Application of an Atmospheric Pressure Sampling Mass Spectrometer to Chlorination Reactions

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APPLICATION OF AN ATMOSPHERIC PRESSURE SAMPLING MASS
SPECTROMETER TO CHLORINATION REACTIONS

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SUMMARY

An atmospheric pressure mass spectrometric sampling system, based on a free jet expansion has been used to study certain M-Cl-O reactions at high temperatures. This apparatus enables the volatile species from a 1-atm chemical process to be directly identified with a mass spectrometer which operates at ~10^-8 torr. Studies for both pure metals and alloys are discussed. It is shown that this mass spectrometer system not only aids in identifying the volatile species, but also provides fundamental information on the reaction mechanism.

INTRODUCTION

The formation of volatile metal chlorides is important in a variety of metallurgical and chemical processes. Numerous stable metal chlorides and oxychlorides are known to exist (refs. 1 to 4). Some extractive metallurgical processes involve the production of metal chlorides as intermediates (ref. 5). Numerous chemical processes release chlorine or hydrogen chloride as a byproduct (ref. 6). Thus chlorine corrosion of the reactor vessel can be a problem. In most cases the chlorine containing gas is one component of a complex gas mixture. There is only limited laboratory work directed at understanding these processes on a fundamental level. Difficulties arise in identifying the volatile species and understanding the complex kinetic behavior. The purpose of this paper is to illustrate the use of an atmospheric pressure sampling mass spectrometer as a tool to help elucidate the chemistry involved.

One of the most commonly used methods of identifying high temperature vapors is a mass spectrometer (ref. 7). Measurements are taken in-situ and generally the peaks are easily identified. However a mass spectrometer must operate at pressures of 10^-6 torr or less. Most chlorination processes occur at 1 atm or greater. Reducing the total pressure in a laboratory study may alter the fundamental nature of the processes involved. Therefore, a method is needed to introduce in-situ a sample of the gaseous product/reactant mixture to a mass spectrometer, while preserving the chemical integrity of that mixture.

A method using the technique of a free-jet expansion meets this requirement and has been discussed by numerous investigators (refs. 8 to 11). It will only be briefly summarized here. When a high pressure source gas is allowed to pass through a small orifice into a low pressure region, it undergoes a rapid expansion. Generally the mean free path of the gas is much greater than the diameter of the orifice and flow in the continuum regime is maintained on the downstream side of the orifice. However the velocity vectors of these
molecules tend to be more aligned and an abrupt transition to collisionless, directed flow occurs at a specific distance from the orifice. This is shown schematically in figure 1. In order to achieve collimation and higher beam intensity, a collimating cone or skimmer is placed downstream from the orifice typically after the transition to collisionless flow. A second collimator is placed after the skimmer and directs the molecular beam into the ion source of the mass spectrometer.

A free jet expansion should preserve the chemical integrity of the source gas. However there are certain difficulties (ref. 9) which the experimenter must be aware of when interpreting the results. One problem is cluster formation. After expansion the beam undergoes rapid cooling and molecules may coalesce to form clusters. The mass spectrum of laboratory air often shows water clusters (ref. 10). Another problem is clogging of the expansion orifice by condensable vapors. This orifice is typically a very small opening (0.022 cm diameter) and is difficult to keep hot enough to avoid condensation. A third difficulty results from the sensitivity of the instrument. The mass spectrometer will detect trace impurities in the reaction gases. An example is oxygen, which often shows peaks corresponding to xenon. It is important to separate these peaks from the product species of interest. Finally it should be noted that the peak intensities only semi-quantitative -- they are not simply related to vapor pressures. This is because the expansion characteristics and fragmentation patterns are different for each specie and generally unknown. Nonetheless the mass spectra does show what species are evolving from the sample and some general trends in intensities can be noted.

Figure 2 shows the experimental set-up for the metal-chlorine reaction and method of introducing the vapors into the sampling orifice. This assembly consists of a quartz reaction tube in a small tube furnace which is directly adjacent to the sampling orifice. The metered reaction gases were admitted at the bottom of the tube and allowed to flow up and escape around the orifice. The entire reaction furnace assembly and sampling cone flange are surrounded by a sheet metal enclosure connected to an exhaust pipe to remove the exhaust gases. Solid sample coupons were introduced into the hot zone by the push rod shown in figure 2. Initially the metal coupon was hooked onto the push rod and the sample pulled into the reactor tube cold zone below the furnace. Then the furnace was positioned up against the sampling cone and the reaction gases were passed through the tube. Moving the coupon up into the hot zone and adjacent to the thermocouple initiated the high temperature reaction. In a typical experiment several mass scans were taken with the gases flowing and the furnace hot -- some scans with the sample in the hot zone and some with the sample in the cold zone. Comparing these spectra clearly established which peaks were due to volatile species from the sample.

