PREDICTION OF THE SELECTIVE CHLORINATION OF OXIDES
BY GASEOUS MIXTURES IN MOLTEN LiCl-KCl EUTECTIC

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ABSTRACT

Ores constituted by mixtures of oxides are among the principal mineral sources of metals. These ores can be treated in molten salts, in order to be transformed in compounds allowing the obtaining of the corresponding metals in an easy way. In particular, it is possible to use gaseous mixtures for the chlorination of oxides in suspension in molten chlorides.

The use of mixtures like HCl + H₂O, HCI + H₂ + H₂O, HCl + CO + H₂, Cl₂ + O₂, Cl₂ + CO or COCl₂ and also Cl₂ + C(s), has been explained in terms of oxidation-reduction and acidity. As an example, molten LiCl-KCl eutectic at various temperatures is considered and selective chlorinations of mixtures of oxides are predicted from potential-pO² diagrams.

INTRODUCTION

The development of metal electrowinning in molten salts has caused an increase in the interest of using these media for the treatment of raw materials (salts or ores), in order to prepare salts for feeding electrolytic cells.

Chlorides are among the most used molten salts; however, oxides are often insoluble in them and, as a consequence, must be transformed into the corresponding soluble chlorides. An interesting way in this aim could consist in selectively chlorinating mixtures of oxides in suspension in molten chlorides.

The purpose of this paper is to show how it is possible to take up this problem, from a thermodynamic point of view.
CHLORINATION REACTIONS AND CHLORINATING REACTANTS

Chlorination reactions.

Chlorination of a metallic oxide corresponds to a reaction of exchange of $O^{2-}$ by $Cl^-$ ions. Thus, for example, the chlorination reaction of an oxide like $MO$ can be written:

$$MO (+ 2Cl^-) \rightleftharpoons MCl_2 (+O^{2-})$$

In order to realize it, it is necessary to provide a donor of $Cl^-$ ions and of an acceptor of $O^{2-}$, or of a compound which would be both a donor of $Cl^-$ and an acceptor of $O^{2-}$. In a chloride melt, the introduction of an oxide gives rise to the equilibrium:

$$MO + 2 (M^+, Cl^-) \rightleftharpoons MCl_2 + M_2O$$

(solid) (melt) (solvated) (solvated)

which can be written in a simpler manner:

$$MO(s) \rightleftharpoons M^{2+} + O^{2-}$$

This equilibrium corresponds to the partial dissolution of $MO(s)$ characterized by the solubility product:

$$K_s(MO) = [M^{2+}][O^{2-}]$$

In order that chlorination may occur this dissolution equilibrium must be shifted towards the formation of metallic ions. In general, the action of the melt is not sufficient (except in the rare cases of soluble oxides for which chlorination is only due to the effects of solvation). We must therefore use a compound called chlorinating agent (or reactant) whose role is to shift the oxide dissolution equilibrium.

Among the most efficient chlorinating mixtures, the oldest to be used is carbon with either chlorine (6) or hydrogen chloride (7). It was proven at the beginning of this century (8) that no oxide can hold out against this method of chlorination. However, it is usable only for the preparation of volatile chlorides for which one does not fear a contamination by the excess of carbon necessary to obtain a complete transformation. In order to overcome this limitation, carbon monoxide (9) and even hydrocarbons (10) have been used instead of carbon. This process is still in use now (11,12).

A widespread method for the preparation of anhydrous chlorides from oxides makes use of volatile carbon-, sulfur- or nitrogen-containing compounds. One of the oldest chlorinations calls for the use of carbon tetrachloride (13). Methyl chloride and chloroform have also been envisaged (14), as well as phosgene (15). Sulfur dichloride and sulfur monochloride with chlorine or not (16,17), as well as thionyl chloride (18), have also been used; above 400°C thionyl chloride is dissociated and the chlorination reaction is similar to...
the one obtained with a $S_2Cl_2 + Cl_2$ mixture. Among the nitrogen compounds, ammonium chloride is one of the most efficient (19); nitrosyl chloride has also been considered sometimes (20).

