Intrinsic Kinetics of the Chlorination of RuO_2 with Cl_2 Between 973 K and 1073 K (700 °C and 800 °C)

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Ruthenium, as well as the rest of the platinum-group metals, is of crucial importance for industry due to its extraordinary catalytic activity and high-tech applications. Because of its scarcity and high value, there is an increasing interest towards its recovery from wastes. Chlorination metallurgy arises as one possible recovery method. The intrinsic kinetics of the chlorination of ruthenium oxide was studied with the aim of applying this process in a suitable recovery technology. Chlorination of RuO_2 was investigated for temperatures between 973 K and 1073 K (700 °C and 800 °C) and chlorine partial pressure from 50 to 90 kPa. The reaction rate was measured by gravimetry and the rate equation was obtained. An activation energy of 259 ± 6 kJ mol^{-1} and a reaction order of 0.5 with respect of chlorine partial pressure were determined. The reaction product is unstable at atmospheric conditions. Formation of RuO_2Cl_2 is proposed based on experimental evidence; however, such product has not been confirmed yet.

I. INTRODUCTION

PLATINUM-GROUP metals are part of our everyday life; they are used in cars, computers, cell phones, medicine, and are required in many industries. Primary production of these metals occurs mainly in South Africa and Russia and, in lower amounts, in Canada, United States and Zimbabwe. Secondary production, recycling from wastes and recovery from primary production residues, is being also very important to meet the global demand. Ruthenium is mined as a by-product of platinum and palladium. It is used by chemical, electrical, dental, and jewelry industries. In chemistry, it is an important well known catalysts for several chemical reactions such as the oxidation of water to O_2, hydroxylation of olefins and alkanes, epoxidation of alkenes, oxidation of alcohols, among others.[1] In high technology applications, it is used in PC hard disk ultra-thin coatings, chip resistors, electrical contacts, membrane sensors, fuel cells and photovoltaic devices. Besides, it is part of many pharmaceuticals and superalloys.

Recovery of ruthenium from end of use materials or scraps is of major importance due to economic and environmental reasons. Several works and patents have recently appeared on this topic involving hydrometallurgical and pyrometallurgical processes, and the combination of both. The process is chosen according to the type of matrix where ruthenium is contained, the chemical form of the metal, and the product to be obtained. The main available methodologies are leaching ruthenium oxide from fuel cells,[2] solvent extraction of ruthenium compounds from homogeneous catalysts,[3] distillation of ruthenium tetroxide from an oxidant aqueous solution-containing platinum-group metals, and absorption of ruthenium tetroxide in hydrochloric acid,[4] recovery of ruthenium supported on a carrier by reduction of ruthenium compounds at high temperature and dissolution in an oxidizing solution,[5] recovery from waste catalyst of aluminum oxide loaded with ruthenium by roasting, reducing to Ru, oxidizing to RuO_4, dissolving in acid, adding oxidant, filtering, precipitating ammonium hexachloro (IV) ruthenium and reducing to metallic ruthenium,[6] and recuperation from spent catalysts containing ruthenium oxide by reducing in gaseous hydrogen chloride at high temperature and treating with hydrochloric acid to form ruthenium chloride.[7] As can be seen from above, none of these developments involve a pyrometallurgical process like dry chlorination which could be applied in a recovery strategy, but has not been much explored for this metal. On the other hand, there are several patents, not specifically for ruthenium but for valuable or PGM metals in general, that do apply dry chlorination for the recovery process.[8–11] Some of the advantages of this methodology are the high reactivity of chlorine towards many materials, its selectivity, the wide difference in metal chloride vapor pressures that can be used for further separation and purification of these compounds and the absence of liquid residues. Besides, these new

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emerging technologies, based on chlorination, claim to be more efficient and cheaper than traditional methods.[12] For this reason, a better understanding of ruthenium oxide chlorination reaction can contribute in the development of ruthenium recovery strategies involving chlorination.

