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Department of Chemistry and Chemical Engineering  
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ABSTRACT

The reaction of  $\text{MoO}_3$  with  $\text{HCl}$  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.

## GASEOUS MOLYBDENUM OXYCHLORIDE

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N. L. Lofgren<sup>1</sup> ran flow experiments in which a mixture of H<sub>2</sub> and HCl gases was passed over solid molybdenum metal at 1200°K in a silica system. Assuming a reaction of the form  $\text{Mo(s)} + x\text{HCl} = \text{MoCl}_x(\text{g}) + x/2 \text{H}_2$ , Lofgren found that  $x = 4$  satisfied the observed HCl and H<sub>2</sub> 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 MoCl<sub>4</sub>(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<sup>-4</sup> atmosphere of H<sub>2</sub>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 MoO<sub>2</sub>Cl<sub>2</sub> gas.

## (1) Flow method

HCl was passed over heated MoO<sub>3</sub> 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 MoO<sub>3</sub> 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

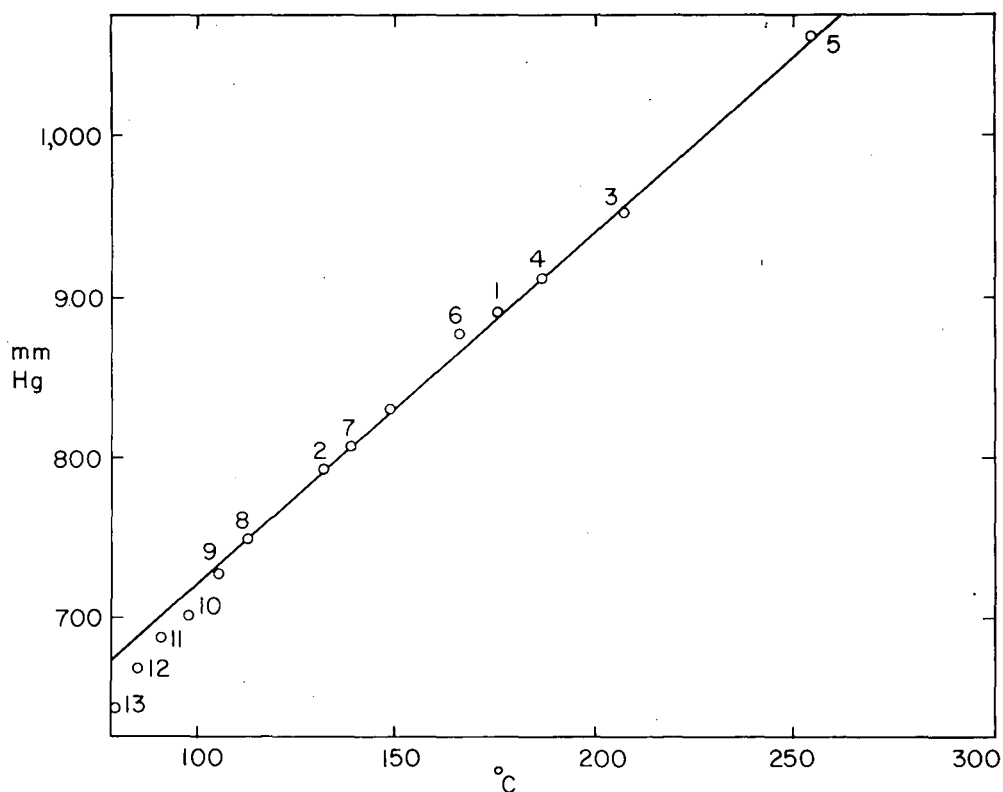
MoO<sub>3</sub> and HCl were heated in a sealed tube. The pressure was measured with a quartz "click" gauge accurate to better than 1 mm of pressure. Between 100°C and 260°C no deviations from the ideal gas law were noted in the pressure as shown in Fig. 1. The numbers given for each point indicate the order of taking the measurements. The reaction  $\text{MoO}_3(\text{s}) +$

