# Molybdates Solid State Synthesis: The MgO—$MoO_3$ System

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The formation reaction of $Mg_2Mo_3O_{11}$ from MgO (single crystal) and $MoO_3$ (pellet) has been investigated in the temperature range 873—973 K.

Supported by an analysis of the transport properties a mechanism is proposed involving a unidirectional transport of $Mo^{6+}$ via $V_{Mo}^{6'}$ and of oxygen via gas phase.

The transport properties of $MgMoO_4$ (the other intermediate compound in the system MgO—$MoO_3$) were also studied and the results were found to agree with the mechanism observed in a previous work on the basis of kinetic and structural considerations.

## Introduction

When studying solid-solid interactions, the transport mechanism is generally determined by means of inert-markers experiments; it must however be noted that sometimes, in this way, one obtains an ambiguous answer, expecially when the contact between the reactants is not as good as desirable.

The phase characterization obtained from the structural and transport properties seems therefore to be a very useful tool to check the validity of the experimental results. In this way it becomes also possible to know the rate determining step of the overall process.

In the present work this analysis is applied to the kinetic results obtained for the reaction between MgO and $MoO_3$.

Preliminary measurements on the system MgO (s.c.)/$MoO_3$(pellet), carried out at 923 K by the contact method, showed that the product layer at the interface consists almost entirely of $Mg_2Mo_3O_{11}$ and contains only traces of $MgMoO_4$, the other compound present in the equilibrium phase diagram [1]. The formation mechanism of $MgMoO_4$ was previously studied [2] in the couple MgO (s.c.)/ $MoO_3$(vapour phase): indeed, in these conditions, by considering the standard free energies of formation of the two compounds from the binary oxides, it can be deduced that the formation of $MgMoO_4$ only is possible.

## Experimental

MgO: Single crystal plates (5 × 5 × 0.5 mm) obtained by cleavage along (100) planes of a boule from Atomergic Chemetals Co.

$MoO_3$: Pellets obtained by pressing at $2 \cdot 10^3$ kg/cm$^2$ a powder material (99.9%) from Alfa Inorganics.

$MgMoO_4$: Precipitated from solutions of Merck pro analysi $MgCl_2$ and $Na_2MoO_4$ according to the literature [3].

$Mg_2Mo_3O_{11}$: Obtained by solid state reaction between $MgCO_3$ (Atomergic Chemetals Co.; 99.99%) and $MoO_3$ in the stoichiometric ratio 2 : 3 for 72 hours at 773 K; formed in pellets and reacted again for 72 hours at 903 K in a sealed quartz tube in the presence of $MoO_3$. After this treatment the X-ray analysis showed the characteristic reflexions [4] of $Mg_2Mo_3O_{11}$ only.

a.c. and d.c. conductivity measurements were carried out in the temperature range 873 – 973 K, the oxygen partial pressure ranging between $10^{-1}$ and $10^5$ Pa; Pt electrodes were used. Whenever the temperature or the surrounding atmosphere was changed, ten hours were always waited before measurements to allow for the attainment of equilibrium. a.c. measurements were performed by means of a Wayne-Kerr Autobalance Bridge Mod. B 331, d.c. measurements with an Amel Potentiostat Mod. 551 by imposing a constant voltage (10 – 100 mv) across the sample and measuring the equilibrium current with an Amel Ammeter Mod. 668.

For the formation reaction of $Mg_2Mo_3O_{11}$ kinetic measurements were carried out by means of the

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contact method in the temperature range 873 – 973 K. An optical microscope was used to measure the product thickness. X-ray analysis was employed to identify the phases in the product.

## Results and Discussion

### $MgMoO_4$

The a.c. conductivity values at two different oxygen partial pressures ($2 \cdot 10^4$ and $1 \cdot 10^{-1}$ Pa) are reported in Fig. 1 as a function of temperature. The intrinsic range begins at about 913 K. It can be seen that in the entire temperature range the conductivity values are practically independent from the oxygen partial pressure.

