GIBBS ENERGIES OF FORMATION OF MoO_2 AND Mo_4O_{11}

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Summary

The Gibbs energies of formation of MoO_2 and Mo_4O_{11} have been determined by means of e.m.f. measurements using the cells Mo, $MoO_2/ZrO_2 \cdot$ CaO or $ThO_2 \cdot Y_2O_3/Fe_{0.95}O$, Fe and Fe, $Fe_{0.95}O/ZrO_2 \cdot CaO/Mo_4O_{11}$, MoO_2. The data may be represented by the equations $^f\Delta G^0 \langle MoO_2 \rangle = -571.8 + 0.1662T \pm 1.1$ (kJ mol^{-1}) between 1070 and 1320 K and $^f\Delta G^0 \langle Mo_4O_{11} \rangle = -2743 + 0.853T \pm 5$ (kJ mol^{-1}) between 840 and 1090 K. The enthalpies of formation and standard entropies of MoO_2 and Mo_4O_{11} at 298 K are calculated by second law evaluations.

$$^f\Delta H^0_{298} \langle MoO_2 \rangle = -(586 \pm 3) \, kJ \, mol^{-1}$$

$$S^0_{298} \langle MoO_2 \rangle = (49 \pm 2) \, J \, K^{-1} \, mol^{-1}$$

$$^f\Delta H^0_{298} \langle Mo_4O_{11} \rangle = -(2807 \pm 12) \, kJ \, mol^{-1}$$

$$S^0_{298} \langle Mo_4O_{11} \rangle = (290 \pm 15) \, J \, K^{-1} \, mol^{-1}$$

The Gibbs energies of formation of MoO_2 and Mo_4O_{11} are given by $^f\Delta G^0 \langle MoO_2 \rangle = -592 - 0.0387T \log T + 0.303T$ (kJ mol^{-1}) between 298 and 2000 K and $^f\Delta G^0 \langle Mo_4O_{11} \rangle = -2776 + 0.886T$ (kJ mol^{-1}) between 298 and 1091 K.

1. Introduction

The oxides MoO_2, MoO_3 and some intermediate phases exist in the molybdenum–oxygen system at elevated temperatures [1]. Thermodynamic data for MoO_2 were previously obtained calorimetrically [2, 3], by gas equilibration methods [4 - 6] and by galvanic cell measurements [7 - 14]. Most of these results are in excellent agreement (see Table 1). However, thermodynamic data for the intermediate oxides are scarce. Investigations on Mo_4O_{11} are restricted to MoO_3 vapor pressure measurements over the $MoO_2-Mo_4O_{11}$ two-phase field [15]. Furthermore, an estimation of the enthalpy of formation of Mo_4O_{11} has been made [16]. Thermodynamic

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data for the molybdenum oxides, for instance, are necessary for the analysis of the chemical state of irradiated nuclear oxide fuels. As the oxygen potential of the molybdenum oxides is comparable with that of the uranium–plutonium dioxide, ranging from -650 to -250 kJ mol^{-1}, the oxidation state of the fission product molybdenum in the fuel is a sensitive indicator of the oxygen potential and of the stoichiometry of the irradiated uranium–plutonium dioxide.
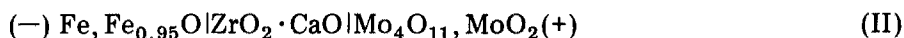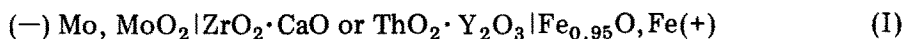
TABLE 1

