

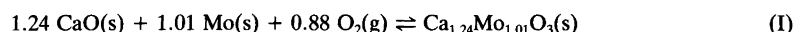
# The Thermodynamic Stability of $\text{Ca}_{1.24}\text{Mo}_{1.01}\text{O}_3$ by Solid-State Emf Measurements in the Temperature Range 1300–1500 K

Bo Lindblom

Department of Inorganic Chemistry, University of Umeå, S-901 87 Umeå, Sweden

Lindblom, B., 1989. The Thermodynamic Stability of  $\text{Ca}_{1.24}\text{Mo}_{1.01}\text{O}_3$  by Solid-State Emf Measurements in the Temperature Range 1300–1500 K. – *Acta Chem. Scand.* 43: 621–623.

The thermodynamic stability of the phase  $\text{Ca}_{1.24}\text{Mo}_{1.01}\text{O}_3$  has been determined by solid-state emf measurements of the equilibrium



in the temperature range 1300–1500 K. The equilibrium oxygen partial pressure were measured by the use of galvanic cells with calcia-stabilized zirconia as solid electrolyte material. From the measured emf data the following Gibbs free energy expression was calculated:

$$\Delta_r G^\circ(\text{I})/\text{J mol}^{-1} = -548761 + 166.23(T/\text{K}) - 3.0898(T/\text{K})\ln(T/\text{K})$$

[1297 < T/K < 1480,  $\delta\Delta_r G^\circ(\text{I}) = \pm 0.3 \text{ kJ mol}^{-1}$ ]

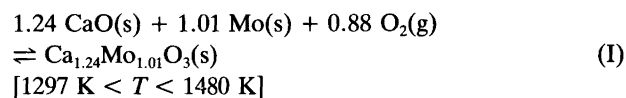
The following expression for the Gibbs free energy of formation of  $\text{Ca}_{1.24}\text{Mo}_{1.01}\text{O}_3$  was calculated by combining literature data for  $\Delta_r G^\circ(\text{CaO})$  with the above equation.

$$\Delta_r G^\circ(\text{Ca}_{1.24}\text{Mo}_{1.01}\text{O}_3)/\text{J mol}^{-1} = -1322000 + 151.98(T/\text{K}) + 13.612(T/\text{K})\ln(T/\text{K})$$

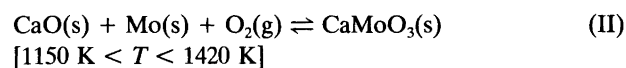
[1297 < T/K < 1480,  $\delta\Delta_r G^\circ(\text{Ca}_{1.24}\text{Mo}_{1.01}\text{O}_3) = \pm 1.3 \text{ kJ mol}^{-1}$ ]

The aim of a project in progress at our department is to establish phase relations and to determine equilibrium conditions in the systems SrO – Mo – O and CaO – Mo – O. In the present paper phase relations and equilibria are investigated in that composition region of the CaO – Mo – O system where the components CaO and Mo are coexistent. As a part of this project a new intermediate phase with the composition  $\text{Ca}_{16.5}\text{Mo}_{13.5}\text{O}_{40}$  has been examined by Lindblom and Strandberg<sup>1</sup> by single-crystal X-ray diffraction.

The aim of this paper is to report the thermodynamic stability of the phase  $\text{Ca}_{16.5}\text{Mo}_{13.5}\text{O}_{40}$  and its coexistence with other phases. From a practical point of view the unit  $\text{Ca}_{1.24}\text{Mo}_{1.01}\text{O}_3$  is chosen here instead of  $\text{Ca}_{16.5}\text{Mo}_{13.5}\text{O}_{40}$ . The thermodynamic stability of the phase  $\text{Ca}_{1.24}\text{Mo}_{1.01}\text{O}_3$  has been examined by solid-state emf measurements of the equilibrium



Two phase-stability studies which are of some interest are reported in the literature. The equilibrium oxygen partial pressure of the following equilibrium



has been determined by Kamata *et al.*<sup>2</sup> and Levitskii *et al.*<sup>3</sup> Kamata *et al.*<sup>2</sup> used a thermogravimetric method, and Levitskii *et al.*<sup>3</sup> used solid-state galvanic cells.

## Experimental

**Chemicals.** The starting materials, Mo (Aldrich, analytical grade),  $\text{MoO}_2$  (Pfalz & Bauer),  $\text{CaCO}_3$  (Riedel – De Haën *p.a.*), Fe (Merck *p.a.*) and  $\text{Fe}_2\text{O}_3$  (Fisher, certified), were used without further purification. The oxide CaO was prepared by heating  $\text{CaCO}_3$  in air at 1300 K for 24 h.

