

Solid State emf Measurements and Phase Studies in the System SrO/Mo/O in the Temperature Range 1200–1600 K

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Lindblom, B. and Rosén, E., 1986. Solid State emf Measurements and Phase Studies in the System SrO/Mo/O in the Temperature Range 1200–1600 K. – Acta Chem. Scand. A 40: 452–458.

The equilibria $\text{SrMoO}_3(\text{s}) + 1/2\text{O}_2(\text{g}) \rightleftharpoons \text{SrMoO}_4(\text{s})$ and $2\text{SrO}(\text{s}) + \text{Mo}(\text{s}) + \text{O}_2(\text{g}) \rightleftharpoons \text{Sr}_2\text{MoO}_4(\text{s})$ were studied by measuring the partial pressure of oxygen at equilibrium using galvanic cells involving calcia-stabilized zirconia and yttria-doped thoria as solid electrolyte materials. The Gibbs free energy of reaction was calculated from the measured emfs and derived equations. To prepare Sr_2MoO_4 , a mixture of Mo and SrO was used as an oxygen partial pressure buffer.

During the past few decades, there has been an increased interest in the use of alkaline earth molybdates in, for example, electronics, metallurgical processes and nuclear waste technology. A helpful tool to achieve optimum conditions in various processes is the method of equilibrium calculations. It is therefore essential that reliable thermodynamic data for all species which can appear in a process be available.

In the system SrO/Mo/O, experimental results concerning the phase relations are contradictory, and apparently very little has been done to determine thermodynamic data for the phases involved. In 1954, Sholder¹ described the preparation of Sr_2MoO_4 by the reduction of Sr_2MoO_5 in a H_2 atmosphere. Balz and Plieth² found that Sr_2MoO_4 has the tetragonal K_2NiF_4 structure. However, some years later, Gooden³ was unable to prepare this compound. He obtained a product with a complex X-ray powder pattern which indicated the coexistence of several phases. In 1973, McCarthy and Gooden⁴ presented a phase study of the ternary system Sr/Mo/O at 1473 K. They identified the three ternary phases SrMoO_3 , SrMoO_4 and Sr_3MoO_6 , but were unable to prepare Sr_2MoO_4 at 1273, 1473 or 1673 K. At the total composition corresponding to Sr_2MoO_4 , the stable phase assemblage obtained was Sr_3MoO_6 and Mo. There are some earlier studies, using the technique of equilibration with H_2 and H_2O , by Zharkova *et al.* of the following equilibria:

$\text{SrO}(\text{s}) + \text{Mo}(\text{s}) + \text{O}_2(\text{g}) \rightleftharpoons \text{SrMoO}_3(\text{s})$ and $\text{SrMoO}_3(\text{s}) + 1/2\text{O}_2(\text{g}) \rightleftharpoons \text{SrMoO}_4(\text{s})$ (I).

The oxygen stability range of SrMoO_3 at 1473 K has been reported by Kamata *et al.*⁶ who used the thermogravimetric method. Thermodynamic data for Sr_2MoO_4 could not be found in the literature. In view of the conflicting phase stabilities and lack of thermodynamic data, an extended re-investigation was needed. The purpose of this study was to show the existence of the phase Sr_2MoO_4 and to present data for equilibrium (I) and equilibrium (II):

$2\text{SrO}(\text{s}) + \text{Mo}(\text{s}) + \text{O}_2(\text{g}) \rightleftharpoons \text{Sr}_2\text{MoO}_4(\text{s})$ (II).

The emf technique using solid electrolytes has proven to be the most accurate and sensitive method for determining equilibrium constants at high temperatures for reactions involving oxygen. Preliminary measurements on equilibrium (II) with calcia-stabilized zirconia (CSZ) electrolytes showed that the partial pressure of oxygen at equilibrium was extremely low, approximately 10^{-21} atm at 1200 K (1 atm = 101.325 kPa). Such oxygen partial pressures are too low for application of CSZ electrolytes because of electronic conduction. Therefore, two different electrolyte materials have been used in the emf measurements, calcia-stabilized zirconia for equilibrium (I) and yttria-doped thoria (YDT) for equilibrium (II). To check the performance of the YDT electrolytes, equilibrium (I) was studied with

both YDT and CSZ, with three different reference systems.

