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Neilen Hultgren and Leo Brewer

September 1955

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Neilen Hultgren and Leo Brewer
Radiation Laboratory and
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University of California, Berkeley, California
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ABSTRACT

The reaction of $\text{MoO}_3$ with HCl was studied and the formation of the gaseous molecule $\text{MoO}_2\text{Cl}_2$ demonstrated. This molecule is probably responsible for the anomalous earlier observations of the reaction of molybdenum metal with hydrogen chloride gas.
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N. L. Lofgren ran flow experiments in which a mixture of H₂ and HCl gases was passed over solid molybdenum metal at 1200°K in a silica system. Assuming a reaction of the form \( \text{Mo(s)} + x\text{HCl(g)} = \text{MoCl}_x\text{(g)} + \frac{x}{2}\text{H}_2\text{(g)} \), Lofgren found that \( x = 4 \) satisfied the observed HCl and H₂ pressure dependences. The calculated \( \Delta S \) for the reaction \( \text{Mo(s)} + 4\text{HCl(g)} = \text{MoCl}_4\text{(g)} + 2\text{H}_2\text{(g)} \) gave a \( \Delta S \) of formation for \( \text{MoCl}_4\text{(g)} \) of +22 eu. This was in marked disagreement with an estimated value of -15 eu and indicated that the proposed reaction was not the correct net reaction.

In the present work it was found that about \( 10^{-4} \) atmosphere of \( \text{H}_2\text{O(g)} \) would suffice to cause the observed volatility of Mo if the reaction were \( \text{Mo(s)} + 2\text{H}_2\text{O(g)} + 2\text{HCl(g)} = \text{MoO}_2\text{Cl}_2\text{(g)} + 3\text{H}_2\text{(g)} \). The calculated and estimated entropy values for this reaction are in good agreement. If the formation of molybdenum halides from the reaction of molybdenum with hydrogen chloride gas is to be studied, it will require a very dry non-oxide system to prevent formation of \( \text{MoO}_2\text{Cl}_2\text{ gas} \).

(1) Flow method

HCl was passed over heated \( \text{MoO}_3 \) and collected in a liquid nitrogen trap. The flow and pressure of HCl were controlled by a series of capillary tubes. After a given time the amount of HCl collected and the weight loss of the \( \text{MoO}_3 \) were measured. Temperatures were about 480°K. Reproducible results could not be obtained, even when the flow was as low as 9 cc/min.

(2) Click gauge

\( \text{MoO}_3 \) and HCl were heated in a sealed tube. The pressure was measured with a quartz "click" gauge accurate to better than 1 mm of pressure. Between 100°C and 260°C no deviations from the ideal gas law were noted in the pressure as shown in Fig. 1. The numbers given for each point indicate the order of taking the measurements. The reaction \( \text{MoO}_3\text{(s)} + \)}
\[ 2\text{HCl}(g) = \text{MoO}_2\text{Cl}_2(g) + \text{H}_2\text{O}(g) \] would show no pressure change. Also, a reaction forming \( \text{MoO}_2\text{OHCl} \) gas would show no pressure change. A reaction such as \( \text{MoO}_3(s) + 2\text{HCl}(g) = \text{MoO(OH)}_2\text{Cl}_2(g) \) would deviate from the ideal gas law by about 35 mm of Hg at 250°C if the equilibrium constants obtained below are correct. At temperatures below 100°C the pressures became too low, indicating formation of the known \( \text{MoO}_3 \cdot 2\text{HCl} \) solid.

Fig. 2 presents the results of heating \( \text{MoO}_3 \cdot 2\text{HCl} \) with HCl gas in a sealed tube. The order of the observations is indicated in Fig. 2. Upon initial heating no deviations from perfect gas law were observed up to 100°C. As the volatility of molybdenum species is very small at these temperatures, no reactions of any type have taken place. Upon heating above 115°C at 475 mm HCl, dissociation of \( \text{MoO}_3 \cdot 2\text{HCl} \) solid to MoO\(_3\) solid and HCl commenced. The steeply rising portion of the curve represents the HCl pressure in equilibrium with the two solid phases \( \text{MoO}_3 \cdot 2\text{HCl} \) and MoO\(_3\). Upon cooling, the system returned to perfect gas behavior at a higher HCl pressure, indicating that the surface MoO\(_3\) had been reconverted to \( \text{MoO}_3 \cdot 2\text{HCl} \) without reconverting the underlying MoO\(_3\). Figs. 1 and 2 correspond to two portions of a pressure-versus-temperature curve at constant volume such as is given in Fig. 3, where the portion corresponding to the univariant three-phase region is independent of volume and amounts of material while the slopes of the straight-line sections depend upon the amounts of material as well as the volume of the system. Thus the intersections of the three curves can be changed by changing the volume of the system or the amounts of material as in the above two experiments.

