JOURNAL OF SOLID STATE CHEMISTRY 8, 14–28 (1973)

The Chemical Transport of Molybdenum and Tungsten and of their Dioxides and Sulfides

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Received December 13, 1972

Experiments have been made and an extensive thermodynamic discussion has taken place concerning the chemical transport of Mo, W, MoO_2, WO_2, MoS_2 and WS_2 in the presence of iodine. Efforts have been made to find the species via which Mo and W can migrate within the gas phase.

Results: In each case the transport proceeds via the oxide iodides MoO_2J_2 and WO_2J_2 respectively, as already known for the dioxides. Thus the chemical transport of Mo, W, MoS_2 and WS_2 needs not only J_2 but also H_2O, usually liberated from the wall of the quartz ampoule.

By means of $J_2 + H_2O$, the metals can be transported into the high temperature region of the ampoule (e.g., 1050 → 1150°C), whereas the transport of the sulfides proceeds in the opposite direction (e.g., 900 → 700°C).

For the sulfide-transport the influence of the ratio of the transport agents J_2/H_2O has been discussed.

The water content of the quartz glass out of which the ampoules are made is an important source for water, influencing the reactions.

The addition of graphite which considerably lowers the H_2O partial pressure prevents any transport of the metals or the sulfides, which proves that the use of J_2 alone as a transport agent is insufficient in these cases.

The gaseous iodides MoJ_x and WJ_x are without any importance under the experimental conditions used for the transport of the metals, their dioxides and sulfides.

The partial pressures of $MoO_2(OH)_2$ and $WO_2(OH)_2$ under the experimental conditions chosen may usually be neglected. But in the system MoO_2/H_2O the transport via $MoO_2(OH)_2$ (1000 → 800°C) has been observed.

The synthesis of MoO_2 and WO_2, starting with the elements or with powder of metal and trioxide is promoted by the addition of J_2. The reaction steps involved are discussed.

1. Introduction

The metals molybdenum and tungsten do not belong to that group of elements which have been purified by means of the classical van Arkel transport method via gaseous iodides. Obviously the reason is the instability of the iodides at temperatures necessary for their evaporation. If this were so, the chemical transport of compounds of these elements via gaseous iodides would be impossible. Contrary to this thermodynamic expectation, the transport by means of iodine of the following compounds has been described:

MoS_2 (*1*) Mo_3Sb_7 (*2*)
WS_2 (*1*) WSe_2 (*3–5*) WTe_2 (*3*)

It has been generally believed that the transport of these substances (as that of many other sulfides) proceeds via gaseous iodides. From the consideration mentioned above this must be evidently wrong. We supposed (*6*), as a solution of this discrepancy, that in these cases the transport in fact proceeds via gaseous oxide iodides. This means, that J_2 and H_2O introduced either as an impurity or coming from the wall of the quartz reaction tube act both together as transport agents. To check this assumption the following investigation has been undertaken.

It should be emphasized that it is very difficult to exclude traces of water, even if one prepares the ampoules from a specially produced kind of quartz glass, with a water content as low as

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possible (~0.01 wt%; ir spectrum), and even if these ampoules are degassed under high vacuum at 1000°C. These precautions can not prevent the diffusion of water out of the wall into the reaction room during long heating times.

2. Experiments and Their Results

2.1. General Remarks Concerning the Experimental Technique

In all experiments chemically pure substances have been used. The graphite in grains of the size of ~0.1–0.5 mm was of highest purity for spectral analysis. The tube material in each case was quartz glass with a very low water content (ir spectrum). For dimensions of the transport ampoules see Tables I–IV. After charging the ampoules are sealed under high vacuum. Both ends of the ampoule are connected with small quartz glass tubes of 2 cm in length and of an inside diameter of 0.4 cm, into which later on the thermocouples are fixed.

The ampoule is heated in horizontal position in an electric furnace with two zones regulated independently.

2.2. Chemical Transport of the Dioxides MoO_2 and WO_2

MoO_2. Transport experiments using MoO_2 as a solid and J_2 as a transport agent proved successful (*7–9*). Table I gives data of our earlier experiments unpublished so far (*7*).

TABLE I

CHEMICAL TRANSPORT OF MoO_2[a]

Expt. No.	Introduced transp. agent [mg/ml]	*P* at av. temp. [atm]	Temperature [0°C]	Yield, MoO_2 crystals [mg]
1	0	0	800 ← 1000	3
2	0.61 H_2O	3.2 H_2O	800 ← 1000	~50
3	J_2 from 1.57 CuJ	0.40 J_2	800 ← 1000	146
4	J_2 from 1.56 CuJ	0.39 J_2	800 ← 1000	164
5	0.52 H_2O	2.3 H_2O	650 ← 730	0
6	1.26 J_2	0.39 J_2	650 ← 730	15

[a] Source material 1.0 g MoO_2; ampoule dimensions 9 mm inside diameter, 150 mm length; heating time 4 days. The arrow gives the transport direction which has been checked.

TABLE II

SYNTHESIS OF WO_2 (CRYSTALS)[a]

Expt. No.	Charge in mmole W	WO_3	O_2	Transport agent [mg/ml]	Yield in the 800°C region
1	5.86	0	1.42	0	0
2	5.53	0	1.29	1.2 J_2	~300 mg WO_2
3	4.00	7.99	0	0	Some mg of blue material
4	4.00	8.02	0	0.30 H_2O	24 mg of blue material
5	3.99	7.95	0	3.1 J_2 + 0.30 H_2O	681 mg WO_2
6	4.01	8.00	0	3.04 J_2	2.06 g WO_2
7	6.01	8.05	0	3.0 J_2	2.18 g WO_2

[a] Ampoule dimensions: 16 mm inside diameter, 170 mm in length; ~34 ml volume. Heating time 24 hr at 1000 → 800°C.

Experiment 1 without a transport agent added nevertheless shows a small transport effect. It is caused by water impurities. The transport proceeds via $MoO_2(OH)_{2,g}$; cf. Sect. 3.4.2.1. The influence of higher pressure of H_2O is shown by Expt. 2. At a lower temperature (Expt. 5) a transport effect caused by H_2O could not be observed.

The iodine transport of MoO_2 is shown by Expts. 3, 4, and 6. In some cases the transport agent J_2 was initially prepared by the reaction of CuJ in a stream of O_2. Compared with the iodine transport of WO_2 the transport rate with MoO_2 is smaller. Nevertheless fair amounts of MoO_2 can be transported if larger tube diameters and (or) higher temperatures are used.

The chemical transport of MoO_2 obviously proceeds similar to the WO_2 transport via $MoO_2J_{2,g}$. This assumption (*6*) was confirmed by quantitative transport experiments in tubes with a well-defined diffusion path and their thermodynamic discussion (*9*) (cf. Sect. 3.4.2.2).

For the MoO_2 synthesis, starting from $Mo + O_2$ or $Mo + MoO_3$ an addition of transport agent (J_2; see WO_2) and a heating within a temperature gradient (1000 → 800°C) is to be recommended. In this way synthesis and chemical transport occur in one and the same experimental process.

WO_2. Chemical transport of WO_2 with J_2 as a transport agent in a temperature gradient 1000 → 800°C proceeds by means of the iodide $WO_2J_{2,g}$. For experimental details and more information see refs. *8*, *10* and *11*; see also Sect. 3.4.2.2. Some experiments regarding the synthesis of WO_2 are given in Table II.

