained at these temperatures at various times along with the reference patterns are shown in Fig. 4. At shorter times at 750 and 800 °C, formation of SmOCl is observed. At longer times, both SmCl<sub>3</sub> and CeCl<sub>3</sub> are detected. These results are the same as the individual carbochlorination of each oxide [12,13]. As observed at the lower temperatures (Figs. 2 and 3), no interaction between cerium and samarium compounds is observed. Mass balances in this temperature range indicate that CeO2 is carbochlorinated according to

$$2CeO_{2}(s) + 3Cl_{2}(g) + 4C(s)$$
  
= 2CeCl<sub>3</sub>(l, s) + 4CO(g) (6)

which is the same stoichiometry as that of the individual carbochlorination [13]. Like the  $Sm_2O_3$ – $Cl_2$ –C system [12], the mass balances indicated that  $Sm_2O_3$  is carbochlorinated in two steps. Between 700 and 850 °C, SmOCl is produced according to Eq. (4). At higher temperatures, the formation of SmOCl as a first step is observed but no stoichiometry can be assigned. At 725 °C, the second step leads to the carbochlorination of SmOCl to produce SmCl<sub>3</sub> according to

$$2SmOCl(s) + 2Cl_2(g) + C(s)$$
  
= 2SmCl\_3(l, s) + CO<sub>2</sub>(g) (7)

And between 750 and 950 °C:

$$SmOCl(s) + Cl_2(g) + C(s) = SmCl_3(l, s) + CO(g)$$
  
(8)

The global reaction at 725 °C is described by:

$$3Sm_2O_3 (s) + 6Cl_2 (g) + 3C (s) = 4SmCl_3 (l, s) + 3CO_2 (g)$$
(9)

While the global reaction between 750 and 950 °C is described by:

$$3Sm_2O_3(s) + 6Cl_2(g) + 6C(s) = 4SmCl_3(l, s) + 6CO(g)$$
(10)

Traces of both CeCl<sub>3</sub> and SmCl<sub>3</sub> were observed on SEM images which is in agreement with their respective melting points of 816 and 681  $^{\circ}$ C [25].

#### 3.5. Effect of the temperature on the reaction rate

Isothermal TG curves are shown in Fig. 5. At  $T \le 675 \,^{\circ}$ C, the carbochlorination is achieved in one step corresponding to the formation of SmOCl according to Eq. (4). The rate increases as the temperature is raised, i.e., time needed to achieve  $\alpha_{\text{Sm}_2\text{O}_3} = 0.9$  is 607, 90 and 20 s at 400, 500 and 600 °C, respectively. Table 1 displays reaction rates calculated at various  $\alpha_{\text{Sm}_2\text{O}_3}$  by Eq. (3) along with the theoretical values obtained from the equation of Ranz-Marshall [12-15] corrected as suggested [26]. Since both sets of values are similar, it is concluded that carbochlorination of the mixture is achieved under external mass transfer control which increases as temperature increases [12,15]. The values are also compared to those for the individual carbochlorination systems [12,13]. The values in the mixture are of the same order of magnitude as those for carbochlorination of  $Sm_2O_3$  [12] indicating that no changes are produced due to the presence of CeO<sub>2</sub> in the mixture. CeO<sub>2</sub> presents no reaction in this temperature range which is also in agreement with the individual system [13].



Fig. 5. (a) Effect of the temperature between 400 and 625 °C. The global stoichiometry is calculated using Eq. (4). (b) Effect of the temperature between 650 and 700 °C. In these curves, the global stoichiometry is calculated according to Eq. (5). Formation of products at each stage from XRD, EDS and SEM measurements are signaled by full circles, hollow circles and full squares, respectively.

