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# DETERMINATION OF THERMODYNAMIC STABILITY OF $CdMoO_4$ BY KNUDSEN EFFUSION VAPOR PRESSURE MEASUREMENT METHOD

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Thermodynamic stability of $CdMoO_4$ was determined by measuring the vapor pressures of Cd and $MoO_3$ bearing gaseous species. Th vaporization reaction could be described as $CdMoO_4(s)+MoO_2(s)=Cd(g)+2/n(MoO_3)_n$ ($n$=3, 4 and 5). The vapor pressures of the cadmium ($p_{Cd}$) and trimer ($p_{(MoO_3)_3}$) measured in the temperature range $987 \leq T/K \leq 1111$ could be expressed, respectively, as $\ln(p_{Cd}/Pa) = -32643.9/T + 29.46 \pm 0.08$ and $\ln(p_{(MoO_3)_3}/Pa) = -32289.6/T + 29.28 \pm 0.08$. The standard molar Gibbs free energy of formation of $CdMoO_4(s)$, derived from the vaporization results could be expressed by the equations: $\Delta_f G^0_{CdMoO_4(s)} = -1002.0 + 0.267T \pm 14.5$ kJ mol$^{-1}$ ($987 \leq T/K \leq 1033$) and $\Delta_f G^0_{CdMoO_4(s)} = -1101.9 + 0.363T \pm 14.4$ kJ mol$^{-1}$ ($1044 \leq T/K \leq 1111$). The standard enthalpy of formation of $CdMoO_4(s)$ was found to be $-1015.4 \pm 14.5$ kJ mol$^{-1}$.

***Keywords:*** *$CdMoO_4$, enthalpy, free energy, Knudsen effusion, vapor pressure*

## Introduction

Thermal methods have been extensively used in the investigation of catalysts [1, 2]. Physico-chemical studies on metal molybdates, that act as catalysts for light alkane oxydehydrogenation or olefins partial oxidation have been carried out using thermal methods [3, 4]. $CdMoO_4(s)$ is widely used as catalyst for the oxidation of olefins in the temperature range 575–625 K [5, 6]. The catalytic behavior of the molybdates strongly depends on oxygen partial pressure [6]. The oxygen pressure is a key factor to modify the selectivity of molybdenum-based catalysts. Therefore, for long-term use of these catalysts the knowledge of thermodynamic stability of these compounds under different oxygen partial pressures is required. The stability data of $CdMoO_4(s)$ is also useful in the thermodynamic evaluation of chemical state of the fission products Cd, Mo in fuel pin accidentally exposed to oxidizing environment during burnup process. It is well established that Cd, Mo, etc. are generated during the fission of $^{235}$U in the light water reactor (LWR) and $^{239}$Pu in fast breeder reactor (FBR) [7]. Though the above fission products remain in their elemental forms inside the nuclear fuel pins, under accidental conditions they can form their oxides. Thermodynamic data for the complex oxides will be helpful in assessing their release behaviors to the environment under the off normal conditions.

In a recent publication [8], Namboodiri *et al*. have reported the phase diagram of ternary Cd–Mo–O system involving the compound $CdMoO_4(s)$ by equilibrating different compositions of Cd metal and $MoO_3(s)$ in sealed quartz ampoules at 773 K. Apart from this, no other thermodynamic information is available on this system. The present paper deals with the determination of Gibbs free energy of formation of $CdMoO_4(s)$ by reacting $CdMoO_4(s)$ with $MoO_2(s)$ inside a Knudsen cell and measuring the vapor pressures of the gaseous products through effusion method.