If the elements $W + O_2$ are used, they are combined in a first reaction step to WO_2 within the hot temperature region. The formation of a WO_2 layer on the surface of the tungsten grains slowing down the reaction velocity is prevented by the transport agent (J_2). Small WO_2 crystals are formed near the source material. During this step the driving force (the concentration gradient) within the hot zone is determined by the stability difference of $W + O_2$ and WO_2 respectively.

TABLE III

CHEMICAL TRANSPORT OF Mo[a]

	Introduced transp. agent				
Expt. No.	[mg/ml]	*P* at av. temp. [atm]	Temperatures [°C]	Heating time [hr]	Yield transp. Mo [mg]
1	0.69 H_2O	3.37 H_2O	$700 \rightarrow 900$	52	0
2	1.50 J_2	0.53 J_2	$710 \rightarrow 940$	106	0
3	1.50 J_2	0.52 J_2	$670 \leftarrow 940$	167	0
4	1.38 J_2	0.50 J_2	$750 \rightarrow 950$	48	17
	0.28 H_2O	1.43 H_2O			
5	1.38 J_2	0.48 J_2	$700 \leftarrow 900$	42	0
	0.28 H_2O	1.37 H_2O			
6	0.51 H_2O	3.19 H_2O	$1050 \rightarrow 1150$	96	0
7	0.17 H_2O	0.99 H_2O	$900 \leftarrow 1100$	96	2 mg Mo (+ MoO_2)
8	3.26 J_2 + 105 mg C[b]	1.45 J_2	$1050 \rightarrow 1150$	96	0
9	3.20 J_2	1.42 J_2	$1050 \rightarrow 1150$	96	259
10	0.25 H_2O	1.51 H_2O			
	1.30 J_2	0.56 J_2	$950 \rightarrow 1150$	98	18
11	0.47 H_2O	2.94 H_2O			
	3.04 J_2	1.35 J_2	$1050 \rightarrow 1150$	97	72
12	0.12 H_2O	0.75 H_2O			
	4.44 J_2	1.97 J_2	$1050 \rightarrow 1150$	94	204

[a] Source material 1.5 g Mo (powder). Dimensions of the quartz ampoule: 17 mm inside diameter, 160 mm in length. The arrow gives the transport direction which has been checked.

[b] Total amount of graphite.

The second (slower) step is the chemical transport of WO_2 into the low temperature region.

In the WO_2 formation starting with $W + WO_3$ we can distinguish several reaction steps again. First WO_3 must be moved onto the tungsten surface. As to this process we should mention the fact that a powder mixture of W and WO_3 is used so that the distance to be overcome is small. For that reason the process can proceed by means of the small saturation pressure of WO_3; $P(W_3O_9) = 5 \times 10^{-7}$ atm at 1300 K. Since traces of H_2O are usually present the WO_3 transport may proceed also via $WO_2(OH)_{2,g}$.

Instead of transporting WO_3 an oxygen carrier would suffice. This oxygen transfer from WO_3 to W will occur by means of the system H_2O/H_2 established automatically in the presence of water.

The last step is the chemical transport of WO_2 by means of J_2 preventing again the formation of a rate limiting surface layer. These considerations are in agreement with the observations.

In some of the experiments, small amounts of a blue material are deposited into the coldest end of the ampoule. Its X-ray diagram shows the pattern of $W_{18}O_{49}$ and some times of oxide phases with compositions between $W_{18}O_{49}$ and WO_3.

2.3. Chemical Transport of the Elements Mo and W

Mo. The similarity of the transport of MoO_2 and WO_2 via $MoO_2J_{2,g}$ and $WO_2J_{2,g}$ respectively suggests the Mo-transport by means of $J_2 + H_2O$, similar to the W-transport (*10*) (800 → 1000°C). Some experiments made in this direction are given in Table III.

Remarks concerning the experiments of Table III: (a) The charging with H_2O was brought about by thermal decomposition of $BaCl_2 \cdot 2H_2O$ and condensation of H_2O in the ampoule. (b) In Expt. 4 the deposition of Mo occurred in form of a mirror. (c) In Expts. 11 and 12 the residue in the low temperature region consists of $Mo + MoO_2$ (X-ray diagram). (d) In Expt. 12 the deposition of Mo crystals happened not only within the

TABLE IV

CHEMICAL TRANSPORT OF MoS_2 AND WS_2[a]

	Introduced					
		Transp. agent				
Expt. No.	Solid [mg]	[mg/ml]	P at av. temp. [atm]	Temp. [°C]	Heating time [h]	Yield [mg]
1	302 MoS_2	0	0	700 ← 830	360	0
				850 ← 990	312	0
2	1000 MoS_2*	0.0225 H_2O	0.11 H_2O	700 ← 900	96	0
3	1000 MoS_2* 105 graphite	1.23 J_2	0.42 J_2	670 ← 890	38	0
4	302 MoS_2	3.81 J_2	1.30 J_2	750 ← 820	350	190 MoS_2
5	1000 MoS_2*	1.23 J_2	0.42 J_2	650 ← 900	20	165 MoS_2
6	300 WS_2	0	0	700 ← 830	360	0
				850 ← 980	288	0
7	1000 WS_2*	0.020 H_2O	0.10 H_2O	700 ← 900	96	14
8	873 WS_2 83 graphite	1.20 J_2	0.42 J_2	700 ← 900	72	0
9	1050 WS_2* 145 graphite	1.17 J_2	0.41 J_2	700 ← 900	450	0
10	306 WS_2	5.0 J_2	1.73 J_2	720 ← 870	720	300 WS_2
11	1003 WS_2*	1.19 J_2	0.41 J_2	700 ← 900	40	667 WS_2

[a] Dimensions of the quartz ampoules: 16 mm inside diameter and 120–170 mm in length. The arrow gives the transport direction which has been checked. The asterisk * denotes that the ampoule is charged with metal and sulfur in stoichiometric amounts.

hottest region but also in the middle of the ampoule. Table III shows that neither H_2O (Expts. 1 and 6) nor J_2 (Expts. 2 and 8) alone causes chemical transport of Mo into the hotter zone at the temperatures used. But H_2O and J_2 together (Expts. 4, *10*, *11*, and *12*) cause a small chemical transport of Mo via $MoO_2J_{2,g}$ into the hotter zone; see Sect. 3.4.3. At temperatures of $1050 \rightarrow 1150°C$ the small amounts of H_2O which are always present are sufficient (Expt. 9). If one lowers the H_2O content by means of graphite (see Sect. 3.3) iodine alone will not cause any transport.

At higher temperatures (1200–1500°C) a remarkable volatilization of Mo and W in a stream of $H_2O + H_2$ is observed by equilibrium measurements (*12*, *13*). In this way chemical transport of Mo from the higher to the lower temperature region will be possible (see also Expt. 7).

Recently new investigations have been published (*14*) concerning the chemical transport of Mo and W in an H_2O/H_2-atmosphere between different places of filaments of the metals at temperatures about 2500°C.

W. As mentioned above if both J_2 and H_2O are present, W is transported in a temperature gradient $800 \rightarrow 1000°C$ into the hotter region. Responsible for this behaviour is the exothermic formation of $WO_2J_{2,g}$ (and HJ). For transport experiments see (*10*).

If H_2O alone is used as transport agent, W is transported into the lower temperature region; e.g., with ampoules as in Table III, with 0.17 mg H_2O/ml and 1100 (W) → 900°C we observed the deposition of 42 mg W $(+WO_2)$/100 hr within the 900°C zone. Iodine alone will not cause any transport of W (*10*).