Preparations

Starting materials. Mo (Aldrich, analytical grade), MoO₂ (Pfaltz & Bauer), Sr(NO₃)₂ (Merck *p.a.*) and NaOH (EKA, *puriss*) were used without further purification.

Preparation of Sr(OH)₂ and SrO. Sr(OH)₂ was precipitated in aqueous solution by adding an excess of 18 M NaOH to a 2 M Sr(NO₃)₂ solution. The precipitate was filtered, washed with cold water and dried at 473 K. The sodium content was analysed by flame spectrometry and was found to be below 0.2 mol percent. The oxide SrO(s) was prepared by heating Sr(OH)₂ in a stream of flowing Ar at 1073 K for 2 h, then at 1373 K for 15 h.

Preparation of SrMoO₄ and SrMoO₃. The phase SrMoO₄ was prepared by heating an equimolar mixture of SrO and Mo at 1270 K for 24 h in air. After this treatment, the sample was shown to be a mixture of SrMoO₄ and Sr₃MoO₆ probably due to loss of gaseous MoO₃. After adding more Mo and further heating for 3 d, Sr₃MoO₆ disappeared. The preparation of SrMoO₃ was carried out in two steps. An equimolar mixture of SrO and MoO₂ was placed at the bottom of a 60 cm long Al₂O₃ tube which was closed at one end. This ampoule was evacuated and sealed with a pyrex tube which was glued to the top of the Al₂O₃ tube. The ampoule was then heated at 1273 K for about 12 h. After this treatment, the sample consisted mainly of SrMoO₃ but considerable amounts of SrMoO₄ were also present. The SrMoO₄ formed could be reduced by heating the mixture in a H₂ atmosphere for 1 h at 1270 K.

The cell parameters were calculated from X-ray powder data: $a = 5.3935(2)$ Å and $c = 12.0217(7)$ Å for SrMoO₄; and $a = 3.974(1)$ Å for SrMoO₃. These data correspond with those given in the literature.^{7,8}

Preparation of Sr₂MoO₄. A mixture of SrO and Mo was placed at the bottom of a closed end Al₂O₃ tube to provide an oxygen partial pressure buffer. An Al₂O₃ crucible was filled with Sr(OH)₂ and MoO₂ in a molar ratio of about 3:1, and placed on top of the SrO, Mo mixture. The Al₂O₃

ampoule was then evacuated, sealed and heated first to 1073 K for a few h then to 1373 K for 72 h. Sr(OH)₂ decomposed to SrO(s) and H₂O(g) with increasing temperature. The SrO thus formed reacted with MoO₂ to produce Sr₂MoO₄. The H₂O expelled would react with the SrO + Mo mixture according to the reaction $2\text{SrO(s)} + \text{Mo(s)} + 2\text{H}_2\text{O(g)} \Rightarrow \text{Sr}_2\text{MoO}_4\text{(s)} + 2\text{H}_2\text{(g)}$ which means that the gas buffer generated gave a stable condition for the formation of Sr₂MoO₄. Subsequently, the ampoule was cooled by removing it from the furnace. The crucible then contained a mixture of Sr₂MoO₄ and SrO. Excess SrO was removed by treating the sample with boiling methanol. The formation of Sr₂MoO₄ was checked by X-ray powder diffraction. All 23 diffraction peaks could be fitted to a tetragonal unit cell with cell parameters $a = 3.9175(3)$ Å and $c = 12.867(1)$ Å (Table 1), in good agreement with the cell parameters obtained by Balz and Plieth² ($a = 3.92$ Å and $c = 12.84$ Å).

Preparation of sample mixtures for emf measurements. The samples for studying equilibrium

Table 1. X-ray powder diffraction data for Sr₂MoO₄ taken with CuKα₁ radiation ($\lambda = 1.5405981$ Å).