Separation of metallic ruthenium from platinum-group metal alloys by dry chlorination has already been investigated and formation of insoluble ruthenium chloride has been reported.[13] However, chlorination of other ruthenium compounds such as oxides has not been studied thoroughly, even though some aspects of RuO_2 physicochemical interaction with chlorine at elevated temperatures were reported.[14,15] In a previous work, we studied the kinetics of RuO_2 chlorination under mixed control of reaction rate regime, and obtained an apparent activation energy of 173 ± 8 kJ mol^{-1}.[16] In the present work, we have obtained the experimental conditions for chemical reaction rate control. This has allowed determining the intrinsic kinetic parameters for the reaction and the rate equation that contains the effect of temperature and chlorine partial pressure.

II. EXPERIMENTAL

A. Materials and Methods

The gases used were The gases used were Ar 99.99 pct purity (Linde, Neuquen, Argentina), Cl_2 99.8 pct purity (PRAXAIR, Rosario, Argentina) y N_2 99.99 pct purity (Linde, Neuquén, Argentina). The solid starting material was RuO_2 powder 99.9 pct purity (Sigma-Aldrich, Co., USA). Solid reactive was extensively characterized in a previous work,[16] Figure 1 shows (A) a scanning electron microscopy image (SEM NanoNova 230, FEI) of the RuO_2 powder, agglomerates of nonporous spherical particles can be observed, and (B) the DRX profile of initial sample and the reference pattern of RuO_2.

The solid RuO_2 powder samples used in the experiments were placed in a quartz plate forming a loose packed bed and inside a tubular horizontal reactor.

Before starting the reaction, the RuO_2 samples were maintained in an Ar flow of 1 L $h^{-1}$and heated in Ar up to the target reaction temperature. To begin the reactions the flow of chlorine was injected into the reactor by one end. To interrupt the reactions chlorine was closed, argon flow was increased to 10 L h^{-1} for half hour, and the furnace was turned off. A schematic diagram of the experimental set up is shown in Figure 2.

The effects of temperature and chlorine partial pressure on the reaction rate were investigated gravimetrically in the 973 K to 1073 K (700 °C to 800 °C) temperature range and chlorine partial pressure between 50 and 90 kPa. The following experimental conditions were used: flow rate 6 L h^{-1} and sample mass 2 mg.

Reactions were interrupted to obtain the degree of reaction vs time data. The degree of transformation of ruthenium oxide was defined as the ratio between the mass change and the initial mass: $\alpha = (m_o - m)/m_o$, were m_o is the initial mass and m is the final mass. The weighting precision was ± 0.05 mg (analytical balance Radwag AS220/C/2).

Repeated measurements were preformed to verify the reproducibility of the experiments. The value of α for a reaction time of 574 seconds was determined under the following conditions: flow rate 6 L h^{-1}, chlorine partial pressure 90 kPa and temperature 1073 K (800 °C) (Table I shows the results obtained). Two estimations of α error were considered: the standard deviation of repeated measurements (SD_M) and the error propagation from the weighing precision (E_W). The results obtained with both methods are of the same order, indicating that the experimental error is mainly due to the precision of weighing and other contributions are negligible. We use $\alpha \pm E_W$ for elsewhere calculations.
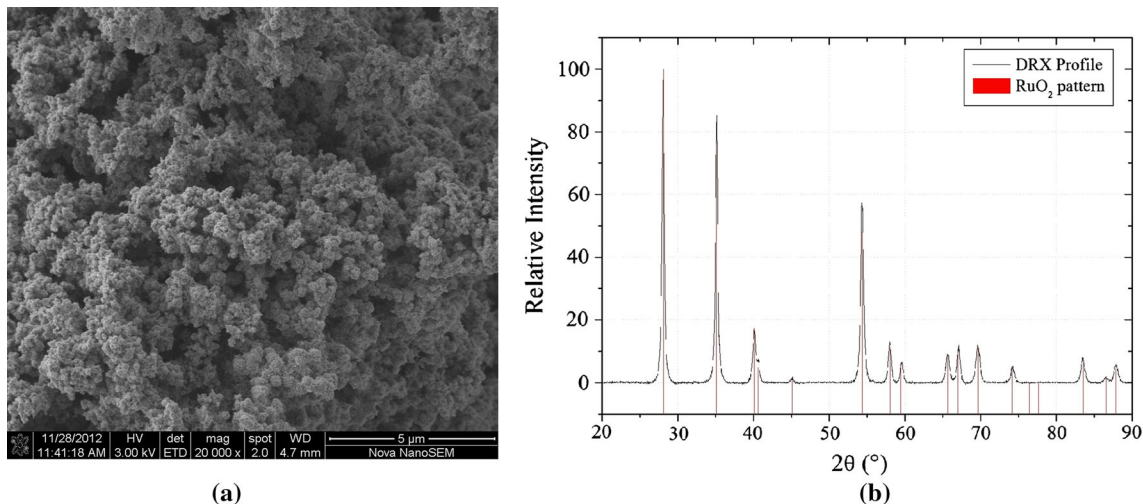

