GASEOUS MOLYBDENUM OXYCHLORIDE

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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.

N. L. Lofgren¹ ran flow experiments in which a mixture of H_2 and HCl gases was passed over solid molybdenum metal at 1200°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 e.u. This was in marked disagreement with an estimated value of -15 e.u. and indicated that the proposed reaction was not the correct net reaction.

In the present work it was found that about 10^{-4} atm. of H₂O(g) could suffice to cause the observed volatility of Mo if the reaction were Mo(s) + 2H₂O(g) + 2HCl(g) = MoO₂Cl₂(g) + 3H₂(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 MoO₂Cl₂ gas.

Experimental

(1) Flow Method.— $\hat{H}Cl$ was passed over heated MoO₃ 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 MoO₃ 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 Gage.—MoO₃ and HCl were heated in a sealed tube. The pressure was measured with a quartz "click" gage accurate to better than 1 mm. of pressure for several series between 90 and 290°. Between 105 and 290° no deviations from the ideal gas law were noted in the pressure as shown by a typical run presented in Fig. 1. The numbers given for each point indicate the order of taking the measurements. The reaction $MoO_3(s) + 2HCl(g) = MoO_2Cl_3(g) + H_2O(g)$ would show no pressure change. Also, a reaction forming MoO_2OHCl gas would show no pressure change. A reaction such as $MoO_3(s) + 2HCl(g) = MoO(OH)_2Cl_2(g)$ would deviate from the ideal gas law by about 35 mm. of Hg at 250° if the equilibrium constants obtained below are correct. At temperatures below 100° the pressures became too low, indicating formation of the known MoO_3 .

Figure 2 presents the results of heating $MoO_3.2HCl$ 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°. As thevolatility of molybdenum species is very small at these temperatures, no reactions of any type have taken place. Upon heating above 115° at 475 mm. HCl, dissociation of $MoO_3.2HCl$ 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 $MoO_3.2HCl$ 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 $MoO_3.2HCl$ without reconverting the underlying MoO_3 . Figures 1 and 2 correspond to two portions of a pressure *versus* term-

perature curve at constant volume such as is given in Fig. 3, where the portion corresponding to the univariant threephase 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



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 MoO₃·2HCl and gaseous HCl.

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



Fig. 3.—Pressure versus temperature behavior for constant volume system with MoO₃ and HCl components.

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.

amounts of material as in the above two experiments. (3) Quartz Fiber.—MoO₃ 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 MoO₃ 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 con-

Results

The HCl pressure at each temperature can be calculated from the pressure at room temperature, the amount removed due to reaction with MoO_3 , and the perfect gas law.

and the perfect gas law. From 400-600°, ΔC_p for the reaction MoO₃(s) + 2HCl(g) = MoO₂Cl₂(g) + H₂O(g) was estimated to be -6 cal./mole. 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./mole and I = -72.2. Hence for the reaction MoO₃(s) + 2HCl(g) = MoO₂Cl(g) + H₂O(g), $\Delta F = 24,800 + 13.8 T \log T - 72.2T$ and $\Delta S = -d\Delta F/dT = -13.8 \log T + 66.2$. At a temperature of 500°K., $\Delta S = 28.9$ e.u. This

At a temperature of 500°K., $\Delta S = 28.9$ e.u. This gives an entropy of formation for MoO₂Cl₂(g) of -15 e.u., which is in very good agreement with an estimated value of -15 e.u.

Using the above data, it is found that the reaction $Mo(s) + 2HCl(g) + 2H_2O(g) = MoO_2Cl_2(g) + 3H_2(g)$ would account for the volatility of Mo observed at 1200°K. by Lofgren if 10^{-4} atm. of water were present in his vacuum line. He states that the H₂O pressure is less than 10^{-3} atm. in his line.

James Kane² passed HCl, H₂ and H₂O(g) over solid Mo in a short series of experiments yielding the data shown in Table II. The approximate extrapolated K for these temperatures (adding the equations $MoO_3 + 2HCl = MoO_2Cl_2 + H_2O$ and $3H_2O + Mo = MoO_3 + 3H_2$) is 0.02. The MoO₃ and H₂O data were obtained from Coughlin.³ The

TABLE I

$$MoO_{\delta}(s) + 2HCl(g) = MoO_{2}(g) + H_{2}O(g)$$

The P_{HCl} values given at room temperature are the pressures of HCl(g) in atm. introduced into the glass tube at room temperature. The value given for P_{H20} was calculated from the weight of introduced water. W_{M0} is the weight loss, in milligrams, of the MoO₂ on the pan. The volume of the system was 234 cc.