Gibbs energy of formation of MoO_2

$^f\Delta G^0_T$ (J mol^{-1})	T (K)	Method	Ref.
$-553\,300 + 146.9T$	950 - 1330	H_2/H_2O equil.	4
$-596\,100 - 40.66T\log T + 311.6T$	298 - 2000	Calorimetry + C_p	3
$-576\,900 + 168.1T$	1200 - 1350	CO/CO_2 equil.	5
$-575\,300 + 167.4T$	1020 - 1320	e.m.f.	7
$-578\,900 + 177.8T$	840 - 1100	e.m.f.	8
$-575\,600 + 169.4T$	1260 - 1360	e.m.f.	9
$-570\,700 + 159.4T$	1070 - 1670	e.m.f.	10
$-530\,300 + 127.5T$	970 - 1140	H_2/H_2O equil.	6
$-564\,800 + 161.0T$	1150 - 1450	e.m.f.	11
$-565\,600 + 183.3T$	870 - 1670 }	e.m.f.	12
$-516\,890 + 154.4T$	1670 - 1970 }		
$-575\,600 + 168.7T$	1170 - 1370	e.m.f.	13
$-587\,600 + 177.3T$	1070 - 1670 }	e.m.f.	14
$-530\,100 + 143.0T$	1670 - 1970 }		
$-571\,800 + 166.2T$	1070 - 1320	e.m.f.	This work

2. Experimental

The Gibbs energies of formation of MoO_2 and Mo_4O_{11} were determined by means of electromotive force measurements using galvanic cells with solid oxide electrolytes [17]. The following cells were built up using an Fe–$Fe_{0.95}$ reference electrode:

$$(-) \text{ Mo, } MoO_2 | ZrO_2 \cdot CaO \text{ or } ThO_2 \cdot Y_2O_3 | Fe_{0.95}O, Fe(+) \qquad (I)$$

$$(-) \text{ Fe, } Fe_{0.95}O | ZrO_2 \cdot CaO | Mo_4O_{11}, MoO_2(+) \qquad (II)$$

Owing to the low solubility of oxygen in molybdenum [18] and of molybdenum in MoO_2 [19], one can formulate the cell reaction for cell (I) by

$$\text{Mo} + 2Fe_{0.95}O = MoO_2 + 1.9\text{Fe} \qquad (1)$$

with the Gibbs energy of reaction

$$^r\Delta G^0 = -4FE_I = {}^f\Delta G^0 \langle MoO_2 \rangle - 2\,{}^f\Delta G^0 \langle Fe_{0.95}O \rangle \qquad (2)$$

The Mo–MoO_2 electrode is negative only at temperatures below 1200 K. If the homogeneous region of MoO_2 can be neglected, the cell reaction for cell (II) can be expressed as

$$2.85Fe + Mo_4O_{11} = 3Fe_{0.95}O + 4MoO_2 \qquad (3)$$

with the Gibbs energy of reaction

$$^r\Delta G^0 = -6FE_{II} = 3^f\Delta G^0 \langle Fe_{0.95}O \rangle + 4^f\Delta G^0 \langle MoO_2 \rangle - {}^f\Delta G^0 \langle Mo_4O_{11} \rangle \quad (4)$$

E is the measured electromotive force of the cells and F is Faraday's number 96 487 C mol^{-1}.

The Mo–MoO$_2$ electrode was prepared by mixing equal amounts by weight of molybdenum (Fluka) and molybdenum dioxide (Micropure). The mixture was pre-annealed at 1000 °C under high vacuum and either pelleted or sealed into CaO-doped ZrO$_2$ crucibles [20] which simultaneously acted as the electrolyte. Both ZrO$_2 \cdot$CaO and ThO$_2 \cdot$Y$_2$O$_3$ discs were used in the open pellet stack arrangement. Iridium leads were used to avoid any reaction with the electrodes. No reliable e.m.f. data were obtained with tungsten leads (WO$_2$ coating) or Pt or Pt–Rh leads (formation of Pt–Fe alloys). The cells were operated under purified argon ($P_{O_2} < 10^{-10}$ bar). Details have been described elsewhere [20]. The use of an Ni–NiO reference electrode was not suitable in this apparatus because of the high purity of the argon gas. It was observed that NiO is reduced after some hours of operation. The electromotive force measurements were carried out between 1070 and 1320 K. The time for equilibration was much longer for the Mo–MoO$_2$ electrode than for other systems, *e.g.* the platinum metal oxides previously investigated in this laboratory. The time for attaining equilibrium and the e.m.f. data were independent of the type of the electrolyte and the form of the cell. This seems to indicate that a molybdenum oxide coating at the electrolyte–electrode interface is not the reason for the low e.m.f. values, as has sometimes been assumed [7, 8, 12]. However, molybdenum penetration through the electrolyte by grain boundary diffusion was observed by electron microprobe analysis in this study. This resulted in a limited lifetime of the cells at high temperatures.