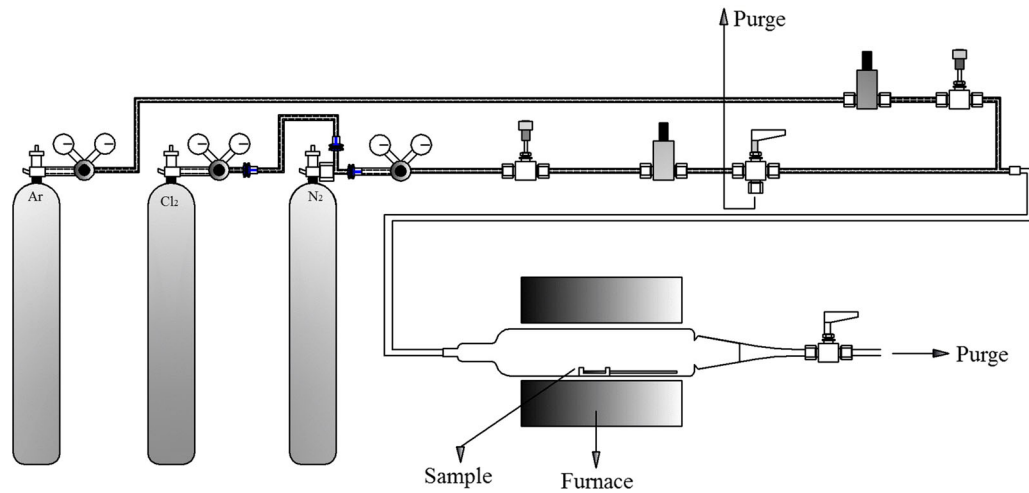Fig. 1—Initial sample: (a) SEM photograph and (b) DRX profile.

Fig. 2—Schematic diagram of the experimental set up.

III. RESULTS AND DISCUSSION

A. Reaction Products

When the reaction starts, formation of a dark gaseous product is observed. This gaseous product, which condensates in the cold zone of the reactor, is unstable when exposed to air. For XRD analysis the product was collected and placed in a well-sealed XRD holder. All manipulation was performed under Argon atmosphere to avoid decomposition. The reaction products contain β-RuCl$_3$ and an amorphous phase. Figure 3 shows (A) a SEM image (SEM 515, Philips Electronic Instruments) and (B) the XRD profile of reaction products (this results were discussed in a previous work[16]). On the XRD profile can be seen the amorphous phase. The peak about 13 deg corresponds to SiO$_2$ contamination. Here, we show new results and propose a possible reaction product in accordance with the experimental evidence.