$2\text{HCl}(\text{g}) = \text{MoO}_2\text{Cl}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$  would show no pressure change. Also, a reaction forming  $\text{MoO}_2\text{OHCl}$  gas would show no pressure change. A reaction such as  $\text{MoO}_3(\text{s}) + 2\text{HCl}(\text{g}) = \text{MoO}(\text{OH})_2\text{Cl}_2(\text{g})$  would deviate from the ideal gas law by about 35 mm of Hg at  $250^\circ\text{C}$  if the equilibrium constants obtained below are correct. At temperatures below  $100^\circ\text{C}$  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  $100^\circ\text{C}$ . As the volatility of molybdenum species is very small at these temperatures, no reactions of any type have taken place. Upon heating above  $115^\circ\text{C}$  at 475 mm HCl, dissociation of  $\text{MoO}_3 \cdot 2\text{HCl}$  solid to  $\text{MoO}_3$  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  $\text{MoO}_3$ . Upon cooling, the system returned to perfect gas behavior at a higher HCl pressure, indicating that the surface  $\text{MoO}_3$  had been reconverted to  $\text{MoO}_3 \cdot 2\text{HCl}$  without reconvertng the underlying  $\text{MoO}_3$ . 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  $\text{MoO}_3$  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  $\text{MoO}_3$  was vastly diminished. The only reaction considered plausible which



MU-10276

Fig. 1. Total Pressure of Constant-Volume System Starting with Solid  $\text{MoO}_3$  and Gaseous  $\text{HCl}$ .



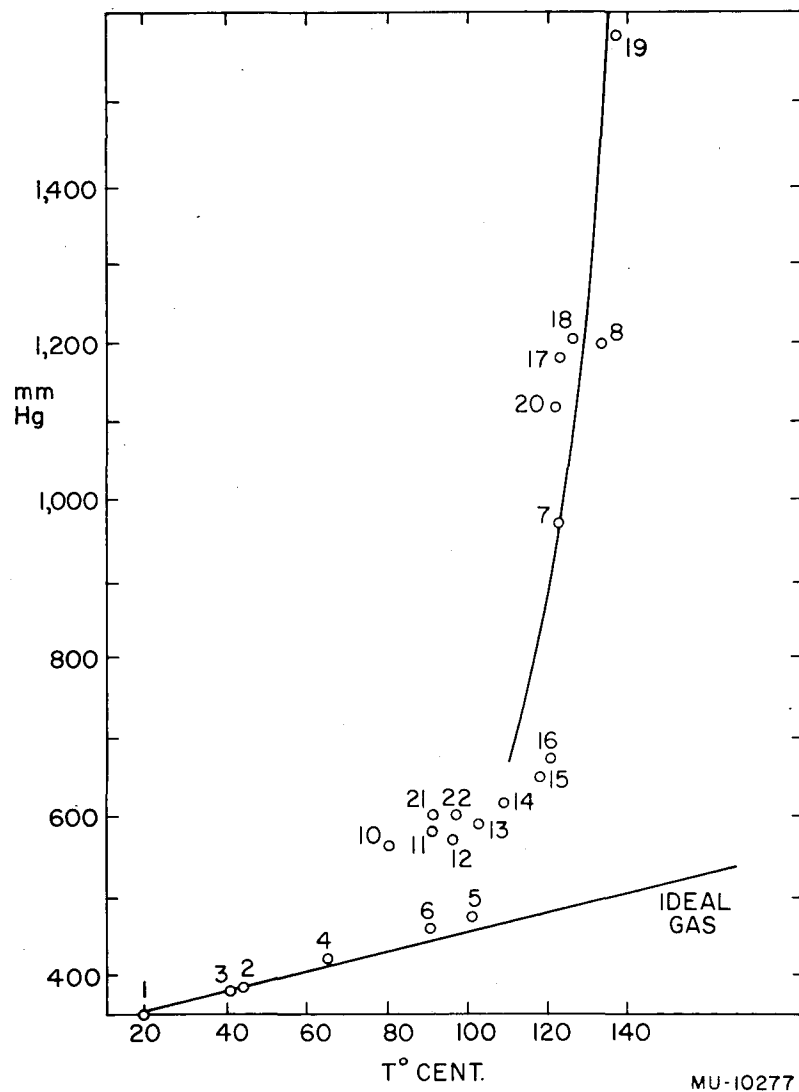


Fig. 2. Total Pressure of Constant-Volume System Starting with Solid  $\text{MoO}_3 \cdot 2\text{HCl}$  and Gaseous  $\text{HCl}$ .

