

# Electrochemistry of Ni(II) and the Behavior of Oxide Ions in Chloroaluminate Melts

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**Abstract:** The electrochemical behavior of Ni(II) has been investigated in chloroaluminate melts between 175 and 210 °C. Ni(II) is completely soluble in acidic mixtures where the pCl is higher than 5.5 (mol kg<sup>-1</sup> scale). A well-defined and behaved reduction wave is observed at 1.2 V vs. an Al reference in a NaCl-saturated reference compartment. When the pCl is decreased, precipitation of NiCl<sub>2</sub> occurs, the result which has been confirmed from electrochemical and x-ray diffraction experiments. A solubility product of 10<sup>-12.9</sup> (mol kg<sup>-1</sup>)<sup>3</sup> was found. This result is also in disagreement with the precipitation of NiO which has been recently proposed in the literature. As a direct consequence, the acid-base behavior of oxide ions in chloroaluminate has been reinvestigated. Precise titrations of the basic strength of oxide ions have been performed in narrow pCl ranges. An equilibrium constant of 1.6 × 10<sup>-2</sup> mol kg<sup>-1</sup> was found for the general reaction  $\text{AlOCl}_2^- \rightleftharpoons \text{AlOCl} + \text{Cl}^-$ , two orders of magnitude higher than the previously reported value.

In the course of our investigations in molten chloroaluminates over the past few years, we have become increasingly aware of problems associated with the presence of oxides in these melts and, most significantly, our inability to determine the oxide content of our melts. The behavior of oxide was studied in an early paper by Letisse and Tremillon<sup>1</sup> who reported that OH<sup>-</sup> (O<sup>2-</sup>) behaved as a tribase as a result of carrying out base-acid titrations in the melt. However, such procedures could not be used to determine the oxide content of a melt of unknown composition.

We have recently studied the behavior of sulfur and sulfides in the melt and had found considerable acid-base chemistry as sulfide ions interact with the solvent sodium tetrachloroaluminate melt.<sup>2</sup> We concluded that S<sup>2-</sup> activity in the melt varied markedly with melt acidity as a result of an acid-base equilibrium:



That is, we found, initially by emf measurements and then by direct titration, that S<sup>2-</sup> behaved as a tribase in these melts. The relation expressed in eq 1 appears to be valid at pCl values in excess of ca. 2.8 on the molal scale; in more basic systems, S<sup>2-</sup> appears to function as a dibase, forming AlS<sub>2</sub>Cl<sup>-</sup>. Similar results have been found for selenide and telluride. Experiments indicated that the solubility of metal sulfides and selenides was dramatically dependent on melt acidity, in keeping with the equilibria given above.

However, S<sup>2-</sup> and Se<sup>2-</sup> are electrochemically active in these melts, and could be studied in some detail. O<sup>2-</sup>, on the other hand, showed no evidence of electrochemical activity, and while we could study, via titration (see below), the O<sup>2-</sup> basicity, we could not otherwise determine the amount of oxide present in these melts.

Recently, however, Tremillon, Bermond, and Molina<sup>3</sup> reported on the determination of O<sup>2-</sup> in the tetrachloroaluminate melts. The basis of their reported determination was the anodic depolarization of Ni, by O<sup>2-</sup> in the melt, to form NiO. It was stated that over a pCl range from NaCl saturated to about 4.5 or so, NiO was insoluble and a diffusion controlled (by O<sup>2-</sup>, or oxide-carrying species) voltammetric wave could be obtained. They also reported, in contrast to their earlier work,<sup>1</sup> that O<sup>2-</sup> was di- rather than tribasic.

From previous investigations, it is, however, surprising that Ni(II) precipitates as NiO and not as NiCl<sub>2</sub>. In KCl-AlCl<sub>3</sub> melts, Øye and Gruen have shown that an acidic solution of Co<sup>2+</sup>, when neutralized by KCl addition, undergoes a precipitation of CoCl<sub>2</sub>, as shown from the x-ray pattern.<sup>4</sup> Following these authors, low solubilities of transition metal

chlorides in melts with KCl-AlCl<sub>3</sub> ratios slightly less than 1 appear to be quite generally encountered. Very low solubilities of UCl<sub>3</sub>, NiCl<sub>2</sub>,<sup>4</sup> and UCl<sub>3</sub>,<sup>5,6</sup> have indeed been observed. By increasing the temperature (up to 750 °C) and making the melt more basic, it has also been shown that NiCl<sub>2</sub> may eventually redissolve by forming chloro complexes.<sup>4,7</sup>

Since we had considerable interest in the determination of oxide in the melts, and since our own work on S<sup>2-</sup>, O<sup>2-</sup>, Se<sup>2-</sup>, and Te<sup>2-</sup> had indicated these species to be tribasic, at least in the neutral to acidic melt, we undertook to verify the experiments of Tremillon, Bermond, and Molina. It will be shown in this paper that indeed Ni(II) precipitates as NiCl<sub>2</sub> and, consequently, the previous results related to the oxide behavior have been reinvestigated.

## Experimental Section

Most of the experiments have been performed with melts prepared following the general procedure of ref 8. Fluka (A.G. anhydrous and iron free) aluminum chloride is sublimed under vacuum and then mixed with the necessary amount of NaCl (Fisher, certified ACS, recrystallized from water and dried for 24 h under vacuum at 400 °C). The mixtures were sealed under vacuum in a Pyrex tube with aluminum metal and kept molten at 250 °C. Water-clear melts have always been obtained, even for the more reactive acidic melts. When necessary, traces of impurities could be removed by electrolyzing the melt inside the electrochemical cell, between two aluminum electrodes.