EDS reveals that the atomic ratio Ru:Cl in the amorphous phase is mainly 1:2. The reaction product was thermally treated in argon at 723 K (450 °C), leading to weight loss and formation of metallic Ru and RuO$_2$. The presence of RuO$_2$ evidences that the amorphous phase in the reaction product is an oxychloride (or a mixture of oxychlorides). This is because the reaction product (*i.e.*, β-RuCl$_3$ and the amorphous phase) was never exposed to oxygen before the treatment. We had already observed that β-RuCl$_3$ was reduced to Ru by the thermal treatment. The relative quantities of Ru and RuO$_2$ obtained by the treatment were calculated by Rietveld analysis of the XRD profile. Assuming that Ru belongs to RuCl$_3$ reduction, and RuO$_2$ arises from oxychloride reduction; and the mass loss corresponds to release of molecular chloride (which was captured with a NaOH solution and identified); the stoichiometry of the oxychloride RuO$_2$Cl$_x$ in the reaction product was calculated. With this procedure a value of x of 2 was obtained corresponding to RuO$_2$Cl$_2$, which is in accordance with the EDS measurements. With this evidence, we propose that the main oxychloride produced by chlorination of RuO$_2$ is RuO$_2$Cl$_2$, which subsequently reacts with Cl$_2$ and produce β-RuCl$_3$. Information about anhydrous ruthenium oxychlorides in the literature is scarce and vague. The following compounds were mentioned by different authors: RuO$_{2-x}$Cl$_x$,[15,17, 18] RuOCl$_2$,[19,20] Ru$_2$OCl$_4$, Ru$_2$OCl$_5$, and Ru$_2$OCl$_6$.[21–23] It has to be pointed out that due to the high instability of the reaction product it could not been directly identified to confirm the stoichiometry proposed until the moment.

In order to set up ruthenium recovery process, dry chlorination might be the first step, which separates the metal from the matrix. The second step could be the transformation of the unstable product into a valuable ruthenium compound for reutilization. Ru and RuO$_2$ can be obtained by thermal treatment of the chlorination product in argon at 723 K (450 °C) for 3 hours, and α-RuCl$_3$ is formed by thermal treatment in chlorine at 793 K (520 °C) for 4 hours.

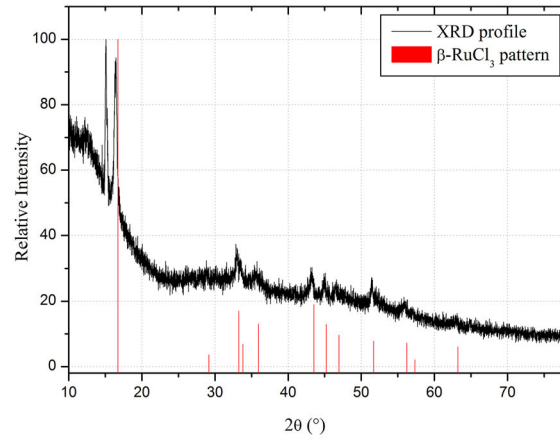### B. Determination of Kinetic Parameters and Rate Equation

As discussed in the section above, the following chlorination reaction is proposed:

$$RuO_2(s) + Cl_2(g) \rightarrow RuO_2Cl_2(g) \qquad [1]$$

Even thought it could not been confirmed yet, knowing univocally the identity of the reaction product is not mandatory for the subsequent kinetic analysis.
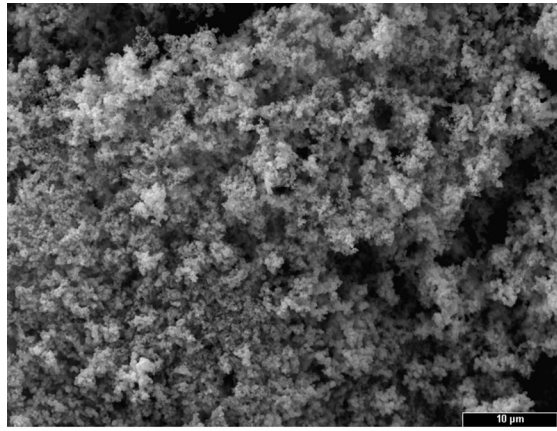
(a)

(b)

Fig. 3—Products of RuO_2 chlorination: (*a*) SEM photograph and (*b*) XRD profile.