(3) Quartz fiber

\( \text{MoO}_3 \) was placed in a quartz pan located at the end of a 20-cm quartz fiber sealed in a glass tube. The weight of the MoO\(_3\) could be calculated from the amount of deflection of the fiber as observed through a cathetometer. HCl was added and the tube was heated in an oven. Air was circulated by means of a fan. Two different series of runs using different temperatures gave fairly consistent results. At high temperatures there was some distillation of greenish crystals. In the third run water was added. All the data are presented in Table I. The weight loss of the MoO\(_3\) was vastly diminished. The only reaction considered plausible which
Fig. 1. Total Pressure of Constant-Volume System Starting with Solid MoO$_3$ and Gaseous HCl.
Fig. 2. Total Pressure of Constant-Volume System Starting with Solid MoO$_3$·2HCl and Gaseous HCl.
Fig. 3. Pressure versus Temperature Behavior for Constant-Volume System with MoO₃ and HCl Components.
shows no volume change and which produces water is MoO$_3$(s) + 2HCl(g) = MoO$_2$Cl$_2$(g) + H$_2$O(g). After a run the formerly pale yellow MoO$_3$ on the tray was bluish black. It does not seem likely that a phase change occurred, since absorption of HCl should have showed up in the click-gauge experiment. On the other hand, the greenish crystals which condensed on cooling did not in the least resemble the original molybdic oxide. These crystals turned dark blue on exposure to air. As even minute reduction of hexavalent molybdenum compounds often causes deeply blue colors, the color changes appear to be due to a slight reduction caused by reducing impurities.

RESULTS

From 400° - 600°C, $\Delta G_p$ for the reaction MoO$_3$(s) + 2HCl(g) = MoO$_2$Cl$_2$(g) + H$_2$O(g) was estimated to be -6 cal/mol. A "$\Sigma$" diagram was plotted against $1/T$ where $\Sigma = -R\ln K + \Delta G_p \ln T = \Delta H_o/T + I$. The slope of the curve gives $\Delta H_o$ and the intercept gives I.

From the graph it is found that $\Delta H_o = 24,800 \pm 2,000$ cal/mol and I = -72.2. Hence for the reaction MoO$_3$(s) + 2HCl(g) = MoO$_2$Cl$_2$(g) + H$_2$O(g), $\Delta F = 24,800 + 13.8 T \log T - 72.2 T$ and $\Delta S = -d\Delta F/dT = -13.8 \log T + 66.2$.

At a temperature of 500°K, $\Delta S = 28.9$ eu. This gives an entropy of formation for MoO$_2$Cl$_2$(g) of -15 eu, which is in very good agreement with an estimated value of -15 eu.

Using the above data, it is found that the reaction Mo(s) + 2HCl(g) + 2H$_2$O(g) = MoO$_2$Cl$_2$(g) + 3H$_2$(g) would account for the volatility of Mo observed at 1200°K by Lofgren if $10^{-4}$ atmos of water were present in his vacuum line. He states that the H$_2$O pressure is less than $10^{-3}$ atmos in his line.
Table I

\[
\text{MoO}_3(s) + 2\text{HCl}(g) = \text{MoO}_2\text{Cl}_2(g) + \text{H}_2\text{O}(g)
\]

<table>
<thead>
<tr>
<th>(o_K)</th>
<th>(P_{\text{HCl}})</th>
<th>(W_{\text{Mo}})</th>
<th>(K)</th>
<th>-(R\ln K)</th>
<th>(\Delta C_p \ln T)</th>
<th>(\Sigma)</th>
<th>(10^3/T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>0.192</td>
<td>0.0</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>511</td>
<td>---</td>
<td>6.7 mg</td>
<td>6.80 \times 10^{-4}</td>
<td>14.49</td>
<td>-37.38</td>
<td>-22.89</td>
<td>1.957</td>
</tr>
<tr>
<td>544</td>
<td>---</td>
<td>15.6</td>
<td>4.29 \times 10^{-3}</td>
<td>10.83</td>
<td>-37.75</td>
<td>-26.92</td>
<td>1.838</td>
</tr>
<tr>
<td>558</td>
<td>---</td>
<td>19.2</td>
<td>6.96 \times 10^{-3}</td>
<td>9.87</td>
<td>-37.90</td>
<td>-28.03</td>
<td>1.792</td>
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<tr>
<td>584</td>
<td>---</td>
<td>26.8</td>
<td>.0156</td>
<td>8.27</td>
<td>-38.18</td>
<td>-29.91</td>
<td>1.712</td>
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<tr>
<td>611</td>
<td>---</td>
<td>36.8</td>
<td>.0548</td>
<td>6.62</td>
<td>-38.45</td>
<td>-31.83</td>
<td>1.637</td>
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</table>