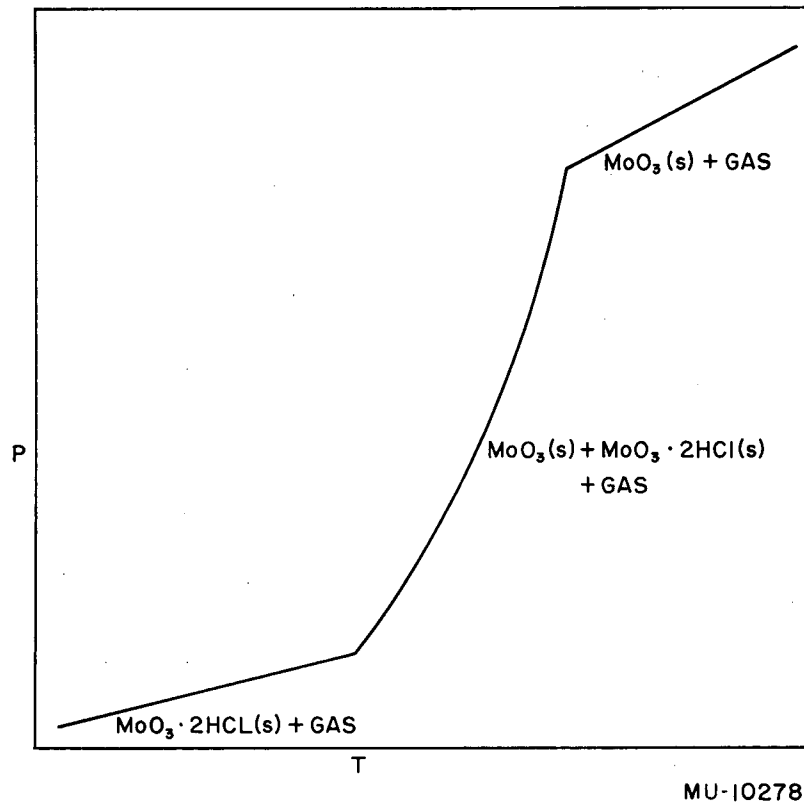


Fig. 3. Pressure versus Temperature Behavior for Constant-Volume System with MoO<sub>3</sub> and HCl Components.

shows no volume change and which produces water is  $\text{MoO}_3(\text{s}) + 2\text{HCl}(\text{g}) = \text{MoO}_2\text{Cl}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$ . After a run the formerly pale yellow  $\text{MoO}_3$  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 molybdenic 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  $400^\circ - 600^\circ\text{C}$ ,  $\Delta C_p$  for the reaction  $\text{MoO}_3(\text{s}) + 2\text{HCl}(\text{g}) = \text{MoO}_2\text{Cl}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$  was estimated to be  $-6$  cal/mol. A " $\Sigma$ " diagram was plotted against  $1/T$  where  $\Sigma = -R \ln K + \Delta C_p \ln T = \Delta H_o/T + I$ . 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  $\text{MoO}_3(\text{s}) + 2\text{HCl}(\text{g}) = \text{MoO}_2\text{Cl}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$ ,  $\Delta F = 24,800 + 13.8 T \log T - 72.2 T$  and  $\Delta S = -d\Delta F/dT = -13.8 \log T + 66.2$ .

At a temperature of  $500^\circ\text{K}$ ,  $\Delta S = 28.9$  eu. This gives an entropy of formation for  $\text{MoO}_2\text{Cl}_2(\text{g})$  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  $\text{Mo}(\text{s}) + 2\text{HCl}(\text{g}) + 2\text{H}_2\text{O}(\text{g}) = \text{MoO}_2\text{Cl}_2(\text{g}) + 3\text{H}_2(\text{g})$  would account for the volatility of Mo observed at  $1200^\circ\text{K}$  by Lofgren if  $10^{-4}$  atmos of water were present in his vacuum line. He states that the  $\text{H}_2\text{O}$  pressure is less than  $10^{-3}$  atmos in his line.