$h k l$	I_{obs}	$10^5 \sin^2 \theta_{\text{obs}}$	$10^5 \Delta$	$d_{\text{calc}}/\text{Å}$
0 0 2	13	1423	-11	6.43375
1 0 1	5	4209	-16	3.74768
1 0 3	100	7079	-13	2.89258
1 1 0	66	7718	-14	2.77010
1 0 5	9	12779	-47	2.15091
0 0 6	23	12875	-26	2.14458
1 1 4	8	13455	-12	2.09909
2 0 0	37	15445	-21	1.95876
2 0 2	4	16880	-19	1.87384
1 1 6	22	20615	-19	1.69578
2 1 3	39	22540	-17	1.62188
0 0 8	3	22918	-18	1.60844
2 0 6	19	28346	-21	1.44629
1 1 8	4	30656	-12	1.39096
2 2 0	10	30920	-10	1.38505
1 0 9	5	32888	-7	1.34307
3 0 3	8	38021	-1	1.24923
2 0 8	5	38413	12	1.24305
3 1 0	10	38664	0	1.23883
2 2 6	8	43844	12	1.16350
3 1 4	2	44427	30	1.15606
1 0 11	5	47250	21	1.12087
2 1 9	5	48389	30	1.10769

(I) were prepared by mixing and grinding SrMoO_4 , SrMoO_3 , and Mo (or Sr_3MoO_6) in the molar ratio of 1:3:3 respectively. Before measurements of equilibrium (II), a sample mixture ($\text{SrO}:\text{MoO}_2:\text{Mo} = 6:1:4$) was ground and equilibrated in hydrogen gas at 1273 K for approximately 10 h to ensure that the equilibrium composition was formed. All phases and sample mixtures prepared were routinely checked by X-ray powder diffraction technique, using a Rigaku D/MAX IIA diffractometer.

The emf cells

Two types of emf cells were used, the *single tube* and the *double tube* arrangement. The two cell configurations can be described as follows. The

Pt, $\text{O}_2(\text{g})$, sample | electrolyte | $\text{O}_2(\text{air})$, Pt (A)

Pt, $\text{O}_2(\text{g})$, sample | electrolyte | Mo,
 MoO_2 , $\text{O}_2(\text{g})$, Pt (B)

single tube arrangement (A) consisted of an evacuated, closed end CSZ tube (for detailed description see Pejryd⁹). About 1.5 g of the sample mixture were placed at the bottom of the electrolyte tube. A platinum wire wound around the lower end of an Al_2O_3 capillary served as inner electrode; a platinum wire wound around the CSZ tube served as reference electrode. The double tube arrangement (B) is also described in detail by Pejryd.⁹ The cell arrangement consisted of a single tube cell, CSZ or YDT, inserted in a closed end Al_2O_3 tube. The reference system (about 1.5 g) was placed at the bottom of the electrolyte tube, and the sample system (about 2 g) at the bottom of the Al_2O_3 tube. In some cases, the indicated reference system Mo, MoO_2 was replaced by Fe, $\text{Fe}_{(1-y)}\text{O}$. Both cell compartments were evacuated and sealed prior to heating.

When using YDT electrolytes, there are some practical aspects to consider. The electrolytic material is capable of exhibiting pure ionic conductivity at high temperatures and very low oxygen partial pressures.¹⁰ On the other hand, p type electronic conduction becomes significant at moderate partial pressures ($p(\text{O}_2) \geq 10^{-6}$ atm). Therefore, direct exposure to air or any other system with high oxygen partial pressure must be avoided. The p type electronic conduction is considered to be caused by excess oxygen entering

the vacancies and creating electron holes. These vacancies act as colour centers explaining the brown colour of highly doped specimens sintered in air. It is therefore important to remove excess oxygen before measurement is started, otherwise the sample mixture will be oxidized during heating of the cell. Prior to a measurement, the YDT tube was heated in flowing hydrogen gas at 1273 K for approximately 10 h. The brown colour then disappeared.

The o. d. of the 60 cm long, closed end tube was 10 mm, the i. d. 6 mm. The tubes were delivered by Zircoa, Ohio, in 1977 and because of difficulty in finding a manufacturer of similar electrolytes at present, the double tube cell arrangement was slightly modified so that the YDT tube could be reused. At about 10 cm from the top of the Al_2O_3 tube, brass rings were inserted and sealed with epoxy glue. When exchanging sample mixtures, the glue was removed with a soldering iron and the Al_2O_3 tube could be pulled apart. To avoid thermal shock to the YDT electrolyte, the rate of temperature change never exceeded 100 degrees/h.

