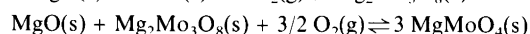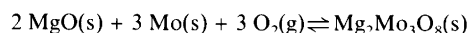# Studies of Phase Equilibria in the System MgO–Mo–O in the Temperature Range 1100–1400 K

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To determine the thermodynamic stabilities of the intermediate phases $Mg_2Mo_3O_8$ and $MgMoO_4$, the following redox equilibria were considered:

$2 MgO(s) + 3 Mo(s) + 3 O_2(g) \rightleftharpoons Mg_2Mo_3O_8(s)$

$MgO(s) + Mg_2Mo_3O_8(s) + 3/2 O_2(g) \rightleftharpoons 3 MgMoO_4(s)$

The equilibrium oxygen pressures, generated in the temperature range 1100–1400 K, were determined by means of the solid-state EMF technique involving calcia-stabilized zirconia as electrolyte material. The results obtained were used to calculate the standard Gibbs free energies of formation ($\Delta_f G^\circ$) for the phases $Mg_2Mo_3O_8$ and $MgMoO_4$.
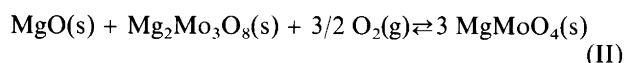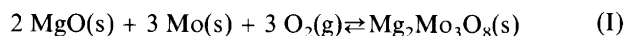
Work has progressed for some years at our department in investigating metal–molybdate systems. Thus, Pejryd[1,2] studied the system Ni–Mo–O and Lindblom[3–5] the systems SrO–Mo–O and CaO–Mo–O. These studies include the determination of redox equilibria and thermochemical data for intermediate phases from solid-state EMF measurements. The present study, dealing with the system MgO–Mo–O, forms a continuation of this work.

In the MgO–Mo–O system, at temperatures above 1100 K three ternary intermediate phases have been reported in the literature: the Mo(IV)-containing phases $MgMoO_3$ and $Mg_2Mo_3O_8$, and the Mo(VI)-compound $MgMoO_4$. However, McCarroll et al.[6,7] have shown convincingly that $Mg_2Mo_3O_8$ is the only stable phase in the binary subsystem $MgO–MoO_2$. The intermediate phases $Mg_2Mo_3O_8$[7] and $MgMoO_4$[8] are both structurally well characterized. On the other hand, reliable stability data for these phases are lacking, and the main object of the present study is to fill this gap.
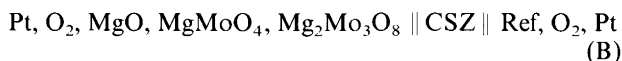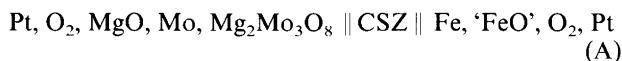
## Experimental

*Equilibria considered.* The phase relations in the system $MgO–Mo–MoO_3$ were examined by thorough equilibrations of sample mixtures, exhibiting various compositions, in the temperature range 1100–1400 K. The phase-relation conditions obtained are presented in Fig. 1. It should be mentioned that no detailed examinations were made in the composition range $MoO_2–MoO_3$, in which several additional solid Mo–O phases occur, e.g.

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$Mo_4O_{11}$, at temperatures below 1130 K. It turns out from this phase diagram that the following redox equilibria can be established:

$2 MgO(s) + 3 Mo(s) + 3 O_2(g) \rightleftharpoons Mg_2Mo_3O_8(s)$ (I)

$MgO(s) + Mg_2Mo_3O_8(s) + 3/2 O_2(g) \rightleftharpoons 3 MgMoO_4(s)$ (II)

The oxygen pressures $p_{O_2}$, generated in accordance with equilibria (I)–(II), have been determined by solid-state EMF measurements.

*Galvanic cells used and cell operation.* To determine the oxygen pressures, the following oxygen concentration cells, involving calcia-stabilized zirconia (CSZ) as solid electrolyte, were used:

Pt, $O_2$, MgO, Mo, $Mg_2Mo_3O_8$ ‖ CSZ ‖ Fe, 'FeO', $O_2$, Pt (A)

Pt, $O_2$, MgO, $MgMoO_4$, $Mg_2Mo_3O_8$ ‖ CSZ ‖ Ref, $O_2$, Pt (B)

where 'Ref' in the cell configuration (B) represents the reference systems Fe,'FeO' or Ni,NiO. The construction of the galvanic cells and furnace equipment has been described in detail by Pejryd.[9]

In a typical run, a cell was initially heated for approximately 24 h at about 1200 K. The temperature was then changed in steps of 20 to 50 K between the readings. The time between a temperature change and taking a data point was 5–50 h, depending on the temperature level. To

establish that equilibrium values were achieved, the EMF measurements were carried out by both increasing and decreasing the cell temperatures.