By comparison of d.c. measurements performed in air at 923 K (the pertinent $\log \sigma$ value is also reported in Fig. 1) with the corresponding a.c. measurements, an electronic transference number of about 0.05 was estimated. These results seems to be consistent with those we reported in a previous work [2], namely:

a) the compound $MgMoO_4$ is stoichiometric in the conditions here considered;

b) for the formation reaction of $MgMoO_4$ from $MgO$ (s.c.) and $MoO_3$ (vapour phase) the values of the kinetic constant are practically independent of the oxygen partial pressure in the examined temperature range;

c) the process is governed by a mechanism involving counterdiffusion of the $Mo^{6+}$ and $Mg^{2+}$ ions.

As the self-diffusion coefficients of $Mg^{2+}$ and $Mo^{6+}$ are not available, it is not possible to individuate the rate determining ion by applying the theory of Schmalzried [5]. On the other hand, if the activation energy value of the reaction ($\Delta E =$ 66 kcal/mole) is taken into account, it can be noted that very close values were obtained in the synthesis of divalent metal molybdates ($MeMoO_4$; Me = Ca, Sr) whose slowest step was the diffusion of $Mo^{6+}$ via $V_{\mathrm{Mo}}^{6'}$ [6].

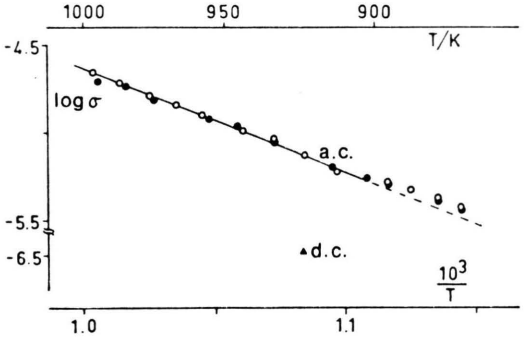

Fig. 1. a.c. conductivity (in $\mathrm{ohm}^{-1}\,\mathrm{cm}^{-1}$) of $MgMoO_4$ as a function of reciprocal temperature. Filled circles: $p_{O_2} = 2 \cdot 10^4$ Pa; open circles: $p_{O_2} = 1 \cdot 10^{-1}$ Pa. A d.c. value ($T = 923$ K, $p_{O_2} = 2 \cdot 10^4$ Pa) is also shown.

Therefore also in this case the transport of $Mo^{6+}$ may be reasonably taken as the rate determining step of the process. Consequently the activation energy obtained from conductivity measurements ($\Delta E = 27.5$ kcal/mole) may be attributed to the transport of the faster ion, $Mg^{2+}$. Assuming such a mechanism the average diffusion coefficient $\overline{D}_{\mathrm{Mo}^{6+}}$ may be drawn from kinetic data by the equation

$$\overline{D}_{\mathrm{Mo}^{6+}} = \frac{k\,R\,T}{\gamma\,|\,\Delta G^0\,|\,z_{\mathrm{Mo}}\,c_{\mathrm{Mo}}},$$

where $k$ is the kinetic constant, $\Delta G^0$ the standard free energy change for the reaction considered and $\gamma$ a numerical factor whose value depends on the mechanism of the process. From the values of $k(\mathrm{eq\,s^{-1}\,cm^{-1}})$ obtained in the temperature range 873 – 973 K, and taking $\Delta G^0 = -12{,}900 - 3.25\,T$ [7] and $\gamma = 4/3$, the following temperature dependence for $\overline{D}_{\mathrm{Mo}^{6+}}$ (in $\mathrm{cm^2/sec}$) is obtained:

$$\log \overline{D}_{\mathrm{Mo}^{6+}} = 2.78 - 67{,}052/4.576\,T\,.$$

### $Mg_2Mo_3O_{11}$

As observed for other molybdates [8], at comparatively high temperatures this compound too exhibits an appreciable volatility of $MoO_3$ and consequently a deficiency of this constituent in the temperature range we selected ($Mg_2Mo_{3-x}O_{11-3x}$). It was verified by thermogravimetry that the $MoO_3$ loss becomes remarkable after protracted heating in air at temperatures above 873 K: conductivity measurements were therefore performed only at this temperature. The a.c. conductivity values obtained at different oxygen partial pressures ($10^{-1} - 10^5$ Pa) are given in Table 1: it can be seen that they depend on $p_{O_2}$: $\sigma \propto p_{O_2}^{1/n}$ with $n = 8 \pm 1$. d.c. measurements carried out in air at the same temperature allow to deduce, by comparison, that this compound is a predominantly electronic conductor.

