Journal of Alloys and Compounds, 187 (1992) 373–379
JALCOM 323

Thermodynamic investigation of the vaporization of molybdenum trioxide

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(Received April 1, 1992)

Abstract

The vapour pressure of MoO_3(s) was measured using a novel thermogravimetric system. The total pressures obtained in this investigation agree well with the best assessed values from data in the literature. The enthalpy of sublimation at 1000 K obtained from this work is 365.2 ± 5.0 kJ mol^{-1} in close agreement with the assessed value of 369.1 ± 0.8 kJ mol^{-1}. The vapour pressure data for pure MoO_3(s) was obtained in the context of our investigations on the vaporization of transition metal molybdates.

1. Introduction

The thermodynamic stabilities of transition metal molybdates are of considerable importance in nuclear fuel chemistry [1]. In this context, a programme has been initiated in our laboratory to study the phase equilibria in the ZrO_2–MoO_3 system and to determine the thermodynamic properties of molybdates such as $ZrMo_2O_8$. As a prerequisite to the study of vaporization behaviour of $ZrMo_2O_8$, the vaporization behaviour of MoO_3(s) was investigated using a novel thermogravimetric system. This system has been designed and fabricated for determining the vapour pressures of materials at high temperatures by the transpiration technique [2]. This paper describes the measurement of the vapour pressure of MoO_3(s), which serves the dual purpose of establishing the reliability of the newly built system as well as providing reference data for future studies on molybdates which will be carried out using the same experimental set-up.

2. Experimental details

The details of construction of the apparatus have been described elsewhere [2]. In the present design (Fig. 1) the sample A under investigation, spread uniformly, is contained in a tiered sample holder B consisting of three pans 10 mm in diameter and 2 mm deep. The pans, which are made of platinum foil, are stacked one above the other, leaving a gap of about a millimetre between each pan. The three-tiered sample holder is suspended on one arm of an electronic recording beam-type microbalance C (Sartorius model 4411)

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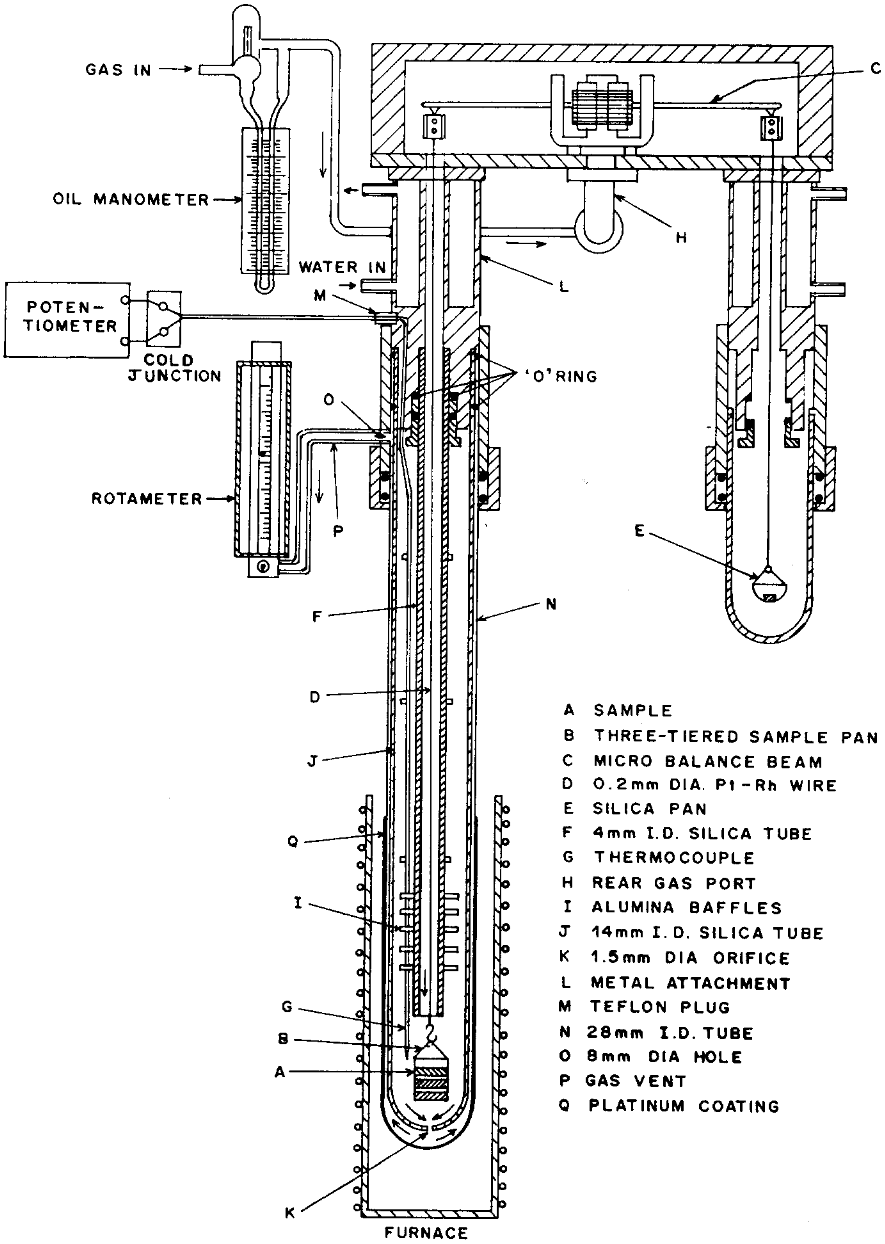