*Chemicals.* The metals Mo (Aldrich, analytical grade), Fe (Merck p.a.), Ni (Merck p.a.) and the oxides $MoO_2$ (Pfalz and Bauer), $Fe_2O_3$ (Fisher certified) were all dried before use, usually at 425–500 K, while the more hygroscopic oxide MgO (Merck p.a.) was dried for 48 h at 1200 K. All the dried chemicals were stored in a desiccator over silica gel. The metal oxide NiO was synthesized by decomposing basic nickel(II) carbonate (Fluka p.a.) at 1100 K. The wustite phase 'FeO' was prepared by mixing and grinding appropriate amounts of Fe and $Fe_2O_3$, and was then heated at 1273 K for 24 h in a 600 mm long, closed-end $Al_2O_3$ ('ampoule'). Before heating, the 'ampoule' was evacuated and sealed via a glass tube glued to the top of the $Al_2O_3$ tube.

The intermediate phase $Mg_2Mo_3O_8$ was prepared by heating equimolar amounts of MgO and $MoO_2$ in an evacuated 'ampoule' at 1350 K for about 200 h with one intermediate grinding. To avoid the formation of any $MgMoO_4$, a mixture of Mo (as a getter) and MgO, kept in a crucible, was also placed inside the 'ampoule'. X-ray powder diffraction data obtained were in good agreement with corresponding data given by McCarroll *et al.*[6,7] Finally, the intermediate phase $MgMoO_4$ could easily be prepared by heating MgO and Mo (in a molar ratio 1:1) in air at 1273 K for 24 h.

All prepared phases and sample mixtures were checked and verified by X-ray powder diffraction, using a Rigaku D/MAX IIA diffractometer.
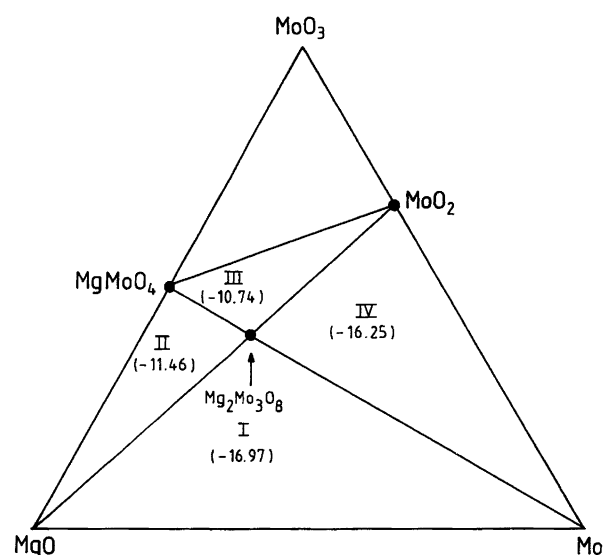
## Results and calculations

*EMF values obtained.* The EMF values obtained at various temperatures ($E_{exp}$/mV, $T$/K) from cell configurations (A) and (B) are given in Tables 1 and 2, respectively. The values given are obtained from 3–4 runs, where each run started with a newly assembled cell charged with 'fresh' chemical mixtures. The measured values were smoothed by a least-squares treatment to evaluate the following $E(T)$ relationships:

$$E(A) = -5.29 + 1.21159\ T - 0.163625\ T \ln T; \qquad (1)$$
$$(1090 \le T \le 1360)$$

$$E(B) = 720.90 + 1.36868\ T - 0.202351\ T \ln T; \qquad (2)$$
$$(1180 \le T \le 1400)$$

Cell configuration (B) contains two different reference systems, and in order to present only one $E(T)$ expression, the measured EMF values in each case were normalized to correspond to a cell with air as the reference system ($p_{O_2} = 0.2123$ bar). In this transformation, necessary relationships were taken from Ref. 10 (Fe,'FeO') and Ref. 11 (Ni,NiO). Relationships (1) and (2) correspond to the assumption of a constant (but non-zero) value of $\Delta C_p$ for the equilibrium reactions considered. Calculated values of the deviations $\Delta E = E_{exp} - E$ are also given in Tables 1 and 2. The mean errors are: $\delta E(A) = \pm 0.3$ mV, $\delta E(B) = \pm 1.0$ mV.