Anhydrous NiCl<sub>2</sub> was obtained following the method described by Taylor and Carter.<sup>9</sup> It involves heating under vacuum a molecularly dispersed mixture of hydrated NiCl<sub>2</sub> with six times more NH<sub>4</sub>Cl until the water and ammonium halide are expelled to leave pure anhydrous NiCl<sub>2</sub>. NiO (Baker, AR) and BaCO<sub>3</sub> (99%, Chemical Services) were dried under vacuum at 200 °C during 8 h. Na<sub>2</sub>CO<sub>3</sub> (Mallinckrodt, AR primary standard) has been dried at temperatures varying from 25 to 300 °C. Whatever was the drying temperature, it was found difficult to obtain complete dissolution of Na<sub>2</sub>CO<sub>3</sub>, especially in the more basic melt.

The electrochemical cell is similar in design to the one described in ref 10 but contains a much smaller volume of melt (≈ 20 mL). A 3-mm diameter vitreous carbon rod electrode, sealed in Pyrex, ground flat on an emery wheel, and polished to a mirrorlike finish using type B alumina powder (Fisher) was used as the working electrode. Buttons or wire nickel electrodes, sealed in Pyrex, were cleaned by anodization in diluted HNO<sub>3</sub> (0.5 M) or with a H<sub>2</sub>SO<sub>4</sub>-H<sub>3</sub>PO<sub>4</sub>-HNO<sub>3</sub> mixture. An Al (m5N, Alfa Inorganics) counter electrode was separated from the main compartment by a fine porosity glass frit. The reference electrode consisted of an Al foil immersed in a melt which is contained in a very thin soft glass bulb. The resistance through the membrane was low enough so that the reference electrode can be used directly, even in cyclic voltammetry experiments. When very precise potential measurements are not needed, the melt of the reference compartment was saturated with NaCl. Otherwise, basic but nonsaturated melts,

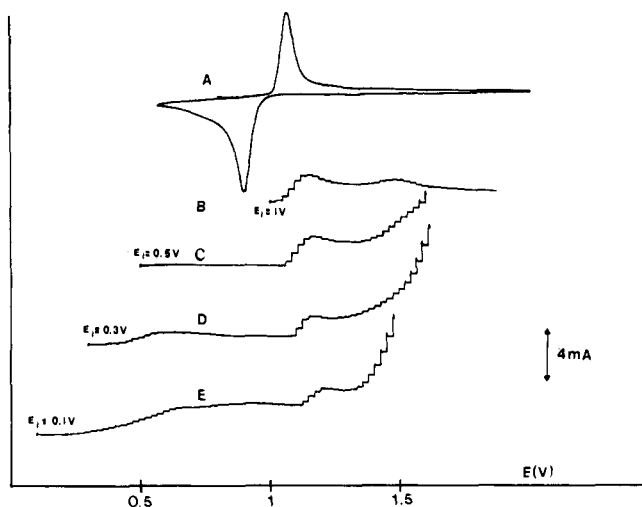


Figure 1. (A) Cyclic voltammograms obtained on a nickel electrode at 175 °C, scan rate 0.200 V s<sup>-1</sup>,  $E_i = 0.8$  V. (B-E) Pulse polarograms obtained on a nickel electrode with different initial potentials: scan rate 5 mV s<sup>-1</sup>, delay time 5 s,  $T^0 = 175$  °C.

which exhibit a much more reproducible potential, have been used in the reference compartment. In this latter case, when the experiment is finished, large amounts of NaCl were added to the bulk melt. The solution is then stirred for several hours in order to ensure saturation of the melt. All the potential measurements are then corrected for the potential difference between the reference electrode and an Al electrode immersed in the saturated main compartment.

All handling of the melts, filtration of precipitates, and electrochemical measurements were performed either under a purified argon atmosphere in a Vacuum Atmosphere drybox as previously described<sup>10</sup> or under vacuum in sealed ampules or in a vacuum line. The x-ray diffraction powder patterns of the precipitates, collected after filtration and sealed under vacuum in very thin Pyrex or silica capillaries, were obtained with a G.E. x-ray diffractometer and a Phillips 90-mm camera using the  $K\alpha$  copper line.

Essentially all the experiments were performed with a PAR Model 174 polarographic analyzer. Cyclic voltammograms on nickel electrodes, which involve high current densities, were performed with a multipurpose instrument described elsewhere.<sup>11</sup> A Sargent coulometric current source, Model IV, was used for melt acidity adjustments, for titration of  $O^{2-}$  and for quantitative anodization of nickel electrodes.

## Results

In a first series of experiments, we tried to reproduce the results obtained by Tremillon during the anodization of a nickel electrode in melts of different compositions.<sup>3</sup>

A cyclic voltammogram obtained on a nickel electrode in a basic melt is shown in Figure 1, curve A. The oxidation wave at 1.1 V is characteristic of the formation of an insoluble product but the results were not reproducible enough to verify that the wave is diffusion controlled. Indeed, past the oxidation wave the current drops to zero, and after successive cycles the oxidation wave decreases and eventually vanishes. This behavior is typical of a partially insulating layer which is not quantitatively reduced after one complete cycle. Anodic passivation behavior has already been observed on a nickel electrode in molten LiCl-KCl and KCl-NiCl<sub>2</sub> melts. Passivation was surmised to be due to the deposition of solid metal chloride or chloro complexes.<sup>12,13</sup>

The shape of normal pulse polarograms (using a PAR 174) or polarograms constructed from current-time curves using a P. D. P. 12 computer show a strong dependence on the initial potential  $E_i$  (Figure 1, curves B-D). If  $E_i \geq 0.8$  V, passivation of the electrode occurs at around 1.6 V. If  $E_i < 0.5$  V, the intensity of the oxidation wave at 1.1 V decreases and is preceded by a broad wave at 0.3 V which may involve some Al oxidation.