Fig. 1. Schematic diagram of an automatic recording transpiration apparatus.

with the help of a suspension wire D made of Pt–10 wt.%Rh alloy and 0.2 mm in diameter. The other arm of the beam carries a silica pan E for taring the weight of the sample and the container located in the furnace. The suspension wire 0.2 mm in diameter carrying the tiered sample pan passes through a silica tube F 4 mm in inside diameter which serves the dual purpose of supporting the thermocouple G with the tip located near the sample pan and of carrying the gas entering from the rear port H of the balance housing to the sample site after being pre-heated to the temperature of the sample on passing through the temperature gradient along its path.

In a typical experiment the carrier gas entering the rear port H of the steel casing of the balance (housing the beam) decends through the centre tube F 4 mm in inside diameter and, after reaching the sample which is maintained isothermally in the hottest zone, sweeps the vapour in equilibrium with the sample through a hole K 1.5 mm in diameter provided in the closed end of the tube J 14 mm in diameter. The vapour escaping through this hole is deposited in the temperature gradient region in an annular space between the middle tube 14 mm in inside diameter and the outer tube N 28 mm in inside diameter. The carrier gas then leaves through the exit port P connected to a rotameter.

In the present study, the vapour pressure of molybdenum trioxide was measured in the presence of flowing dry oxygen in the temperature range 947–1048 K. Oxygen was dried by passing over a column of anhydrous magnesium perchlorate. The Analar grade MoO_3 sample used in this investigation was obtained from Mallinkrodt Chemicals, USA. The desired temperatures of the sample were attained and maintained constant to ± 1 K using the programmer–controller (model MPC-500) supplied by M/s Indotherm Pvt. Ltd. The temperature of the sample was measured with a Pt–(Pt–13 wt.%Rh) thermocouple calibrated at the melting points of tin, antimony, silver, copper and gold, with an ice junction as the reference. The mass changes of the samples at various temperatures and flow rates were monitored with the microbalance (Sartorius model 4411) having a capacity of 25 g and an ultimate sensitivity of 1 μg. The changes were recorded continuously with a sensitivity of 20 μg on a three-pen strip chart recorder (Ohkura model DR 1132-800). The flow rate of oxygen used as a carrier gas in the present study ranged from 0.9 to 3.2 $1\ h^{-1}$. It was regulated with an inlet capillary flowmeter and was measured with a float-type rotameter (supplied by Instrumentation India Pvt. Ltd., Hyderabad). The plot of apparent vapour pressure *vs.* flow rate showed a distinct plateau region in the range 1.30–2.0 $1\ h^{-1}$ (Fig. 2). Therefore in all the vapour pressure measurements a flow rate of 1.55 $1\ h^{-1}$ was employed. The total amount of gas flowing was calculated from the rate of flow and time.

3. Results and discussion

It is known from mass spectrometry investigations [3–6] that MoO_3(s) vaporizes by forming polymers such as trimer, tetramer and pentamer in the vapour phase. Therefore it is necessary to obtain the average molecular weight from the partial pressure ratios in order to calculate the total vapour pressure from the data obtained in this investigation. Brewer and Lamoreaux [7] have given equations for the partial pressure $p_{Mo_3O_9}$ of the trimer, the partial pressure $p_{Mo_4O_{12}}$ of the tetramer and the partial pressure $p_{Mo_5O_{15}}$ of