The intermediate phase  $\text{CaMoO}_3$  was prepared by heating equimolar amounts of CaO and  $\text{MoO}_2$  in a 600 mm long  $\text{Al}_2\text{O}_3$  tube with closed ends (here called an “ampoule”) which was evacuated and sealed. This ampoule was heated at 1470 K for 24 h. X-Ray powder diffraction data obtained for  $\text{CaMoO}_3$  were in good agreement with data given by Kamata *et al.*<sup>4</sup>

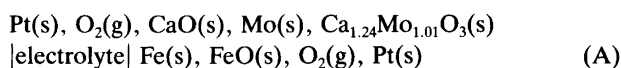
The phase  $\text{Ca}_{1.24}\text{Mo}_{1.01}\text{O}_3$  was prepared by mixing and grinding CaO, Mo and  $\text{MoO}_2$  in proper amounts, and then heating the powder mixture in an ampoule at 1473 K for 4 d. The purity of the phase  $\text{Ca}_{1.24}\text{Mo}_{1.01}\text{O}_3$  was checked by X-ray powder diffraction, and all 44 diffraction peaks obtained could be indexed to a tetragonal unit cell with cell parameters  $a = 8.5575(5)$  and  $c = 11.850(1) \text{ \AA}$  (supplementary data are available from the author upon request). These results are in good agreement with single-crystal data given by Lindblom and Strandberg.<sup>1</sup>

The sample mixtures for the emf measurements were prepared by mixing and grinding CaO, Mo and  $\text{Ca}_{1.24}\text{Mo}_{1.01}\text{O}_3$  in a molar ratio of 5:5:1. The reference mixture consisted of Fe and FeO in a molar ratio of 1:1. The wüstite phase FeO was prepared by mixing and grinding an equimolar mixture of Fe and  $\text{Fe}_2\text{O}_3$ , which then was heated in an ampoule at 1273 K for 24 h.

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

**Phase relation studies.** To demonstrate the proper phase relations, three samples made up with CaO,  $\text{MoO}_2$  and Mo in a molar ratio of 3:1:2 were initially equilibrated in ampoules. The ampoules were heated at three different temperatures, viz. 1273, 1373 and 1473 K, for 5 d. After the heat treatment the samples were examined by X-ray powder diffraction, and all three were found to contain the phases CaO, Mo and  $\text{Ca}_{1.24}\text{Mo}_{1.01}\text{O}_3$ .

**Emf measurements.** In the emf measurements the double-tube arrangement was used (for details, see Pejryd<sup>5</sup>). The cell configuration can be described as follows:



The double-tube arrangement consists of a closed end calcia-stabilized zirconia electrolyte tube, inserted in a closed-end  $\text{Al}_2\text{O}_3$  tube. The reference system Fe, FeO (about 1.5 g) was placed at the bottom of the electrolyte tube. The sample system CaO, Mo,  $\text{Ca}_{1.24}\text{Mo}_{1.01}\text{O}_3$  (about 2.0 g) was placed at the bottom of the  $\text{Al}_2\text{O}_3$  tube. Both cell compartments were evacuated and sealed before heating.

The emf measurements were performed in the temperature range 1300 to 1500 K. Below 1300 K irreproducible conditions arose. At temperatures above 1500 K the emf started to drift towards zero. The temperature was changed in steps of 20–50 K between the readings. The time required for equilibration was 2 to 4 h, depending on the temperature. In a typical run, the cells were heated to approximately 1400 K during the day. To avoid thermal shock to the electrolyte the rate of the temperature change never exceeded 200 K  $\text{h}^{-1}$ . The temperature was kept constant at night to ensure that equilibrium conditions were attained in the morning. The recording of temperature and emf then began.

The cells were heated in two different types of furnaces. For temperatures up to 1400 K, a furnace with non-inductive wound Kantal A-1 resistance wire was used. For temperatures up to 1600 K, a Pt/Pt(40 mass % Rh) resistance furnace was used. The temperature was measured with a Pt/Pt(10 mass % Rh) thermocouple. Both cell and thermal emfs were recorded with a high-precision digital voltmeter (Solartron 7075).

## Results and calculations

**Emf values obtained.** The experimental emf values obtained from four different runs in the temperature range 1297–1480 K are given in Table 1. They were smoothed by a least-squares treatment to give the  $E(T)$  relationship

$$E(\text{II})/\text{mV} = 300.94 - 0.53329(T/\text{K}) + \\ 0.056519(T/\text{K})\ln(T/\text{K}) \quad (1) \\ [1297 < T/\text{K} < 1480]$$

The mean error,  $\sigma E(\text{II})$ , was  $\pm 0.6$  mV.