In order to define the best working conditions, experiments were performed using the computer as a pulse generator. Pulse durations between 10 and 50 ms and delay times between 100 ms and 10 s were applied to the electrode with no improvement in the reproducibility.

In view of the irreproducible nature of the results compared to those of Tremillon and coupled with the complete lack of experimental information, we decided to investigate the electrochemical behavior of Ni(II) more thoroughly.

**A. Electrochemical Behavior of Nickel.** The electrochemical behavior of Ni(II) in acidic melt was first investigated. For pCl higher than 5.5 (pCl expressed in mol kg<sup>-1</sup>), solutions of Ni(II) can easily be obtained by anodization of a nickel electrode. Identical results are obtained by addition of NiCl<sub>2</sub> to the melt, showing that the species formed by anodizing a Ni electrode is indeed Ni(II). Ni(II) is completely soluble (at least up to 10<sup>-2</sup> M) and forms clear, salmon-colored solutions. Typical cyclic voltammograms obtained on such solutions are shown in Figure 2. A well-defined reduction wave can be observed around 1.2 V with respect to an Al electrode in a NaCl-saturated melt and corresponds to the reduction of Ni(II) to Ni metal.

The peak height of the wave is proportional to the Ni(II) concentration and the corresponding diffusion coefficient equals  $3.6 \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup>. Because of the very steep rise in the beginning of the wave, it is, however, possible that the peak height is affected by distortion due to a nucleation effect.<sup>14</sup> Emf measurements obtained on a nickel electrode at different Ni(II) concentrations show the electrode potential to be given by eq 2, for a melt pCl of 5.8

$$E = (1.443 \pm 0.002) + (0.044 \pm 0.001) \log [Ni^{-2+}] \quad (2)$$

where  $1.433 \pm 0.002$  is the value of  $E^0$  at 175 °C. The value of  $E^0$  can also be calculated from the cyclic voltammogram, assuming a constant overpotential and using the following relationship:<sup>15</sup>

$$E_p = E^0 + \frac{RT}{nF} \ln C - 0.854 \frac{RT}{nF} \quad (3)$$

In this case,  $E^0$  calculated from  $E_p$  vs.  $\log C$  plots is 1.33 V and the corresponding nucleation overpotential is then about 115 mV.

The presence of a small oxidation wave (wave b) following the main oxidation wave (wave x) is typical of a layer strongly adhering to the glassy carbon electrode. Its intensity and position are very dependent on the history of the electrode and on the initial concentration of Ni(II). Consequently, in order to obtain reproducible results for the reduction or oxidation waves, it was found necessary to strip the electrode completely by applying a potential of at least 2.3 V before each scan.

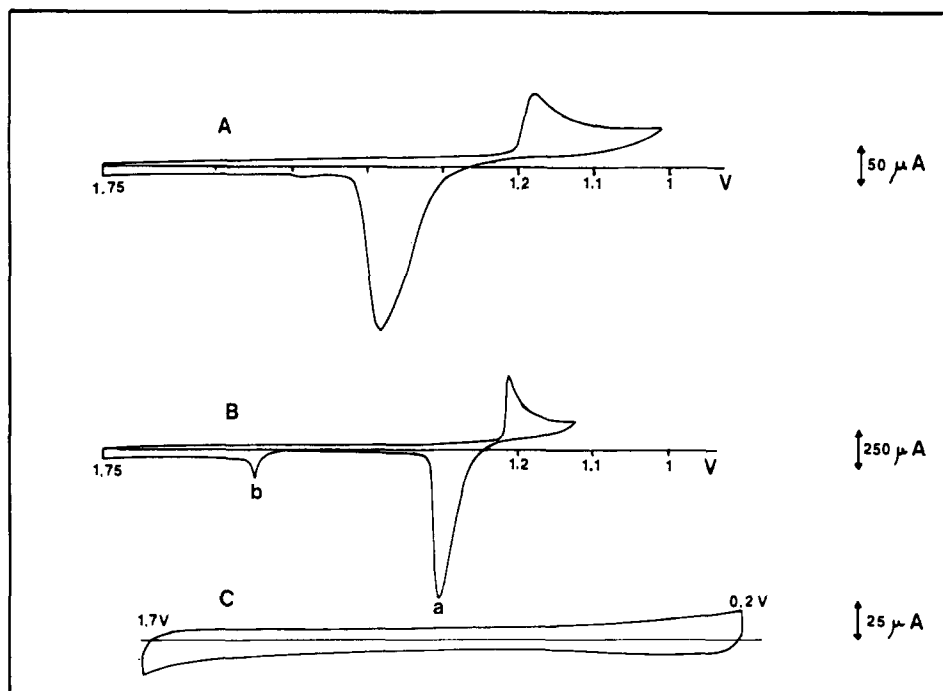
If, starting with a 10<sup>-2</sup> M solution of Ni(II), the pCl is lowered below 5.5 by small additions of NaCl, the reduction wave decreases progressively and finally disappears. A pale yellow precipitate is formed which, according to the work of Tremillon, should be NiO. The color of the precipitate, however, does not correspond to the reported color of NiO (green). In order to characterize the nature of the precipitate, the following experiments have been performed.