The $k$ values obtained in air by employing the diffusion couples $MgO$ (s.c.)/$MoO_3$ (pellet) are shown in Fig. 2 (reaction times ranging between 15 and

| $p_{O_2}$/Pa | $\sigma$/ohm$^{-1}$ cm$^{-1}$ |
|---|---|
| $1 \cdot 10^5$ | $9.8 \cdot 10^{-5}$ |
| $2 \cdot 10^4$ | $7.6 \cdot 10^{-5}$ |
| $1 \cdot 10^3$ | $5.6 \cdot 10^{-5}$ |
| $1 \cdot 10^2$ | $4.1 \cdot 10^{-5}$ |
| $1$ | $2.3 \cdot 10^{-5}$ |
| $1 \cdot 10^{-1}$ | $1.6 \cdot 10^{-5}$ |

Table 1. $\sigma$ values (total conductivity) of $Mg_2Mo_{3-x}O_{11-3x}$ at different oxygen partial pressures ($T = 873$ K).

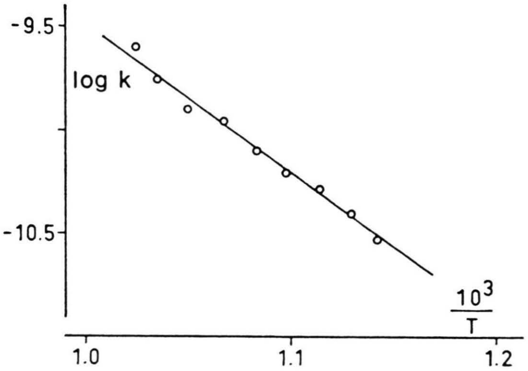

Fig. 2. Arrhenius plot of $k$ (in cm$^2$ s$^{-1}$) for the $Mg_2Mo_3O_{11}$ formation from MgO (s. c.) and $MoO_3$ (pellet).

100 hours). The X-ray analysis showed that the reaction product was almost entirely $Mg_2Mo_3O_{11}$; only traces of $MgMoO_4$ were present in contact with the MgO single crystal. The inert markers (Pt ribbons 5 µm thick) initially located at the reaction interface MgO/MoO$_3$ were always present at the interface product/MoO$_3$ after the thermal treatment. At 873 K kinetic determinations performed at different oxygen partial pressures proved that the kinetic constants become ten times larger by passing from $p_{O_2} = 10^{-1}$ Pa to $p_{O_2} = 2 \cdot 10^4$ Pa.

Taking into account the characteristics of $Mg_2Mo_{3-x}O_{11-3x}$, it seems reasonable to think that the majority defect pair may be constituted by molybdenum and oxygen vacancies. For such a model, in the case of fully ionized vacancies, the following approximated electroneutrality condition is valid:

$$[V_O^{2\cdot}] = 3[V_{Mo}^{6'}].$$

According to Schmalzried and Wagner [9], from the defect generation equilibria we obtain for the minority defect $h^\cdot$, $[h^\cdot] \propto p_{O_2}^{1/8}$. The conductivity dependence of $Mg_2Mo_3O_{11}$ on $p_{O_2}$ ($\sigma \propto p_{O_2}^{1/8}$) may therefore be explained by this model.

It may be concluded that the rate determining step of the formation process (in air) ought not to be the diffusion of oxygen via $V_O^{2\cdot}$, because if this were the case a different dependence of the kinetic constant on $p_{O_2}$ would have to be observed.

We can therefore suppose that the transport of Mo$^{6+}$ is the rate determining step, and that the oxygen is transported via gas phase according to a mechanism already observed in the formation of other molybdates [6].

The observed dependence of the kinetic constants on $p_{O_2}$ may be explained by assuming that the gas-phase oxygen becomes rate-determining when $p_{O_2}$ diminishes, although it cannot be excluded that such a trend might introduce a different mechanism.

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