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GASEOUS MOLYBDENUM OXYCHLORIDE

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ABSTRACT

The reaction of MoO_3 with HCl was studied and the formation of the gaseous molecule MoO_2Cl_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. Lofgren¹ ran flow experiments in which a mixture of H_2 and HCl gases was passed over solid molybdenum metal at $1200^\circ K$ in a silica system. Assuming a reaction of the form $Mo(s) + xHCl = MoCl_x(g) + x/2 H_2$, Lofgren found that $x = 4$ satisfied the observed HCl and H_2 pressure dependences. The calculated ΔS for the reaction $Mo(s) + 4HCl(g) = MoCl_4(g) + 2H_2(g)$ gave a ΔS of formation for $MoCl_4(g)$ 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 $H_2O(g)$ would suffice to cause the observed volatility of Mo if the reaction were $Mo(s) + 2H_2O(g) + 2HCl(g) = MoO_2Cl_2(g) + 3H_2(g)$. 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_2Cl_2 gas.

(1) Flow method

HCl was passed over heated 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 MoO_3 were measured. Temperatures were about $480^\circ K$. Reproducible results could not be obtained, even when the flow was as low as 9 cc/min.

(2) Click gauge

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 $100^\circ C$ and $260^\circ C$ 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 $MoO_3(s) +$

$2\text{HCl}(\text{g}) = \text{MoO}_2\text{Cl}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$ would show no pressure change. Also, a reaction forming MoO_2OHCl 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°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 reconvertng 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

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 $\text{MoO}_3 \cdot 2\text{HCl}$ and Gaseous HCl .

Fig. 3. Pressure versus Temperature Behavior for Constant-Volume System with MoO_3 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 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 $400^\circ - 600^\circ\text{C}$, ΔC_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 " Σ " diagram was plotted against $1/T$ where $\Sigma = -R \ln K + \Delta C_p \ln T = \Delta H_0/T + I$. The slope of the curve gives ΔH_0 and the intercept gives I .

From the graph it is found that $\Delta H_0 = 24,800 \pm 2,000$ 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°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°K by Lofgren if 10^{-4} atmos of water were present in his vacuum line. He states that the H_2O 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_{HCl}	W_{Mo}	K	$-\text{RlnK}$	$\Delta C_p \ln T$	Σ	$10^3/T$	
Run No. 1								
293	0.192	0.0	---	---	---	---	---	
511	---	6.7 mg	6.80×10^{-4}	14.49	-37.38	-22.89	1.957	
544	---	15.6	4.29×10^{-3}	10.83	-37.75	-26.92	1.838	
558	---	19.2	6.96×10^{-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	2.26×10^{-4}	16.68	-37.00	-20.32	2.083	
529	---	19.5	8.2×10^{-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_{HCl}	W_{Mo}	K	$-\text{RlnK}$	$\Delta C_p \ln T$	Σ	$10^3/T$
535	---	---	.1	2.78×10^{-3}	11.69	-37.65	-25.96	2.083
296	0.576	0.141	0.00					

P_{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_{Mo} is the weight loss, in milligrams, of the MoO_3 on the pan.

P_{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_{Mo} is the weight loss, in milligrams, of the MoO_3 on the pan.

James Kane passed HCl , H_2 , and $\text{H}_2\text{O}(\text{g})$ over solid Mo in a short series of experiments yielding the data of Table II.

Table II

Volatility of Molybdenum Metal in HCl , H_2 , H_2O Gaseous Mixtures					
$^{\circ}\text{K}$	P_{Mo} Species $\times 10^6$	P_{HCl}	$\text{P}_{\text{H}_2\text{O}}$ $\times 10^3$	P_{H_2}	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_3 and H_2O data were obtained from Coughlin.³ The uncertainties are large for both the high-temperature determinations and the extrapolated value of the equilibrium constant for the reaction $\text{Mo}(\text{s}) + 2\text{H}_2\text{O}(\text{g}) + 2\text{HCl}(\text{g}) = \text{MoO}_2\text{Cl}_2(\text{g}) + 3\text{H}_2(\text{g})$. 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 $\text{Mo}(\text{s}) + 3\text{H}_2\text{O}(\text{g}) + \text{HCl}(\text{g}) = \text{MoO}_2\text{OHCl}(\text{g}) + 3\text{H}_2$ may account for the large volatility observed by Kane.

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