Initial measurements (Fe,'FeO' as reference system) indicated that the equilibrium reaction (II) is rather sluggish, and for this reason the EMF values may be influenced if any oxygen diffusion occurs through the electrolyte wall. It therefore seemed advisable to use also Ni,NiO as a reference system, in which case the potential differences are reduced. As can be seen from Table 2,



*Fig. 1.* Phase relations in the system MgO–Mo–$MoO_3$ in the temperature range 1100–1400 K, stable-phase areas being labelled by the Roman numerals (I)–(IV). The figures indicated (inside the brackets) correspond to the logarithms of the equilibrium oxygen pressures (in bar) generated at 1200 K in the various phase areas.

*Table 1.* Basic experimental data, $E_{exp}$/mV and $T$/K, and calculated values $\Delta E = E_{exp} - E$, obtained for cell arrangement (A).

| $T$/K | $E_{exp}$/mV | $\Delta E$/mV |
|---|---|---|
| 1097.9 | 57.48 | +0.28 |
| 1118.4 | 55.07 | −0.10 |
| 1139.5 | 52.95 | −0.06 |
| 1160.6 | 50.79 | −0.00 |
| 1181.3 | 48.10 | −0.46 |
| 1197.1 | 46.65 | −0.16 |
| 1206.9 | 46.09 | +0.38 |
| 1223.6 | 43.59 | −0.20 |
| 1233.9 | 42.46 | −0.15 |
| 1250.1 | 40.52 | −0.17 |
| 1260.2 | 40.18 | +0.69 |
| 1276.1 | 37.42 | −0.14 |
| 1286.7 | 36.50 | +0.24 |
| 1302.5 | 34.09 | −0.20 |
| 1312.3 | 33.55 | +0.50 |
| 1329.2 | 30.62 | −0.27 |
| 1355.9 | 27.22 | −0.19 |

Table 2. Experimental EMF values ($E_{exp}$/mV), normalized to air as reference system ($p_{O_2}^*$=0.2123 bar), and calculated values, $\Delta E = E_{exp} - E$, obtained at various temperatures ($T$/K) for cell arrangement (B).

| $T$/K | $E_{exp}$/mV | $\Delta E$/mV |
|-------|--------------|---------------|
| 1187.2 | 645.76 | -0.65 |
| 1200.4 | 640.38 | +1.20[a] |
| 1207.5 | 640.18 | -0.51[a] |
| 1217.8 | 637.33 | -0.44 |
| 1236.7 | 631.10 | +0.63 |
| 1243.8 | 630.47 | -0.69 |
| 1253.6 | 625.32 | +1.70[a] |
| 1260.4 | 625.83 | -0.65[a] |
| 1269.8 | 623.40 | -0.84 |
| 1289.2 | 615.94 | +1.16 |
| 1295.9 | 616.10 | -0.90 |
| 1309.0 | 610.29 | +1.18[a] |
| 1321.7 | 609.73 | -1.91 |
| 1341.7 | 601.48 | +0.55 |
| 1400.0 | 584.71 | +0.11 |

[a] Values obtained with Ni,NiO as the reference system.

there is no significant difference in the EMF values between the two reference systems.

*Calculation of oxygen pressures.* The equilibrium oxygen pressures of the equilibria studied [$p_{O_2}$(I)/bar and $p_{O_2}$(II) /bar] are related to the EMF ($E$/mV) and temperature ($T$/K) values and the reference oxygen pressures ($p_{O_2}^*$/bar) by the equations (1 bar = $10^5$ Pa)

$$\lg p_{O_2}(I) = \lg p_{O_2}^* - 4F/(R \ln 10) \times E(A)/T \qquad (3)$$

$$\lg p_{O_2}(II) = - 0.673 - 4F/(R \ln 10) \times E(B)/T \qquad (4)$$

where $R$ is the gas constant (8.31441 J K$^{-1}$ mol$^{-1}$), $F$ is the Faraday constant (96484.56 C mol$^{-1}$) and lg denotes base 10 logarithms. The reference oxygen pressures $p_{O_2}^*$, which originate from the Fe–'FeO' equilibrium reaction, can be expressed by the equation[10]

$$\lg p_{O_2}^* = - 0.884 - 26506/T + 2.2012 \lg T \qquad (5)$$

the uncertainty in lg $p_{O_2}^*$ being $\pm 0.004$ at 1300 K.