Emf measurements. The cells were heated in two different types of resistance furnaces. For temperatures up to 1400 K, a furnace with Kanthal A-1 resistance wire was used, for temperatures up to 1600 K, a Pt/Pt (40 mass % Rh) resistance furnace was used. The furnace design is described in Ref. 9. The temperature was measured with a Pt/Pt (10 mass % Rh) thermocouple. Cells emfs and thermal emfs were measured with a Solartron 7075 digital voltmeter with a high input impedance ($10^{12} \Omega$).

A typical run can be described as follows. The cell was heated during the day to approximately 1300 K. To ensure equilibrium conditions, the temperature was maintained for at least 5 h. The temperature was then changed in steps of 20–50 K. For all reactions studied, the rate was rather sluggish at temperatures below 1200 K, and unreproducible conditions arose. The time required for equilibration was more than 2 h below 1300 K and between 1–2 h above 1300 K. After a run, the YDT cells were slowly cooled to room temperature to avoid thermal shock to the electrolyte material. Since the CSZ tubes were not recycled, these cells were quenched to maintain the equilibrium phase composition of the sample. All sample mixtures were analysed by X-ray powder

diffraction technique to check the sample composition after the measurements.

Emf values obtained with the CSZ electrolyte were stable and reproducible for 4–7 d. During a run, the amount of SrMoO₃ in the sample decreased due to oxygen diffusion through the electrolyte wall. The measurements with the YDT electrolyte, on the other hand, could be run for more than a week without any problems; the emf values remained stable during the entire period, with no noticeable signs of oxidation of the sample. This indicated that the YDT electrolyte functioned just as well as the CSZ electrolyte at moderate oxygen partial pressures [equil. (I)]. At lower oxygen partial pressures [equil. (II)] pure ionic conduction was maintained for the YDT electrolyte, which was not the case with the CSZ electrolyte.

Results and calculations

Emf values obtained. An emf value (E) obtained in the measurements is described by the expres-

$$E = RT \ln 10 / 4F [\log p^*(\text{O}_2) - \log p(\text{O}_2)] \quad (1)$$

sion (1) where R is the gas constant, F the Faraday constant, $p^*(\text{O}_2)/\text{atm}$ and $p(\text{O}_2)/\text{atm}$ are the partial pressures of oxygen in the reference and the sample system, respectively. Emf values for equil. (I) were determined in five different runs with Mo, MoO₂ or Fe, Fe_(1-y)O or air as a reference system (see Table 2). To compare the various measurements, normalized emf values were calculated assuming O₂(g) at 1 atm as the reference system. This was done by combining eqn.

(1) with $\log p^*(\text{O}_2)$ expressions (2) or (3), which are shown below, for the equilibria Mo(s) + O₂(g) \rightleftharpoons MoO₂(s) (III) and (1-y)Fe(s) + 1/2O₂(g) \rightleftharpoons Fe_(1-y)O(s), or $\log[p^*(\text{O}_2)/\text{atm}] = -0.67890$ for air at 1 atm as reference system. (The slight variation of the atmospheric pressure was considered in the calculations.) Expressions (2) and (3) were taken from Refs. 11 and 12, respectively. It should be mentioned that eqn. (2) was derived from measurements up to 1450 K. However, we have shown from separate emf measurements on equil. (III) that eqn. (2) is valid within stated uncertainties up to 1600 K. In the study of equil. (II), three different runs were carried out with Mo, MoO₂ as the reference system (Table 2).