The peaks were identified from both the mass-to-charge ratio and the isotopic distribution, which is quite distinctive for chlorine containing molecules. Actual distributions were compared to those calculated from an isotopic distribution computer program (ref. 12) for a particular molecule. Ion intensities were calculated from the following expression (ref. 7):

$$I = \frac{V}{\sigma R_Y}$$  \hspace{1cm} (1)
Here $V$ is the sum of the voltage peaks for each of the major isotopes, $\sigma$ is the ionization cross section, calculated from the additivity rules (ref. 13). $R$ is the resistor across which $V$ is measured, and $\gamma$ is the gain of the instrument. Metal chloride and metal oxychloride peaks are normalized to $I(\text{Cl}_2)$ or $I(\text{HCl}^+)$, depending on the reactive gas used.

One would expect that chlorination of various metals would produce many volatile chlorides. Indeed, a stable chloride might be expected for each oxidation state of a particular metal. Figure 3 lists some volatile chlorides and oxychlorides which have been observed for the transition metals (refs. 1 to 4). These are only vapors for which thermodynamic data is readily available. It is not intended to be an exhaustive list, but rather a general indication of what molecules have been observed. Nonetheless some interesting trends are evident. As expected, metals with multiple oxidation states have several stable chlorides. In some cases dimers were observed. Note also that oxychlorides have been observed for Al, Ti, Cr, Mo, and W. These are metals with known volatile oxides (ref. 1). Other oxychlorides may exist but there is not information readily available on them.

In what follows results presented for several studies of specific systems with emphasis on the studies performed at NASA Lewis. Atmospheric pressure mass spectrometric sampling aided in understanding the reactions involved.

**Cobalt + Cl$_2$-O$_2$ Mixtures at 650 °C**

The reaction of 1, 10, and 50% O$_2$/1% Cl$_2$/Ar has recently been studied by Jacobson, McNallan, and Lee (ref. 14). In this study kinetic data and morphology information are correlated with mass spectrometric data. Table I lists the principal ion intensities-normalized to Cl$_2^+$. There are several important points relative to this table. First, thermodynamic calculations indicates that CoCl$_2$(g) and CoCl$_3$(g) are the principal vapor species expected for this system; CoCl and Co$_2$Cl$_4$ are not formed in any appreciable quantities. The ions listed in table I very likely result from CoCl$_2$(g) and CoCl$_3$(g) with CoCl$^+$ being a fragment ion. The important point to note from table I is that the quantities of CoCl$_2$(g) and CoCl$_3$(g) do not show a strong dependence on oxygen partial pressure. This yields some information on the primary reaction occurring. Clearly, if the chlorine reacts with the metaloxide, the intensity of CoCl$_2$ would decrease with increasing P$_{O_2}$:

$$\text{Co}_3\text{O}_4 + 3\text{Cl}_2 = 3\text{CoCl}_2 + 2\text{O}_2 \quad P_{\text{CoCl}_2} = \left(\frac{K_P^3}{P_{\text{Cl}_2}}\right)^{1/3}$$

(2)

This does not occur and the initial reaction appears to be the reaction of Cl$_2$ with the metal. An examination of a section of scale which had cracked or spalled reveals a microstructure which corroborates this explanation (fig. 4 and 5). The scale appears to consist of an outer layer of oxide over
condensed cobalt chloride which forms on the metal. The stable condensed phase chlorine is CoCl₂(s) and thus a likely reaction scheme is:

\[
\begin{align*}
\text{Co} + \text{Cl}_2 &= \text{CoCl}_2(s) \\
\text{CoCl}_2(s) &= \text{CoCl}_2(g) \\
\text{CoCl}_2(s) + \frac{1}{2} \text{Cl}_2(g) &= \text{CoCl}_3(g)
\end{align*}
\]

As this occurs an oxide grows above the CoCl₂(s).