## Experimental

High purity $MoO_2(s)$ (Aldrich USA, 99.0% purity), $CdCO_3(s)$ (Loba-Chemie purity 99.9%) and $MoO_3(s)$ (AR grade, Mallinkrodt Chemicals, USA) were used in the experiment. $CdMoO_4(s)$ was prepared by heating a mixture of freshly prepared $CdO(s)$ (obtained from decomposition of $CdCO_3$) and $MoO_3(s)$ in equal molar proportions at 925 K for 12 h with two intermittent grindings. The compound was characterized by TG-DTA, X-ray diffraction and chemical analysis techniques. The XRD pattern of the compound obtained using a Phillips X-ray diffractometer with CuK∝ radiation was found to match with the pattern reported in JCPDS file no. (07–0209). From the chemical analysis of the sample the observed cadmium content was found to be 41.0±1.5 mass% as against the calculated 41.3%. Mo content was found to be 34.5±2.0 mass% as against the calculated 35.2%. Thermal characterization of the sample was done using a Setaram TG-DTA instrument (Model 92–16.18). The following exploratory experiments were made for

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working out the scheme of thermodynamic stability study of the molybdate.

Thermogravimetric runs for pure $CdMoO_4(s)$, mixture of $CdMoO_4(s)+MoO_2(s)$, and mixture of $CdO(s)+MoO_2(s)$ were taken separately. The TG analysis of the last mixture was made for understanding the thermal behavior of the $CdMoO_4(s)+MoO_2(s)$ mixture. Thermogravimetric run for the mixture of CdO and $MoO_2$ mixture recorded in vacuum showed vaporization of the sample at about 800 K. In order to know the vaporizing species in the TG experiment, a mixture of $CdO(s)$ and $MoO_2(s)$ was sealed in a quartz tube and heated at about 975 K. The partially reacted $CdO(s)$ and $MoO_2(s)$ mixture at 975 K with the vapor deposits in the cooler part of the sealed quartz tube along with the XRD pattern of the volatile products is shown in Fig. 1. The XRD analysis of the vapor deposit from the equilibration showed the presence of $MoO_3(s)$ and $Cd(s)$.

Taking the above fact together with the observation that $CdMoO_4(s)+MoO_2(s)$ showed similar TG loss at higher temperatures (998 to 1110 K) where pure $CdMoO_4(s)$ did not, the chemical reaction leading to the mass loss could be expressed as

$$CdMoO_4(s)+MoO_2(s)=2MoO_3(g)+Cd(g) \quad (1)$$

The $MoO_3(g)$ species according to the reported information [9, 10] will exist in different polymeric forms. The indicated reaction path leaves the phase mixture unchanged as confirmed in the XRD pattern of the TG residue.

The equilibrium state of reaction (1) involves vapor with the two solids phases and therefore is bivariant. In the Knudsen effusion there is possibility that the compound $CdMoO_4(s)$ may deviate from its oxygen stoichiometry. The XRD analysis of the TG residue showed that the tetragonal cell parameters of the compound are $a$=5.154(3) Å, $c$=11.191(4) Å, which agree well within the experimental uncertainty with the literature values of $a$=5.154 Å and $c$=11.194 Å; the cell parameters of the as prepared compound were same as those analyzed in the residue. Further, the TG residue of the equimolar mixture of $MoO_2(s)$ and $CdMoO_4(s)$ at 1073 K was reduced by Ar – 8% $H_2$ mixture in the microbalance. Mass loss due to the reduction started at about 800 and completed at 1075 K, and the residue was found to be pure $MoO_2(s)$. The observed mass loss due to the chemical reaction, $CdMoO_{4-x}(s)+MoO_2(s)+(2–x)H_2(g)=2MoO_2(s)+Cd(g)+(2–x)H_2O(g)$ indicated that the oxygen stoichiometry of the compound did not have observable deviation from that in $CdMoO_4$ in the presence of the reductant $MoO_2(s)$. From this observation it is believed that the $CdMoO_4(s)+MoO_2(s)$ mixture attains the congruently evaporating composition very close to the stoichiometric compound. The congruency reducing the degrees of freedom by one, the effusion experiment could be carried out on the system and the thermodynamic property derived thereof could be assigned to the stoichiometric compound.