The experimental emf values obtained for equil. (I) (normalized) and equil. (II) were smoothed by a least squares treatment (Tables 3 and 4). The $E(T)$ relationships were obtained by eqns. (4) and (5) for equil. (I) and equil. (II) respectively. Calculated values of the deviations $\Delta E = E_{\text{exp}} - E$ are also given in Tables 3 and 4. The mean errors are $\sigma E(\text{I}) = \pm 1.3$ mV and $\sigma E(\text{II}) = \pm 0.5$ mV.

$$\log[p^*(\text{O}_2)/\text{atm}] = -6.622 - 27643/(T/K) + 1.89091 \ln(T/K) \quad (\sigma = \pm 0.020 \text{ at } 1400 \text{ K}) \quad (2)$$

$$\log[p^*(\text{O}_2)/\text{atm}] = 9.1513 - 27967/(T/K) - 0.282031 \ln(T/K) \quad (\sigma = \pm 0.015 \text{ at } 1400 \text{ K}) \quad (3)$$

$$E(\text{I})/\text{mV} = 1397.8 + 0.32518(T/K) - 0.087983(T/K) \ln(T/K) \quad (4)$$

$$E(\text{II})/\text{mV} = 167.12 + 0.33974(T/K) - 0.036139(T/K) \ln(T/K) \quad (5)$$

Table 2. The different cell types used in the emf measurements.

Cell no.	Cell type	Electrolyte	Sample group	Reference system	No. of points
1	Double	YDT	SrMoO ₃ , SrMoO ₄ , Mo	Mo, MoO ₂	22
2	Single	CSZ	SrMoO ₃ , SrMoO ₄ , Mo	Air	5
3	Single	CSZ	SrMoO ₃ , SrMoO ₄ , Mo	Air	9
4	Single	CSZ	SrMoO ₃ , SrMoO ₄ , Sr ₃ MoO ₆	Air	3
5	Double	CSZ	SrMoO ₃ , SrMoO ₄ , Mo	Fe/Fe _{1-y} O	3
6	Double	YDT	Sr ₂ MoO ₄ , SrO, Mo	Mo, MoO ₂	17
7	Double	YDT	Sr ₂ MoO ₄ , SrO, Mo	Mo, MoO ₂	10
8	Double	YDT	Sr ₂ MoO ₄ , SrO, Mo	Mo, MoO ₂	4

Table 3. Experimental data, $E(\text{exp})/\text{mV}$ and T/K , and calculated values $\Delta E = E(\text{exp}) - E$, obtained from measurements on equilibrium (I), normalized to $\text{O}_2(\text{g})$ at 1 atm as reference system.

T/K	$E(\text{exp})/\text{mV}$	ΔE	Cell No.
1202.2	1038.2	-0.36	1
1208.5	1036.1	-0.02	1
1225.6	1027.5	-1.96	1
1226.0	1027.6	-1.58	1
1239.9	1023.4	-0.54	1
1251.7	1018.5	-0.84	1
1257.2	1015.5	-1.67	1
1258.5	1016.9	0.24	1
1265.8	1013.3	-0.52	1
1274.0	1010.9	0.29	1
1278.3	1008.8	-0.12	1
1289.5	1003.5	-1.05	1
1300.9	1000.2	0.12	1
1301.9	998.6	-1.00	1
1318.1	992.4	-0.81	1
1327.0	989.7	0.00	1
1344.4	981.7	-1.17	1
1354.9	978.5	-0.20	1
1364.4	974.5	-0.44	1
1379.7	968.4	-0.39	1
1386.9	965.4	-0.52	1
1399.7	960.3	-0.52	1
1210.6	1036.9	1.60	2
1222.3	1031.0	0.18	2
1250.1	1020.9	0.96	2
1275.0	1011.4	1.22	2
1292.3	1004.7	1.29	2
1220.6	1033.7	2.25	3
1273.4	1012.8	1.99	3
1303.3	1000.4	1.33	3
1325.9	991.8	1.65	3
1329.5	989.0	0.23	3
1346.1	983.7	1.48	3
1357.2	978.3	0.55	3
1369.2	974.2	1.26	3
1389.0	966.0	0.94	3
1222.6	1031.6	0.90	4
1247.8	1021.7	0.88	4
1274.9	1011.2	0.99	4
1241.3	1020.6	-2.76	5
1297.7	999.3	-1.99	5
1349.4	979.0	-1.89	5

Calculation of $\log p(\text{O}_2)$ values. The $\log p(\text{O}_2)$ values for equil. (I) were calculated by combining eqns. (1) and (4); for equil. (II), eqns. (1), (2) and (5) were combined. Expressions obtained for

Table 4. Experimental data, $E(\text{exp})/\text{mV}$ and T/K , and calculated values $\Delta E = E(\text{exp}) - E$, obtained from measurements on equilibrium (II), with Mo, MoO_2 as reference system.