During a run the ion intensities decayed dramatically for the first 15 min. This is shown with thermogravitmetric kinetic curves in figure 6. These curves show that the 10 and 50% O₂/1% Cl₂/Ar mixtures have similar behavior as pure oxidation. However the 1% O₂/1% Cl₂/Ar shows continuous volatilization at a rate close to that calculated for mass transfer of CoCl₂(g) from a flat plate. These results suggest that in the high oxygen cases the intensity decay is due to a thick oxide scale overgrowing and stopping the transport of cobalt chlorides out or chlorine in. In the low chlorine case, the continuous volatilization observed in the kinetic curves indicates that a porous oxide scale must be above the CoCl₂(s). The observed decay of mass-spectral ion intensities was found to be due to clogging of the sampling orifice in the low oxygen case.

In summary, the atmospheric pressure sampling mass spectrometer not only identified the principal vapor species of the reaction, but also helped elucidate the fundamental reaction mechanism.

Iron + HCl - O₂ Mixtures

The reaction of pure iron and 0 to 50% O₂/1% HCl/Ar mixtures at 550 °C has recently been studied by the author (ref. 15). Table II lists the major results in this case. As in the cobalt case, the principal vapor species can be inferred from this data and known volatile iron chlorides. Thus it appears that the principal vapor species for the 1% HCl/Ar case is FeCl₂, whereas the oxygen containing gases also produce FeCl₃. Free energy calculations for the compounds in their standard states clearly suggest that the presence of oxygen is necessary for the formation of FeCl₃(g):

\[
\begin{align*}
\text{Fe} + 3\text{HCl}(g) &= \text{FeCl}_3(g) + \frac{3}{2} \text{H}_2(g) \quad \Delta G = 60.7 \text{ kJ/mol} \\
\text{Fe} + 3\text{HCl}(g) + \frac{3}{4} \text{O}_2 &= \text{FeCl}_3(g) + \frac{3}{2} \text{H}_2\text{O} \quad \Delta G = -242.8 \text{ kJ/mol}
\end{align*}
\]

These conclusions are in agreement with other investigators (ref. 16) who predict the presence of FeCl₃(g) in oxidizing environments.

Figure 7 is a stability diagram for the condensed phases under O₂-Cl₂ mixtures. This diagram shows that a stable condensed iron chloride can only exist in a region of low oxygen potential. Thus one expects a situation
similar to that observed in the Co-O-Cl case where the metal chloride forms below the oxide in a region with a low oxygen potential. Peeling away the oxide and exposing a region of the metal showed that the iron chloride forms as patches below the oxide scale (fig. 8). This is consistent with the fact that the ion intensities show no clear dependence on the partial pressure of oxygen. The oxide scales also seemed to be very poorly adherent, which may be a consequence of iron chloride at the oxide/metal interface.

Silicon, Silica + HCl

This system was studied by Lin (ref. 17) with an instrument at AMMRC. He reports a number of interesting results. For SiO$_2$ a reaction only occurs at $T > 1250$ °C and the principal vapor species are SiCl$_2$ and SiCl$_3$. Although SiCl$_4$ is predicted to be the most abundant thermodynamically, it is only observed in very small quantities. The author concludes that there may be kinetic limitations to the formation of SiCl$_4$. In the case of pure silicon, a reaction occurs more readily – producing SiCl$_4$ as the major species. The lower chlorides may become important at higher temperatures.

Aluminum + Cl$_2$

This reaction was also studied by Lin (ref. 18) in the context of a larger study to examine the CVD (chemical vapor deposition) of alumina. He observes a number of species: AlCl, AlCl$_3$, and Al$_2$Cl$_6$. Above 1000 °C AlCl is the dominant species. This observation coupled with the observation of other species in the CVD process, suggests the primary reaction for deposition of alumina is:

$$2\text{AlCl}(g) + \text{H}_2\text{O}(g) + \text{O}_2(g) = \text{Al}_2\text{O}_3(s) + 2\text{HCl}(g)$$  \hspace{1cm} (5)

Reaction of Chromia Formers with Cl$_2$

Thus far only pure metals have been examined. However, the actual systems used in Cl$_2$ or HCl containing environments are usually involve complex alloys. Alloys which form a dense protective chromia layer often offer good resistance to harsh chemical environments. However this oxide may volatilize to CrO$_3$ at temperatures >1000 °C. Figure 9 shows the vapor pressure of CrO$_3$(g) (ref. 19) formed by the reaction

$$\text{Cr}_2\text{O}_3(s) + \frac{3}{2} \text{O}_2(g) = 2\text{CrO}_3(g)$$  \hspace{1cm} (6)