The TG curves corresponding to 650–700 °C are displayed in Fig. 5b. At 650 and 675 °C, carbochlorination of  $Sm_2O_3$ leads to a complete formation of SmOCl in the first stage but not to the full formation of SmCl<sub>3</sub> in the second. At temperatures higher than 675 °C, formation of SmCl<sub>3</sub> is complete according to Eq. (5). This behavior was previously observed in the carbochlorination of  $Sm_2O_3$  [12]. The experimental

Table 1

Comparison between r	(experimental) and	N (theoretical)	reaction rates
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reaction rates are compared to those of the Ranz-Marshall equation [12–15] in Table 1. The first stage reaction rate is similar to those of the Ranz-Marshall equation indicating the first stage is controlled by mass transfer. The second stage is two orders of magnitudes lower suggesting a different reaction regime closer to chemical-mixed control. Similar experimental reaction rates values and the presence of two reaction stages in this temperature range were observed in the individual carbochlorination of  $Sm_2O_3$  [12] suggesting no interaction with CeO<sub>2</sub> in the mixture. As discussed in Section 3.3, the carbochlorination of CeO<sub>2</sub> is not achieved in this temperature range.

The TG curves at 725–950 °C are displayed in Fig. 6. In this case, curves are expressed as the consumption of carbon because this reactant is the one common to reaction of both oxides. Like that of Sm<sub>2</sub>O<sub>3</sub> [12], the carbochlorination of the mixture occurs in two stages. In the first, formation of SmOCl is achieved. (Fig. 4a and c). In the second, the formation of both SmCl<sub>3</sub> and CeCl<sub>3</sub> is achieved (Fig. 4b, d and e). As also observed in the carbochlorination of Sm<sub>2</sub>O<sub>3</sub> [12], the rate in the second stage is more dependent on temperature than the first. The time to reach  $\alpha_{\rm C} = 0.20$  is 10, 17 and 20 s at 950, 800 and 725 °C, while the time to reach  $\alpha_{\rm C} = 0.80$  is 50, 168 and 461 s at the same temperatures, respectively.

Table 1 displays the carbochlorination rate at various temperatures and  $\alpha_{\rm C}$  using Eq. (3) with the global stoichiometry of Eqs. (6), (9) and (10). The carbochlorination rates at lower  $\alpha_{\rm C}$  values are faster, by at least one order of magnitude, than those at higher  $\alpha_{\rm C}$  values at the same temperatures. This indicates the reaction evolves under different kinetic regimes. As discussed in the previous section, the first stage is un-

<i>T</i> (°C)	$D ({\rm cm}{\rm s}^{-2})$	$\nu (\mathrm{cms^{-2}})$	$N (\mathrm{mol}\mathrm{Cl}_2\mathrm{s}^{-2})$	Equation used	α	$R \pmod{\operatorname{Cl}_2 \operatorname{s}^{-2}}$		
						This work	[12]	[13]
400	0.43	0.39	$6.01 \times 10^{-8}$	(4)	0.2 0.5	$\begin{array}{c} 3.28 \times 10^{-8} \\ 2.71 \times 10^{-8} \end{array}$	$\begin{array}{c} 1.15 \times 10^{-8} \\ 1.27 \times 10^{-8} \end{array}$	
600	0.76	0.67	$4.30 \times 10^{-7}$	(4)	0.2 0.5	$9.64 \times 10^{-8}$ $4.78 \times 10^{-8}$	$4.42 \times 10^{-7}$ $5.98 \times 10^{-7}$	-
650	0.83	0.74	$4.57 \times 10^{-7}$	(4) (5)	0.2 0.45	$9.75 \times 10^{-7}$ $7.00 \times 10^{-10}$	$3.76 \times 10^{-7}$ $7.37 \times 10^{-10}$	_
700	0.92	0.81	$5.00 \times 10^{-7}$	(5)	0.2 0.5	$8.16 \times 10^{-7}$ $1.25 \times 10^{-9}$	$8.05 \times 10^{-7}$ $1.67 \times 10^{-9}$	_
750	1.00	0.89	$5.28  imes 10^{-7}$	(6), (10)	0.2 0.5	$8.45 \times 10^{-7}$ $7.10 \times 10^{-9}$	$5.25 \times 10^{-7}$ $2.0 \times 10^{-9}$	_
800	1.09	0.96	$6.00 \times 10^{-7}$	(6), (10)	0.2 0.5	$8.62 \times 10^{-7}$ $9.02 \times 10^{-9}$	$3.02 \times 10^{-7}$ $6.02 \times 10^{-9}$	$3.67 \times 10^{-7}$ $1.50 \times 10^{-7}$
850	1.18	1.04	$7.52 \times 10^{-7}$	(6), (10)	0.2 0.5	$8.76 \times 10^{-7}$ $5.00 \times 10^{-8}$	$\begin{array}{c} 5.86 \times 10^{-7} \\ 8.04 \times 10^{-9} \end{array}$	$4.70 \times 10^{-7}$ $3.27 \times 10^{-7}$
950	1.36	1.21	$8.01 \times 10^{-7}$	(6), (10)	0.2 0.5	$9.90 \times 10^{-7}$ $5.78 \times 10^{-8}$	$7.32 \times 10^{-7}$ $1.78 \times 10^{-8}$	$6.91 \times 10^{-7}$ $2.40 \times 10^{-7}$

