

Mo-MoO₂ (MOM) oxygen buffer and the free energy of formation of MoO₂

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ABSTRACT

The chemical potential of oxygen defined by the Mo-MoO₂ equilibrium has been measured between 1000 and 1400 K using an electrochemical method. The results are

$$\mu_{\text{O}_2}^{\text{Mo-MoO}_2} = -603\,268 + 337.460T - 20.6892T \ln T$$

in joules per mole ($\pm 140 \text{ J}\cdot\text{mol}^{-1}$). These results show that the small increment to the calorimetrically measured entropy of MoO₂, suggested in the JANAF tables is unwarranted. The standard enthalpy of formation of MoO₂ is $-591.50 \pm 0.14 \text{ kJ}\cdot\text{mol}^{-1}$.

INTRODUCTION

The Mo-MoO₂ (MOM) equilibrium is a potentially useful oxygen buffer in experimental petrology, not least because of the advantages of using relatively inert Mo as a capsule material. However, there is considerable disagreement among the previous calibrations of this buffer (see Table 1 for a summary). Moreover, a couple of question marks hang over the calorimetric data for MoO₂. First, since the entropy of MoO₂ has been determined from heat-capacity measurements that extend only down to 53 K (King, 1958), the compilers of the JANAF thermochemical tables (Stull and Prophet, 1971) suggested that an additional contribution of up to $9.2 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ might need to be added to the experimental value to allow for a supposed antiferromagnetic to paramagnetic transition in MoO₂ below 50 K. However, the rather unusual structure of MoO₂ (deformed rutile with some unusually close metal-metal distances) suggests that a simple magnetic model based on the properties of a d^2 ion may not be appropriate, owing to the formation of Mo-Mo bonds. Indeed, electrical resistivity measurements down to 4.2 K have failed to reveal any anomaly (Rogers et al., 1969). Nevertheless, for the JANAF assessment, a compromise of $3.8 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ was added to the measured entropy, largely in order to bring the emf measurements of Rapp (1963) into agreement with the calorimetrically determined heat of formation. This addition has subsequently been used in other compilations of thermodynamic data [e.g., Barin and Knacke (1973), Robie et al. (1978), but not Pankratz (1982)]. However, the enthalpy of formation of MoO₂ selected by JANAF is based on measurements of the enthalpy of combustion of MoO₂ to MoO₃ by Staskiewicz et al. (1955) and Mah (1957). Since in both determinations, combustion was incomplete, a correction to the measured heats needed to be applied: this correction might well be in error, as the presence of the host of intermediate phases between MoO₂ and MoO₃ (e.g., Magnéli, 1953) was not allowed for.

In order to settle these uncertainties and to provide a

more accurate calibration of the MOM equilibrium, a series of experiments was therefore undertaken using an electrochemical method.

EXPERIMENTAL DETAILS

The experimental method and apparatus used are fully described in O'Neill (ms. in prep.). Two runs were performed, both with Fe-“FeO” as the reference electrode. In the first run, the Mo + MoO₂ electrode occupied the usual sample position; in the second, the position of the two electrodes was reversed.

The chemicals used were of greater than 99.5% purity. MoO₂ was synthesized by mixing Mo and MoO₃ in the appropriate ratio, but with a slight excess of Mo, and then sintering at 1000°C under highly purified argon for ~10 h. This MoO₂ was then mixed with more Mo (<2- μm grain size) in the molar ratio 3Mo to 1MoO₂. “FeO” was prepared in an identical manner from Fe and Fe₂O₃.

Perhaps surprisingly, the Mo + MoO₂ electrode proved rather unreactive. In the first run (Mo + MoO₂ in the normal sample position) equilibrium could not be achieved below ~1000 K; in the second run, with the Mo + MoO₂ electrode having to equilibrate with a larger gas space, equilibrium was not reached initially below 1150 K, although matters improved after the Mo + MoO₂ compartment was flushed out with a reducing Ar + 10% CH₄ gas mixture. In both runs, the emf at low temperatures was displaced in a direction indicating that the Mo + MoO₂ electrode was too oxidized. The symmetrical cells Fe + “FeO” vs. Fe + “FeO” and Mo + MoO₂ vs. Mo + MoO₂ were also run as calibration checks. The first gave essentially zero ($< \pm 0.2 \text{ mV}$) emf values, even down to 900 K; the second confirmed the unreactive nature of the Mo + MoO₂ electrode at lower temperatures by giving almost zero ($< \pm 0.4 \text{ mV}$) above ~1150 K, but rather erratic results at temperatures below this. Nevertheless, all cells performed very well at higher temperatures.