Ways of action of a chlorinating reactant.

A chlorinating reactant (labelled in the following by CR) can act either as an acid, i.e. an acceptor of $O^{2-}$ (1-4), or as an oxidant, or as both.

A chlorinating reactant which only works as an acid has to be stronger than $M^{2+}$; then, chlorination is reduced to the simple reaction of exchange of oxide ion:

$$MO(s) + acid \rightleftharpoons M^{2+} + base$$

Hydrogen chloride reacts in this way, giving water vapor (as the base).

A chlorinating reactant can also act by oxidizing $O^{2-}$ into oxygen according to the following reaction:

$$MO(s) + Ox \rightleftharpoons M^{2+} + \frac{1}{2} O_2(g) + R$$

which is the sum of the oxide dissolution equilibrium and of the two redox systems:

$$Ox + 2e^- = R$$

and:

$$O^{2-} - 2e^- = \frac{1}{2} O_2(g)$$

Chlorine reacts in this way. Side reactions such as oxidation of the metallic cation to an upper oxidation state can also take place at the same time.

When one deals with very stable oxides, no sufficiently strong acceptor or oxidant of $O^{2-}$ does exist and one must have recourse to compounds or mixtures whose action calls into play both acidity and oxidation-reduction at the same time. This latter method of chlorination brings about multiple chemical reactions which often allow one to obtain the selectivity desired.

Thus, from a thermodynamic point of view, two sorts of data permit one to obtain the knowledge of the reactions for chlorinating metallic oxides in molten chlorides: on the one hand, the solubility products of the oxides, and more generally the dissociation constants of the oxide complexes of metallic cations, and on the other hand, the acid-base constants and redox potentials of the chlorinating reactants under consideration.

Solubility products of oxides as well as acid-base constants of oxide complexes of metallic cations have been the aim of numerous determinations (5). On the contrary, the equilibrium constants of the chlorinating reactants had not yet been determined.
Obtaining of the chlorination equilibrium constants.

In this study, we have only considered the main chlorinating mixtures whose reactions on oxide ion are given in table 1. Only equilibrium constant $K_1$ corresponding to the acidic strength of hydrogen chloride has been experimentally determined at various temperatures (21-23). The log $K_1$ vs T function which results from these experimental values has permitted us to deduce the variation, as a function of temperature, of the equilibrium constants relative to the other chlorinating gases (equilibria (2) to (10), table 1).

The method used consists in comparing the chlorinating strengths of the different gaseous mixtures to that of hydrogen chloride. As an example, constant of equilibrium (3):

$$\text{Cl}_2(g) + O^2- \rightleftharpoons \frac{1}{2} \text{O}_2(g) + 2\text{Cl}^-$$

has been calculated from constant $k_3$ of the Deacon equilibrium:

$$\text{Cl}_2(g) + \text{H}_2\text{O}(g) \rightleftharpoons 2\text{HCl}(g) + \frac{1}{2} \text{O}_2(g)$$

obtained from thermochemical data from the literature (25). We thus obtain:

$$\log K_3 = \log k_3 + \log K_1$$

Analogous calculations for the other chlorinating gaseous mixtures have led to the variations given in table 1.

Comparison of strengths of the chlorinating gaseous mixtures.

Preliminary classification.

The logarithm of the constant of each equilibrium can be expressed as:

$$\log K = pO^2- + \Sigma \log P,$$

an expression in which $\Sigma \log P$ is the algebraic sum of the logarithm of the partial pressures of the gases intervening in the reaction. The strength of a chlorinating mixture is related to the $pO^2-$ value which it can impose. A classification is thus possible by comparing the logarithms of the constants of equilibria (1) to (10).

Figure 1, which represents the variations of these constants as a function of temperature, brings to the fore three groups of mixtures of increasing strengths: (i) Equilibria (1), (2) and (3) correspond to the weakest chlorinating mixtures; (ii) equilibria (9) and (10) (containing sulfur and chlorine) correspond to mixtures of intermediate strengths; (iii) equilibria (4) to (8) correspond to the most powerful chlorinating mixtures.