By combining eqns. (1), (3) and (5), and (2), (4) and (5), respectively, the following equations can be derived:

$$\lg p_{O_2}(I) = - 25.300 - 26198/T + 9.7963 \lg T \qquad (6)$$
$$(1090 \leq T \leq 1360; \delta \lg p_{O_2}(I) = \pm 0.01)$$

$$\lg p_{O_2}(II) = - 28.264 - 14533/T + 9.3927 \lg T \qquad (7)$$
$$(1180 \leq T \leq 1400; \delta \lg p_{O_2}(II) = \pm 0.02)$$

*Calculation of $\Delta G^\circ$ values.* The Gibbs free energies ($\Delta G^\circ$) for the various equilibria can be evaluated from the general expression

$$\Delta G^\circ = - R \ln 10 \times T \times \lg K$$

where the equilibrium constant $K$ can be substituted as follows:

$$\lg K(I) = - 3 \lg p_{O_2}(I) \qquad (8)$$

$$\lg K(II) = - 3/2 \lg p_{O_2}(II) \qquad (9)$$

Using eqns. (6)–(9), the following relationships are derived:

$$\Delta G^\circ(I) = - 1504650 - 1453.1\,T + 562.64\,T\lg T \qquad (10)$$
$$(1090 \leq T \leq 1360; \delta \Delta G^\circ(I) = \pm 700\,J)$$

$$\Delta G^\circ(II) = - 417340 - 811.66\,T + 269.73\,T\lg T \qquad (11)$$
$$(1180 \leq T \leq 1400; \delta \Delta G^\circ(II) = \pm 600\,J)$$

*Calculation of $\Delta_f G^\circ$ values.* The Gibbs free energy of formation of $Mg_2Mo_3O_8$ and $MgMoO_4$ was derived from the equilibria (I) and (II), giving the expressions:

$$\Delta_f G^\circ(Mg_2Mo_3O_8) = \Delta G^\circ(I) + 2\Delta_f G^\circ(MgO) \qquad (12)$$

$$\Delta_f G^\circ(MgMoO_4) = 1\,3\{\Delta G^\circ(II) + \Delta_f G^\circ(MgO)$$
$$+ \Delta_f G^\circ(Mg_2Mo_3O_8)\} \qquad (13)$$

In the temperature range considered, the following $\Delta_f G^\circ - T$ relationship for MgO was derived using data from Barin[12] and JANAF tables[13]

$$\Delta_f G^\circ(MgO) = - 608700 + 115.8\,T; (\pm 500\,J\,mol^{-1}) \qquad (14)$$

Using eqns. (10), (11) and (14), the following relationships can be calculated:

$$\Delta_f G^\circ(Mg_2Mo_3O_8) = - 2722050 - 1221.5\,T$$
$$+ 562.64\,T\lg T \qquad (15)$$
$$(1100 \leq T \leq 1360; \delta \Delta_f G^\circ = \pm 1500\,J\,mol^{-1})$$

$$\Delta_f G^\circ(MgMoO_4) = - 1249370 - 639.17\,T$$
$$+ 277.46\,T\lg T \qquad (16)$$
$$(1180 \leq T \leq 1360; \delta \Delta_f G^\circ = \pm 800\,J\,mol^{-1})$$

## Discussion

There are very few earlier studies presented in the literature on the MgO–Mo–O system at higher temperatures. The only thermodynamic study seems to be the work by Rezukhina and Levitskij,[14] who carried out solid-state EMF measurements with galvanic cells similar to cell configurations (A) and (B) in the present study. Their values are on the same order of magnitude, but deviate from the present values by about 5–20 mV. However, as they considered the intermediate Mo(IV) phase to be $MgMoO_3$, instead of $Mg_2Mo_3O_8$, any comparisons of $\Delta G^\circ$ values are out of place.

To survey the reducing conditions of the various stable-phase combinations in the system $MgO–Mo–MoO_3$, the logarithms of the oxygen pressures, generated at 1200 K, are also indicated in Fig. 1. For areas (I) and (II) in this diagram, the oxygen pressure values, which refer to equilibria (I) and (II), can be calculated by using eqns. (6) and (7).

For area (III), the given $\lg p_{O_2}$ value is derived from the following equilibrium reaction

$$Mg_2Mo_3O_8(s) + O_2(g) \rightleftarrows 2\ MgMoO_4(s) + MoO_2(s) \quad (III)$$

using $\Delta_f G°$ values for $Mg_2Mo_3O_8$ and $MgMoO_4$, according to eqns. (15) and (16), and for $MoO_2$ from Pejryd.[1] Finally, the value indicated in area (IV) is calculated by considering the equilibrium reaction

$$Mo(s) + O_2(g) \rightleftarrows MoO_2(s) \quad (IV)$$

As can be seen from the diagram, most reducing conditions occur in phase area (I).

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