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<i>т</i> , °к.	$P_{\rm H_2O}$, atm.	WMo, mg.	K	$-R \ln K$	$\Delta C_{\rm p} \ln T$	Σ	$10^{3}/T$
			Run no. 1 ($P_{\rm HCl}$ =	= 0.192 atm. at 2	293°K.)		
511	••	6.7	6.80×10^{-4}	14,49	-37.38	-22.89	1.957
544		15.6	$4.29 imes 10^{-3}$	10.83	-37.75	-26.92	1.838
558	••	19. 2	$6.96 imes 10^{-3}$	9.87	-37.90	-28.02	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 ($P_{\rm HCl}$ =	= 0.518 atm. at 2	296°K.)		
480		10.5	$2.26 imes10^{-4}$	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
	Ra	in no. 3 (with	water) $(P_{\rm HCl} = 0.141$	atm. at 297°K.	and 0.255 atm. a	at 535°K.)	
535	1 04	1	2.78×10^{-8}	.11 69	-37.65	-25.96	2.083

densation of greenish crystals on the glass tube. In the third run water was added. All the data are presented in Table I. The weight loss of the MoO₃ was vastly diminished by addition of water. The only reaction considered plausible which shows no volume change and which produces water is $MoO_3(s) + 2HCl(g) = MoO_2Cl_2(g) + H_2O(g)$. After a run the formerly pale yellow MoO_3 on the tray was bluish black. The greenish crystals which condensed on cooling 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 or slight loss of oxygen.

uncertainties are large for both the high temperature determinations and the extrapolated value of the equilibrium constant for the reaction $Mo(s) + 2H_2O(g) + 2HCl(g) = MoO_2Cl_2(g) + 3H_2(g)$. 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

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

VOLATILITY OF MOLYBDENUM METAL IN HCl. H2, H2O GASEOUS MIXTURES

<i>T</i> , °K.	P_{Mo} species atm. \times 10^6	P _{HCl} , atm.	$P_{\mathrm{H20}}, \\ \mathrm{atm.} \times 10^{\mathrm{s}}$	$P_{\mathrm{H2}},$ atm.	K
1156	20.3	0.307	5.3	0.652	2.0
1177	2.0	.303	5.3	.646	0.2
1175	8.7	. 303	5.3	.650	0.9

 $OHCl(g) + 3H_2$ may account for the large volatility observed by Kane.

It is clear from these results that the study of the reaction $Mo(s) + 4HCl(g) = MoCl_4(g) + 2H_2(g)$ cannot be carried out in an oxide system due to the formation of MoO₂Cl₂ gas and possibly other oxyand hydroxy-chlorides of Mo at high temperatures and a completely metallic system will be necessary.

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THE ENTROPY OF SOLUTION OF BROMINE IN PERFLUORO-n-HEPTANE

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The solubility of Br₂ in n-C₇F₁₆ between -5 and 25° conforms closely with the equation: $\log_{10} x_2 = 1.5398 - 849.58/T$. x_2 denotes mole fraction of Br₂. At 25°, $x_2 = 0.0490$. The mole fraction of C₇F₁₆ in Br₂ is of the order of 5×10^{-5} . The partial molal volume of Br₂ in C₇F₁₆ at saturation is 72 cc., an enormous expansion over its molal volume, 51.5 cc. Its partial molal entropy of solution is 13.05 cal. deg.⁻¹, whereas the entropy of dilution according to Raoult's law would be only 6.0 e.u. The discrepancy can be accounted for by considering the entropy that would accompany (a) an expansion of the solvent by 20.5 cc., (b) the resultant increase in the free volume available to the Br₂, (c) a "Flory-Huggins" entropy for mixing at constant volume, and (d) a small decrease in molecular order of C₇F₁₆ molecules adjacent to Br₂ molecules.