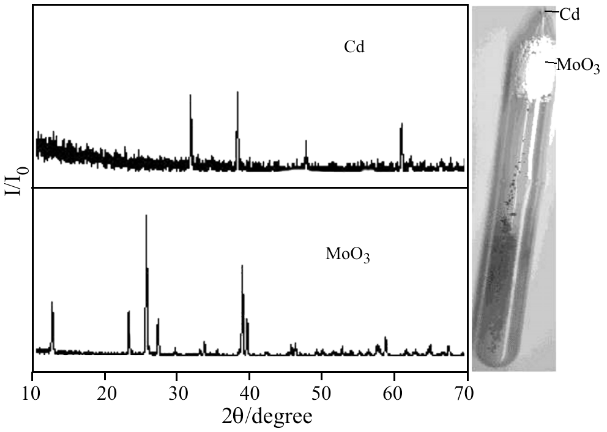

**Fig. 1** Picture of sealed quartz tube containing partially reacted CdO and $MoO_2$ mixture with deposits of Cd and $MoO_3$ in the top cooler part; the XRD patterns of the deposit shown at the left

Taking the above fact into consideration, the determination of thermodynamic stability of $CdMoO_4(s)$ was attempted by following the $CdMoO_4(s)+MoO_2(s)$ reaction with the help of Knudsen effusion mass loss technique. The vapor pressure of $Cd(g)$ and $MoO_3(g)$ formed during the chemical reaction (1) was obtained in the temperature range of 998 to 1110 K by the mass loss analysis using a micro-thermobalance (Setaram, Model B24). The mass losses due to Cd and $MoO_3$ bearing species were calculated by apportioning the total mass loss of the sample to Cd and molybdenum trioxide in their molar ratios. Detailed description about the apparatus and the procedure for the data collection are described elsewhere [11].

About 200 mg of 1:1 molar mixture of $CdMoO_4(s)$ and $MoO_2(s)$ in powder form was spread on a quartz crucible put on a stand inside a hermetically sealed quartz Knudsen cell of 10 mm inner diameter and 1.5 mm orifice diameter. The Clausing factor for the Knudsen cell was determined experimentally by measuring the vapor pressures of the standard substances and comparing the pressures with the corresponding literature values. The ratios of the observed vapor pressure data of the standard materials: $Ag(s)$, $TeO_2(s)$, $CdCl_2(s)$ and the reported vapor pressures for the respective cases in the temperature ranges of 1025–1100, 825–900 and 525–600 K were found to be 0.93, 0.947 and 0.961. The mean Clausing factor for the cell calculated from the above consideration was 0.946. It may be noted here that the measured vapor pressures of the standard materials are quite close to the equilibrium values reported in the literature for all the cases.

In order to ensure the quick equilibrium between sample and its vapor products, the mixture of $CdMoO_4(s)$+$MoO_2(s)$ was well spread in the crucible keeping the ratio of the sample-surface to the orifice is high (about 40). This ratio as such was an order of magnitude higher than that involved in the measurement of the Clausing factor of the cell orifice using silver standard in globular form. The nearly unit value of the Clausing factor was indicative of the fact that Ag vapor over the globule could attain saturation under the effusive loss. Considering that the average particle size in the mixture was 10 micron, the actual evaporating surface was $10^5$ times higher than the projected surface of the sample mixture. The surface augmentation using fine particles was made to tackle any kinetic impedance from the heterogeneous reaction (1). The vapor pressures were measured both in ascending and descending mode of temperatures to ensure the absence of kinetic impediments of the vapor generation inside the cell.

A Pt, Pt – 13% Rh thermocouple protected by a thin alumina sheath was used for measuring the sample temperature. The tip of the thermocouple was located about 1 mm away from the sample but well within the isothermal zone of the reaction tube. The whole system was closed in a vacuum-tight, recrystallized alumina tube of diameter 30 mm. The system as well as the balance was attached to a high-vacuum system. The effusion experiments were done under dynamic vacuum of $10^{-8}$ bar.

The mass calibration of the microbalance was done using standard masses at room temperature. The temperature calibration for the sample was done by the drop method [12], using high purity metal standards: Sn, Sb, Ag and Au. Temperature of the sample was varied using a microprocessor based temperature programmer cum controller with an accuracy of ±0.5 K using a Pt, Pt – 13% Rh thermocouple.