The pressure of oxygen is taken as 1 atm. Figure 9 also shows the vapor pressure of CrO$_2$Cl$_2$(g) (ref. 3) formed by:

$$\text{Cr}_2\text{O}_3(s) + 2\text{Cl}_2(g) + \frac{1}{2} \text{O}_2(g) = 2\text{CrO}_2\text{Cl}_2(g)$$  \hspace{1cm} (7)

The pressure of oxygen is taken as 1 atm and chlorine as 0.01 atm. Note how the small amount of chlorine enhances the volatility of chromia – especially at the lower temperatures. This is similar to the effect of water vapor,
which enhances the volatility of chromia by forming \( \text{Cr}_2\text{O}_3(\text{OH})_x \) (g) (refs. 19 and 20).

Two chromia forming alloys were examined (ref. 21) — Alloy 600\(^1\) (N1-8% Fe-16% Cr) and Hastelloy S\(^1\) (N1-3% Fe-15.5% Cr-14.4% Mo). Both were preoxidized for 2 hr in flowing oxygen (0.88 cm/sec). Then they were reacted with 1% \( \text{Cl}_2 \)-50% \( \text{O}_2 \)-Ar (1.75 cm/sec) at 850 °C. A second set of samples was preoxidized and reacted with the same gas mixture at 900 °C. Both alloys seemed to release a constant amount of volatile species — this is corroborated by the thermogravimetric data (ref. 22) which shows linear weight losses. The peaks listed in tables III and IV were measured in the first 15 min of reaction. As expected both alloys show clear evidence of \( \text{Cr}_2\text{O}_3\text{Cl}_2 \) (g). Hastelloy S also shows \( \text{MoO}_2\text{Cl}_2 \) (g), which is also expected since this alloy contains a large percentage of molybdenum and \( \text{MoO}_2\text{Cl}_2 \) (g) is a very stable molecule (ref. 22). However, the major difference is that the Hastelloy S produces a large amount of \( \text{NiCl}_2 \) (g). An analysis of the deposit on the sampling orifice after an experiment showed it contained large amounts of nickel. This very likely explains TGA results (ref. 22), which show Hastelloy S corrodes several times faster in \( \text{Cl}_2\text{-O}_2 \) mixtures than Alloy 600. Apparently the chromia scale formed on Hastelloy S is less protective than the chromia scale formed on Alloy 600. Current work is under way to understand this further.

**CONCLUSIONS**

An atmospheric pressure mass spectrometric sampling system has been described. This type of instrument can directly sample high temperature vapors from a corrosion process occurring at 1 atm and therefore is ideally suited for studying the reactions of metals with chlorine and hydrogen chloride. A large number of volatile chlorides can potentially form. In the case of cobalt and iron in chlorination-oxidation atmospheres, condensed phase chlorides form below the oxide scale and then volatilize. In the case of chromia forming alloys, the protective chromia layer appears to volatilize by formation of \( \text{Cr}_2\text{O}_3\text{Cl}_2 \) (g). In each case, it is shown that the mass spectrometer not only helps identify the volatile species, but also can provide some insights into fundamental reaction mechanisms.

**REFERENCES**


\(^1\)Cabot Corporation, Kokomo, Indiana.


21. Jacobson, N. S.; McNallan, M.J.; and Fox, D.S.: NASA Lewis Research Center, Cleveland, OH research in progress, to be published.

### TABLE I. - MASS SPECTROMETER INTENSITIES FOR COBALT + Cl₂/O₂/Ar

<table>
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<tr>
<th>Gas mixture</th>
<th>I(CoCl⁺)/I(Cl₂⁺)</th>
<th>I(CoCl₂⁺)/I(Cl₂⁺)</th>
<th>I(CoCl³⁺)/I(Cl₂⁺)</th>
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<tr>
<td>1% O₂/1% Cl₂/Ar</td>
<td>1.1x10⁻³</td>
<td>1.2x10⁻³</td>
<td>1.2x10⁻⁴</td>
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<td>10% O₂/1% Cl₂/Ar</td>
<td>1.5x10⁻³</td>
<td>1.7x10⁻³</td>
<td>1.9x10⁻⁴</td>
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<tr>
<td>50% O₂/1% Cl₂/Ar</td>
<td>1.3x10⁻³</td>
<td>1.4x10⁻³</td>
<td>1.2x10⁻⁴</td>
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### TABLE II. - MASS SPECTROMETER INTENSITIES FOR IRON + HCl/O₂/Ar