T/K	$E(\text{exp})/\text{mV}$	ΔE	Cell No.
1208.6	267.6	-0.13	6
1223.6	269.4	0.96	6
1228.4	269.5	0.78	6
1242.0	269.0	-0.30	6
1255.9	270.5	0.55	6
1271.5	270.4	-0.22	6
1275.6	270.0	-0.85	6
1286.0	271.4	0.07	6
1288.2	271.7	0.28	6
1296.7	271.7	-0.10	6
1307.2	272.4	0.11	6
1318.4	273.2	0.45	6
1336.4	273.0	-0.49	6
1336.7	273.6	0.06	6
1349.1	274.5	0.41	6
1369.0	275.3	0.37	6
1393.8	276.6	0.64	6
1223.9	268.1	-0.35	7
1249.2	268.4	-1.28	7
1251.4	269.6	-0.18	7
1264.7	270.1	-0.24	7
1283.8	271.4	0.22	7
1302.9	271.8	-0.28	7
1314.2	272.7	0.16	7
1328.8	273.5	0.28	7
1353.4	274.5	0.23	7
1379.0	275.2	-0.21	7
1415.3	276.3	-0.54	8
1463.6	278.4	-0.41	8
1523.3	280.8	-0.37	8
1565.5	283.2	0.39	8

$\log p(\text{O}_2)$ are given as (6) and (7) below. The estimated uncertainties at 1400 K are

$$\delta \log p_{\text{O}_2}(\text{I}) = \pm 0.03 \text{ and } \delta \log p_{\text{O}_2}(\text{II}) = \pm 0.025.$$

Calculation of Gibbs free energy. The Gibbs free energy ($\Delta G^\circ/\text{J} \cdot \text{mol}^{-1}$) is related to the partial pressure of oxygen at equilibrium, ($p(\text{O}_2)/\text{atm}$) by the equations [$\Delta G^\circ = 1/2RT \ln 10 \log p(\text{O}_2)$] (for equil. (I)) and [$\Delta G^\circ = RT \ln 10 \log p(\text{O}_2)$] (for equil. (II)). By using the expressions (6) and (7), respectively, relationships (8) and (9) were derived which are shown below. The estimated maximum uncertainty was $\pm 400 \text{ J} \cdot \text{mol}^{-1}$, and

$\pm 670 \text{ J} \cdot \text{mol}^{-1}$ for (8) and (9) respectively. The Gibbs free energy of formation of Sr_2MoO_4 was derived from eqn. (10), also shown below. Unfortunately calculation of $\Delta_f G^\circ(\text{Sr}_2\text{MoO}_4)$ gives rather uncertain values because of the uncertainty of $\Delta_f G^\circ(\text{SrO})$ amounting to approximately $\pm 3.5 \text{ kJ} \cdot \text{mol}^{-1}$.

Discussion

Thermodynamic data for equil. (I) obtained in this study is in fairly good agreement with data found in the literature.^{5,6} The difference is of the magnitude of $2 \text{ kJ} \cdot \text{mol}^{-1}$ in ΔG° at 1300 K. The discrepancy decreases with increasing temperature (see Table 5).

The phase relations at 1373 K so far obtained in the system Sr–Mo–O are shown in Fig. 1. Dotted lines are tentative phase area boundaries and have to be confirmed in additional studies.

Emf measurements on equil. (I) were carried out with either Mo or Sr_3MoO_6 as a third inert phase in addition to SrMoO_3 and SrMoO_4 . This implies that the phase assemblages described by areas (a) and (b) in Fig. 1 constitute compatibility triangles. These results are in agreement with

$$\log[p(\text{O}_2)(\text{I})/\text{atm}] = -6.5553 - 28178/(T/\text{K}) + 1.7737\ln(T/\text{K}) \quad (6)$$

$$\log[p(\text{O}_2)(\text{II})/\text{atm}] = -13.471 - 31012/(T/\text{K}) + 2.6194\ln(T/\text{K}) \quad (7)$$