The MoO$_2$–Mo$_4$O$_{11}$ electrode was prepared by mixing one mole of molybdenum and five moles of MoO$_3$ (Schuchardt) and by reacting this mixture in a closed stainless steel capsule at 930 K. The resulting orthorhombic γ-Mo$_4$O$_{11}$ was identified by X-ray analysis. Monoclinic η-Mo$_4$O$_{11}$ was prepared in the same way at 840 K. The η–γ transformation of Mo$_4$O$_{11}$ is observed at 888 K [21]. The oxide decomposes peritectically at 1091 ± 7 K [1]. The e.m.f. measurements were performed in sealed ZrO$_2 \cdot$CaO crucibles between 840 and 1090 K as described previously [20]. Equilibrium was reached in less than 1 h depending on temperature and was tested by cell polarizations.

3. Results

3.1. *MoO$_2$*

E.m.f. *versus* temperature was measured in various type (I) cells identified by different symbols (Fig. 1). The straight line in Fig. 1 evaluated by
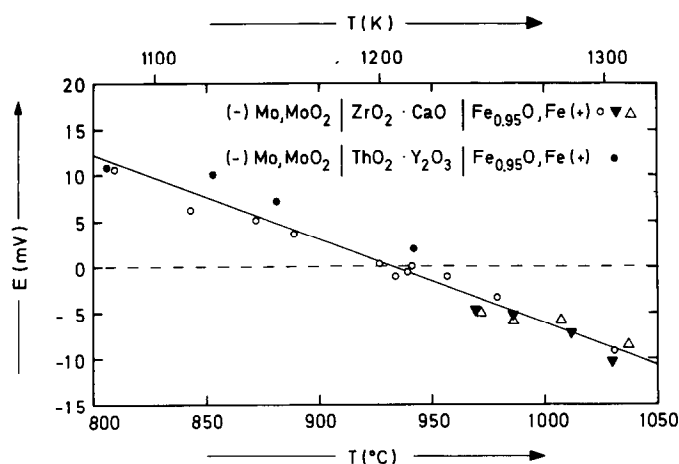
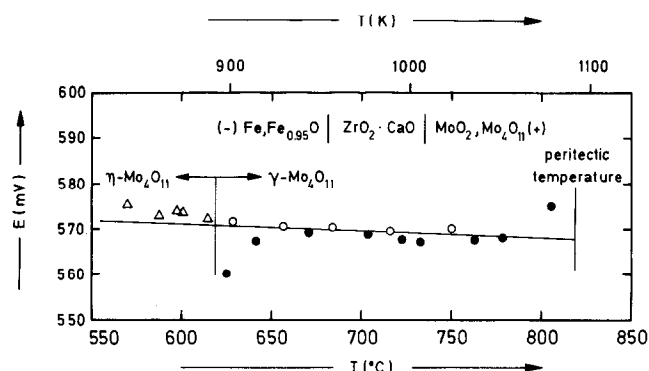Fig. 1. Electromotive force vs. temperature of cell (I). The different symbols represent different experiments.