Table II. Analysis of Effect of Gas Flow and Sample Mass in the Reaction Rate

	$\alpha \pm E_W$		
	Time: 403 s	Time: 574 s	
Flow Rate (L h^{-1})	Sample Mass: 2.1 mg	Sample Mass: 1.6 mg	Sample Mass: 2.1 mg
4	0.21 ± 0.04	0.50 ± 0.05	–
6	0.38 ± 0.04	0.57 ± 0.04	0.52 ± 0.04
8.44	0.33 ± 0.04	–	0.57 ± 0.04
9	–	0.56 ± 0.04	–

The reaction rate of heterogeneous gas–solid reactions can be decrypted mathematically assuming that the hypothesis of variable separation holds:

$$\text{Rate} = \frac{d\alpha}{dt} = k_o \cdot G(\alpha) \cdot K(T) \cdot F(P_{Cl_2}), \qquad [2]$$

Where k_o is the reaction rate constant, $G(\alpha)$ is a function that describes the geometric evolution of the reacting solid, $K(T)$ is the temperature dependence according to Arrhenius equation, and $F(P_{Cl_2})$ expresses the dependence of the reaction rate on chlorine partial pressure.

To verify that reactions were not occurring under gaseous reactant starvation condition, the rate of chlorine supply in moles of Cl_2 s^{-1} corresponding to a gaseous flow of 6 L h^{-1} was compared with the experimental rate. A difference of three orders was obtained confirming that starvation effect is absent.

To analyze whether gaseous mass transfer affects the overall rate, the effect of gas flow rate and sample mass in the reaction rate was analyzed at two reaction times (403 and 574 seconds), 1073 K (800 °C), and 90 kPa. From the results shown in Table II, it can be seen that there is no significant difference in the degree of reaction achieved for each reaction time for gas flow rates of 6, 8.44, and 9 L h^{-1} and sample masses of 1.6 and 2.1 mg. The degree of transformation was slightly lower at 4 L h^{-1} of gas flow rate. These results and the non-linear relationship obtained between reaction degree and time are indicating that the overall rate is controlled by intrinsic particle kinetics for temperatures below 1073 K (800 °C), gas flow rates higher than 6 L h^{-1} and sample masses lower than 2.1 mg.

To determine the kinetic parameters, experiments were performed at different temperatures between 973 K and 1073 K (700 °C and 800 °C) with 90 kPa partial pressure of Cl_2, 6 L h^{-1} of Cl_2-Ar flow and 2.1 mg samples, for which mass transfer processes had no effect on the overall rate.

The experimental weight loss data were fitted with a conversion function that describes the solid evolution during the reaction according to a topochemically contracting geometry[24]:

$$g(\alpha) = 1 - (1 - \alpha)^{1/n} = k_{app}t, \qquad [3]$$

where k_{app} is an apparent reaction constant that depends on temperature and gaseous reactant pressure, t is the chlorination time and n is a particle shape factor that depends on the solid geometry, being 1 for infinite slabs, 2 for long cylinders, and 3 for spheres. Equation [3] describes the temporal evolution of the reaction of a shrinking nonporous particle, chemically controlled.

Our experimental results were well correlated with $n = 3$, which is shown in Figure 4. This is consistent with the spherical morphology of the particles observed by SEM (Figure 1). The values of k_{app} obtained at each temperature are shown in Table III together with its error and the correlation coefficient.
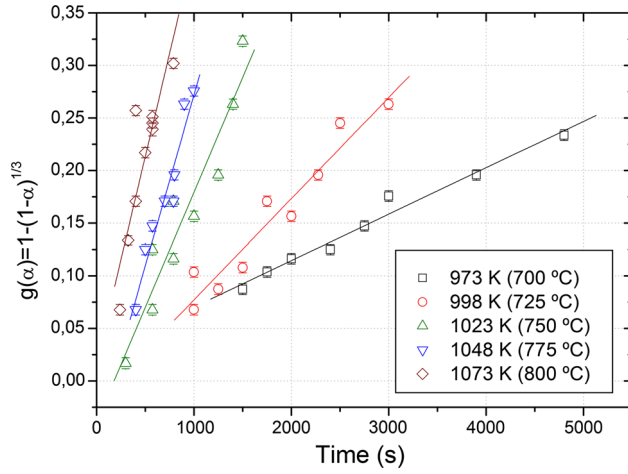
Fig. 4—Conversion function $g(\alpha)$ vs time plot for the chlorination data at temperature between 973 K and 1073 K (700 °C and 800 °C), linear fitting also shown.