2.4. Chemical Transport of the Disulfides of MoS_2 and WS_2

We investigated the influence of the vapour pressure of the disulfides themselves, and the transport effect caused by H_2O, by J_2, and by both $J_2 + H_2O$; see Table IV. In some experiments the sulfide as starting material was replaced by a powder mixture of the elements in stoichiometric amounts. The experiments yielded the same results whether or not there was an isothermal (800°C) heating period of ~10 hr to combine the elements before the heating in the temperature gradient.

In each case the products (residue and material transported to the low temperature region) were characterized by X-ray powder methods as disulfides.

As an experimental result we may register (a) that MoS_2 and WS_2 under the given condition are not volatile themselves (Expts. 1 and 6); (b) that H_2O alone causes no observable transport of MoS_2 but a small transport of WS_2 (Expts. 2 and 7); (c) that no transport by means of J_2 occurs if by addition of graphite the water content is diminished (Expts. 3, 8, and 9); (d) that the addition of J_2 in the presence of water impurities causes a chemical transport into the lower temperature region (Expts. 4, 5, 10, and 11). Water leads to some extent to the formation of H_2S observable by its smell.

3. Discussion

3.1. Thermodynamic Values

The discussion is based on the thermodynamic equilibria involved. Janaf data (*15*) have been used when available. Additional data are given in Table V.

3.2. Vapour Species Possibly Involved in the Observed Transport Reactions

3.2.1. Iodides

So far no conclusive observations have been published concerning gaseous molybdenum- and tungsten iodides. They are indeed undetectable during the thermal decomposition (thermobalance, mass spectrometer) of Mo_6J_{12} and W_6J_{12} (see Expts. A and B). On the other hand observations concerning the synthesis of MoJ_3 and WJ_3 from the elements (see Expts. C, D) achieved at low temperatures and with high J_2 pressure (WJ_3), where the products are deposited in the low temperature zone of an ampoule can be explained by migration via gaseous iodides. However, such an interpretation is not conclusive. By participation of small H_2O pressures, certainly being present, a chemical transport of $MJ_{3,s}$ via $MO_2J_{2,g}$ (M = Mo, W) may be possible, e.g.,

$$MJ_{3,s} + 1.5J_{2,g} + 2H_2O_{,g} = MO_2J_{2,g} + 4HJ_{,g}.$$

Because of the present lack of data a decision between both possibilities can not be taken. Be that as it may, discussing the transport experiments with the metals, the dioxides and the sulfides at higher temperatures, gaseous iodides of Mo and W need not be taken into consideration.

TABLE V

Log $Kp,_{f(\text{atm})}$. Data for Formation from the Elements. Log $Kp,_f \equiv 0$ for $Mo,_s$; $W,_s$; $S_{2,g}$, $J_{2,g}$ at the Temperatures Used

Substance	Temperature, K					Notes
	900	1000	1100	1200	1300	
$Mo_3O_{9,g}$	83.495	72.666	63.824	56.467	50.253	*a*
$MoO_2J_{2,g}$	20.914	18.126	15.854	13.969	12.380	*b*
$WO_2J_{2,g}$	22.623	19.795	17.490	15.574		*c*
$MoS_{2,s}$		11.095		7.886		*d*
$WS_{2,s}$	11.349	9.397	7.800	6.469		*e*

[a] $\Delta H_{900}(Mo_3O_9, \text{subl.}) = 80.5$ kcal (*16*); fef($W_3O_{9,g}$) (*15*).

[b] MoO_2J_2 data from (*9*) in combination with MoO_2 data (*15*).

[c] WO_2J_2 data from (*17*) in combination with WO_2 data (*15*).

[d] MoS_2 data are taken from (*18*). They agree well with recent ΔH (*19*) and Cp (*20*) values.

[e] WS_2 data are taken from equilibrium measurements (*21*). log $Kp,_f$ data calculated from ΔH°_{298}, S°_{298} (*22, 15*) and Cp; Cp(MoS_2) from (*20*) are smaller (−1.0), and log $Kp,_f$-data from (*23*) are higher (+0.5).

Expt. A. If the "dibromide" Mo_6Br_{12} is heated up to 1000°C on a thermobalance under 1 atm argon (*24*), about 50–60% of Mo are volatilized as bromides. The residue is Mo metal. The main species observed when Mo_6Br_{12} is decomposed in the vacuum of a mass spectrometer are Br_2 and $MoBr_4$ (Mo_6Br_{12}; up to 750°C; 50 eV) (*25*).

If the same experiments are made with Mo_6J_{12} as starting material the decomposition leads quantitatively to the formation of J_2 and Mo (thermobalance). No Mo-containing species are observed in the mass spectrometer (Mo_6J_{12}; 20–430°C; 70 eV).

Expt. B. In decomposition experiments with W_6Br_{12} and W_6J_{12} (thermobalance) (*24*); mass spectrometer (*25*) (70 eV) similar to the experiments with Mo compounds, we observed the volatilization of W bromides, but gaseous iodides could not be detected.

Expt. C. An ampoule (2.5 cm in diameter, 16 cm in length) is charged with 0.96 g Mo (powder) and 4.5 g J_2. After heating the ampoule for 24 hr in the gradient 500 → 250°C one finds MoJ_3 crystals in the 250°C zone in a good yield (*26*), see also (*27*).

Expt. D. An ampoule is charged with W powder of high reactivity and an excess of J_2. The ampoule is situated in inclined position in a temperature gradient of 500/350°C in such a manner, that W in the lower position has 500°C and the upper end empty at the beginning has 350°C. During the heating process J_2 is continually condensed in the 350°C region and flows down to the 500°C region, where it vaporizes again. The vapour pressure of liquid J_2 at 350°C equals 18.5 atm. After a reaction time of several days one finds grey needles of WJ_3 in the 350°C zone.

3.2.2. *Oxides and Oxide Hydroxides*

Molybdenum and tungsten form gaseous oxides and oxide hydroxides:

$(MoO_3)_n$; $n = 1, 2, 3, 4, 5$; (*15*) (*16*)

$MoO_2(OH)_2$ (*15*)

$(WO_3)_n$; $n = 1, 2, 3, 4$; (*15*) $WO_2(OH)_2$ (*15*)

3.2.3. *Oxide Iodides*

MoO_2J_2 involved as a molecule in the chemical transport of MoO_2 with J_2 has been suggested (*6*) by analogy with WO_2J_2. This assumption has been confirmed by quantitative transport experiments (*9*).

$WO_2J_{2,g}$ has been observed by measuring the equilibrium established by reaction of $WO_{2,s}$ and $J_{2,g}$ (*17, 30*), and by mass spectroscopy (*30, 31*). WO_2J_2 has also been prepared as a crystalline solid (*32*).

3.2.4. *Sulfide Iodides*

Some gaseous sulfide chlorides and bromides of heavy transition elements are known (X = Cl, Br):

$NbSX_3$ (*33*)
$TaSCl_3$ (*33*) WSX_4 (*34, 35*) $ReSCl_4$ (*36*)
WS_2Cl_2 (*35*)

$NbSCl_3$ and $NbSBr_3$ are observed in a mass spectrometer when the solides NbS_2Cl_2 and NbS_2Br_2 are decomposed. On the other hand during the thermal decomposition of solid NbS_2J_2 iodine was liberated and no sulfide iodide could be detected (*33*). A mixed oxide-sulfide-chloride, the molecule $WOSCl_2$ is also reported (*35*).