The mass loss due to the vaporization of Cd+$MoO_3$ from the Knudsen cell was measured at different temperatures. The mass loss with time plotted in isothermal runs was used to calculate the vapor pressure. Mass loss measurements were taken at different temperatures in increasing as well as decreasing orders of successive isotherms. The observed reproducibility in the mass loss rate in each isothermal run confirms the absence of kinetic hindrance in the evaporative loss. Several measurements were carried out in the temperature range of 987 to 1111 K. The equilibrium vapor pressures of Cd, $MoO_3$ bearing species derived from mass loss data were used to calculate the thermodynamic stability $CdMoO_4(s)$. After the experiment the residue in the silica crucible was analyzed by XRD method and also by chemical means to confirm the presence of the coexisting phases.

## Results and discussion

Thermogravimetric and differential thermal analysis (TG-DTA) plot (Fig. 2) for $CdMoO_4(s)$ recorded under flowing-argon showed that the compound started decomposing at about 1440 K after melting at 1400 K. From the available thermodynamic information [12] on $MoO_2$ solid and its vapor, it can be seen that $MoO_2$ will have negligible vapor pressure in the temperature range of measurements and under the background oxygen partial pressure of $10^{-8}$ bar prevailing during the measurement.

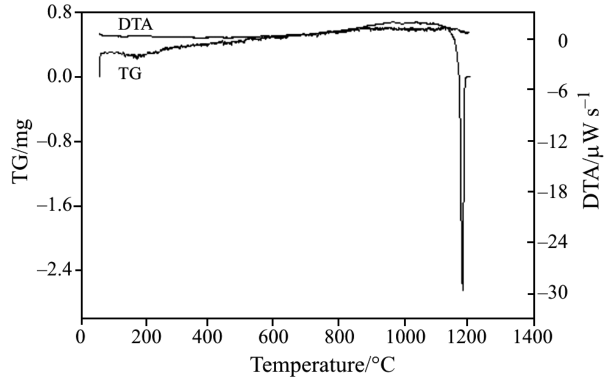

**Fig. 2** TG-DTA plot of $CdMoO_4$ recorded under argon atmosphere, heating rate=10 K min$^{-1}$

The vapor pressure of $MoO_2(s)$ at 1000 K for example, calculated using the literature data [13] is found to be of the order of $10^{-18}$ bar. The mass loss corresponding to the above pressure from the Knudsen cell will be negligible. However, an intimate mixture of $CdMoO_4(s)$ and $MoO_2(s)$ under similar experimental conditions started losing mass at about 1000 K, which was much lower temperature than the decomposition of $CdMoO_4(s)$. It can also be seen that the contribution of $MoO_3(g)$ to the total pressure from oxidation reaction, $MoO_2(s)+O_2(g)=MoO_3(g)$, at the background oxygen pressure at 1000 K [12] is negligible. The XRD and chemical analyses of the condensates collected at the cooler regions of the Knudsen assembly shows the presence of $Cd(s)$ and $MoO_3(s)$. Analysis of the residue from the Knudsen cell after the effusion studies revealed that $CdMoO_4(s)$ and $MoO_2(s)$ were present in the same molar ratio (1:1) as before the reaction. Figure 3 gives the XRD pattern of the residual mixture from effusion studies along with those of the pure $CdMoO_4(s)$ and $MoO_2(s)$.