Table I

$\text{MoO}_3(\text{s}) + 2\text{HCl}(\text{g}) = \text{MoO}_2\text{Cl}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$								
$^{\circ}\text{K}$	$P_{\text{HCl}}$	$W_{\text{Mo}}$	K	$-\text{RlnK}$	$\Delta C_p \text{lnT}$	$\Sigma$	$10^3/\text{T}$	
Run No. 1								
293	0.192	0.0	---	---	---	---	---	
511	---	6.7 mg	$6.80 \times 10^{-4}$	14.49	-37.38	-22.89	1.957	
544	---	15.6	$4.29 \times 10^{-3}$	10.83	-37.75	-26.92	1.838	
558	---	19.2	$6.96 \times 10^{-3}$	9.87	-37.90	-28.03	1.792	
584	---	26.8	.0156	8.27	-38.18	-29.91	1.712	
611	---	36.8	.0548	6.62	-38.45	-31.83	1.637	
Run No. 2								
296	0.518							
480	---	10.5	$2.26 \times 10^{-4}$	16.68	-37.00	-20.32	2.083	
529	---	19.5	$8.2 \times 10^{-4}$	14.12	-37.58	-23.46	1.890	
572	---	60.5	0.00367	11.14	-38.05	-26.91	1.748	
609	---	96.5	0.0348	6.672	-38.43	-31.76	1.642	
637	---	168	0.194	3.298	-38.70	-35.44	1.570	
Run No. 3 (with water)								
$^{\circ}\text{K}$	$P_{\text{H}_2\text{O}}$	$P_{\text{HCl}}$	$W_{\text{Mo}}$	K	$-\text{RlnK}$	$\Delta C_p \text{lnT}$	$\Sigma$	$10^3/\text{T}$
535	---	---	.1	$2.78 \times 10^{-3}$	11.69	-37.65	-25.96	2.083
296	0.576	0.141	0.0					

$P_{\text{HCl}}$  and  $P_{\text{H}_2\text{O}}$  are respectively the pressures of the  $\text{HCl}(\text{g})$  and  $\text{H}_2\text{O}(\text{g})$

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, H<sub>2</sub>, and H<sub>2</sub>O(g) over solid Mo in a short series of experiments yielding the data of Table II.

Table II

Volatility of Molybdenum Metal in HCl, H <sub>2</sub> , H <sub>2</sub> O Gaseous Mixtures					
°K	P <sub>Mo</sub> Species x 10 <sup>6</sup>	P <sub>HCl</sub>	P <sub>H<sub>2</sub>O</sub> x 10 <sup>3</sup>	P <sub>H<sub>2</sub></sub>	K
1156	20.3 atmos	0.307 atmos	5.3 atmos	0.652 atmos	2.0
1177	2.0	0.303	5.3	0.646	0.2
1175	8.7	0.303	5.3	0.650	0.9

The extrapolated K for these temperatures (adding the equations  $\text{MoO}_3 + 2\text{HCl} = \text{MoO}_2\text{Cl}_2 + \text{H}_2\text{O}$  and  $3\text{H}_2\text{O} + \text{Mo} = \text{MoO}_3 + 3\text{H}_2$ ) is 0.02. The MoO<sub>3</sub> and H<sub>2</sub>O data were obtained from Coughlin.<sup>3</sup> The uncertainties are large for both the high-temperature determinations and the extrapolated value of the equilibrium constant for the reaction  $\text{Mo(s)} + 2\text{H}_2\text{O(g)} + 2\text{HCl(g)} = \text{MoO}_2\text{Cl}_2\text{(g)} + 3\text{H}_2\text{(g)}$ . The 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  $\text{Mo(s)} + 3\text{H}_2\text{O(g)} + \text{HCl(g)} = \text{MoO}_2\text{OHCl(g)} + 3\text{H}_2$  may account for the large volatility observed by Kane.

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

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- (2) J. S. Kane, unpublished work, University of California, 1954.
- (3) J. P. Coughlin, Bur. of Mines Bull. 542 (1954).