In order to test the validity of any theory based upon a model, it is proper to select cases that subject it to considerable strain. It is for this reason that we have carefully studied solutions of iodine in f-heptane, where its activity coefficient is 1400, as to conformity with the theory of regular solutions.¹ There is one respect, however, in which that system is not altogether satisfactory. In that theory, the standard state chosen for both components is the pure liquid, and a wide extrapolation below the melting point of iodine is required to obtain the essential properties of liquid iodine at ordinary temperatures. The pair bromine and f-heptane, on the other hand, are both liquid above -7.7° ; both have zero dipole moment; they are chemically inert toward each other, and the difference between their solubility parameters is very large. These considerations led us to undertake the study here reported.

Materials.—The f-heptane was from the stock purified by Glew and Reeves.² The bromine was "analytical grade" from Baker and Mallinckrodt, density 3.10235 g. ml.⁻¹ at

from Baker and Malinekrodt, density 3.10235 g. ml. ¹⁴ at 25°. Precautions were taken to keep it dry. Solubility of Br₂ in C_7F_{16} .—f-Heptane was saturated with bromine for periods of 8 to 24 hours in the apparatus described by Glew and Hildebrand¹ at temperatures constant to 0.002°. Portions were drawn off into a solution of KI and titrated with N/20 thiosulfate from a microburet. The equilibrium temperatures selected were all below room temperature in order to avoid loss of bromine during the temperature, in order to avoid loss of bromine during the withdrawal of each sample. The results are given in Table I.

with the way of each sample. The results are given in Faster: x_2 denotes the mole fraction of Br₂. Log x_2 plotted against 1/T gives a straight line whose equation is $\log_{10}x_2 = 1.5398 - 849.58/T$. The values in the last column were calculated by this equation.

•	I ADUE I		
SOLUBILITY OF	BROMINE IN f-HEPTANE,	MOLE FRACTION	
	100 x2,	100 x2,	
<i>t</i> , °C.	obsd.	calcd.	
-11.93	1.766 (solid)		
- 4.97	2.343	2.345	
-0.12	2.693	2.690	
4.41	3.019	3.013	
9.84	3.453	3.456	
14.78	3.887	3.882	
19.94	4.366	4.377	
25.00		4,898	

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Solubility of C₇F₁₆ in Br₂.—This was determined from the diminution in volume of a small globule of f-heptane after equilibrating with a large volume of bromine. The apparatus consists of a glass bulb to which are at-

tached two tubes, one a calibrated capillary, both with stopcocks near their outer ends, lubricated with fluorocarbon grease. The apparatus is filled with bromine through the larger tube. A small amount of f-heptane is added at the top of the capillary, and its volume measured with a cathe-tometer. The bromine wets the glass preferentially, there-fore the f-heptane is a well-defined globule. The apparatus is then tilted so that the globule runs out of the capillary into the bulb and the apparatus is rocked so that the globule rolls around in contact with the bromine. After at least 24 hours rocking, the capillary is raised to a vertical position, whereupon the globule runs up to the top where its volume is again measured.

The solubility is extremely small, therefore the results, shown in Table II, show considerable percentage fluctuation. They could not be improved by using a much smaller

tion. They could not be improved by using a much smaller capillary, because then the bromine would not displace the fluorocarbon. We can assert only that the mole fraction of f-heptane in bromine at 25° is approximately 5×10^{-5} . Partial Molal Volume of Br₂ in C₇F₁₆.—The densities of pure C₇F₁₆ and of solutions of Br₂ therein, were determined, using a graduated, double stem pycnometer, having a volume of 28 cc. The mole fraction of Br₂ in each solution was determined by titration. The density of the C₇F₁₆ was 1.72004 \pm 0.00005 at 25°. The results are given in Table III. \bar{v}_2 is the partial molal volume and v_2° is the molal volume. volume.

⁽¹⁾ H. A. Benesi and J. H. Hildebrand, J. Am. Chem. Soc., 70, 3978 (1948); J. H. Hildebrand, H. A. Benesi and L. M. Mower, ibid., 72, 1017 (1950); D. N. Glew and J. H. Hildebrand, THIS JOURNAL, 60, 616 (1956); J. H. Hildebrand and D. N. Glew, ibid., 60, 618 (1956).

⁽²⁾ D. N. Glew and L. W. Reeves, ibid., 60, 615 (1956).