$$\Delta G^\circ(\text{I}) \text{ J} \cdot \text{mol}^{-1} = -269732 - 62.749(T/\text{K}) + 16.978(T/\text{K})\ln(T/\text{K}) \quad (8)$$

$$\Delta G^\circ(\text{II}) \text{ J} \cdot \text{mol}^{-1} = -593713 - 257.90(T/\text{K}) + 50.148(T/\text{K})\ln(T/\text{K}) \quad (9)$$

$$\Delta_f G^\circ(\text{Sr}_2\text{MoO}_4) = \Delta G^\circ(\text{II}) + 2\Delta_f G^\circ(\text{SrO}) \quad (10)$$

those put forward by McCarthy *et al.*⁴ Phase area (c) in Fig. 1 shows the phase assemblage SrO, Sr_2MoO_4 and Mo obtained when a mixture of SrO, MoO_2 and Mo in proportions 6:1:4 was equilibrated with hydrogen gas at 1373 K. As the equilibrium mixture (SrO, Sr_2MoO_4 and Mo) was maintained when the emf cells were slowly cooled, this phase assemblage is stable over a broad temperature range. The phase relations in the region between Sr_2MoO_4 , SrMoO_3 and Mo (Fig. 1) will be studied in the near future by using the solid buffer technique.

Experimental difficulties arose when the synthesis of Sr_2MoO_4 was carried out in ampoules without any solid mixture to buffer the oxygen partial pressure. When a mixture of SrO and MoO_2 in proportions 2:1 was heated in an evacuated ampoule, the phase assemblage Sr_3MoO_6 , SrMoO_3 , Sr_2MoO_4 and Mo was obtained. There were also X-ray diffraction peaks which indicated the presence of a fifth phase. These non-equilibrium conditions in the ampoules can be due to the extremely low equilibrium oxygen partial pressures involved in this system. Thus if the system consists of Sr_2MoO_4 only, the gas phase is unbuffered and a small leakage can change the $p(\text{O}_2)$ conditions to levels where Sr_2MoO_4 is unstable. To overcome these problems, the synthesis of Sr_2MoO_4 can be performed successfully by using a proper buffer, such as a mixture of SrO and Mo.

The exact composition of the phase Sr_2MoO_4 has not been fully confirmed. Therefore a single crystal structure investigation is planned, not only to reveal the composition but also to examine the detailed structure of the phase.

Acknowledgements. The authors wish to thank Lars-Olof Öhman and Dan Boström for valuable discussions, Gunnar Eriksson for comments on

Table 5. $\log p(\text{O}_2)$ values and thermodynamic data ΔG° for equil. (I) from the present study and from data given in the literature.

	$\Delta G^\circ/\text{J} \cdot \text{mol}^{-1}$ 1300 K	$\Delta G^\circ/\text{J} \cdot \text{mol}^{-1}$ 1473 K	$\log[p(\text{O}_2)/\text{atm}]$ 1300 K	$\log[p(\text{O}_2)/\text{atm}]$ 1473 K
Present work	-193052	-179723	-15.51	-12.75
Ref. 5	-195071	-180022	-15.68	-12.77
Ref. 6	-	-	-	-12.62

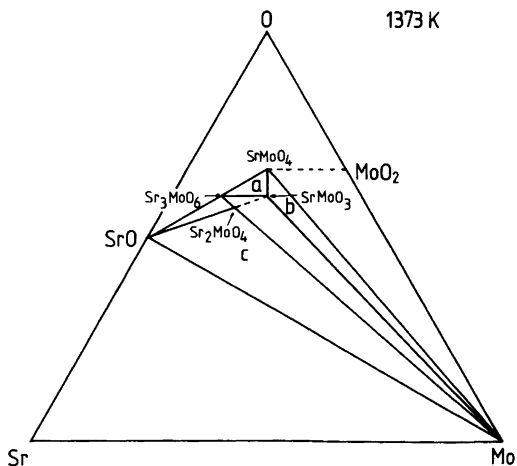


Fig. 1. Phase relations in a part of the system Sr/Mo/O at 1373 K. Dotted lines are tentative three-phase boundaries.

the manuscript and Michael Sharp for revision of the English text.

This work was financially supported by the Swedish Natural Science Research Council.

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Received April 2, 1986.