<table>
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<tr>
<th>Gas mixture</th>
<th>I(FeCl⁺)/I(HCl⁺)</th>
<th>I(FeCl₂⁺)/I(HCl⁺)</th>
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<tr>
<td>1% HCl/Ar</td>
<td>7.9x10⁻⁴</td>
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<td>1% O₂/1% HCl/Ar</td>
<td>9.1x10⁻⁵</td>
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<tr>
<td>10% O₂/1% HCl/Ar</td>
<td>6.7x10⁻⁵</td>
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<td>50% O₂/1% HCl/Ar</td>
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### TABLE III. - ALLOY 600

(a) React with 1% Cl₂-50% O₂-Ar at 850 °C

<table>
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<tr>
<th>Mass/charge number of major peak</th>
<th>Probable ion specie</th>
<th>I(MOₓClʸ⁺)/I(Cl₂⁺)</th>
<th>Probable parent vapor specie</th>
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<tr>
<td>103</td>
<td>CrOCl⁺</td>
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<td>119</td>
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<td>154</td>
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(b) React with 1% Cl₂-50% O₂-Ar at 900 °C

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<th>Mass/charge number of major peak</th>
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<th>I(MOₓClʸ⁺)/I(Cl₂⁺)</th>
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### TABLE IV. - HASTELLOY S

(a) React with 1% Cl₂-50% O₂-Ar at 850 °C

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<th>Mass/charge number of major peak</th>
<th>Probable ion specie</th>
<th>( \frac{I(\text{MO}_x\text{Cl}_y^+)}{I(\text{Cl}_2^+)} )</th>
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<td>165</td>
<td>MoO₂Cl⁺</td>
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(b) React with 1% Cl₂-50% O₂-Ar at 900 °C

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Figure 1. - Schematic of atmospheric pressure sampling apparatus, based on a free jet expansion.

Figure 2. - Schematic of reactor.
**REFERENCES**

1. JANAF TABLES, 1978
2. DANIEL AND RAPP, 1976
3. SANO AND BELTON, 1974
4. PANKRATZ, 1984

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<th>AuCl3</th>
<th>Hg</th>
<th>HgCl</th>
<th>Te</th>
<th>TeCl2</th>
<th>Pb</th>
<th>PbCl</th>
</tr>
</thead>
</table>

**Figure 3.** Volatile chlorides and oxychlorides.
Figure 4. - Cobalt specimen surface and elemental maps after 15 min exposure to 1\% O_2-1\% Cl_2-Ar (ref. 14).
Figure 5. - Cobalt specimen surface and elemental maps after 15 min exposure to 50% $O_2$-1% $Cl_2$-Ar.
Figure 6. - Kinetics for the reaction of cobalt with chlorine-oxygen mixtures (ref. 14).
Figure 7. Stability diagram for condensed phases in Fe-O-Cl system (ref. 15).
Figure 8. - Surface of iron reacted with 1% HCl/10% HCl/10% O₂/Ar. Entire oxide layer removed (ref. 15).
\[
\begin{align*}
Cr_2O_3(s) + 2Cl_2(g) + \frac{1}{2} O_2(g) &= 2CrO_2Cl_2(g) \\
Cr_2O_3(s) + \frac{3}{2} O_2(g) &= 2CrO_3(g)
\end{align*}
\]

Figure 9. - Vapor pressure of CrO_3 above Cr_2O_3 with P_{O_2} = 1 \text{ atm} and vapor pressure of CrO_2Cl_2 above Cr_2O_3 with P_{O_2} = 1 \text{ atm} and P_{Cl_2} = 0.01 \text{ atm.}
Application of an Atmospheric Pressure Sampling Mass Spectrometer to Chlorination Reactions

An atmospheric pressure mass spectrometric sampling system, based on a free jet expansion has been used to study certain M-Cl-O reactions at high temperatures. This apparatus enables the volatile species from a 1-atm chemical process to be directly identified with a mass spectrometer which operates at \( \sim 10^{-8} \) torr. Studies for both pure metals and alloys are discussed. It is shown that this mass spectrometer system not only aids in identifying the volatile species, but also provides fundamental information on the reaction mechanism.