3.3. Equilibria Involved in the Presence of Graphite

The addition of graphite has been proved to be very useful to decrease the water content of a gasphase to a low level. This was observed for the first time by Dettingmeijer (*10*) in connection with the chemical transport of tungsten. The effect is caused by the endothermic reaction (1)

$$C_{,s} + H_2O = CO + H_2. \qquad (1)$$

An initial H_2O pressure of 1 [atm·10^2] by reaction with graphite is diminished to 0.004, 0.0009, 0.0003, 0.00009 [atm·10^2] at 1000, 1100, 1200, 1300 K, respectively, when the equilibrium is established (calculation with data given by (*15*)).

Equilibrium (1) could be a transport system for carbon. But in fact this is not the case: At the highest temperatures used (1300 K) the equilibrium position is too far to the right, and at lower temperatures, the formation of C from CO is slow because of kinetic reasons.

In transport reactions of sulfides S_2 is one of the constituents of the gasphase. The addition of graphite leads to the formation of CS_2,

$$C_{,s} + S_{2,g} = CS_{2,g}. \qquad (2)$$

For this reaction the following equilibrium constants are known (*15*):

T, K	1000	1100	1200	1300
Kp	8.13	7.23	6.55	6.03

In our transport experiments of sulfides with iodine if graphite is used it is situated in the higher temperature region. By equilibration of the graphite with the small S_2-pressure existing in the ampoule in agreement with the given *Kp* values a small CS_2 pressure is established. It is to be expected that this CS_2 pressure will be of an unimportant influence only. Experiments in which the H_2O content is lowered by the addition of graphite will not behave noticeably different from those without graphite, and the same very low equilibrium pressure of H_2O.

3.4. Equilibria Responsible for the Observed Transport Effects

3.4.1. *General Remarks Concerning the Transport Rate*

Usually the transport rate is determined by diffusion between spaces 2 and 1 in which a thermodynamic equilibrium between solid and gas is established. This leads to the semi-empirical formula (*37*) for the amount of transported material

$$n = \frac{\Delta P}{\sum P} \frac{T^{0.8} \cdot q \cdot t'}{s} 1.8 \times 10^{-4} \text{ [mole]}$$

which includes an average diffusion coefficient of 0.1 [$cm^2\ sec^{-1}$] at 1 atm and 273 K, the difference of the partial pressures $\Delta P = P_2 - P_1$ of a gas species related to the transported solid, the average temperature of the diffusion path T [K], the cross section q [cm^2] of the ampoule, the length of the diffusion path [cm] between source and deposit, and the heating time t' [hr]. Under given experimental conditions the diffusion is proportional to the difference of the equilibrium pressures of species involved ΔP, and inversely proportional to the total pressure $\sum P$. The value of $\Delta P/\sum P$ gives a first, rough approximation of the transport rate. For average experimental conditions ($T = 1000$ K, $q = 2.7$ cm^2, $s = 10$ cm, $t' = 100$ hr, molecular weight of transported solid = 100) the lower suitable limit of $\Delta P/\sum P$ equals 10^{-5}, which gives a transport rate as low as about 1 mg/100 hr (*6*). Reactions for which the calculated $\Delta P/\sum P$ is $<10^{-5}$ may be neglected.

The simple model using the same (average) diffusion coefficient for all the gas species involved introduces the assumption that diffusion and thermodiffusion will not cause any gas separation. This however is not correct with regard to our system containing light (H_2) and very heavy molecules (J_2, WO_2J_2). Therefore, the results of the thermodynamic calculations should be considered only in a semiquantitative sense, although this manner leads to very valuable information.

The model can also be understood in the following way: We take a volume element of equilibrium gas from region 1 and transfer it to region 2, where new equilibration with deposition of a solid occurs. The total pressure during this process is kept constant. The change of the number of gaseous molecules, mainly caused by the dissociation of J_2 has been neglected. This effect is unimportant in the systems involved in our investigation. For further information see (*37*).

3.4.2. Transport of the Oxides

3.4.2.1. The influence of water. The elements under investigation form volatile oxides and oxide hydroxides. Therefore the possibility must be discussed, that small pressures of water vapour may act as a transport agent.

MoO_2/H_2O. We assume that under the experimental conditions (temperature, charging with MoO_2 and small H_2O pressures) MoO_2 is the only stable solid. The endothermic equilibrium (3) is of importance.

$$MoO_{2,s} + 2H_2O_{,g} = MoO_2(OH)_{2,g} + H_2. \quad (3)$$

On the other hand the formation of $Mo_3O_{9,g}$ [eq. (4)] and generally $(MoO_3)_{n,g}$ may be neglected,

$$3MoO_2(OH)_{2,g} = Mo_3O_{9,g} + 3H_2O_g. \quad (4)$$

Data for the equilibria (3 and 4) are given in Table VI.

The equilibrium (*3*) is independent of pressure. When the ampoule is charged with MoO_2 and H_2O then $P(MoO_2(OH)_2)$ increases proportionally to $P(H_2O)$. Proceeding to Eq. (4) the influence of changes in $P(H_2O)$ and $P(MoO_2(OH)_2)$ compensate each other. Therefore, $P(Mo_3O_9)$ is independent of the charge ($MoO_2 + H_2O$). Table VI shows, that the total pressure $\sum P$ is about $P(H_2O)$. For chemical transport of MoO_2, 1300 → 1100 K one gets

$$\frac{\Delta P[MoO_2(OH)_2]}{\sum P} = \frac{P[MoO_2(OH)_2]_{1300} - P[MoO_2(OH)_2]_{1100}}{\sum P} = 181 \times 10^{-5}.$$

TABLE VI

EQUILIBRIUM PRESSURES ABOVE $MoO_{2,s}$; $P(H_2O) \equiv 1 \cdot 10^{-2}$ atm; $P(H_2) = P(MoO_2(OH)_2)$

T [K]	Log K_3	Log K_4	$P[MoO_2(OH)_2]$ [atm·10^7]	$P(Mo_3O_9)$ [atm·10^7]
900	−9.445	3.152	1.9	0.0001
1000	−8.119	2.751	8.7	0.004
1100	−7.029	2.411	30.6	0.07
1200	−6.120	2.116	87.1	0.9
1300	−5.349	1.860	211.6	7

This value holds generally because of the pressure independence of reaction (3). It follows from $\Delta P/\sum P$ and Sect. 3.4.1. that at higher temperatures (e.g., 1300 → 1100 K) a chemical transport of MoO_2 by means of H_2O via $MoO_2(OH)_{2,g}$ is to be expected. On the other hand at lower temperatures (e.g., 1000 → 900 K) the transport effect must be very small next to the limit of observation. These conclusions agree well with the experimental results (see Sect. 2.2., Table I, Expts. 2 and 5).

In the presence of small H_2O pressures the addition of foreign gases, (e.g., increasing the $\sum P$ by a factor of 100 by addition of J_2) will considerably diminish the MoO_2 transport via $MoO_2(OH)_{2,g}$.