The relatively poor ability of the Mo + MoO₂ electrode to reach equilibrium at temperatures below ~1150 K may be contrasted with other simple metal-metal oxide electrodes, such as Fe + “FeO”, Ni + NiO, and Cu + Cu₂O, which I have used without undue difficulty in identical apparatus down below 900 K. One advantage that the Mo + MoO₂ electrode does have over Fe + “FeO” or Cu + Cu₂O electrode is that it does not stick to the electrolyte even after extended periods above 1400 K, which enables the electrolyte tube to be used for several experiments.

Table 1. Previous investigations of the Mo-MoO₂ equilibrium (since 1962)

Reference	T(K) range	Method
Gleiser & Chipman (1962)	1200-1350	CO/CO ₂ gas mixing
Rapp (1963)	1023-1323	e.m.f. vs Fe+“FeO” and Ni+NiO
Drobyshev et al. (1965)	1264-1362	e.m.f. vs Fe+“FeO”
Berglund & Klerkegaard (1969)	1150-1450	e.m.f. vs air
Alcock & Chan (1972)	1273-1873	e.m.f. vs CO/CO ₂ mixtures
Katayama & Kozuka (1973)	1173-1373	e.m.f. vs Fe+“FeO”
Iwase et al. (1979)	1223-1723	e.m.f. vs Co+CoO and air
Kleykamp & Supawan (1979)	1070-1320	e.m.f. vs Fe+“FeO”
Prabhakar (1980)	1100-1473	e.m.f. vs air
Pejryd (1984)	940-1450	e.m.f. vs air

EXPERIMENTAL RESULTS

The experimental results are given in Table 2. The value of the oxygen potential at the Fe-“FeO” electrode has been taken from O'Neill (ms. in prep.) to be, in J·mol⁻¹ (of O₂),

$$-605\,812 + 1366.718T - 182.7955T \ln T + 0.103\,592T^2 \quad (T < 1042\text{ K})$$

$$-519\,357 + 59.427T + 8.9276T \ln T \quad (1042\text{ K} < T < 1184\text{ K})$$

$$-551\,159 + 269.404T - 16.9484T \ln T \quad (T > 1184\text{ K})$$

with an error of ± 90 J·mol⁻¹. The reference pressure of O₂ is 1 bar (10⁵ Pa). Temperatures (in kelvins) are based on the IPTS 1968 scale.

Each datum was analyzed by the third-law method, using the entropies and heat capacities listed in Table 3, to give the standard enthalpy of formation of MoO₂. Note that for the entropy of MoO₂, the unadulterated value of King (1958) has been used. The results of this analysis are plotted against the temperature of the datum in Figure 1, from where it will be seen that agreement with the calorimetric data is excellent. The slight negative slope suggested by the data of run 2 may perhaps be explained by the procedure of flushing out the Mo + MoO₂ electrode compartment with a reducing gas, leaving the Mo + MoO₂ electrode slightly out of equilibrium in the direction of being too reduced. In any event, the sense of this slope is opposite to that which would be produced by the addition to the entropy suggested in the JANAF tables, and hence the present results definitely show that this correction to King's original entropy is unwarranted. Incidentally, the rest of the calorimetric data is unusually well known: $S_{298.15\text{ K}}$ for Mo has recently been redetermined by Khriplovich and Paukov (1983) with an essentially identical result, and Mo is often used as a standard for high-temperature heat-capacity experiments. The heat capacity of MoO₂ in the range 350-950 K has also been recently redetermined (Inaba et al., 1984), with again good agreement with the

