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THE STABILITY OF GASEOUS MANGANOUS OXIDE

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The Stability of Gaseous Manganous Oxide

1. Introduction.

In view of the instability of gaseous FeO[1],[2] and NiO[3] with respect to dissociation into the gaseous elements, it is of interest to investigate the stability of gaseous MnO.

Relatively little is known concerning the manganese-oxygen Phase diagram. Le Blanc and Wehner[4] have found that MnO prepared in a vacuum takes up oxygen up to the composition $MnO_{1.13}$ with no change in phase. Assuming the activity of MnO to be essentially unity throughout the MnO solid solution range, one may investigate the volatilization of MnO by measuring the rate of weight loss from an effusion cell containing manganese oxide whose composition falls within this range. Such measurements may be conducted by heating Mn_3O_4 to high temperatures in vacuum. At 1767°K the partial pressure of oxygen over Mn_3O_4 is about 1.9 atm and therefore the composition changes rapidly by loss of oxygen until the MnO solid solution edge is reached. During this time interval a negligible amount of Mn will volatilize since the Mn activity is very low in the Mn_3O_4 region. These measurements are described in the following paper.

By comparison of the results of the effusion measurements with the known heat of dissociation of MnO(s)[5] the most probable mechanism for the volatilization of MnO is given.

2. Experimental.

The Mn_3O_4 used in these determinations was prepared by heating Merck's Reagent grade MnO_2 at 950°C in vacuum. Krüll[6] has observed that dissociation of MnO_2 and Mn_2O_3 occur readily in the range 900-1000°C, whereas Mn_3O_4 was not observed to dissociate to MnO at

an appreciable rate below 1300°C. The MnO_2 was consequently heated at 950°C until the pressure in the vacuum line dropped to a value which indicated that rapid gas evolution was occurring no longer. The resultant Mn_3O_4 was a deep rust color and upon X-ray diffraction examination was shown to contain no other phases than Mn_3O_4. The tetragonally distorted spinel structure had the lattice constants $a = 5.76 \pm 0.01$Å, $c = 9.44 \pm 0.01$Å with $CuK\alpha_1$ radiation. Spectrochemical analysis indicated the following level of impurities: As, Co, Ni, Sn, Pb, Cr not detected; Mo 0.1-1%; Na, 0.2%; Fe <.01%.

The Mn_3O_4 was contained in a platinum effusion cell whose hole area was 7.94×10^{-2} cm^2. The equipment and techniques involved in conducting the effusion measurement by heating inductively in high vacuum have been described elsewhere.(2) The ratio of the weight on the collector to the total weight effusing was 15.4. Spectrochemical analysis of the resultant MnO after a 40 minute heating at 1767°K showed < 0.01% platinum was picked up from the container. The deposit was dissolved from the 2 mil platinum collector plate with 36N H_2SO_4, oxidized with KIO_4 and determined colorimetrically as permanganate on a Carey Recording Spectrophometer. X-ray diffraction patterns of the residue in the effusion cell after each run showed only the MnO phase was present. The lattice constants for the face-centered cubic phase were $a_o = 4.438 \pm 0.004$Å and $a_o = 4.441 \pm 0.002$Å for the MnO resulting from runs 1 and 2 respectively (Table I), as determined with $CuK\alpha_1$ radiation.

Table I gives the results of the effusion measurements. Columns 5 and 6 were calculated from the data assuming the gaseous manganese species in equilibrium with MnO(s) to be Mn(g) and MnO(g), respectively. The relation used in this calculation as derived from gas

Table I

Run	°K	Time secs x 10^{-3}	Wt. Mn collected (gm x 10^{6})	P_{Mn} (atm) assuming Mn(g) species	P_{MnO} (atm) assuming MnO(g) species
1	1767	1.80	49	6.50×10^{-7}	7.80×10^{-7}
2	1767	2.40	73	7.58×10^{-7}	9.10×10^{-7}

kinetics is

$$p = \frac{z\sqrt{MT}}{44.383 \cdot a \cdot t}$$

wherein p is the pressure in atm, z the number of moles of a particular species effusing from the effusion cell, M and molecular weight, T the temperature in °K, a the area of the effusion hole in cm^2 and t the duration of the run in seconds.