WO_2/H_2O. Heating an ampoule charged with WO_2 and H_2O will lead to some extent to the formation of $WO_{2.72,s}$ and H_2, see Eq. (5).

$$WO_{2,s} + 0.72H_2O_{,g} = WO_{2.72,s} + 0.72H_2. \quad (5)$$

Our primary interest is to get an impression of the influence of small H_2O pressures that are difficult to be excluded in transport experiments with WO_2 and J_2 as a transport agent. Besides Eq. (5) we take into account Eqs. (6 and 7); see Table VII.

$$WO_{2,s} + 2H_2O_{,g} = WO_2(OH)_{2,g} + H_2 \quad (6)$$

$$3WO_2(OH)_{2,g} = W_3O_{9,g} + 3H_2O_{,g}. \quad (7)$$

The calculation (Table VII) shows that $P(W_3O_9)$ is without any importance.

If $WO_{2,s}$ has to coexist, then $P(WO_2(OH)_2)$ has the highest possible value above the solids WO_2 and $WO_{2.72}$. Let us assume that an ampoule is charged with WO_2 and H_2O in such a manner, that WO_2 is partially situated at both ends of the ampoule. Table VII shows that if the ampoule is heated in a temperature gradient, some part of

TABLE VII

Equilibrium Pressures above $WO_{2,s} + WO_{2.72,s}$; $P(H_2O) \equiv 1 \times 10^{-2}$ atm

T [K]	Log K_5	Log K_6	Log K_7	$P(H_2)$ [atm·10^2]	$P(WO_2(OH)_2)$ [atm·10^5]	$P(W_3O_9)$ [atm]	ΣP [atm]
900	−0.0186	−6.595	2.558	0.942	0.000270	1×10^{-17}	0.0194
1000	−0.0816	−5.573	2.327	0.770	0.00347	1×10^{-14}	0.0177
1100	−0.1288	−4.731	2.124	0.662	0.0281	3×10^{-12}	0.0166
1200	−0.1643	−4.025	1.943	0.591	0.160	4×10^{-10}	0.0159
1300	−0.1931	−3.424	1.777	0.539	0.699	2×10^{-8}	0.0154

WO_2 will be transformed into $WO_{2.72}$ after some time in the low temperature region and equilibrium (5) will be established. WO_2 in the hot region will not be changed.

This is the situation which we have to consider in order to get an impression of the WO_2 transport via $WO_2(OH)_{2,g}$. As an example we ask for a chemical transport in the gradient 1300 → 1100 K. For the 1100°C-region we find the gas composition in Table VII. Taking the same pressures of H_2O and H_2 and going to the 1300 K region by means of K_6 we calculate $P[WO_2(OH)_2] = 0.569 \times 10^{-5}$ atm. Thus

$$\frac{\Delta P(WO_2(OH)_2)}{\sum P} = \frac{(0.569 - 0.028) \times 10^{-5}}{0.0166} = 33 \times 10^{-5}$$

This value shows that in this temperature range a small WO_2 transport is to be expected.

As in the case of MoO_2, the dioxide transport by means of small H_2O pressures will be of smaller influence, if larger amounts of other gases, e.g., J_2 are added, thereby increasing $\sum P$.

3.4.2.2. Iodine as transport agent for MoO_2 and WO_2. The chemical transport of MoO_2 and WO_2 proceeds by means of the reversible reactions (8 and 9), respectively,

$$MoO_{2,s} + J_{2,g} = MoO_2J_{2,g} \qquad (8)$$

$$WO_{2,s} + J_{2,g} = WO_2J_{2,g}. \qquad (9)$$

Both reactions are endothermic. The transport of the dioxides, therefore, goes into the low-temperature region. Both proceed without change of the number of gaseous molecules, which means, that the value of $\Delta P/\sum P$ is independent of pressure. These conclusions are modified to some extent by the partial dissociation of J_2 into atoms. The composition of the gasphase and the

TABLE VIII

Calculation for the Systems MoO_2/J_2 and WO_2/J_2[a]

System ΣP[atm]	T [K]	Log K for Eq. (8) and (9) resp.	P [atm·10^3] J_2	J_1	MO_2J_2	$(\Delta P/\Sigma P)\cdot 10^5$
MoO_2/J_2	1273	−2.121	213.3	185.1	1.614	290
0.400	1073	−2.882	339.7	59.9	0.446	
WO_2/J_2	1273	−0.427	170.7	165.6	63.8	10300
0.400	1073	−1.150	319.2	58.1	22.6	
MoO_2/J_2	1273	−2.121	667.3	327.5	5.05	390
1.000	1073	−2.882	901.1	97.6	1.18	
WO_2/J_2	1273	−0.427	517.9	288.5	193.7	13400
1.000	1073	−1.150	845.6	94.5	59.9	

[a] Data for MoO_2/J_2 see (*9*), data for WO_2/J_2 see (*17*).

informative values of log K and $\Delta P/\sum P$ are given in Table VIII.

From the log K and $\Delta P/\sum P$ values one can see, that the transport rate for MoO_2 must be small, compared with that for WO_2. But even with MoO_2 the transport rate should be large enough for preparative purposes. This is in agreement with experimental results (see Table I, Expts. 3 and 4).

3.4.3. Transport of the Metals Mo and W

3.4.3.1. The metals and water. If an ampoule charged with Mo or W and H_2O is heated to about 1000°C, this leads to the partial conversion of the metal into its dioxide, Eqs. (10 and 11).

$$0.5Mo_{,s} + H_2O_{,g} = 0.5MoO_{2,s} + H_2 \quad (10)$$

$$0.5W + H_2O_{,g} = 0.5WO_{2,s} + H_2. \quad (11)$$

The hydrogen, produced in this way influences the equilibrium position of the reactions (12 and 13)

$$Mo_{,s} + 4H_2O_{,g} = MoO_2(OH)_{2,g} + 3H_2 \quad (12)$$

$$W_{,s} + 4H_2O_{,g} = WO_2(OH)_{2,g} + 3H_2. \quad (13)$$

The formation of $(MoO_3)_{n,g}$ and $(WO_3)_{n,g}$ can be neglected. Examples for equilibrium pressures are given in Table IX.

From the data given in Table IX we conclude: (a) Starting with an ampoule containing Mo (or W) at both ends and H_2O and heating it in a temperature gradient (e.g., 1200/1400 K) some part of the metal in the low temperature region will be transformed into its dioxide (Eqs. 10 and 11). (b) With a total pressure of 1 atm the $MO_2(OH)_2$ pressures of Table IX are the highest possible. If the formation of a solid dioxide in the low temperature region must be avoided, a higher quotient H_2/H_2O has to be used, yielding a smaller $P(MO_2(OH)_2)$. (c) Finally Table IX, remembering the importance of $\Delta P/\sum P$ shows, that the endothermic chemical transport of Mo and W via $MoO_2(OH)_{2,g}$ and $WO_2(OH)_{2,g}$ respectively, is small with regard to W and near the limit of observation with regard to Mo within the temperature range under investigation; (see Expt. 7 in Table III). Changing to higher temperatures the transport rate clearly becomes larger.