Values of *D* and *v* at various temperatures are estimated for  $pCl_2 = 30.3$  kPa. *N* values are calculated according to the Ranz-Marshall equation and corrected as suggested [15,26]. In this equation, L = 0.30. The experimental values of *R* are obtained for 10 mg of Sm<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub>–C under a  $pCl_2 = 30.3$  kPa and a total gas flow rate of 7.911h<sup>-1</sup> at each temperature. Eighth and ninth columns display these values for the individual carbochlorination of Sm<sub>2</sub>O<sub>3</sub> [12] and CeO<sub>2</sub> [13].



Fig. 6. Effect of the temperature between 725 and 950 °C. In this case, g = 0.5399. Sm<sub>2</sub>O<sub>3</sub> global consumption is expressed according to Eqs. (9) and (10) at 725 and 750 to 950 °C, respectively. CeO<sub>2</sub> global consumption is calculated according to Eq. (6).

der external mass transfer. Unlike the 625–700 °C temperature range in which the first and second stages differ by at least two orders of magnitude, both stages in this temperature range differs by only one order of magnitude, as observed in Table 1. This indicates that external mass transfer controls the first stage and influences, not controls, the second stage in this temperature range [27]. This behavior was observed previously in the Sm<sub>2</sub>O<sub>3</sub>–C–Cl<sub>2</sub> system [12].

#### 3.6. The activation energy and regimes of reaction

### 3.6.1. The formation of SmOCl

The calculation of the activation energy for the formation of SmOCl in the 400–850  $^{\circ}$ C range is shown in Fig. 7. Be-



Fig. 7. Plot of  $\ln t$  vs.  $T^{-1}$  at various conversions for 10 mg of CeO<sub>2</sub>–Sm<sub>2</sub>O<sub>3</sub>–C between 400 and 850 °C. The stoichiometry considered corresponds to Eq. (4).

#### Table 2

Activation energy for the formation of SmOCl and SmCl<sub>3</sub>–CeCl<sub>3</sub> in the carbochlorination of the CeO<sub>2</sub>–Sm<sub>2</sub>O<sub>3</sub> mixture

Process	Temperature range (°C)	α Range	$E_{\rm ap}  (\rm kJ  mol^{-1})$
SmOCl formation	400–625 650–850	0.10-0.90 0.10-0.90	$79 \pm 3$ $12 \pm 4$
SmCl <sub>3</sub> –CeCl <sub>3</sub> formation	725–950	0.10–0.50 0.60–0.90	$\begin{array}{c} 12\pm 4\\ 75\pm 3\end{array}$

tween 400 and 625 °C, the  $E_{ap}$  value is  $79 \pm 3 \text{ kJ mol}^{-1}$ . At 625 °C, the lines break. The  $E_{ap}$  value calculated between 625 and 850 °C is  $12 \pm 3 \text{ kJ mol}^{-1}$ , only some reaction degrees are shown, but calculation was done for values between 0.1 and 0.9. The  $E_{ap}$  values are lower and the temperature were the lines break is higher than those of the carbochlorination of Sm<sub>2</sub>O<sub>3</sub> [12] (see Table 2). This effect is attributed to the presence of a higher amount of C available to react with the Sm<sub>2</sub>O<sub>3</sub> present in the mixture.