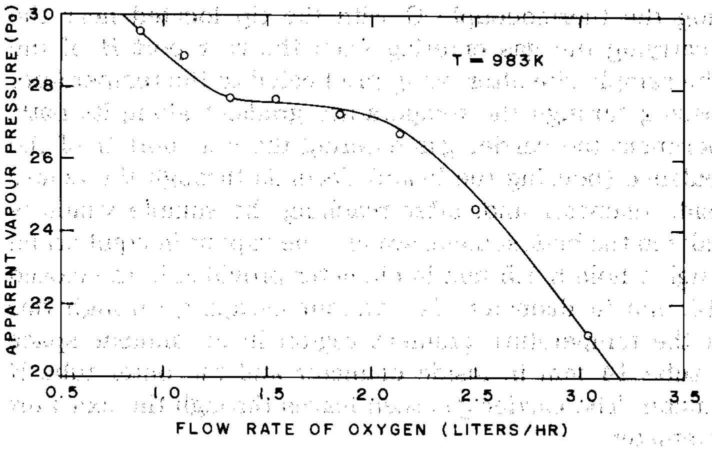

Fig. 2. Apparent pressure *vs.* flow rate plot for vaporization of molybdenum trioxide at 983 K.

the pentamer in their recent review. They have given maximum weightage to the transpiration study of Ackermann *et al.* [8], who in turn have used the ion intensity ratios of Berkowitz *et al.* [3] to calculate the average molecular weight. Since the assessment of Brewer and Lamoreaux, two more mass spectrometry investigations have been reported [5, 6]. Of these two, the work of Ikeda *et al.* [6] appears to be more reliable and provides equations for calculating the partial pressures of the trimer, tetramer and pentamer. Thus we have two sets of equations for the partial pressures of the trimer, tetramer and pentamer to calculate the average molecular weight. From the weight w of oxide transported and the average molecular weight M, the vapour pressures were calculated according to the ideal gas equation:

$$p=\frac{w}{V_c}\frac{R}{M}T_c \tag{1}$$

in which V_c is the volume of the carrier gas measured at a temperature T_c. The results are presented in Tables 1 and 2. It can be seen that the total pressures obtained from the present investigation agree well with the assessed values of Brewer and Lamoreaux [7] and not with those expected from the data of Ikeda *et al.* [6]. The vapour pressure values of Ikeda *et al.* [6] given in Table 2 are extrapolated from their equations for partial pressures as their measurements were only taken up to 940 K, whereas our measurements began at 947 K. The equations given by Brewer and Lamoreaux [7] are valid for the temperature range 800–1074 K, which includes the range of our measurements.

The heats of sublimation to trimer, tetramer and pentamer from the above-mentioned investigations are presented in Table 3. It can be seen that the values of Ikeda *et al.* [6] and Kazenas and Tsuvetkov [4] agree with each other and differ from those of other investigators whose values are close to the assessed values of Brewer and Lamoreaux [7]. Figure 3 gives

TABLE 1

Total pressure of molybdenum-containing species over $MoO_3(s)$

Temperature (K)	Average molecular weight M	Mass transfer per litre of carrier gas (mg l^{-1})	Total pressure	
			This work (Pa)	Ref. 7 (Pa)
947	485.56	1.01	5.08	4.86
954	487.63	1.29	6.54	6.83
963	490.33	2.46	12.42	10.50
980	495.49	5.15	25.73	23.24
983	496.51	5.42	27.02	26.67
998	501.24	11.15	55.08	52.41
1014	506.30	22.87	111.84	105.58
1031	511.77	45.63	220.66	217.34
1048	517.28	92.07	440.72	437.77

TABLE 2

Total pressure of molybdenum-containing species over $MoO_3(s)$ assuming the partial pressure values of Ikeda *et al.* [6]

Temperature (K)	Average molecular weight M	Mass transfer per litre of carrier gas (mg l^{-1})	Total pressure	
			This work (Pa)	Ref. 6 (Pa)
947	514.72	1.01	4.86	6.40
954	517.24	1.29	6.18	8.62
963	520.38	2.46	11.70	12.56
980	526.44	5.15	24.22	25.22
983	527.43	5.42	25.44	28.46
998	532.78	11.15	51.82	51.61
1014	538.33	22.87	105.19	95.86
1031	544.18	45.63	207.61	181.86
1048	549.95	92.07	414.52	339.21

TABLE 3

Various heats of sublimation of $MoO_3(s)$

Reaction	$\Delta H_{1000\ K}$ (kJ mol^{-1})			$\Delta H_{900\ K}$ (kJ mol^{-1})		
	This work	Ref. 7	Ref. 8	Ref. 4	Ref. 5	Ref. 6
$3MoO_3(s)=(MoO_3)_3(g)$	332.7 ± 6.7	341.0 ± 1.4	338.9	285.3	343.9 ± 8.4	291.0 ± 3.5
$4MoO_3(s)=(MoO_3)_4(g)$	388.6 ± 5.7	395.9 ± 0.7	387.9	331.4	397.5 ± 10	338.9 ± 4.8
$5MoO_3(s)=(MoO_3)_5(g)$	447.8 ± 5.2	450.5 ± 2.2	447.7	387.9	470.2 ± 15	387.9 ± 6.9