TABLE IX

Equilibrium Pressures above Mo + $MoO_{2,s}$ and W + $WO_{2,s}$ Respectively. $\Sigma P = 1$ atm

T [K]	Solids	P[atm]		
		H_2	H_2O	$MO_2(OH)_2$
1200	Mo + MoO_2	0.651	0.349	1.41×10^{-7}
1300	Mo + MoO_2	0.582	0.418	1.35×10^{-6}
1400	Mo + MoO_2	0.524	0.476	8.82×10^{-6}
1200	W + WO_2	0.624	0.376	2.13×10^{-5}
1300	W + WO_2	0.551	0.449	1.38×10^{-4}
1400	W + WO_2	0.489	0.511	6.60×10^{-4}

3.4.3.2. The metals, iodine and water. With iodine alone one can not expect chemical transport of Mo and W because of the very low stability of the gaseous iodides, (see Sect. 3.2.1.). This is confirmed by the negative result of experiments using J_2 as a transport agent in the absence of H_2O (Table III, Expt. 8 (*10*). H_2O alone may produce small transport effects, expecially with W. But the transport reactions [Eqs. (12 and 13)] are endothermic, thus causing a chemical transport into the low temperature region. $J_2 + H_2O$ together produce chemical transport of Mo and W by means of exothermic processes, transporting the metals into the hot zone. For this process especially that of W, traces of water (which can be removed by addition of graphite) are sufficient. The thermodynamic discussion in (*10*) for the W-transport taking into account the species J_1, J_2, HJ, H_2, H_2O, $WO_2(OH)_2$, WO_2J_2 leads to the prevailing reaction Eq. (14).

$$W_{,s} + 2H_2O_{,g} + 3J_{2,g} = WO_2J_{2,g} + 4HJ \quad (14)$$

The discussion of molybdenum transport by iodine and water using the similar species as in the tungsten transport leads to Eqs. (15–18).

$$0.5Mo_{,s} + H_2O_{,g} = 0.5MoO_{2,s} + H_2 \quad (15)$$

$$Mo_{,s} + 4H_2O_{,g} = MoO_2(OH)_{2,g} + 3H_2 \quad (16)$$

$$Mo_{,s} + 2H_2O_{,g} + 3J_{2,g} = MoO_2J_{2,g} + 4HJ \quad (17)$$

$$2HJ = J_2 + H_2 \quad (18)$$

$$J_2 = 2J_1. \quad (19)$$

If an ampoule charged with Mo, H_2O, and J_2 is heated within a temperature gradient, e.g., 1300 -> 1400 K with the starting molybdenum in

TABLE X

EQUILIBRIUM PRESSURES RELATED TO TRANSPORT OF Mo[a]

T[K]	Solid	H_2O	$MoO_2(OH)_2$	MoO_2J_2	J_2	J_1	HJ	H_2	ΣP	H/O	J/O	J/H	$\Delta P/\Sigma P$
1300	Mo + MoO_2	0.05446	1.75×10^{-7}	10.03×10^{-3}	1.0892	0.4870	1.2840	0.07586	3.000	20.73	53.27	2.570	64×10^{-5}
1400	Mo	0.05480	3.59×10^{-7}	8.10×10^{-3}	0.9145	0.7457	1.1915	0.08531	3.000	20.73	53.27	2.570	

[a] Ampoule charged with Mo + H_2O + J_2. P in atm.; $\Delta P = P(MoO_2J_2)_{1300} - P(MoO_2J_2)_{1400}$.

the 1300 K region some part of molybdenum is oxidized until the equilibrium (15) is established. MoO_2 formed in this way remains on further heating in the low temperature region (T_1). Furthermore, at T_1 the equilibria (16–19) are established. Taking a volume element of 1300 K equilibrium gas and transferring it into the 1400 K region (T_2) (keeping the total pressure constant) causes a deposition of Mo, whilst the new equilibrium positions (Eqs. 16–19) are established. This means molybdenum transport from the 1300 into the 1400 K zone.

The result of a corresponding calculation for $\sum P = 3$ atm and J_2/H_2O (initial) = J/H (end) = 2.570, suitable to be compared with one of the experiments (Table III, Expt. 12), is given in Table X.

Table X shows that the Mo transport proceeds via MoO_2J_2, whereas $MoO_2(OH)_2$ may be neglected. Furthermore from the temperature dependence of $P(MoO_2J_2)$ follows that the transport proceeds into the high temperature region. Finally $\Delta P(MoO_2J_2)/\sum P$ tells us that the transport rate will be small. This thermodynamic expectation agrees with the experimental results (Table III).

3.4.4. *Transport of the Sulfides MoS_2 and WS_2*

In the introduction the fact was mentioned that the chemical transport of MoS_2, WS_2 and related compounds by means of iodine have been described earlier. The main reason for our investigation was to find the gas species involved. The transport via the gaseous iodides can not proceed because of their instability. The transport via sulfide iodides is to be excluded because it can not be prevented by addition of graphite as it is actually the case (see Table IV). Two possibilities remain: a transport via the known oxide iodides MO_2J_2 as with the metals and the dioxides, or (less probable) a transport via unknown gaseous sulfide-oxide iodides. To arrive at a decision between these two possibilities, the following thermodynamic calculation was made.

We checked whether the observed transport of MoS_2 and WS_2 can be explained quantitatively by a formation of the gaseous oxide iodides MoO_2J_2 and WO_2J_2. In this calculation the reactions (20)–(24) have to be taken into consideration; all species with the exception of MoS_2 and WS_2 being gases.

$$MoS_{2,s} + 2H_2O + 3J_2 = MoO_2J_2 + 4HJ + S_2 \tag{20a}$$

$$WS_{2,s} + 2H_2O + 3J_2 = WO_2J_2 + 4HJ + S_2 \tag{20b}$$

$$2HJ = J_2 + H_2 \tag{21}$$

$$2H_2 + S_2 = 2H_2S \tag{22}$$

$$4H_2O + S_2 = 2SO_2 + 4H_2 \tag{23}$$

$$J_2 = 2J_1. \tag{24}$$

The calculation of the partial pressures of 9 gas species requires 9 conditions. These are 5 equilibria (20–24), the total pressure $\sum P$, and (charging the ampoule with MS_2, J_2, and H_2O) the 3 conditions S/M = 2; H/O = 2; J/O corresponding the charge, where S, M, H, O, J stand for the total contents of the gas phase.

The results are given in Tables XI and XII and Figs. 1 and 2. The general picture is the same for both MoS_2 and WS_2 (Figs. 1 and 2): Keeping the total pressure constant, the curve showing the

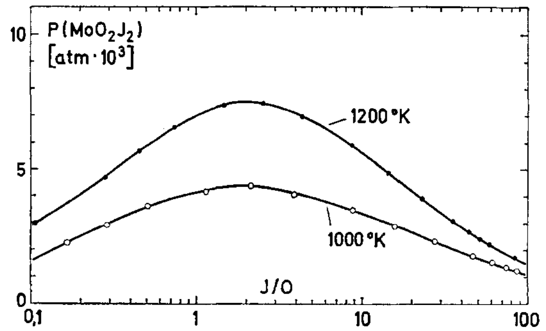

FIG. 1

dependence of $P(MO_2J_2)$ on the J/O ratio passes a maximum near J/O ≅ 2.

For the sake of simplification let us assume that the equilibria (21–24) could be neglected, so that the situation would be determined only by the reaction (20). In such a case the $P(MO_2J_2)$ maximum will be reached if the ratio of the equilibrium pressures J_2/H_2O equals the ratio of the corresponding stoichiometric coefficients of Eq. (20) that is $3/2 = 1.5$. In fact the systems under investigation are much more complicated. A large part of sulfur is transformed into SO_2 (see Tables XI and XII), so that another "main equation" can be written [Eq. (27)],

$$MS_{2,s} + 6H_2O + 3J_2 = MO_2J_2 + 4HJ + 2\,SO_2 + 4H_2 \qquad (25)$$

having a J_2/H_2O ratio of $3/6 = 0.5$.