3. Thermodynamic Treatment.

In view of the agreement between the results of runs 1 and 2 the average values $P_{Mn} = 7.04 \times 10^{-7}$ atm and $P_{MnO} = 8.45 \times 10^{-7}$ atm are used in the calculation of the value of $\frac{\Delta F}{T}$ for the two possible reactions under consideration:

$$MnO(s) = Mn(g) + \frac{1}{2} O_2(g) \qquad (1)$$

$$MnO(s) = MnO(g) \qquad (2)$$

Within the desired accuracy of this research it is assumed that $P_{Mn} = \frac{1}{2} P_{O_2}$ in reaction (1) and that the pressures of Mn(g) and MnO(g) given above are upper limits. For reaction (1) $\frac{\Delta F}{T} = 42.23$ kcal/mole. Combining this value with available $\frac{F - H_o}{T}$ values[5],[7],[8] for the species in reaction (1) one obtains the heat for the reaction: $\Delta H_{298} = -92.0$ kcal/mole for the reaction $M(s) + \frac{1}{2} O_2 = MnO(s)$. Brewer[9] also gives the value $\Delta H_{298} = 68.63$ kcal/mole for the heat of sublimation of manganese. Thus for the reaction (1) the thermochemical value for the heat is $\Delta H_{298} = 160.6$ kcal/mole. Since the difference of one kcal/mole is probably within the accuracy allowed by the assumptions made herein, this constitutes very good agreement between the value calculated on the assumption of a dissociation mechanism and the thermochemical value for the same reaction.

The $\frac{\Delta F}{T}$ value for reaction (2) as calculated from the experimental P_{MnO} is $\frac{\Delta F}{T} = 27.6$ kcal/mole. Assuming the $\frac{F - H_0}{T}$ functions for MnO(g) to be essentially equal to those for NiO(g),[10] and allowing for the difference in molecular weights, the experimentally determined lower limit to the heat for reaction (2) is $\Delta H_0 \geq 112$ kcal/mole. Combining this value with those for the heat of formation of MnO(s),[5] the heat of sublimation of Mn(s)[9] and the heat of dissociation of $\frac{1}{2}$ O_2(g)[9] one calculates the value $\Delta H_0 \leq 107$ kcal/mole for the reaction

$$MnO(g) = Mn(g) + O(g).$$

The value given for this reaction by Gaydon[11] from an inspection of spectroscopic data is $D_0 = 92$ kcal/mole. The divergence between these two values is indication that the vapor-pressure of MnO(g) is much lower than the upper limit given above if the value given by Gaydon is for the dissociation of the MnO molecule from its ground state. The upper limiting value obtained in this work establishes Gaydon's value as resulting from the ground state or one quite close to the ground state.

4. Summary.

The measurement of the rate of vaporization of MnO(s) at high temperatures in vacuum has been combined with available thermochemical data to yield the values for the heats of the following reactions:

$MnO(s) = Mn(g) + \frac{1}{2} O_2(g)$	$\Delta H_{298} \geq 160$ kcal/mole
$MnO(g) = Mn(g) + O(g)$	$\Delta H_0 \leq 107$ kcal/mole
$MnO(s) = MnO(g)$	$\Delta H_{298} \geq 112$ kcal/mole

Since the thermochemical value[5] for the first reaction is

$\Delta H_{298} = 160.6$ kcal/mole, the experimental measurements lead one to conclude that the gaseous species in equilibrium with MnO(s) at 1767°K are Mn(g) and $\frac{1}{2}$ O_2(g) and that MnO(g) is not an important species in the vaporization of MnO. Gaydon[11] gives D_0(MnO) = 92 kcal/mole from an inspection of spectroscopic data. Comparison of this value with $\Delta H_0 \leq 107$ kcal/mole for the second reaction indicates that the upper limit set for the vapor-pressure of MnO(g) is quite high if the spectroscopic data result from the ground state of the MnO(g) molecule. This then is supplementary indication that MnO vaporizes by dissociation to the gaseous elements and that MnO(g) is not a predominate gaseous species.

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