In the following we shall only consider the most currently employed chlorinating mixtures, belonging to the first and third groups.
Potential-pO$_2^-$ domains of action of some chlorinating gaseous mixtures.

We have seen that the chemical action of these mixtures implies in general the intervention of acid-base and oxidation-reduction properties, so that it can be represented in the potential-pO$_2^-$ diagram as it will be shown through the following example.

A Cl$_2$ + O$_2$ mixture imposes a pO$_2^-$ value given by:

\[ pO_{2^-} = \log K_3 + \log P(Cl_2) - \frac{1}{2} \log P(O_2) \]

In the potential-pO$_2^-$ diagram (fig. 2), this value is the abscissa of the point of intersection of the straight lines representative of the two electrochemical systems Cl$_2$(g)/Cl and O$_2$(g)/O$_2^-$. It characterizes the chlorinating strength of the mixture: the higher this value is, the greater the chlorinating strength. Moreover, the mixture imposes a potential value (which characterizes its oxidizing strength) given by:

\[ E = \frac{2.3RT}{2F} \log P(Cl_2) \]

These potential and pO$_2^-$ values depend on the partial pressures of the different gases. In fig. 2, points corresponding to two compositions [mixture M$_1$: Cl$_2$(0.1 atm) + O$_2$(10$^{-2}$ atm) + inert gas; mixture M$_2$: Cl$_2$(0.5 atm) + O$_2$(0.5 atm)] have been represented.

By making the partial pressures vary, between definite limits, a domain of potential and pO$_2^-$ can be covered by means of one type of mixture. In fig. 2, we have chosen arbitrarily the upper limit of 1 atm for the total pressure and the lower limit of 10$^{-3}$ atm for each component.

For each of the gaseous mixtures we have considered, such domains have been calculated by using data from tables 1 and 2; they are represented in fig. 3a and 3b, for the temperatures of 723 K and 1023 K.

HCl + H$_2$O mixtures fix the pO$_2^-$ but not the potential, which can be imposed by the addition of hydrogen. HCl + CO + H$_2$ mixtures have an oxidizing power close to the HCl + H$_2$O + H$_2$ mixtures, but a greater chlorinating strength. Chlorine (whether or not in the presence of oxygen) alone possesses a weak chlorinating strength, whereas, in the presence of carbon, it leads to the greatest chlorinating action (like phosgene).

PRINCIPLE OF CONCEIVING A SELECTIVE METHOD OF CHLORINATION

As an example we shall consider the chlorination of a mixture of iron, titanium, aluminium and silicon oxides in molten LiCl-KCl at 743 K. Such a case can correspond to practical applica-
tions concerning the treatment of aluminum and titanium ores.

The reactions of aluminum and iron chlorides with $O^2-$ ion have been studied experimentally. The solubility products and other acid-base constants in molten LiCl-KCl have been determined by titrations followed by means of an yttria-stabilized zirconia membrane electrode indicator of $pO_2$ (15,26-29). Similar constants for titanium and silicon have been deduced from literature data (25,30). The potential-$pO_2^-$ diagrams so obtained are given in fig. 4.

The simple superimposition of each of these diagrams with the one representing the reactivity domains of the chlorinating gaseous mixtures demonstrate which mixtures are capable of chlorinating one particular oxide, and consequently show a method appropriate to selectively chlorinate the mixture of oxides.

From the iron diagram, for example, it can be noticed that all the iron oxides can be easily chlorinated by all the chlorinating mixtures, with the one restriction that chlorine-oxygen mixtures must have a sufficiently weak oxygen partial pressure. Moreover the reducing mixtures HCl + H$_2$O + H$_2$ and HCl + CO + H$_2$ lead to chlorination of ferric oxide into ferrous chloride and not into (volatile) ferric chloride as with the other mixtures.

Titanium dioxide is a more stable oxide than Fe$_2$O$_3$, so that the HCl + H$_2$O mixture (with H$_2$ or not) and the Cl$_2$ + $O_2$ mixture will be inefficient on it. Only the HCl + CO + H$_2$ mixture (at an appropriate composition) and the Cl$_2$ + CO mixture (or COCl$_2$) are able to extract the volatile tetrachloride TiCl$_4$.