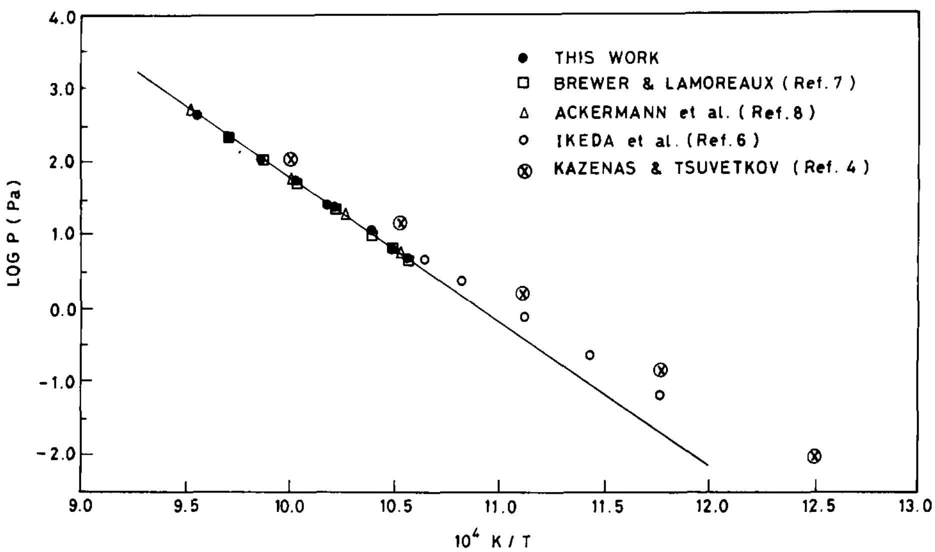

Fig. 3. log *P* *vs.* 1/*T* plot for vaporization of molybdenum trioxide in the temperature range 947–1048 K.

TABLE 4

Partial pressures of the trimer, tetramer and pentamer over $MoO_3(s)$

Temperature (K)	Data of Brewer and Lamoreaux [7]			Data of Ikeda *et al.* [6] (extrapolated)		
	p_3 (Pa)	p_4 (Pa)	p_5 (Pa)	p_3 (Pa)	p_4 (Pa)	p_5 (Pa)
947	3.1467	1.5545	0.1193	3.1572	2.8145	0.4326
954	4.3409	2.2528	0.1825	4.1410	3.8592	0.6210
963	6.5109	3.5988	0.3122	5.8345	5.7531	0.9808
980	13.7093	8.5019	0.8279	10.9597	11.9895	2.2725
983	15.5889	9.8630	0.9910	12.2208	13.6113	2.6278
998	29.2850	20.4190	2.2816	20.8689	25.3805	5.3629
1014	56.1199	43.2668	5.3934	36.2994	48.3504	11.2124
1031	103.1489	93.5118	13.0405	64.1210	93.7994	23.9442
1048	208.2630	196.6009	30.5627	111.2244	178.1148	49.8770

the log *P* *vs.* 1/*T* plot for the total pressures obtained by various investigators. It can be seen that, although the enthalpies of sublimation given by Ikeda *et al.* [6] and Kazenas and Tsuvetkov [4] agree, their total pressures are not in agreement. Our total pressures are in agreement with those of Brewer and Lamoreaux [7] and Ackermann *et al.* [8].

The partial pressures of the trimer, tetramer and pentamer obtained from the equations given by Brewer and Lamoreaux [7] are presented in Table 4 together with those obtained from the equations given by Ikeda *et al.* [6] by extrapolation to higher temperatures. The partial pressures given by Brewer and Lamoreaux [7] are based on the ion intensity ratios obtained by Berkowitz *et al.* [3] in their mass spectrometry investigation. Clearly, one can see the differences in the partial pressures obtained from two different mass spectrometry investigations. This observed discrepancy cannot be accounted for on the basis of possible non-stoichiometry of MoO_3(s) in the high temperature region of Knudsen effusion measurements. Moreover, the existing details in the published Knudsen effusion mass spectrometry work in refs. 3–6 are too inadequate to explain this discrepancy owing to other factors such as ionization cross-sections for the different polymeric species and their fragmentation.

The total enthalpy of sublimation at 1000 K from this work is 365.2 ± 5.0 kJ mol^{-1} which is in close agreement with the value of 369.1 ± 0.8 kJ mol^{-1} obtained by Brewer and Lamoreaux [7]. In view of the excellent agreement of both the total pressure of molybdenum-containing species and the enthalpy of sublimation of the present work with the recent best assessed values [7], our present data will be used to evaluate the free energies of formation of transition metal molybdates, which is in progress in our laboratory. It is felt that a more careful mass spectrometry investigation in the temperature range 950–1050 K would be helpful in resolving the discrepancy between the partial pressures of polymeric species existing in the reported data [3–6].

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