Run No. 2

<table>
<thead>
<tr>
<th>(o_K)</th>
<th>(P_{\text{HCl}})</th>
<th>(W_{\text{Mo}})</th>
<th>(K)</th>
<th>-(R\ln K)</th>
<th>(\Delta C_p \ln T)</th>
<th>(\Sigma)</th>
<th>(10^3/T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>296</td>
<td>0.518</td>
<td>480</td>
<td>---</td>
<td>10.5</td>
<td>2.26 \times 10^{-4}</td>
<td>16.68</td>
<td>-37.00</td>
</tr>
<tr>
<td>529</td>
<td>---</td>
<td>19.5</td>
<td>8.2 \times 10^{-4}</td>
<td>14.12</td>
<td>-37.58</td>
<td>-23.46</td>
<td>1.890</td>
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<tr>
<td>572</td>
<td>---</td>
<td>60.5</td>
<td>0.00367</td>
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<td>-38.05</td>
<td>-26.91</td>
<td>1.748</td>
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<tr>
<td>609</td>
<td>---</td>
<td>96.5</td>
<td>0.0348</td>
<td>6.672</td>
<td>-38.43</td>
<td>-31.76</td>
<td>1.642</td>
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<tr>
<td>637</td>
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<td>168</td>
<td>0.194</td>
<td>3.298</td>
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<td>-35.44</td>
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</table>

Run No. 3 (with water)

<table>
<thead>
<tr>
<th>(o_K)</th>
<th>(P_{\text{H}_2\text{O}})</th>
<th>(P_{\text{HCl}})</th>
<th>(W_{\text{Mo}})</th>
<th>(K)</th>
<th>-(R\ln K)</th>
<th>(\Delta C_p \ln T)</th>
<th>(\Sigma)</th>
<th>(10^3/T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>535</td>
<td>---</td>
<td>---</td>
<td>.1</td>
<td>2.78 \times 10^{-3}</td>
<td>11.69</td>
<td>-37.65</td>
<td>-25.96</td>
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<tr>
<td>296</td>
<td>0.576</td>
<td>0.141</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

\(P_{\text{HCl}}\) and \(P_{\text{H}_2\text{O}}\) are respectively the pressures of the \(\text{HCl}(g)\) and \(\text{H}_2\text{O}(g)\) introduced into the glass tube before any reaction occurs.

\(W_{\text{Mo}}\) is the weight loss, in milligrams, of the \(\text{MoO}_3\) on the pan.
James Kane passed HCl, H₂, and H₂O(g) over solid Mo in a short series of experiments yielding the data of Table II.

**Table II**

<table>
<thead>
<tr>
<th>P&lt;sub&gt;Mo&lt;/sub&gt; Species</th>
<th>P&lt;sub&gt;HCl&lt;/sub&gt; x 10&lt;sup&gt;6&lt;/sup&gt;</th>
<th>P&lt;sub&gt;H₂O&lt;/sub&gt; x 10&lt;sup&gt;3&lt;/sup&gt;</th>
<th>P&lt;sub&gt;H₂&lt;/sub&gt;</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1156</td>
<td>20.3 atmos</td>
<td>0.307 atmos</td>
<td>5.3 atmos</td>
<td>0.652 atmos</td>
</tr>
<tr>
<td>1177</td>
<td>2.0</td>
<td>0.303</td>
<td>5.3</td>
<td>0.646</td>
</tr>
<tr>
<td>1175</td>
<td>8.7</td>
<td>0.303</td>
<td>5.3</td>
<td>0.650</td>
</tr>
</tbody>
</table>

The extrapolated K for these temperatures (adding the equations MoO<sub>3</sub> + 2HCl = MoO<sub>2</sub>Cl<sub>2</sub> + H₂O and 3H₂O + Mo = MoO<sub>3</sub> + 3H₂) is 0.02. The MoO<sub>3</sub> and H₂O data were obtained from Coughlin. The uncertainties are large for both the high-temperature determinations and the extrapolated value of the equilibrium constant for the reaction Mo(s) + 2H₂(g) + 2HCl(g) = MoO<sub>2</sub>Cl<sub>2</sub>(g) + 3H₂(g). The difference may be due to experimental errors but under the condition of large water pressures the possibility of the formation of other molybdenum compounds should be considered. Reactions such as Mo(s) + 3H₂O(g) + HCl(g) = MoO₂OHCl(g) + 3H₂ may account for the large volatility observed by Kane.

This work was performed under the auspices of the U.S. Atomic Energy Commission.
References

(1) N. L. Lofgren, "Gaseous Molybdenum Chlorides in HCl and H₂ Atmospheres," unpublished work, University of California, 1948.

(2) J. S. Kane, unpublished work, University of California, 1954.