#### 3.6.2. The formation of CeCl<sub>3</sub> and SmCl<sub>3</sub>

Like that of the carbochlorination of  $\text{Sm}_2\text{O}_3$  [12], the formation of SmCl<sub>3</sub> occurs as a second stage after the formation of SmOCl. No total conversion of the SmOCl is achieved at temperatures lower than 690 °C as observed in both Figs. 5b and 3a–c. The formation of solid SmCl<sub>3</sub> hindering the progress of the reaction is attributed to this discontinuity of the reaction curves at temperatures lower than 690 °C as observed in Fig. 5b.

If compared with the curves of the carbochlorination of Sm<sub>2</sub>O<sub>3</sub> [12], those of the carbochlorination of the CeO<sub>2</sub>-Sm<sub>2</sub>O<sub>3</sub> mixture shown in Fig. 5 are quicker. As example, the time to reach  $\alpha_{\text{Sm}_2\text{O}_3} = 0.4$  and 0.8 at 700 °C are 27 and 141 s for the CeO2-Sm2O3 mixture, while it is 119 and 3046 s for the individual carbochlorination of  $\text{Sm}_2\text{O}_3$  [12]. This effect is attributed to the presence of a higher amount of carbon available to react with the Sm<sub>2</sub>O<sub>3</sub> in the mixture than that available in the individual carbochlorination [12]. Despite the fact that the percentage of carbon in the Sm<sub>2</sub>O<sub>3</sub>-C [12] and that in Sm<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub>-C are approximately the same, the total amount of C in the samples of the mixture are higher because these samples have a total mass four times higher. As studied in a previous work [13], carbon produces a kinetic effect which accelerates the ratio of reaction [13]. It is attributed to the presence of intermediaries of reaction incremented with the amount of carbon present in the sample and available to react [13]. At temperatures higher than 700 °C, this increment on the reaction ratio is also due to the formation of liquid SmCl<sub>3</sub>. As discussed in a previous work [12], the formation of SmCl<sub>3</sub> (l) enhances the diffusion of reactive species from or to the reactive SmOCl surface and favoring the carbochlorination of Sm<sub>2</sub>O<sub>3</sub> in the process. This process also favors the carbochlorination of CeO<sub>2</sub>. As observed in Fig. 6, the carbochlorination of  $CeO_2$  according to Eq. (6) and that of Sm<sub>2</sub>O<sub>3</sub> according to Eqs. (9) and (10) in the mix-



Fig. 8. Plot of  $\ln t$  vs.  $T^{-1}$  at various conversions for 10 mg of CeO<sub>2</sub>–Sm<sub>2</sub>O<sub>3</sub>–C between 700 and 950 °C. The stoichiometries considered correspond to Eqs. (6), (9) and (10).

ture are completed. Although the individual carbochlorination of  $Sm_2O_3$  is completed in this temperature range [12], that of  $CeO_2$  is not [13]. This last reaction only achieves the maximum  $\alpha_{CeO_2}$  at temperatures higher than 790 °C [13]. In CeO<sub>2</sub> carbochlorination, the formation of liquid CeCl<sub>3</sub> enhances the completion of the reaction at higher temperatures by coalescing and leaving unreacted CeO<sub>2</sub> surface exposed to chlorine chemical attack [13]. When CeO<sub>2</sub>-Sm<sub>2</sub>O<sub>3</sub>-C is chlorinated, the formation of liquid SmCl<sub>3</sub> at lower temperatures due to its mp of 681 °C [25] not only coalesces and exposes the SmOCl surface to further carbochlorination as observed in Fig. 6, but also exposes the CeO<sub>2</sub> surface to react and the full carbochlorination of both oxides is favored in the process. At temperatures higher than 800 °C, the presence of carbon which accelerates the carbochlorination rate of the mixture and the simultaneous formation of  $SmCl_3$  (1) and CeCl<sub>3</sub> (l) (mp 816 °C [25]) produces a global increment of the reaction rate. This combined effect is observed in the  $E_{\rm ap}$  values of the reaction. The  $E_{\rm ap}$  values calculated in this temperature range are shown in Fig. 8. Although only four  $\alpha$  values are shown, the calculation was done for  $\alpha$  between 0.1 and 0.9. The calculation of  $\alpha$  between 0.1 and 0.5 (not shown here) led to  $E_{ap}$  values of  $12 \pm 4 \text{ kJ mol}^{-1}$  similar to those obtained for the formation of SmOCl in the 625-850 °C range which is reasonable if considering that this stage is also occurring at this temperature range. The  $E_{ap}$  values found indicate that this stage occurs under external mass transfer control [28,29]. It is confirmed by observing that experimental and theoretical reaction rates are of the same order as displayed in Table 1. The  $E_{ap}$  values for  $\alpha$  values between 0.6 and 0.9 shown in Fig. 8 are parallel indicating that the mechanism of reaction remains the same. The values are of the order of  $75 \pm 3 \text{ kJ mol}^{-1}$ . These values suggest the presence of chemical-mixed control influenced by external mass transfer. The shift from low to high  $E_{ap}$  values as the values of  $\alpha$  raise is attributed to the evolution of two different mechanisms of reaction: the formation of SmOCl in the first step and the formation of both SmCl<sub>3</sub> and CeCl<sub>3</sub> in the second. Although this behavior was observed previously [12], the  $E_{ap}$  values for the second step are lower in the case of the present work. It is due to the kinetic effect produced by the presence of a higher amount of C allowable to react [13]. Its combined effect with the formation of both liquid chlorides shifts the chemical-mixed control observed in the case of the carbochlorination of Sm<sub>2</sub>O<sub>3</sub> [12] to chemical-mixed influenced by external mass transfer observed in the present work.