(1) By measuring the decrease of height of the Ni(II) reduction wave from cyclic voltammetry at known pCl values, it should be possible to distinguish between NiCl<sub>2</sub> and NiO.

As it will be shown below and in agreement with the first paper of Tremillon about oxide behavior in chloroaluminates,<sup>1</sup> the  $O^{2-}$  ions act as a strong tribase in acidic melt and the following reaction is practically quantitative:



If the solubility product  $K_{sp}$  of the precipitate is given by



**Figure 2.** Cyclic voltammograms obtained from solutions of Ni(II) in acidic melts (pCl 5.6). Glassy carbon electrode, surface area 0.070 cm<sup>2</sup>, scan rate 100 mV s<sup>-1</sup>,  $T = 175\text{ }^{\circ}\text{C}$ . Ni(II) concentration of the solutions: curve A,  $1.215 \times 10^{-3}$  mol kg<sup>-1</sup>; curve B,  $7.3 \times 10^{-3}$  mol kg<sup>-1</sup>; curve C, 0.

**Table I.** X-Ray of the Precipitate (Ni Anodization Experiment)

Precipitate <i>d</i> Found	NiCl <sub>2</sub>		NaAlCl <sub>4</sub> (pCl 3.5)		NiO	
	Found	Lit. <sup>16</sup>	Found	Lit. <sup>17</sup>	Found	Lit. <sup>18</sup>
5.78 (100)	5.76 (100)	5.8 (100)				
5.26 (60)			5.28 (40)	5.3 (50)		
3.56 (40)			3.57 (40)	3.58 (50)		
3.083 (70)			3.09 (100)	3.09 (75)		
2.949 (60)	2.96 (30)	2.96 (40)	2.955 (80)	2.95 (100)		
2.873 (50)			2.879 (80)	2.88 (100)		
2.798 (30)			2.783 (60)			
2.544 (60)			2.539 (100)	2.54 (75)		
2.469 (60)	2.47 (100)	2.48 (100)		2.47 (10)		
					2.405 (40)	2.41 (91)
					2.084 (100)	2.088 (100)
1.760 (30)			1.762 (40)	1.76 (34)		
1.739 (50)	1.736 (60)	1.74 (26)				
1.660 (40)	1.662 (30)	1.666 (12)				
			1.653 (30)	1.64 (10)		
					1.476 (50)	1.476 (54)
					1.258 (30)	1.259 (16)
					1.203 (20)	1.206 (13)
					0.9562 (5)	0.958 (7)
					0.9335 (20)	0.9338 (21)
					0.8525 (10)	0.8527 (17)

$[\text{Ni}][\text{X}]^y = K_{\text{sp}}$  where  $\text{X} = \text{Cl}$  or  $\text{O}$ , a plot of  $\log [\text{Ni}^{2+}]$  with respect to the pCl should have a slope of 2 in case of NiCl<sub>2</sub> and a slope of 3 in case of NiO.

Since Ni(II) ions would react with an Al electrode employed for pCl measurements, the pCl has been measured precisely with an aluminum electrode only after complete precipitation of the insoluble Ni(II) compound. The pCl of the solution can then be calculated from the NaCl added and the amount of chloride consumed by the nickel chloride precipitation. The pCl correction due to NiX<sub>y</sub> precipitation was found to be negligible with respect to the experimental errors.

The resulting plot is indeed a straight line which for an initial Ni(II) concentration of  $7.3 \times 10^{-3}$  mol kg<sup>-1</sup> is defined by the equation

$$\log [\text{Ni}^{2+}] = (-12.81 \pm 0.5) + (1.98 \pm 0.1)\text{pCl} \quad (5)$$

The slope of  $1.98 \pm 0.1$  indicates that the precipitate is most probably NiCl<sub>2</sub>; the corresponding solubility product was found to be  $10^{-12.8}$  (mol kg<sup>-1</sup>)<sup>3</sup> at 175 °C.

(2) In order to confirm this result, the precipitate was filtered under vacuum and an x-ray analysis was performed; in spite of the filtration, it was found very difficult to remove all the solvent and the precipitate was contaminated by NaAlCl<sub>4</sub>. In Table I, the main lines of the precipitate and of the possible components NiCl<sub>2</sub>, NiO, and NaAlCl<sub>4</sub> are summarized. NiCl<sub>2</sub> and NiO give strong patterns and can be distinguished very easily. NiCl<sub>2</sub> is characterized by the line at 5.76 Å and NiO at 2.08 Å. Al<sub>2</sub>Cl<sub>6</sub> also gives a line at 5.8 Å but can be ruled out

Table II<sup>a</sup>

$\eta_{\text{O}^{2-}}$ - added, mol kg <sup>-1</sup>	$\Delta E$ Ni/Al (NaCl-saturated melt), V	$\eta_{\text{O}^{2-}}$ - added, mol kg <sup>-1</sup>	$\Delta E$ Ni/Al (NaCl-saturated melt), V
0	1.220	$5.2 \times 10^{-2}$	1.2225
$1.14 \times 10^{-2}$	1.2205	$8.5 \times 10^{-2}$	1.219
$2.9 \times 10^{-2}$	1.221	$11 \times 10^{-2}$	1.218
$\bar{x} = 1.220 \pm 0.0015$			

by the absence of the 1.71-Å line and also because the presence of  $\text{Al}_2\text{Cl}_6$  in detectable amounts at such a pCl is impossible. Several experiments were performed in which, starting from an acidic melt,  $\text{NiCl}_2$  or  $\text{NiO}$  was dissolved, or Ni was anodized to yield Ni(II) in solution. NaCl was then added to lower the pCl and a precipitate was obtained. In each case, even after  $\text{NiO}$  dissolution, only  $\text{NiCl}_2$  was identified in the precipitate.