Table III. Apparent Reaction Constant Obtained from Fitting Experimental Data Using Eq. [3]

Temperature [K (°C)]	$k_{app} \pm$ Er $(10^{-5}\ s^{-1})$	Correlation Coefficient R
973 (700)	4.41 ± 0.17	0.98854
998 (725)	9.58 ± 0.25	0.96531
1023 (750)	20.89 ± 0.42	0.94000
1048 (775)	44.19 ± 4.87	0.96366
1073 (800)	38.82 ± 10.39	0.88309

Integrating Eq. [2], considering $K(T)$ as an Arrhenius type function and rearranging, the apparent reaction constant can be written as follows:

$$k_{app} = k_o \cdot e^{-\frac{E}{RT}} \cdot F(p_{Cl_2}) \quad [4]$$

The value of the activation energy E can be obtained from the slope of the $\ln k_{app}$ vs T^{-1} plot, according to the following equation:

$$\ln k_{app} = -\frac{E}{RT} + \ln[k_o \cdot F(p_{Cl_2})] \quad [5]$$

This is shown in Figure 5 where an activation energy of 259 ± 6 kJ mol^{-1} indicating a strong temperature dependence was calculated. At low temperatures, where the intrinsic reactivity of the solid is low, the concentration of the gaseous reactant is uniform throughout the solid, the activation energy of the overall reaction is the same as the intrinsic value. At somewhat higher temperatures, the probability of a gaseous reactant molecule penetrating deeply into the solid powder before reacting is small, diffusion within the pores of the solid limits the reaction rate, measured values of activation energy are about one-half of the intrinsic value. In each regime the plot of $\ln k$ vs T^{-1} is a straight line with negative slope which corresponds to $-E$ (Eq. [5]).[24] The low value of k_{app} for 1073 K (800 °C) is indicating that the change in the reaction regime is
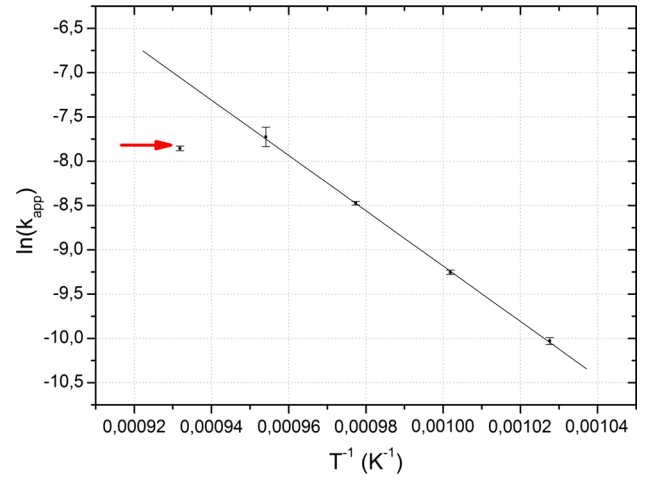

Fig. 5—Arrhenius plot for chlorination of RuO$_2$.

taking place around that temperature. The linear fit for the lower temperatures is included in the error bar of the corresponding values. The value at 1073 K (800 °C), and its error bar, has no correlation with that fitting. For that reason, it was not taken into account to obtain the intrinsic kinetic parameters (Figure 5).

A power dependency $p_{Cl_2}^m$ for chlorine partial pressure was proposed. Where m is the order with respect to chlorine partial pressure and can be calculated from the slope of the $\ln k_{app}$ vs $\ln p_{Cl_2}$. Thus, relationship follows from Eq. [4]:

$$\ln k_{app} = m \cdot \ln(p_{Cl_2}) + \ln k_o - \frac{E}{RT} \quad [6]$$

A value of 0.5 for m is in good agreement with the experimental results. This is shown in Figure 6 where data of $\ln k_{app}$ vs $\ln p_{Cl_2}$ were fitted with a straight line of slope 0.5.