Table 2. Experimental results for the cell Pt, Fe + “FeO” | CSZ | Mo + MoO₂, Pt

T (K)	EMF (mV)	$\Delta_{\text{F}}H^{\circ}(298.15\text{K})$ (kJ mol ⁻¹)	T (K)	EMF (mV)	$\Delta_{\text{F}}H^{\circ}(298.15\text{K})$ (kJ mol ⁻¹)
Run #1					
1034	22.7	-591.26	1151	10.7	-591.47
1061	19.7	.26	1163	9.3	.41
1113	14.3	.33	1175	8.1	.42
1139	11.6	.34	1187	7.0	.46
1163	9.0	.29	1200	5.7	.45
1126	13.0	.36	1211	4.6	.44
1101	15.8	.42	1223	3.4	.44
1075	18.2	.26	1235	2.3	.46
1048	21.0	.21	1247	1.2	.49
1106	25.8	.20	1259	0.0	.48
1020	24.3	.25	1271	-1.1	.51
1034	23.2	.45	1281	-2.1	.50
1047	21.8	.47	1293	-3.2	.53
1061	20.2	.45	1304	-4.3	.51
1074	18.9	.49	1314	-5.3	.50
1088	17.4	.50	1325	-6.4	.49
1100	16.0	.45	1335	-7.3	.51
1113	14.5	.41	1345	-8.3	.50
1126	13.3	.47	1356	-9.2	.56
Run #2					
1153	11.3	-591.78	1248	1.6	-591.69
1142	12.4	.77	1259	0.4	.64
1129	13.6	.71	1270	-0.6	.67
1103	16.1	.62	1281	-1.7	.65
1090	17.2	.50	1292	-2.9	.60
1076	18.1	.27	1237	2.7	.69
1090	17.4	.58	1303	-4.0	.59
1103	16.1	.62	1314	-5.1	.58
1116	14.9	.68	1324	-6.1	.57
1128	13.8	.75	1335	-7.2	.55
1141	12.6	.81	1225	3.7	.63
1152	11.4	.78	1248	1.7	.72
1165	10.1	.80	1270	1.7	.72
1177	8.9	.80	1325	-6.2	.57
1189	7.6	.77	1346	-8.4	.50
1201	6.5	.80	1356	-9.5	.45
1213	5.3	.79	1367	-10.6	.43
1125	4.1	.78	1376	-11.7	.34
1236	2.6	.62	1303	-4.0	.59
1201	6.1	.64	1346	-8.3	.54
1213	5.0	.67	1377	-11.4	.50
1225	3.9	.70	1387	-12.4	.48
1236	2.8	.70	1397	-13.6	.39

values used here (apart from a blip in the C_p vs. T curve of unknown provenance at ~ 865 K).

The small degree of oxygen deficiency noted by Zador and Alcock (1970) for MoO₂ in equilibrium with Mo would have but a trivial effect on the calorimetric data and need

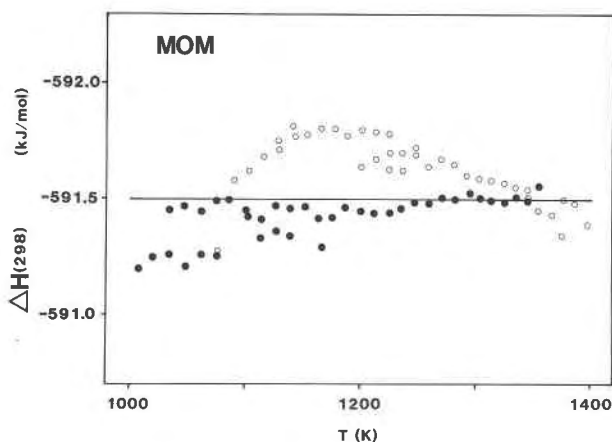


Fig. 1. Standard enthalpy of formation of MoO₂ calculated using the calorimetric data listed in Table 3 for each experimental datum plotted against the temperature of the datum. Closed circles, run 1. Open circles, run 2.