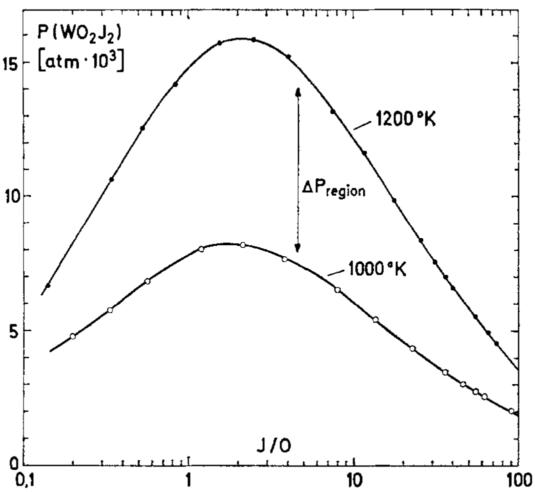

FIG. 2

The maximum value on the J/O scale of Figs. 1 and 2, taking into consideration all the equilibria involved is at about J/O = 2, corresponding to the ratio of the equilibrium pressures $J_2/H_2O \sim 0.8$ and therefore within the limits (0.5–1.5) of the simplified considerations given above.

The temperature dependence of the $P(MO_2J_2)$ maximum position is small. Therefore, in the same position on the J/O scale we find the maximum value of $\Delta P = P(MO_2J_2)_{T_2} - P(MO_2J_2)_{T_1}$, corresponding to the maximum transport rate.

TABLE XI

SYSTEM $MoS_2/H_2O/J_2$[a]

T[K]	J/O	H_2O	J_2	MoO_2J_2	HJ	S_2	H_2	H_2S	SO_2	J_1
1000	8.82	8.537 E-2	4.268 E-1	3.492 E-3	4.139 E-2	3.782 E-6	1.379 E-4	3.796 E-5	6.972 E-3	3.574 E-2
1000	15.87	4.721 E-2	4.721 E-1	2.868 E-3	3.429 E-2	4.047 E-6	8.556 E-5	2.437 E-5	5.731 E-3	3.759 E-2
1000	27.57	2.509 E-2	5.018 E-1	2.326 E-3	2.732 E-2	4.195 E-6	5.112 E-5	1.482 E-5	4.614 E-3	3.875 E-2
1000	46.69	1.302 E-2	5.206 E-1	1.780 E-3	2.148 E-2	4.320 E-6	3.044 E-5	8.955 E-6	3.555 E-3	3.947 E-2
1000	61.92	8.805 E-3	5.283 E-1	1.543 E-3	1.846 E-2	4.362 E-6	2.217 E-5	6.555 E-6	3.082 E-3	3.976 E-2
1000	75.27	6.656 E-3	5.325 E-1	1.389 E-3	1.658 E-2	4.359 E-6	1.774 E-5	5.242 E-6	2.751 E-3	3.991 E-2
1000	87.14	5.355 E-3	5.355 E-1	1.273 E-3	1.524 E-2	4.381 E-6	1.491 E-5	4.417 E-6	2.526 E-3	4.003 E-2
1200	8.69	6.188 E-2	3.094 E-1	5.913 E-3	6.731 E-2	8.861 E-5	6.602 E-4	1.437 E-4	1.155 E-2	1.430 E-1
1200	14.36	3.438 E-2	3.438 E-1	4.843 E-3	5.611 E-2	9.493 E-5	4.128 E-4	9.299 E-5	9.439 E-3	1.507 E-1
1200	22.91	1.842 E-2	3.684 E-1	3.905 E-3	4.521 E-2	9.868 E-5	2.501 E-4	5.744 E-5	7.527 E-3	1.560 E-1
1200	35.17	9.642 E-3	3.857 E-1	3.091 E-3	3.565 E-2	1.012 E-4	1.486 E-4	3.457 E-5	5.916 E-3	1.596 E-1
1200	44.38	6.554 E-3	3.933 E-1	2.675 E-3	3.081 E-2	1.028 E-4	1.088 E-4	2.551 E-5	5.134 E-3	1.612 E-1
1200	52.25	4.972 E-3	3.978 E-1	2.401 E-3	2.778 E-2	1.033 E-4	8.743 E-5	2.054 E-5	4.589 E-3	1.621 E-1
1200	58.95	4.009 E-3	4.009 E-1	2.213 E-3	2.558 E-2	1.036 E-4	7.359 E-5	1.732 E-5	4.217 E-3	1.627 E-1
1200	84.28	2.043 E-3	4.086 E-1	1.714 E-3	1.973 E-2	1.040 E-4	4.294 E-5	1.013 E-5	3.225 E-3	1.643 E-1

[a] P in atm; $\Sigma P \equiv 0.600$ atm; S/Mo ≡ 2.00; H/O ≡ 2.00.

TABLE XII

SYSTEM $WS_2/H_2O/J_2$[a]

T[K]	J/O	H_2O	J_2	WO_2J_2	HJ	S_2	H_2	H_2S	SO_2	J_1
1000	7.97	8.013 E-2	4.007 E-1	6.524 E-3	6.512 E-2	5.603 E-4	3.637 E-4	1.219 E-3	1.075 E-2	3.462 E-2
1000	13.62	4.481 E-2	4.481 E-1	5.427 E-3	5.456 E-2	5.982 E-4	2.282 E-4	7.902 E-4	8.818 E-3	3.662 E-2
1000	22.59	2.406 E-2	4.812 E-1	4.327 E-3	4.419 E-2	6.225 E-4	1.394 E-4	4.925 E-4	6.950 E-3	3.795 E-2
1000	35.77	1.259 E-2	5.036 E-1	3.495 E-3	3.483 E-2	6.266 E-4	8.278 E-5	2.934 E-4	5.417 E-3	3.882 E-2
1000	46.11	8.558 E-3	5.135 E-1	3.054 E-3	3.016 E-2	6.247 E-4	6.087 E-5	2.154 E-4	4.622 E-3	3.920 E-2
1000	54.71	6.490 E-3	5.192 E-1	2.779 E-3	2.715 E-2	6.213 E-4	4.879 E-5	1.722 E-4	4.125 E-3	3.941 E-2
1000	62.39	5.230 E-3	5.230 E-1	2.574 E-3	2.503 E-2	6.169 E-4	4.115 E-5	1.447 E-4	3.753 E-3	3.956 E-2
1000	90.86	2.662 E-3	5.325 E-1	2.058 E-3	1.928 E-2	5.991 E-4	2.399 E-5	8.313 E-5	2.820 E-3	3.992 E-2
1200	7.53	5.524 E-2	2.762 E-1	1.319 E-2	9.742 E-2	5.401 E-3	1.549 E-3	2.632 E-3	1.305 E-2	1.351 E-1
1200	11.59	3.123 E-2	3.123 E-1	1.162 E-2	8.249 E-2	5.512 E-3	9.822 E-4	1.686 E-3	1.048 E-2	1.436 E-1
1200	17.46	1.701 E-2	3.402 E-1	9.851 E-3	6.796 E-2	5.409 E-3	6.121 E-4	1.041 E-3	7.931 E-3	1.499 E-1
1200	25.46	9.031 E-3	3.613 E-1	8.333 E-3	5.482 E-2	5.098 E-3	3.751 E-4	6.192 E-4	5.781 E-3	1.545 E-1
1200	31.17	6.186 E-3	3.712 E-1	7.542 E-3	4.795 E-2	4.897 E-3	2.793 E-4	4.519 E-4	4.794 E-3	1.566 E-1
1200	35.94	4.715 E-3	3.772 E-1	6.973 E-3	4.355 E-2	4.745 E-3	2.267 E-4	3.610 E-4	4.161 E-3	1.579 E-1
1200	39.76	3.815 E-3	3.815 E-1	6.613 E-3	4.032 E-2	4.618 E-3	1.921 E-4	3.018 E-4	3.745 E-3	1.588 E-1
1200	54.38	1.963 E-3	3.926 E-1	5.535 E-3	3.176 E-2	4.133 E-3	1.158 E-4	1.722 E-4	2.579 E-3	1.611 E-1
1200	64.74	1.326 E-3	3.978 E-1	4.953 E-3	2.754 E-2	3.879 E-3	8.595 E-5	1.238 E-4	2.070 E-3	1.621 E-1
1200	73.20	1.002 E-3	4.009 E-1	4.573 E-3	2.490 E-2	3.672 E-3	6.975 E-5	9.772 E-5	1.747 E-3	1.627 E-1