From the mass spectrometric data [9, 10] it can be shown that the molybdenum bearing gaseous species effusing out from the Knudsen cell under the experimental conditions, consist predominantly of $(MoO_3)_3$, $(MoO_3)_4$ and $(MoO_3)_5$ in addition to negligible amounts of $(MoO_3)_2$. Considering this along with the present observations, the reaction between

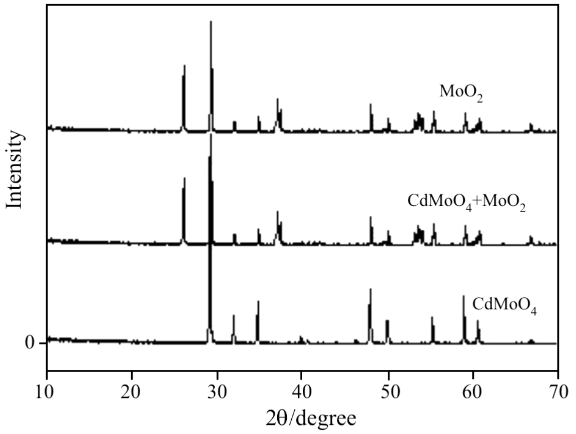

**Fig. 3** XRD plots for pure CdMoO$_4$, reacted CdMoO$_4$+MoO$_2$ mixture and pure MoO$_2$

CdMoO$_4$ and MoO$_2$ taking place during the effusion process could be expressed by the following equation

$$\mathrm{CdMoO_4}(s)+\mathrm{MoO_2}(s)=\mathrm{Cd}(g)+2/n(\mathrm{MoO_3})_n(g) \quad (2)$$

where $n$=3, 4, 5.

In the present case the total mass loss from the Knudsen cell per unit time ($w_T$) is equal to the sum of the mass loss due to Cd and polymeric species of molybdenum trioxides, i.e.,

$$w_T=w_{Cd}+w_3+w_4+w_5 \quad (3)$$

where $w_{Cd}$, $w_3$, $w_4$ and $w_5$ are the mass loss of Cd, and tri-, tetra- and pentamers of MoO$_3$ per unit time. Using the kinetic theory of gases the vapor fluxes of the species, $f_{Cd}$ and $f_{(\mathrm{MoO_3})_n}$, from the Knudsen cell and the total mass loss ($w_T$) can be correlated by the equation

$$w_T=\frac{AK}{\sqrt{2\pi RT}}(p_{Cd}\sqrt{M_{Cd}}+p_3\sqrt{M_3}+ +p_4\sqrt{M_4}+p_5\sqrt{M_5}) \quad (4)$$

where, $A$ the orifice area, $K$ the Clausing factor, $T$ the absolute temperature in K, $M_{Cd}$ and $M_n$ ($n$=3, 4 and 5) are the molecular mass of Cd and molybdenum oxide species, $R$ the universal gas constant and $p_{Cd}$, $p_3$, $p_4$ and $p_5$ are respectively the partial pressures of cadmium, and trimer, tetramer and pentamer of molybdenum trioxide. From Eq. (2) it is observed that the total vapor fluxes of molybdenum trioxide species as MoO$_3$ will be twice that of the vapor fluxes of Cd. Therefore, considering the individual masses involved in Eq. (3) the molecular flux balance equation can be constructed as

$$\frac{2w_{Cd}}{M_{Cd}}=\left(3\frac{w_3}{M_3}+4\frac{w_4}{M_4}+5\frac{w_5}{M_5}\right) \quad (5)$$

With the consideration of effusive flow of the individual vapor species, the flux balance Eq. (5) can be rewritten in terms of the partial pressures as

$$2\frac{p_{Cd}}{\sqrt{M_{Cd}}}=\left(3\frac{p_3}{\sqrt{M_3}}+4\frac{p_4}{\sqrt{M_4}}+5\frac{p_5}{\sqrt{M_5}}\right) \quad (6)$$

or

$$p_{Cd}=\left(3\frac{p_3}{\sqrt{M_3}}+4\frac{p_4}{\sqrt{M_4}}+5\frac{p_5}{\sqrt{M_5}}\right)\frac{\sqrt{M_{Cd}}}{2} \quad (7)$$

Putting the value of $p_{Cd}$ from Eq. (7) in Eq. (4), the total mass loss ($w_T$) per unit time can be expressed as

$$w_T=\frac{AK}{\sqrt{2\pi RT}}\left[\begin{array}{l}\frac{M_{Cd}}{2}\left(3\frac{p_3}{\sqrt{M_3}}+4\frac{p_4}{\sqrt{M_4}}+5\frac{p_5}{\sqrt{M_5}}\right)\\ +p_3\sqrt{M_3}+p_4\sqrt{M_4}+p_5\sqrt{M_5}\end{array}\right] \quad (8)$$