Concerning aluminum and considering only $\alpha$-alumina, its chlorination can take place through the action of chlorine in presence of carbon or of carbon monoxide, or through the action of phosgene.

Finally silica, which is the most stable oxide, can only be chlorinated by using the Cl$_2$ + CO mixture, or phosgene.

To sum up, a selective chlorination process of the oxide mixture can be the following. Ferric oxide can be chlorinated at first by HCl, then TiO$_2$ by a HCl + CO + H$_2$ mixture at a suitable composition (i.e. not corresponding to the highest chlorinating power in order to avoid chlorination of alumina). Finally aluminum trichloride and silicon tetrachloride can be obtained with chlorine and carbon monoxide mixtures (aluminum and silicon chlorides are then separable by a fractional condensation).

CONCLUSION

By consideration of potential-$pO_2^-$ diagrams it appears possible to predict the thermodynamic conditions which have to be satisfied in order to realize the selective chlorination of mixtures.
of various oxides in suspension in molten chlorides, by means of
gaseous chemical agents. Obviously this estimated approach has to be
completed by experimental kinetical studies (31,32).

Such a method can also be applied to investi-
gate the possibility of separation by selective precipitation. In fact,
the way of reasoning, here described, demonstrates the interest of the
potential-pO₂ diagrams as a very useful tool to conceive, in a more
general manner, any chemical process of metallurgical treatment of ores
in molten salts.

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Table 1 - Values of constants $K$ of some chlorination equilibria in molten LiCl-KCl eutectic (concentrations in mol kg$^{-1}$, pressures in atm, $T$ in Kelvins).

| CHLORINATION EQUILIBRIA | log $K = A \cdot 10^B \cdot T^{-1}$ |
|--------------------------|-----------------------------------|
| (1) $\text{HCl}(g) + O^2- \rightleftharpoons \text{H}_2\text{O}(g) + 2\text{Cl}^-$ | $A$ | $B$ |
| (2) $\text{HCl}(g) + \text{CO(g)} + O^2- \rightleftharpoons \text{CO}_2(g) + \text{H}_2\text{O(g)} + 2\text{Cl}^-$ | -3.477 | 9.980 |
| (3) $\text{Cl}_2(g) + O^2- \rightleftharpoons \frac{1}{2} \text{O}_2(g) + 2\text{Cl}^-$ | -5.264 | 11.88 |
| (4) $\text{Cl}_2(g) + \text{CO(g)} + O^2- \rightleftharpoons \text{CO}_2(g) + 2\text{Cl}^-$ | -2.651.10^{-2} | 6.912 |
| (5) $\text{COCl}_2(g) + O^2- \rightleftharpoons \text{CO}_2(g) + 2\text{Cl}^-$ | -4.583 | 21.62 |
| (6) $\text{Cl}_2(g) + \frac{1}{2} \text{C(s)} + O^2- \rightleftharpoons \frac{1}{2} \text{CO}_2(g) + 2\text{Cl}^-$ | 2.465 | 15.01 |
| (7) $\text{Cl}_2(g) + \text{C(s)} + O^2- \rightleftharpoons \text{CO}_2(g) + 2\text{Cl}^-$ | 2.086.10^{-2} | 17.14 |
| (8) $\frac{1}{2} \text{CCl}_4(g) + O^2- \rightleftharpoons \frac{1}{2} \text{CO}_2(g) + 2\text{Cl}^-$ | 4.603 | 12.68 |
| (9) $\text{SOCl}_2(g) + O^2- \rightleftharpoons \text{SO}_2(g) + 2\text{Cl}^-$ | 3.503 | 14.77 |
| (10) $\frac{1}{4} \text{S}_2\text{Cl}_2(g) + \frac{3}{4} \text{Cl}_2(g) + O^2- \rightleftharpoons \frac{1}{2} \text{SO}_2(g) + 2\text{Cl}^-$ | -0.3999 | 14.48 |