Fig. 2. Electromotive force vs. temperature of cell (II). The different symbols represent different experiments.

the least-squares method can be represented by $E_I = 110.40 - 0.09156T$ (mV). The Gibbs energy of formation of MoO_2 is calculated from eqn. (2) between 1070 and 1320 K using the data for $Fe_{0.95}O$ from ref. 22:

$$^f\Delta G_T^0 \langle MoO_2 \rangle = -(571.8 \pm 2.9) + (0.1662 \pm 0.0023)T \pm 1.1 \ (kJ \ mol^{-1}) (5)$$

The high temperature heat capacity of MoO_2 has been measured [3]. Taking the corresponding data for Mo and O_2 from ref. 16, the difference in the heat capacities is

$$\Delta C_P = 4.937 + 18.995 \times 10^{-3}T - 7.448 \times 10^5 T^{-2} - 2.259 \times 10^{-6} T^2$$

$$(J \ mol^{-1}) \qquad (6)$$

The second law evaluation results in

$$^f\Delta H^0_{298}\langle MoO_2\rangle = -(586 \pm 3) \text{ kJ mol}^{-1} \tag{7}$$

$$S^0_{298}\langle MoO_2\rangle = (49 \pm 2) \text{ J K}^{-1} \text{ mol}^{-1} \tag{8}$$

for the enthalpy of formation and the standard entropy of MoO_2 at 298 K.

3.2. Mo_4O_{11}

E.m.f. *versus* temperature was measured in various type (II) cells identified by different symbols (Fig. 2). No inflection point in the e.m.f. *versus* T curve owing to the $\eta - \gamma$ transition of Mo_4O_{11} at 888 K was detected. Therefore an enthalpy of transformation can be disregarded. The straight line in Fig. 2 evaluated by the least-squares method can be represented by $E_{II} = 583.38 - 0.01395T$ (mV). The Gibbs energy of formation of Mo_4O_{11} is calculated from eqn. (4) between 840 and 1090 K using the data for $Fe_{0.95}O$ [22] and eqn. (5):

$$^f\Delta G^0_T\langle Mo_4O_{11}\rangle = -(2743 \pm 10) + (0.853 \pm 0.012)T \pm 5 \text{ (kJ mol}^{-1}) \tag{9}$$

The high temperature heat capacity of Mo_4O_{11} has been measured [23]. Taking the corresponding data for Mo and O_2 [16], the difference in the heat capacities is

$$\Delta C_P = -3.598 + 146.36 \times 10^{-3}T - 9.037 \times 10^{-6}T^2 + 9.205 \times 10^5 T^{-2}$$
$$\text{(J mol}^{-1}) \tag{10}$$

The second law evaluation results in

$$^f\Delta H^0_{298}\langle Mo_4O_{11}\rangle = -(2807 \pm 12) \text{ kJ mol}^{-1} \tag{11}$$

$$S^0_{298}\langle Mo_4O_{11}\rangle = (290 \pm 15) \text{ J K}^{-1} \text{ mol}^{-1} \tag{12}$$

for the enthalpy of formation and the standard entropy of Mo_4O_{11} at 298 K.

4. Discussion

The Gibbs energy of formation measurements on MoO_2 by the e.m.f. method [7 - 14] agree very well in most cases, although some authors have described difficulties in equilibrating the cells. However, the quoted errors in the Gibbs energy of formation [7, 11, 13] are probably too small because the error of $2^f\Delta G^0\langle Fe_{0.95}O\rangle$ of the reference electrode already amounts to 1090 J mol^{-1} [22]. The set of e.m.f. results is complemented by higher and lower values based on the gas equilibrium methods [4 - 6]. The Gibbs energy of formation data for MoO_2, together with the results of this paper, are given in Table 1. The enthalpy of formation and the standard entropy of MoO_2 at 298 K were evaluated by the second law method using the published heat capacity of MoO_2 [3]. These values are in excellent agreement with the data determined calorimetrically [2, 3]; they are given in Table 2. From these results, the following three-term expression is recom-

TABLE 2

Enthalpy of formation and standard entropy of MoO_2

$^f\Delta H^0_{298}$ (kJ mol^{-1})	S^0_{298} (J K^{-1} mol^{-1})	Method	Ref.
-553.3^a	—	H_2/H_2O equil.	4
-588.4 ± 0.5	—	Calorimetry	2
-589.1 ± 0.8	46.3 ± 0.2	Calorimetry	3
-592.0^a	—	CO/CO_2 equil.	5
-587.4 ± 2.9^a	—	e.m.f.	9
-586.0 ± 2.5^a	48.9 ± 2.4	e.m.f.	This work

^{a}Second law.