Substituting $F(p_{Cl_2})$ by $p_{Cl_2}^{0.5}$, the value of k_o can be obtained from the y intercept of the $\ln k_{app}$ vs T^{-1} plot (Figure 5) according to Eq. [5]. The following relationship between conversion and time was established, where t is in seconds and p in kPa:

$$g(\alpha) = 1 - (1 - \alpha)^{1/3}$$
$$= 3.92 \times 10^8 (kPa^{-0.5}\ s^{-1}) e^{-\frac{259 kJ mol^{-1}}{RT}} p_{Cl_2}^{0.5} t \quad [7]$$

The corresponding conversion vs time curves according to Eq. [7] are plotted in Figure 7 together with the experimental values. It shows that a good correlation exists between experimental and calculated conversions for temperatures between 973 K and 1048 K (700 °C and 775 °C).

Finally, by differentiating Eq. [7] with respect to time and rearranging, the reaction rate expression can be presented as follows:

$$\frac{d\alpha}{dt} = 1.18 \times 10^9 (kPa^{-0.5}\ s^{-1}) e^{-\left(\frac{259 kJ mol^{-1}}{RT}\right)} p_{Cl_2}^{0.5} (1 - \alpha)^{2/3}$$
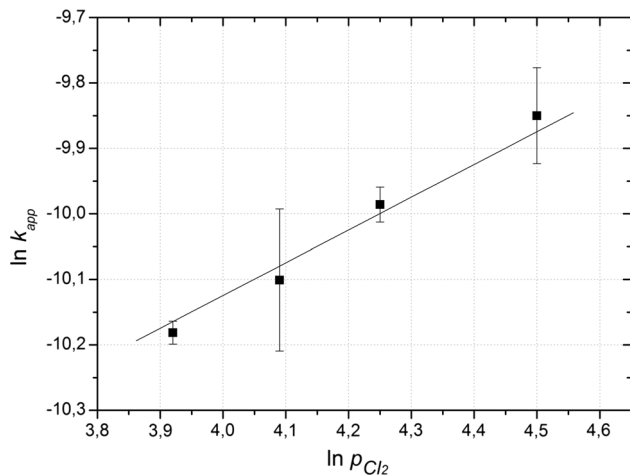$$[8]$$

Fig. 6—Determination of the order with respect to the chlorine partial pressure at 973 K (700 °C).
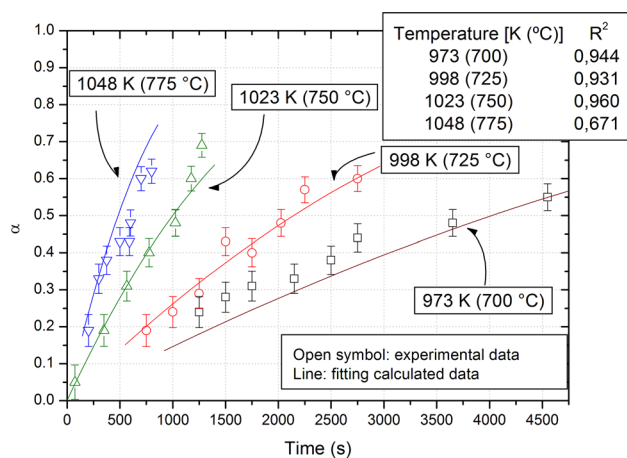

Fig. 7—Experimental conversion *vs* time curves for different temperatures together with calculated conversion *vs* time curves according to Eq. [7]. Inset table shows the correlation coefficient (R^2) between experimental data and α data according to Eq. [7].

It is noticed that the value of the pre-exponential constant in Eq. [8] is not an intrinsic value and corresponds to the solid morphology and particle size of the sample studied in this work.

IV. CONCLUSIONS

The kinetic of ruthenium oxide chlorination has been studied at temperature between 973 K and 1073 K (700 °C and 800 °C) and chlorine partial pressures ranging from 50 and 90 kPa. The reaction rate is controlled by intrinsic particle kinetics between 973 K and 1048 K (700 °C and 775 °C)

Under these conditions, dependences of rate on gaseous reactant pressure, solid conversion, and temperature were determined. Two intrinsic parameters were obtained: the activation energy of about 259 ± 6 kJ mol^{-1} and the reaction order with respect to chlorine partial pressure of 0.5, while the Arrhenius

pre-exponential factor was estimated. Finally, a complete rate equation was formulated for the reaction.

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