Since the bulk precipitate was shown to be  $\text{NiCl}_2$ , it is reasonable to conclude that upon anodization of a Ni electrode in the tetrachloroaluminate melt,  $\text{NiCl}_2$  is formed on the electrode surface. Emf measurements similar to those carried out by Tremillon were performed; the potential at a Ni electrode immersed in the melt for pCl values more basic than pCl 5.5 was determined as a function of pCl. Stable and reproducible measurements were obtained only if the Ni electrodes were anodized slightly prior to use, presumably to obtain a thin layer of  $\text{NiCl}_2$  on the electrode surface. A plot of  $E$  vs. pCl is a straight line which is defined by the equation

$$E = (0.877 \pm 0.005) + (0.090 \pm 0.002)\text{pCl} \quad (6)$$

The slope of the plot is thus 90 mV, compared to the  $2.3RT/F$  value of 89 mV at 175 °C. If the electrode functions as a second-class electrode, i.e., as  $\text{Ni}/\text{NiCl}_2/\text{Cl}^-$ , then the potential of the electrode would be given by

$$E = E^0_{\text{Ni}/\text{Ni}^{2+}} + \frac{2.3RT}{2F} \log K_{\text{spNiCl}_2} + \frac{2.3RT}{2F} 2 \text{pCl} \quad (7)$$

From eq 6 and making use of the  $E^0$  value of  $\text{Ni}/\text{Ni}^{2+}$  of 1.443 V determined in acidic melt as described previously, a  $K_{\text{sp}}$  value of  $\text{NiCl}_2$  can be determined and was found to be  $10^{-13}$  (mol kg<sup>-1</sup>)<sup>3</sup>, which is in excellent agreement with the value of  $10^{-12.8}$  calculated from the cyclic voltammetric data. Thus, the standard potential for the  $\text{Ni}/\text{NiCl}_2/\text{Cl}^-$  couple would be 0.87 V vs. Al. Furthermore, on the basis of the results which will be described in the next paragraph, a straight line in the range of pCl between 1 and 5 cannot be expected if the electrode corresponds to the  $\text{Ni}/\text{NiO}$  system, simply because the nature of the oxide-containing species changes with the pCl.

Finally, oxide ions were added to the melt by dissolution of  $\text{BaCO}_3$ . While  $\text{BaCO}_3$  is completely and quickly solubilized, the dissolution of  $\text{Na}_2\text{CO}_3$  is very slow and always incomplete. Attempts to dry  $\text{Na}_2\text{CO}_3$  at different temperatures (from 25 to 300 °C) did not improve its solubility. No or only partial reaction has also been reported by Sherer<sup>19</sup> and by Letisse and Tremillon<sup>1</sup> for the  $\text{Na}_2\text{CO}_3$  dissolution. The potential of an anodized nickel electrode with respect to the Al reference electrode was then monitored as a function of the oxide concentration.

After each  $\text{BaCO}_3$  addition, the pCl (measured with a separate Al electrode) was readjusted to its initial value by Coulometric anodization of an Al electrode or  $\text{AlCl}_3$  addition. In order to obtain reproducible and stable potential measurements, the large nickel electrode was anodized for 2 s at 10 mA to restore the surface layer after each pCl adjustment. The results are summarized in Table II; the potential was

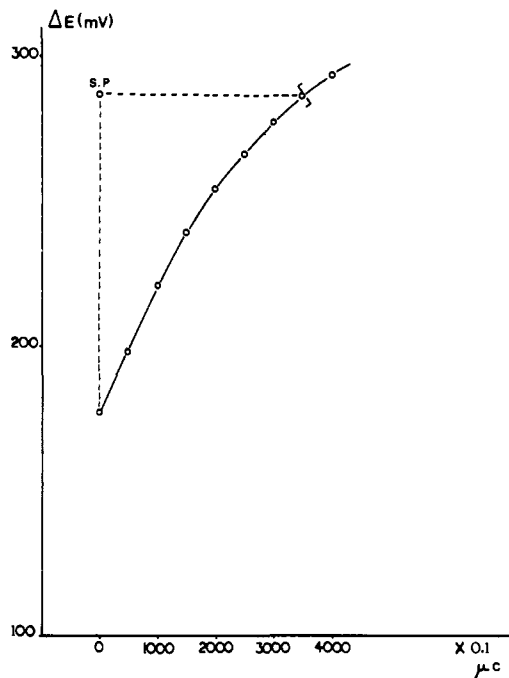


Figure 3. Titration curve of  $\text{O}^{2-}$  in an acidic melt ( $T^0 = 200$  °C). Starting potential (SP) = 286.5 mV (pCl 3.46);  $\eta_{\text{O}^{2-}}$ - added  $156 \times 10^{-6}$  mol;  $\mu\text{C}$  of charge passed through the Al electrode ( $\mu\text{C}$ ) 353;  $\eta$  measured 3.01.

found constant within 2 mV, despite a variation of the oxide concentration of a factor of 10. This is in marked contrast to the behavior reported by Tremillon.