Calculated values of the deviations  $\Delta E = E(\text{exp}) - E$  are also given in Table 1.

**Calculation of  $p(\text{O}_2)$  values.** The emf values ( $E$ ) obtained in the measurements are related to the oxygen partial pressures of the reference and the sample systems by expression (2).

$$E = RT\ln 10/4F[\log p^*(\text{O}_2) - \log p(\text{O}_2)] \quad (2)$$

where  $R$  is the gas constant,  $F$  the Faraday constant, and  $p^*(\text{O}_2)$  and  $p(\text{O}_2)$  are the partial pressures of oxygen in the reference and the sample system, respectively. In all four different runs Fe, FeO was used as reference system. The following  $\log p^*(\text{O}_2)$  expression for the reference system is taken from Fredriksson and Rosén<sup>6</sup>

$$\log [p^*(\text{O}_2)/\text{atm}] = -0.8839 - 26506/(T/\text{K}) +$$

Table 1. Experimental data,  $E(\text{exp})/\text{mV}$  and  $T/\text{K}$ , and calculated values  $\Delta E = E(\text{exp}) - E$  obtained for galvanic cell (A).

$T/\text{K}$	$E(\text{exp})/\text{mV}$	$\Delta E/\text{mV}$	Cell No.
1297.0	134.8	0.10	1
1317.7	133.0	-0.22	1
1325.2	133.5	0.81	1
1336.5	131.4	-0.50	1
1343.2	131.5	0.07	1
1357.9	131.0	0.59	1
1386.2	129.1	0.63	1
1305.7	134.0	-0.07	2
1330.7	132.0	-0.30	2
1357.3	130.6	0.15	2
1384.5	128.7	0.11	2
1316.8	132.9	-0.38	3
1383.1	129.3	0.62	3
1393.0	126.9	-1.11	3
1411.5	127.1	0.33	3
1426.5	124.6	-1.17	3
1442.6	124.4	-0.31	3
1463.8	123.4	0.07	3
1361.0	129.9	-0.30	4
1393.2	128.3	0.03	4
1440.4	125.5	0.64	4
1452.5	123.6	-0.46	4
1479.9	122.7	0.41	4

$$0.95597 \ln(T/K) \quad (3)$$

[862 < T/K < 1405,  $\delta \log p^*(O_2) = \pm 0.004$  at 1400 K]  
 (1 atm = 101.325 kPa)

The  $\log p(O_2)$  values for equilibrium (I) were calculated by combining eqns. (1), (2) and (3), giving the expression

$$\log [p(O_2)(I)/\text{atm}] = 9.8667 - 32573/(T/K) - 0.18340(T/K) \ln(T/K) \quad (4)$$

[1297 < T/K < 1480,  $\delta \log p(O_2) = \pm 0.01$  at 1400 K]

**Calculation of Gibbs energy.** For equilibrium (I), the Gibbs free energy ( $\Delta G^\circ/\text{J mol}^{-1}$ ) is related to the equilibrium oxygen partial pressure,  $[p(O_2)/\text{atm}]$ , by the following expression:

$$\Delta G^\circ = 0.88RT \ln 10 \log p(O_2) \quad (5)$$

By introducing eqn. (4) into eqn. (5), the relationship (6) is derived:

$$\Delta G^\circ(I)/\text{J mol}^{-1} = -548761 + 166.23(T/K) - 3.0898(T/K) \ln(T/K) \quad (6)$$

[1297 < T/K < 1480,  $\delta \Delta G^\circ(I) = \pm 0.3 \text{ kJ mol}^{-1}$ ]

The Gibbs free energy of formation of Ca<sub>1.24</sub>Mo<sub>1.01</sub>O<sub>3</sub> can be written

$$\Delta_f G^\circ(\text{Ca}_{1.24}\text{Mo}_{1.01}\text{O}_3) = \Delta G^\circ(I) + 1.24 \Delta_f G^\circ(\text{CaO}) \quad (7)$$

The following  $\Delta_f G^\circ - T$  relationship for CaO was derived using data from JANAF tables<sup>7</sup>

$$\Delta_f G^\circ(\text{CaO})/\text{J mol}^{-1} = -623580 - 11.490(T/K) + 13.469(T/K) \ln(T/K) \quad (8)$$

[900 < T/K < 1700,  $\delta \Delta_f G^\circ(\text{CaO}) = \pm 1.0 \text{ kJ mol}^{-1}$ ]

Finally, combining eqn. (7) and eqn. (8) gives the expression

$$\Delta_f G^\circ(\text{Ca}_{1.24}\text{Mo}_{1.01}\text{O}_3)/\text{J mol}^{-1} = -1322000 + 151.98(T/K) + 13.612(T/K) \ln(T/K) \quad (9)$$

[1297 < T/K < 1480]

The estimated uncertainty in  $\Delta_f G^\circ(\text{Ca}_{1.24}\text{Mo}_{1.01}\text{O}_3)$  is  $\pm 1.3 \text{ kJ mol}^{-1}$ .