Table 2 - Equilibrium potential expressions and standard potential values (in V vs standard chlorine electrode), as a function of temperature $T$ (in K), for some electrochemical systems in molten LiCl-KCl eutectic (concentrations in mol kg$^{-1}$ and pressures in atm).

| Electrochemical systems | Equilibrium potentials | Standard potentials $E^\circ = A + B \cdot 10^{C \cdot T}$ |
|-------------------------|------------------------|---------------------------------------------------------|
| $\text{H}_2(g) + 2e^- + 2\text{Cl}^-$ $\rightleftharpoons 2\text{HCl(g)}$ | $E = E^\circ + 2.3 RT \cdot F^{-1} \cdot \log P(\text{HCl}) - 2.3 RT \cdot 0.5 F^{-1} \cdot \log P(\text{H}_2)$ | $A$ | $B$ |
| $\text{H}_2(g) + 2e^- + \text{O}_2 \rightleftharpoons \text{H}_2\text{O}(g)$ | $E = E^\circ + 2.3 RT \cdot 0.5 F^{-1} \cdot \log \frac{P(\text{H}_2\text{O})}{P(\text{H}_2)} + 2.3 RT \cdot 0.5 F^{-1} \cdot \log \frac{P(\text{O}_2)}{P(\text{H}_2)}$ | -0.977^6 | -67.27 |
| $\text{O}_2(g) + 2e^- \rightleftharpoons 2\text{O}^-$ | $E = E^\circ + 2.3 RT \cdot 0.5 F^{-1} \cdot \log \frac{P(\text{O}_2)}{P(\text{H}_2)}$ | -1.466 | 281.9 |
| $\text{C(s)} + 2e^- + 2\text{Cl}^-$ $\rightleftharpoons \text{C} + 2\text{Cl}^-$ | $E = E^\circ + 2.3 RT \cdot 0.5 F^{-1} \cdot \log P(\text{Cl}_2) + 2.3 RT \cdot 0.5 F^{-1} \cdot \log P(\text{C})$ | -0.639 | 3.48 |
| $\text{CO}_2(g) + 2e^- \rightleftharpoons 2\text{CO}_2$ | $E = E^\circ + 2.3 RT \cdot 0.5 F^{-1} \cdot \log P(\text{CO}_2)$ | -1.709 | -2.66 |
| $\text{CO} + 2e^- \rightleftharpoons 2\text{CO}_2$ | $E = E^\circ + 2.3 RT \cdot 0.5 F^{-1} \cdot \log P(\text{CO}_2)$ | -2.146 | -659.6 |
| $\text{CO}_2(g) + 2e^- + \text{O}_2 \rightleftharpoons 2\text{CO}_2$ | $E = E^\circ + 2.3 RT \cdot 0.5 F^{-1} \cdot \log P(\text{CO}_2) + 2.3 RT \cdot 0.5 F^{-1} \cdot \log P(\text{O}_2)$ | -657.0 | 702.0 |

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Fig. 1. - Constants of chlorination equilibria corresponding to various gaseous mixtures in molten LiCl-KCl (see table 1).
1: HCl + H₂O; 2: HCl + CO + H₂; 3: Cl₂ + O₂;
4: Cl₂ + CO; 5: COCl₂; 6-7: Cl₂ + C (s);
8: CCl₄; 9: SOCl₂; 10: S₂Cl₂ + Cl₂

Fig. 2. - Potential-pO²⁻ domain of Cl₂ + O₂ mixtures in molten LiCl-KCl at 743 K.
Fig. 3.- Potential–pO$_2$- domains of various gaseous mixtures in molten LiCl–KCl eutectic at 743K (a) and 1023 K (b)

I : Cl$_2$ + O$_2$  
II : Cl$_2$ + CO  
III : Cl$_2$ + C(s)  
IV : HCl + H$_2$O  
V : HCl + H$_2$O + H$_2$  
VI : HCl + CO + H$_2$
Fig. 4.- Chlorination by various gaseous mixtures in molten LiCl-KCl at 743 K.