#### Acid-Base Behavior of $\text{O}^{2-}$ Ions in Chloroaluminate Melts.

The preceding results show clearly that the nickel electrode is a good pCl indicator (up to pCl 5) electrode, but is insensitive to the oxide content. As a direct consequence, the oxide ion behavior in chloroaluminate melt which had been proposed<sup>3</sup> was reinvestigated. For instance, it had been assumed that the oxide-containing species  $\text{AlOCl}_2^-$  stays unchanged from pCl 1 to pCl 4 on the basis of the linearity of an emf plot of an anodized nickel electrode vs. pCl.<sup>3</sup> If the precipitate is in fact  $\text{NiCl}_2$ , that conclusion is no longer valid and more accurate measurements of the basicity of  $\text{O}^{2-}$  ions are needed.

Precise titration of  $\text{O}^{2-}$  basic strength has been performed as a function of pCl as follows. The melt was first adjusted to the desired pCl which was continuously monitored with a separate Al electrode. A weighed amount of  $\text{BaCO}_3$  was then added. Because the  $\text{O}^{2-}$  acts as a base, the pCl drops and so does the potential of the monitoring aluminum electrode. When all the  $\text{BaCO}_3$  is completely dissolved, the melt is progressively readjusted to its initial pCl by coulometric anodization of another Al electrode. The resulting titration curves are shown in Figure 3 for an acidic ( $2.85 < \text{pCl} < 3.85$ ) melt and in Figure 4 for a basic ( $2.00 < \text{pCl} < 2.43$ ) melt. From the equivalents of Al oxidized in order to restore the initial pCl exactly, the basic strength of  $\text{O}^{2-}$  ion can be calculated from the following relation:

$$\eta = \frac{\text{equiv of Al} \times 4/3}{\text{equiv of BaCO}_3 \text{ added}} \quad (8)$$

and

$\eta$  = the ratio of number of  $\text{Cl}^-$  ions produced the number of  $\text{O}^{2-}$  added

Because the amount of  $\text{BaCO}_3$  added can be very small ( $\approx 10$  mg), the titration can be performed in narrow pCl ranges and  $\eta$  can be followed as a function of the pCl. Such a procedure is much preferable to a titration of a known amount of

**Table III.** Evolution of  $\eta$  as a Function of pCl

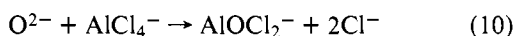
$\eta$	pCl	$\eta$	pCl
3.01	3.46	2.63	2.1
2.99	3.34	2.65	2.03
2.92	2.64	2.48	1.97
2.87	2.61	2.47	1.91
2.73	2.26	2.38	1.84

$\text{Al}_2\text{Cl}_7^-$  by  $\text{O}^{2-}$  addition because the value of  $\eta$  may change drastically along the titration curve and only an average value is obtained.

As it is shown in Table III, the  $\text{O}^{2-}$  ions behave as a tribase as long as the melt is kept acidic. This result is in very good agreement with the first experiments of Tremillon but disagrees with the newest results. When the basicity is increased, the value of  $\eta$  decreases markedly and trends toward 2. Such a behavior is very similar to what has been observed for S, Se, and Te.<sup>2</sup> In the case of oxide ions, however, the pCl range in which such titrations can be performed is limited in the low pCl region by the precipitation, apparently of  $\text{BaCl}_2$ .

In order to explain the decrease of  $\eta$  as a function of pCl, we will retain, as a first hypothesis, the species proposed by Tremillon, i.e.,  $\text{AlOCl}$  and  $\text{AlOCl}_2^-$ , but the range of their existence will be quite different. One also has to remember that electrochemical measurements do not really say very much about the structure of the oxide-containing species, especially about solvation by  $\text{AlCl}_4^-$  and that other methods will be necessary to eventually confirm the proposed species.

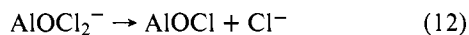
The  $\text{O}^{2-}$  ions may then react with the melt as follows:



with the corresponding equilibrium constants:

$$K_1 = \frac{[\text{AlOCl}][\text{Cl}^-]^3}{[\text{O}^{2-}][\text{AlCl}_4^-]} \text{ and } K_2 = \frac{[\text{AlOCl}_2^-][\text{Cl}^-]^2}{[\text{O}^{2-}][\text{AlCl}_4^-]} \quad (11)$$

In a first step, the dissociation of the oxide-containing species  $\text{AlOCl}$  and  $\text{AlOCl}_2^-$  was supposed negligible or, in other words, the free  $\text{O}^{2-}$  content is very low. The only other equilibrium to consider is then



and

$$K = \frac{K_1}{K_2} = \frac{[\text{AlOCl}][\text{Cl}^-]}{[\text{AlOCl}_2^-]} \quad (13)$$

In this case, the stoichiometric balance can be written as

$$\eta_{\text{O}^{2-}} = [\text{AlOCl}] + [\text{AlOCl}_2^-] \quad (\eta_{\text{O}^{2-}} = \text{mole number of oxide added}) \quad (14)$$

$$\eta_{\text{Cl}^-} = 3[\text{AlOCl}] + 2[\text{AlOCl}_2^-] \quad (\eta_{\text{Cl}^-} = \text{mole number of Cl}^- \text{ produced}) \quad (15)$$