### 3.7. Separation method for this mixture

The separation of these oxides at temperatures lower than 700 °C was discussed in previous works [16,30]. At higher temperatures, the simultaneous formation of CeCl<sub>3</sub> and SmCl<sub>3</sub> is achieved as discussed in the previous section. Then, the separation method should consist in two steps:

- The carbochlorination of the CeO<sub>2</sub>–Sm<sub>2</sub>O<sub>3</sub> mixture using the minimum amount of C needed according to the stoichiometries of Eqs. (6), (9) and (10) to produce CeCl<sub>3</sub> and SmCl<sub>3</sub> chlorides.
- (2) Since no interaction between the initial oxides and the produced chlorides is observed, the chlorides can be separated using differential volatilization or any other physical method taking advantage of the differences on their vapor pressure [25].

# 4. Conclusions

In this work, the effect of the temperature on the carbochlorination of a CeO<sub>2</sub>–Sm<sub>2</sub>O<sub>3</sub> mixture was studied. The starting temperature of the carbochlorination is observed at 400 °C where only Sm<sub>2</sub>O<sub>3</sub> is carbochlorinated. Between this temperature and 625 °C, this oxide reacts in one stage forming SmOCl (s). Over 650 °C and up to 950 °C, the formation of SmCl<sub>3</sub> occurs as a second step. The stoichiometries and temperature ranges of reaction coincide with those of the individual carbochlorination of this oxide [12]. Over 700 °C, the full carbochlorination of CeO<sub>2</sub> in the mixture is achieved with the same stoichiometry of its individual [13].

The  $E_{ap}$  values involved in the formation of SmOCl (s) are  $79 \pm 3 \text{ kJ} \text{ mol}^{-1}$  between 400 and 625 °C and  $12 \pm 4 \text{ kJ} \text{ mol}^{-1}$  between 650 and 850 °C, respectively. The same value is obtained at higher temperatures. The formation of SmOCl is achieved under external mass transfer control. The  $E_{ap}$  value involved on the formation of SmCl<sub>3</sub> and CeCl<sub>3</sub> is of the order of  $75 \pm 3 \text{ kJ} \text{ mol}^{-1}$ . The stage is assumed to be under chemical-mixed control influences by external mass transfer.

Although no interactions between the oxides are observed, a global acceleration of the carbochlorination ratio of the mixture is observed. It is attributed to the presence of a higher amount of carbon available to react per surface area [13] and the formation of liquid SmCl<sub>3</sub> which not only enhances the further carbochlorination of SmOCl formed in the first stage but also favors the full carbochlorination of CeO<sub>2</sub> between 700 and 800 °C by coalescing and exposing the unreacted CeO<sub>2</sub> surface to chlorine chemical attack. The simultaneous formation of both liquids at higher temperatures also increases the global reaction rate of the carbochlorination.