## Discussion

The Gibbs free energies could be calculated from measured emf data obtained for equilibrium (I). The uncertainty in the calculated Gibbs energy of reaction for equilibrium (I) is of the magnitude of  $\pm 0.3 \text{ kJ mol}^{-1}$ . The estimated uncertainty in the Gibbs free energy of formation of Ca<sub>1.24</sub>Mo<sub>1.01</sub>O<sub>3</sub> becomes higher,  $\pm 1.3 \text{ kJ mol}^{-1}$ , because of the uncertainty in  $\Delta_f G^\circ(\text{CaO})$ , which has a magnitude of  $\pm 1 \text{ kJ mol}^{-1}$ .

Table 2.  $\log p(O_2)$  values from the present study [equil. (I)] and from data given in the literature [equil. (II)].

	$\log [p(O_2)/\text{atm}]$ (1300 K)	$\log [p(O_2)/\text{atm}]$ (1473 K)	Estimated uncertainty
Present work	-16.50	-13.58	$\pm 0.02$
Kamata <i>et al.</i> <sup>2</sup>	-	-13.20	$\pm 0.10$
Levitskii <i>et al.</i> <sup>3</sup>	-16.29	-13.43	$\pm 0.08$

The results from the present study prove that the intermediate phase which coexists with the components CaO and Mo is Ca<sub>1.24</sub>Mo<sub>1.01</sub>O<sub>3</sub> [equilibrium (I)], and *not* CaMoO<sub>3</sub> [equilibrium (II)] as reported by Kamata *et al.*<sup>2</sup> and Levitskii *et al.*<sup>3</sup> The results presented by Kamata *et al.*<sup>2</sup> and Levitskii *et al.*<sup>3</sup> which they assumed to be valid for equilibrium (II), should rather be applicable to equilibrium (I). It may therefore be appropriate to compare their results with the present results for equilibrium (I) (Table 2). The  $\log p(O_2)$  values reported by Kamata *et al.*<sup>2</sup> and Levitskii *et al.*<sup>3</sup> are 0.2–0.3 units higher than the values obtained in the present study. A possible reason for their higher  $\log p(O_2)$  values could be that their samples, which were initially composed of CaO, Mo and CaMoO<sub>3</sub>, still contained some unreacted CaMoO<sub>3</sub> as well as Ca<sub>1.24</sub>Mo<sub>1.01</sub>O<sub>3</sub>.

The fact is that the intermediate phase CaMoO<sub>3</sub> will be formed only under certain conditions. It therefore seemed important to make a more thorough examination of phase relations in those composition regions of the system CaO – Mo – O where CaMoO<sub>3</sub> and Ca<sub>1.24</sub>Mo<sub>1.01</sub>O<sub>3</sub> appear together with other phases, and also to determine the thermodynamic stability of CaMoO<sub>3</sub>. A full description of results from that study is given by Lindblom.<sup>8</sup>

**Acknowledgements.** The author wishes to thank Prof. Erik Rosén for valuable discussions, Barbro Saitton for technical assistance and Steven Swanson for having revised the English text. This work was financially supported by the Swedish Natural Science Research Council.

## References

1. Lindblom, B. and Strandberg, R. *To be published.*
2. Kamata, K., Nakamura, T. and Sata, T. *Mater. Res. Bull.* 10 (1975) 373.
3. Levitskii, V. A., Frenkel', M. Ya. and Rezukhina, T. N. *Sov. Electrochem.* 1 (1965) 1229.
4. Kamata, K., Nakamura, T. and Sata, T. *Chem. Lett.* (1975) 81.
5. Pejryd, L., *Thesis*, University of Umeå, Umeå, Sweden 1985.
6. Fredriksson, M. and Rosén, E. *Scand. J. Metall.* 13 (1984) 95.
7. *JANAF Thermochemical Tables*, 3rd ed., *J. Phys. Chem. Ref. Data*, 14 (1985) Suppl. 1.
8. Lindblom, B. *Scand. J. Metall.* *In press.*

Received September 19, 1988.