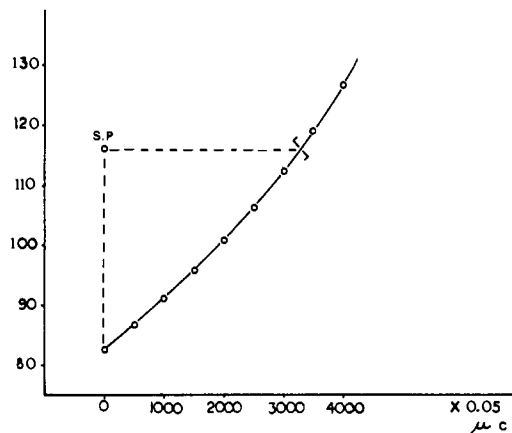
and

$$\eta = \eta_{\text{Cl}^-} / \eta_{\text{O}^{2-}}$$

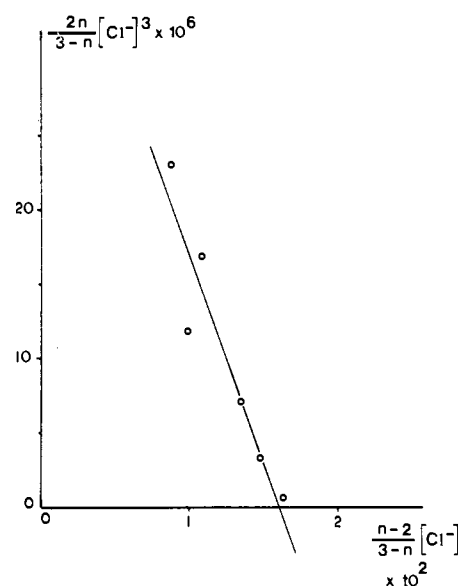
By solving these equations, one obtains

$$\log \left( \frac{3 - \eta}{\eta - 2} \right) = \log [\text{Cl}] - \log K \quad (16)$$

Simple calculations show also that the preceding relation is also valid, whatever the initial oxide content of the melt is. In such a hypothesis, a plot of  $\log \left( \frac{3 - \eta}{\eta - 2} \right)$  as a function of pCl should be a straight line with a slope equal to 1. The experimental results lead indeed to a straight line but the mea-



**Figure 4.** Titration curve of  $\text{O}^{2-}$  in a basic melt ( $T^0 = 200^\circ\text{C}$ ). Starting potential (SP) = 116.0 mV (pCl 2.1);  $\eta_{\text{O}^{2-}}$ -added  $82.6 \times 10^{-6}$  mol;  $\mu\text{equiv}$  of charge ( $\mu\text{C}$ ) 163;  $\eta$  measured 2.63.



**Figure 5.** Plot of  $\left( \frac{2\eta}{3-\eta} \right) [\text{Cl}]^3$  as a function of  $\left( \frac{\eta-2}{3-\eta} \right) \cdot [\text{Cl}]$ .

sured slope is close to 1.5 and the hypothesis made cannot then explain the results.

In a second step, we have assumed that the reactions 9 and 10 are not complete and that some free  $\text{O}^{2-}$  can exist in the solution, most probably in very basic melt. In this case, relation 14 has to include the amount of free oxide:

$$\eta_{\text{O}^{2-}} = [\text{AlOCl}] + [\text{AlOCl}_2^-] + [\text{O}^{2-}] \quad (17)$$

and because that amount comes from the dissociation of  $\text{AlOCl}$  and  $\text{AlOCl}_2^-$ , we can write

$$[\text{O}^{2-}] = \frac{[\text{AlOCl}][\text{Cl}]^3}{[\text{AlCl}_4^-]K_1} + \frac{[\text{AlOCl}_2^-][\text{Cl}]^2}{[\text{AlCl}_4^-]K_2} \quad (18)$$

and

$$\eta_{\text{O}^{2-}} = [\text{AlOCl}] \left\{ 1 + \frac{[\text{Cl}]^3}{K'_1} \right\} + [\text{AlOCl}_2^-] \left\{ 1 + \frac{[\text{Cl}]^2}{K'_2} \right\} \quad (19)$$

with  $K'_1 = K_1[\text{AlCl}_4^-]$  and  $K'_2 = K_2[\text{AlCl}_4^-]$ .

Equation 15 is still valid and the system can be solved and lead to the following relationship:

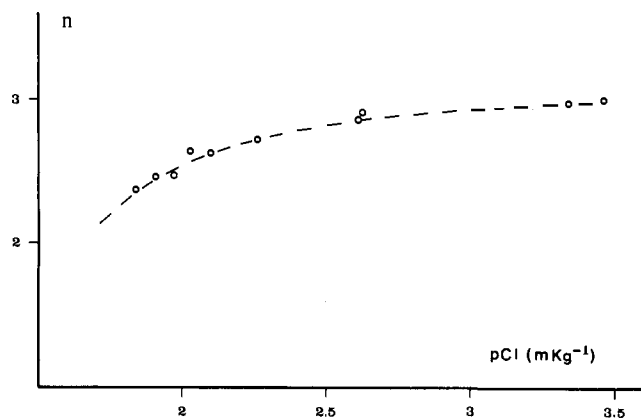


Figure 6.  $\eta$  plot as a function of pCl: O, experimental points; ---, calculated curve from  $\eta = (3K'_1 + 2[Cl]K'_2)/(K'_1 + K'_2[Cl] + 2[Cl]^3)$ .