The equilibrium between trimer, tetramer and pentamer in the vapor phase could be expressed by the following equations:

$$4/3(\mathrm{MoO_3})_3 \Leftrightarrow (\mathrm{MoO_3})_4 \quad K_1=p_4/p_3^{4/3} \quad (9)$$

and

$$5/3(\mathrm{MoO_3})_3 \Leftrightarrow (\mathrm{MoO_3})_5 \quad K_1=p_5/p_3^{5/3} \quad (10)$$

Using the values as of $p_4$ and $p_5$ in terms of $K_1$ and $K_2$ from Eqs (9) and (10) respectively, Eq. (8) can be expressed as

$$w_T=\frac{AK}{\sqrt{2\pi RT}}\left[\begin{array}{l}p_3\left(\frac{3}{2}\frac{M_{Cd}}{\sqrt{M_3}}+\sqrt{M_3}\right)+\\ +K_1p_3^{4/3}\left(2\frac{M_{Cd}}{\sqrt{M_4}}+\sqrt{M_4}\right)+\\ +K_2p_3^{5/3}\left(\frac{5}{2}\frac{M_{Cd}}{\sqrt{M_5}}+\sqrt{M_5}\right)\end{array}\right] \quad (11)$$

Putting the values of $A$, $K$, $K_1$, $K_2$, $M_{Cd}$, $M_3$, $M_4$, $M_5$ and $w_T$ in SI units and the non-linear equation (Eq. (11)) was solved for the equilibrium partial pressures of the trimmer ($p_3$). The constants $K_1$ and $K_2$ could be obtained from the data compiled by Brewer and Lamoreaux [14]. The partial pressure ($p_{Cd}$) was calculated using the Eqs (11) and (7).

The vapor pressure of Cd($g$), (MoO$_3$)$_3$($g$) over the CdMoO$_4$($s$) and MoO$_2$($s$) mixture in the temperature range 987 to 1111 K as calculated from experimentally determined parameters involved in Eqs (7) and (11) respectively, are given in Table 1 for all the runs. The linear least-square fits of ln$p_{(Cd)}$, ln $p_{(\mathrm{MoO_3})_3}$ *vs.* 1/$T$ are represented in Fig. 4. The least square fitted equations are represented as

$$\ln(p_{Cd}/\mathrm{Pa})=-32643.9/T+29.46\pm0.08 \quad (987\leq T/\mathrm{K}\leq1111) \quad (12)$$

**Table 1** Vapor pressure data for Cd and $P_3$ in the temperature range 987 to1111 K

| $T$/K | Time | Mass loss/μg | $p_{Cd}$/Pa | $K_1$/Pa$^{-1/3}$ | $K_2$/Pa$^{-2/3}$ | $p_3$/Pa | $\Delta_f G^0_{CdMoO_4}$/kJ mol$^{-1}$ |
|---|---|---|---|---|---|---|---|
| 987 | 200 | 41 | 0.023 | 1649 | 10190 | 0.006 | –738.5 |
| 988 | 700 | 167 | 0.027 | 1612 | 9751 | 0.007 | –738.2 |
| 1001 | 300 | 104 | 0.040 | 1204 | 5580 | 0.010 | –734.7 |
| 1007 | 300 | 136 | 0.052 | 1055 | 4335 | 0.012 | –733.1 |
| 1011 | 600 | 329 | 0.064 | 966.9 | 3669 | 0.014 | –732.0 |
| 1022 | 400 | 311 | 0.091 | 763.6 | 2336 | 0.020 | –729.1 |
| 1031 | 200 | 183 | 0.107 | 632.0 | 1626 | 0.024 | –726.7 |
| 1033 | 800 | 874 | 0.128 | 606.3 | 1502 | 0.027 | –726.2 |
| 1044 | 200 | 292 | 0.172 | 483.8 | 975.1 | 0.036 | –722.9 |
| 1053 | 300 | 495 | 0.195 | 403.7 | 689.5 | 0.041 | –719.7 |
| 1055 | 250 | 533 | 0.252 | 388.0 | 639.0 | 0.050 | –718.9 |
| 1066 | 400 | 1027 | 0.305 | 312.6 | 422.5 | 0.061 | –714.9 |
| 1078 | 200 | 776 | 0.464 | 248.0 | 271.7 | 0.088 | –710.6 |
| 1088 | 300 | 1379 | 0.553 | 205.8 | 189.5 | 0.105 | –706.9 |
| 1111 | 100 | 802 | 0.974 | 135.4 | 85 | 0.178 | –698.6 |