TABLE 3

Enthalpy of formation and standard entropy of Mo_4O_{11}

$^f\Delta H^0_{298}$ (kJ mol^{-1})	S^0_{298} (J K^{-1} mol^{-1})	Method	Ref.
-2778 ± 27	372 ± 6	MoO_3 pressure	15
-2846 ± 10	—	Estimated	16
-2807 ± 12^a	290 ± 15	e.m.f.	This work

^{a}Second law.

mended for the Gibbs energy of formation of MoO_2 between 298 and 2000 K:

$$^f\Delta G^0\langle MoO_2\rangle = -592 - 0.0387T\log T + 0.303T \text{ (kJ mol}^{-1}) \tag{13}$$

with an error of ± 2 kJ mol^{-1} below 1400 K and ± 4 kJ mol^{-1} above 1400 K.

The measured Gibbs energy of formation of Mo_4O_{11} cannot be compared directly with the results of other authors. The enthalpy of formation value at 298 K [15] based on MoO_3 partial pressure measurements over solid MoO_2–Mo_4O_{11} agrees reasonably well with the second law value of this paper which has been calculated from the heat capacity of Mo_4O_{11} [23] (see Table 3). In this calculation, a possible heat of transformation of the η–γ transition of Mo_4O_{11} at 888 K is disregarded. From these results one can obtain a two-term expression:

$$^f\Delta G^0_T\langle Mo_4O_{11}\rangle = -2776 + 0.886T \pm 15 \text{ (kJ mol}^{-1}) \tag{14}$$

for the Gibbs energy of formation of Mo_4O_{11} between 298 K and the temperature of the peritectic decomposition at 1091 K. The partial molar Gibbs energy of oxygen in the MoO_2–Mo_4O_{11} two-phase field is calculated using eqns. (5), (7), (8) and (13) to give

$$\Delta \overline{G}_{O_2} = -289 + 0.112T \pm 12 \text{ (kJ mol}^{-1}) \tag{15}$$

between 298 and 1091 K. This relation reveals an oxygen partial pressure of 1×10^{-8} bar at the peritectic temperature of Mo_4O_{11}. The partial molar Gibbs energy of oxygen and the oxygen partial pressure in the Mo–O system
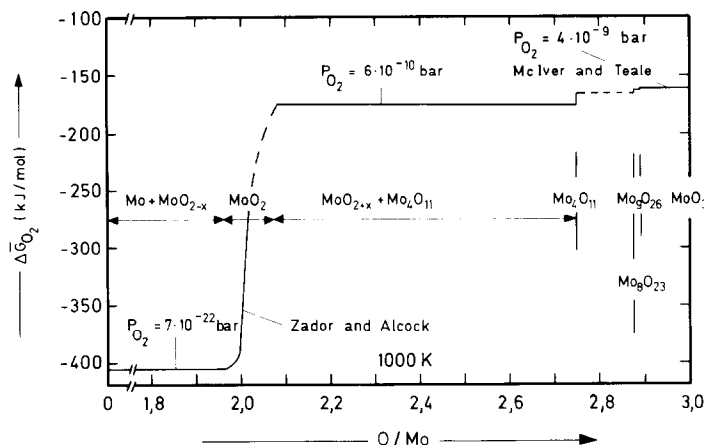
Fig. 3. Partial molar Gibbs energy of oxygen in the Mo–O system at 1000 K.

at 1000 K are given in Fig. 3. The results are complemented by the thermo-dynamic studies [19] in the homogeneous region of $MoO_{2\pm x}$ which is suggested to be in the O/Mo range between 1.97 and 2.08 [16]. Furthermore, the partial molar Gibbs energy of oxygen measured over the gross composition $MoO_{2.90}$ [10] is given in Fig. 3. The value is consistent with the measurements reported here.

It can be deduced from these results that at 1000 K the formation of Mo_4O_{11} by oxidation of MoO_2 is not possible in the fuel surface region of irradiated uranium–plutonium dioxide.

Acknowledgment

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