[a] P in atm; $\Sigma P \equiv 0.600$ atm; $S/W \cong 2.00$; $H/O \equiv 2.00$.

In our experiments J/O is situated on the right hand side of the maximum. Therefore the data given in Tables XI and XII cover only this part of the system. Comparing the ΔP values of Figs. 1 and 2 we find that $\Delta P/\sum P$ and therefore the chemical transport for WS_2 is about 3 times larger than for MoS_2.

In our experiments (Table IV) we charged the ampoules with metalsulfide and iodine, but we did not introduce known amounts of water. Therefore, we have to discuss the possibility of a water content.

We know from a large number of experiments with quartz glass ampoules how difficult it is to exclude traces of water. Taking an ampoule with a volume of 32 ml at 1000 K only 0.07 mg H_2O will produce an H_2O pressure of 0.01 atm. Such small amounts of water may easily be introduced with the charge. But a much more important source of water is the wall of the quartz ampoule. One knows (*38*, *39*), that the water content of the usual kinds of quartz glass is about 0.01–0.1 wt%. This means that an ampoule with the wall thickness of 1 mm, an inside diameter of 16 mm, and a length of 160 mm, has a water content within the wall between 2.2 and 22 mg. This value compared with the 0.07 mg H_2O necessary for producing an H_2O pressure of 0.01 atm at 1000 K demonstrates that the diffusion of H_2O out of the wall must produce water pressures which are possibly important for chemical transport reactions. Returning to the chemical transport of WS_2 we take as an example the data given in the last but one row of Table XII with J/O = 64.74 and get

$$P(J_2, \text{initial}) = P(J_2) + P(WO_2J_2) + 0.5P(HJ) + 0.5P(J_1) = 0.498 \text{ atm } (1200 \text{ K})$$

$$P(H_2O, \text{initial}) = P(H_2O) + 2P(WO_2J_2) + 2P(SO_2) = 0.0154 \text{ atm } (1200\text{K})$$

Regarding the foregoing considerations this is no doubt a possible water content. Turning to Fig. 2 for J/O ≡ 64.74 we read $\Delta P(WO_2J_2) = (4.95 - 2.5) \times 10^{-3} = 2.45 \times 10^{-3}$ [atm]. Now the semi-empirical formula for a chemical transport by gas diffusion between equilibrium spaces is applied, see Sect. 3.4.1. With the average temperature T[K], the cross section q [cm^2] of the ampoule, the length of the diffusion path s [cm]

between source and deposit and the heating time t' [hr], from all this follows

$$
\begin{aligned}
\mathrm{n}(\mathrm{WS_2}) = {} & \\
& \frac{\varDelta P(\mathrm{WO_2J_2})}{\sum P} \cdot \frac{T^{0.8} \cdot q \cdot t'}{s} \cdot 1.8 \times 10^{-4} \text{ [mole]} \\
& = \frac{2.45 \times 10^{-3}}{0.6} \cdot \frac{1100^{0.8} \cdot 2.7 \cdot 40}{10} \cdot 1.8 \times 10^{-4} \\
& = 2.15 \times 10^{-3} \text{ mole } \mathrm{WS_2} \mathrel{\hat{=}} 533 \text{ mg } \mathrm{WS_2}.
\end{aligned}
$$

This result is of the order of magnitude of the transport rates observed (see Table IV, Expt. 11). Furthermore, Fig. 2 shows that changing to higher water contents (smaller J/O ratios) the result will not be changed considerably. Another important point to be discussed is the hindrance of WS_2 or MoS_2 transport by the addition of graphite. From Sect. 3.3. we know that at 1200 K an initial H_2O pressure of 0.01 atm by the reaction with graphite with the formation of $CO + H_2$ is diminished to 0.000003 atm. Simultaneously an H_2 pressure of 0.01 atm is produced. Looking for Eq. (25) we notice that both, the very strong reduction of the H_2O pressure and the increasing H_2 pressure shift the equilibrium position very much to the left. It is evident, that in this way the MO_2J_2 pressure becomes so small that no sulfide transport can be observed. Finally the equilibria (26) deserve consideration.

$$\mathrm{MoO_2J_{2,g}} + 2\mathrm{H_2O_{,g}} = \mathrm{MoO_2(OH)_{2,g}} + 2\mathrm{HJ_{,g}} \tag{26a}$$

$$Kp(1000\ \mathrm{K}) = 3.81 \times 10^{-4}; \quad Kp(1200\ \mathrm{K}) = 3.94 \times 10^{-3}$$

$$\mathrm{WO_2J_{2,g}} + 2\mathrm{H_2O_{,g}} = \mathrm{WO_2(OH)_{2,g}} + 2\mathrm{HJ_{,g}} \tag{26b}$$

$$Kp(1000\ \mathrm{K}) = 2.38 \times 10^{-3}; \quad Kp(1200\ \mathrm{K}) = 9.64 \times 10^{-3}$$

The formation of the molecules $MoO_2(OH)_2$ and $WO_2(OH)_2$ is not included in the calculation of Tables XI and XII and in Figs. 1 and 2. In fact this is allowed on that side of the systems rich in iodine and it is only this region which is important as far as our experiments are concerned. Moving on the J/O scale on Fig. 1 and 2 from right to left $P[MO_2(OH)_2]$ will clearly increase. It starts with pressures as low as $<10^{-7}$ atm at $J/O = 100$ and reaches $P[MO_2(OH)_2] \lessapprox 0.02\ P(MO_2J_2)$ at the $P(MO_2J_2)$ maximum of the curves. Proceeding further to the side rich in water, that is to small values on the J/O scale in Figs. 1 and 2, clearly $P[MO_2(OH)_2]$ gains of importance. At $J/O \sim 0.1$ one calculates $P[MO_2(OH)_2] \approx P(MO_2J_2)$.

4. Closing Remarks

The chemical transport of MoS_2 and WS_2 and certainly of some other Mo and W compounds using iodine as a transport agent proceeds via the gaseous oxide iodides MoO_2J_2 and WO_2J_2. These are produced by the presence of small amounts of water. It is obvious that the influence of water especially in closed tube reactions at high temperatures deserves more consideration.

Acknowledgments

We wish to thank Mrs. B. Plautz for experiments in the MoO_2/J_2 system and Dr. F. Wehmeier for first observations with MoS_2/J_2 and WS_2/J_2.

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