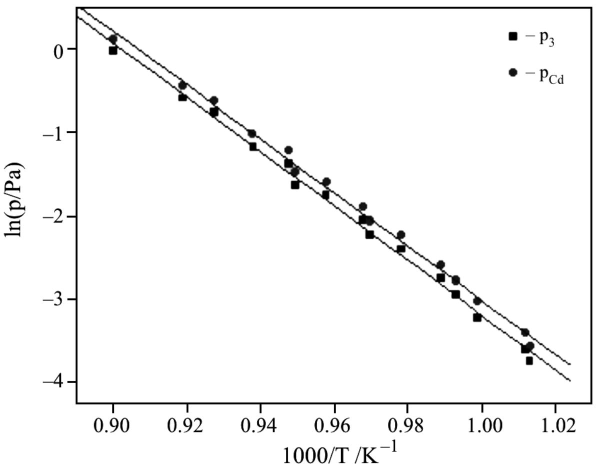

**Fig. 4** Plot of $\ln(p_{Cd}/Pa)=-32643.9/T+29.46\pm0.08$ and $\ln(p_3/Pa)=-32289.6/T+29.28\pm0.08$ *vs*. $1/T$ for the vaporization reaction between $CdMoO_4$ and $MoO_2$

$$\ln(p_{(MoO_3)_3}/\mathrm{Pa})=-32289.6/T+29.28\pm0.08 \quad (987\leq T/\mathrm{K}\leq1111) \tag{13}$$

The standard free energy of formation of $CdMoO_4$ was derived from the following equilibrium reaction

$$CdMoO_4(s)+MoO_2(s)= 2/3(MoO_3)_3(g)+Cd(g) \tag{14}$$

The standard free energy change for this reaction can expressed by

$$\Delta rG^0=2/3\Delta_f G^0_{(MoO_3)_3(g)}+\Delta_f G^0_{Cd(g)}- -\Delta_f G^0_{CdMoO_4(s)}-\Delta_f G^0_{MoO_2(s)} \tag{15}$$

$\Delta_r G^0$ in terms of the equilibrium constant ($K_{eq}$) for the reaction can be expressed as

$$\Delta rG^0=-RT\ln K_{eq}=-RT\ln(p_3^{2/3}p_{Cd}) \tag{16}$$

In the derivation of the Gibbs energy of formation of $CdMoO_4$, it was assumed that there is negligible $MoO_2$ solubility in $CdMoO_4$ [8]. From Eqs (15) and (16) $\Delta_f G^0_{CdMoO_4(s)}$ can be expressed as

$$\Delta_f G^0_{CdMoO_4(s)}=2/3\Delta_f G^0_{(MoO_3)_3(g)}+\Delta_f G^0_{Cd(g)} -\Delta_f G^0_{MoO_2(s)}+RT\ln(p_3^{2/3}p_{Cd}) \tag{17}$$