As a conclusion, a two-step method based on the carbochlorination and further vaporization of the chlorides to separate the oxides in the initial mixture is proposed.

# Appendix A

### A.1. Refinements

SmOCl phase was refined with the *P4/nmm* space group. Cell parameters *a*, *b* and *c* are equal to 3.982, 3.982 and 6.712 Å, respectively.  $\alpha$ ,  $\beta$  and  $\gamma$  angles are equal to 90°. Atoms Wyckoff position of SmOCl used during Rietveld refinements were Sm (2c), O (2a) (*z*=0.17) and Cl (2c) (*z*=0.63). *z* stands for the adjustable parameter.

Cubic Sm<sub>2</sub>O<sub>3</sub> phase was refined with the *Ia*<sup>3</sup> space group. Cell parameter *a* is equal to 10.92 Å.  $\alpha$ ,  $\beta$  and  $\gamma$  angles are equal to 90°. Atoms Wyckoff positions were Sm1 (8b), Sm2 (24d) and O (48e).

Cubic CeO<sub>2</sub> phase was refined with the *Fm3m* space group. Cell parameter *a* is equal to 5.398 Å.  $\alpha$ ,  $\beta$  and  $\gamma$  angles are equal to 90°. Atom Wyckoff positions are Ce (4a) and O (8c).

#### A.2. Mass balances

As used in previous works [12,13], mass balances were performed in this system to assess the reaction stoichiometries. Two representative temperatures were selected to explain how the mass balances were done: 700 and 950 °C. Both TG curves are displayed in Fig. 9a and b, respectively. In "A" point at Fig. 9a, the initial constituents are:  $Sm_2O_3$ (s),  $CeO_2$  (s) and C (s). At that point,  $Cl_2$  (g) is injected. Between "A" and "B", only  $Sm_2O_3$  reacts according to Eq. (5). CeO<sub>2</sub> presents no reaction at this temperature. At "B" point,  $SmCl_3$  (s, 1),  $CeO_2$  (s) and C (s) are present. At this point,  $Cl_2$  (g) injection is closed and  $SmCl_3$  (l, s) is vaporized in Ar at 950 °C. After that, only  $CeO_2$  (s) and C (s) remain in the crucible. Crucible is weighed and removed. C (s) is burning in air at 950 °C. Remaining  $CeO_2$  (s) is weighed. A resume of results is displayed in Table 3.

In "A" point in Figs. 9b, the initial constituents are the same as the previous case. Between "A" and "B"  $Sm_2O_3$  and  $CeO_2$  react according to Eqs. (10) and (6), respectively. At "B" point, the compounds present are  $SmCl_3$  (l, s),  $CeCl_3$  (l, s) and remaining C (s). At this point,  $Cl_2$  (g) injection is closed and the chlorides mixture is evaporated in Ar (g) at



Fig. 9. (a) TG curve at 700  $^\circ C$  and (b) at 950  $^\circ C.$  Both curves are used to exemplify the mass balances performed in this system.

Table 3

Examples of mass balances used to determine the stoichiometries of the reactions involved in this system

<i>T</i> (°C)	Substances	Masses points s Fig. 9 (	measured in shown in mg)	Masses measured after evaporation in Ar (g)* and burning
		A	В	in Air <sup>**</sup> (mg)
700	Sm <sub>2</sub> O <sub>3</sub>	4.468	0	0
	CeO <sub>2</sub>	4.468	4.468	4.468
	CeCl <sub>3</sub>	0	0	0
	SmCl <sub>3</sub>	0	6.550	0
	С	0.995	0.764	$0.764^*, 0^{**}$
950	$Sm_2O_3$	4.490	0	0
	CeO <sub>2</sub>	4.490	0	0
	CeCl <sub>3</sub>	0	6.610	0
	SmCl <sub>3</sub>	0	6.429	0
	С	1.066	0.166	0.166*, 0**

950 °C. After that, remaining C (s) is burning in air and the crucible is weighed. A resume of results is also displayed in Table 3. In all cases, chlorine adsorption on C surface and oxidation of C was considered in the mass balances [31].

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