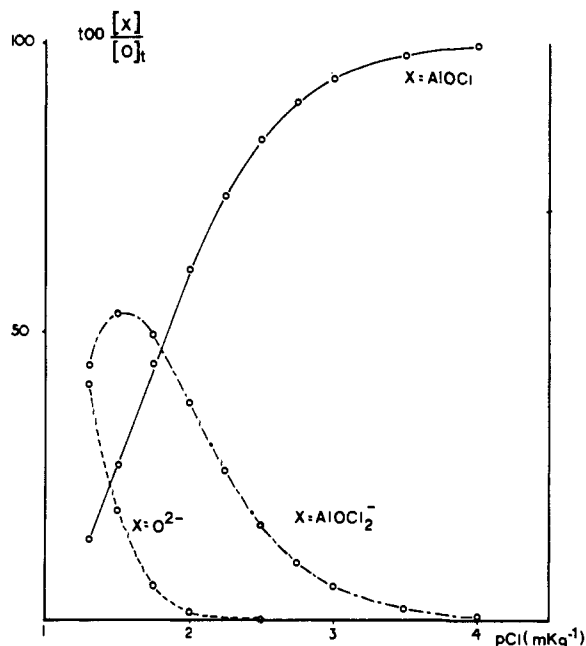


Figure 7. Distribution function of AlOCl, AlOCl<sub>2</sub><sup>-</sup>, and O<sup>2-</sup> as a function of pCl.  $100 ([X]/[O]_t) =$  percentage of the oxide-containing species under the form X.

$$\frac{2\eta}{3-\eta} [Cl]^3 = -K'_2 \left( \frac{\eta-2}{3-\eta} \right) [Cl] + K'_1 \quad (20)$$

A plot of  $(2\eta[Cl]^3)/(3-\eta)$  vs.  $(\eta-2)/(3-\eta)[Cl]$  is shown in Figure 5 and the corresponding values of  $K_1$ ,  $K_2$ , and  $K$  are summarized in Table IV. By using the  $K_1$  and  $K_2$  values, the  $\eta$  plot as a function of pCl can be recalculated in order to check the validity of the hypothesis. The calculated curve is shown in Figure 6 together with the experimental points.

Knowing the stoichiometric constants  $K_1$ ,  $K_2$ , and  $K$ , it is then possible to calculate the distribution of AlOCl, AlOCl<sub>2</sub><sup>-</sup>, and O<sup>2-</sup> as a function of the pCl and this is shown in Figure 7. As one can see, the amount of free O<sup>2-</sup> is only important at very low pCl values and decreases drastically when the pCl is increased. In order to emphasize that effect, we have plotted the  $\log ([O^{2-}]/[O]_{total})$  as a function of pCl (Figure 8). It can be seen that, above a pCl of 3, the quantity  $\log ([O^{2-}]/[O]_t)$  simply corresponds to the relation

$$-\log \frac{[O^{2-}]}{[O]_t} = \log \frac{K_1[AlCl_4^-]}{[Cl]^3} = -4.35 + 3 \text{ pCl} \quad (21)$$

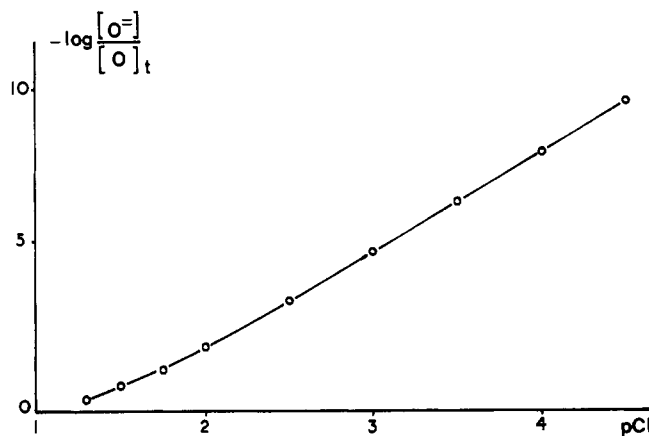


Figure 8. Plot of the fraction of free oxide ions as a function of pCl.

Table IV. Stoichiometric Equilibrium Constants

$K_1 = (8.4 \pm 1.1) \times 10^{-6}$	(mol kg <sup>-1</sup> ) <sup>2</sup>
$K_2 = (5.2 \pm 1) \times 10^{-4}$	(mol kg <sup>-1</sup> )
$K = (1.6 \pm 0.5) \times 10^{-2}$	(mol kg <sup>-1</sup> )

The most important point of these measurements is that, although the precision obtained on the equilibrium constants is not very high, even an error of an order of magnitude will not change the main conclusion that the amount of free oxide ions is definitely very small, especially in acidic melt. For instance, at a pCl of 5, if the total amount of oxides is 10<sup>-2</sup> mol kg<sup>-1</sup>, a solute at a concentration of 10<sup>-3</sup> will only precipitate as an oxide if its solubility product is <10<sup>-15</sup>.

The very high affinity of aluminum for oxygen resulting in a very low free oxide content can then explain why, except for Tremillon's work,<sup>3</sup> no oxide precipitation has been reported in chloroaluminate melt.

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## References and Notes

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