Table 3. Calorimetric data used in calculating $\Delta H_{(298,15K)}^{\circ}$ for MoO₂
 $C_p = A + BT + CT^2 + DT^{-1/2} + ET^{-2}$

Substance	Ref. T (K)	T range (K)	S _(T) (J K ⁻¹ mol ⁻¹)	H _(T) -H ₍₂₉₈₎ (J mol ⁻¹)	C _p				
					A	B(x10 ³)	C(x10 ⁶)	D	E(x10 ⁻⁵)
Mo ^a	1000	700-1500	60.38	18690	33.9113	-11.919	6.958	-	-9.2048
MoO ₂ ^b	1000	700-1500	133.82	50246	59.99	18.011	3.407	-	-
O ₂ ^c	1000	298-1800	243.58	22694	48.318	-0.6913	-	-420.66	4.9923

a Barin et al. (1977)
b Stull & Prophet (1971) : authors own fit to tabulated C_p values.
c Robie et al. (1978)

not therefore be taken into account when comparing with the phase-equilibrium measurements.

Since run 1 should be more accurate than run 2, I have given it more weight in calculating the mean standard enthalpy of formation of MoO₂, -591.50 ± 0.14 kJ·mol⁻¹. This is slightly more negative than the values obtained from combustion calorimetry by Staskiewicz et al. (1955) (-589.36 ± 0.53 kJ·mol⁻¹) and Mah (1957) (-588.44 ± 0.53 kJ·mol⁻¹). As mentioned previously, this small discrepancy may result from the presence of unidentified Magnéli phases in the products of the calorimetric experiments.

The above value for the standard enthalpy of formation of MoO₂ together with the calorimetric data of Table 3 has been used to calculate, at 50-K intervals, values for the oxygen potential (in J·mol⁻¹; ± 140 J·mol⁻¹) of the

MOM equilibrium, from which the following expression was obtained by a least-squares regression:

$$\mu_{O_2} = -603\,268 + 337.460T - 20.6892T \ln T \quad (800 \text{ K} < T < 1500 \text{ K}).$$

The present results are 2.25 ± 0.1 kJ·mol⁻¹ more negative than those recently given by Pankratz (1982), based on calorimetric data.

The difference in the chemical potential of oxygen defined by the MOM buffer as found in this study and that given by some previous investigations is shown in Figure 2. For the sake of comparison, the results of those emf studies that used a Fe + "FeO" reference electrode have been recalculated using the same values for the Fe + "FeO" equilibrium as used in this work. Having done this, it may be seen that the results of Rapp (1963) are actually in quite good agreement; moreover, his results using the Ni + NiO equilibrium as the reference (which have not been plotted for lack of space) are in even slightly better agreement.

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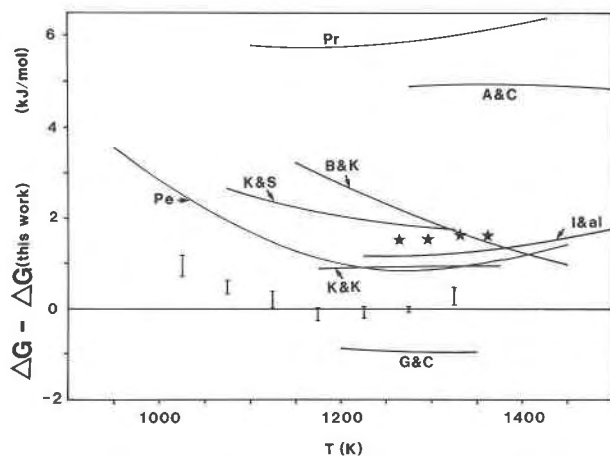


Fig. 2. Comparison of previous experimental determinations of the free energy of formation of MoO₂ with that of this study. Pr = Prabhakar (1980); A & C = Alcock and Chan (1972); B & K = Berglund and Kierkegaard (1969); K & S = Kleykamp and Supawan (1979); I & al = Iwase et al. (1979); K & K: Katayama and Kozuka (1973); Pe = Pejryd (1984); G & C = Gleiser and Chipman (1962). Stars = Drobyshev et al. (1965). Bars = Rapp (1963), his data obtained vs. Fe + "FeO."

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