The values for standard free energy of formation of $(MoO_3)_3(g)$, $MoO_2(s)$ were taken from reference [15, 16]. Since the boiling point of Cd is 1038 K, the values of the standard free energy of formation Cd($g$) is taken as zero for the measurements above 1038 K. The free energy of formation of Cd($g$) below 1038 K was taken from the literature [11]. The standard free energy of formation of $CdMoO_4(s)$ calculated using the values of the above quantities in Eq. (17) is given in Table 1. The linear graph showing the variation of Gibbs free energy of formation of $CdMoO_4(s)$ with temperature is shown in Fig. 5. The least square fitted equation for the Gibbs free energy of formation below and above the boiling point of Cd could be expressed as

$$\Delta_f G^0_{CdMoO_4(s)}=-1002.0+0.267T\pm14.5\ \mathrm{kJ\ mol^{-1}} \quad (987\leq T/\mathrm{K}\leq1033) \tag{18}$$

and

$$\Delta_f G^0_{CdMoO_4(s)}=-1101.9+0.363T\pm14.4\ \mathrm{kJ\ mol^{-1}} \quad (1044\leq T/\mathrm{K}\leq1111) \tag{19}$$

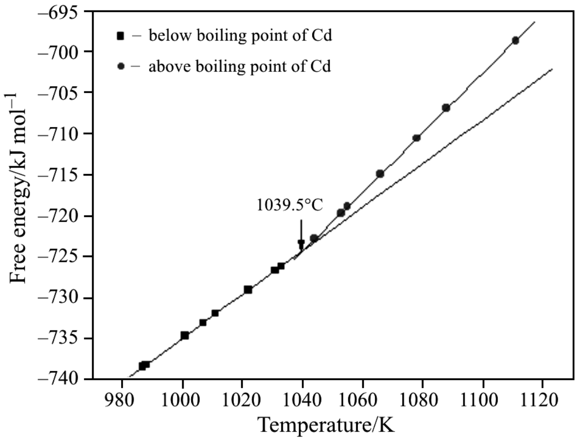

**Fig. 5** Variation of Gibbs free energy of formation of $CdMoO_4$ as a function of temperature

The standard enthalpy and entropy of formation $CdMoO_4(s)$ below and above the boiling point of Cd are –1002.0 and 1101.9 kJ mol$^{-1}$, and 267 and 363 J K$^{-1}$ mol$^{-1}$, at the mean temperature 1010 and 1078 K, respectively. The average standard enthalpy of formation of $CdMoO_4(s)$ at the room temperature derived from the free energy data using the estimated heat capacity of $CdMoO_4(s)$ was found to be –1015.4±14.4 kJ mol$^{-1}$.

## Conclusions

Thermodynamic stability of $CdMoO_4(s)$ was determined by measuring the vapor pressures of Cd(*g*) and $MoO_3$ bearing species from the reaction of $CdMoO_4(s)$ and $MoO_2(s)$ carried out with Knudsen effusion mass loss method. The equilibrium partial pressures of Cd(*g*) and molybdenum oxide bearing species were calculated by apportioning the total mass loss in the molar ratios of the reaction products and by using the values of equilibrium constants of polymerization of the molybdenum bearing vapor species. The standard Gibbs free energy of formation of $CdMoO_4(s)$ derived using the above vapor pressure data and other auxiliary data below and above the boiling point of Cd, could be expressed by the equations, $\Delta_f G^0_{CdMoO_4(s)} = -1002.0+0.267T\pm14.5$ kJ mol$^{-1}$ ($987\leq T$/K$\leq1033$) and $\Delta_f G^0_{CdMoO_4(s)} = -1101.9+0.363T\pm14.4$ kJ mol$^{-1}$ ($1044\leq T$/K$\leq1111$). The average standard enthalpy of formation of $CdMoO_4(s)$ at the room temperature derived from the free energy data using the estimated heat capacity of $CdMoO_4$ was found to be –1015.4±14.5 kJ mol$^{-1}$.

## References

1 A. Tungler, J. Therm. Anal. Cal., 79 (2005) 521.
2 J. A. Moura, A. S. Araujo, A. C. S. L. S. Coutinho, J. M. F. B. Aquino, A. O. S. Silva and M. J. B. Souza, J. Therm. Anal. Cal., 79 (2005) 435.
3 P. K. Sinhamahapatra and S. K. Bhattachayya, J. Thermal Anal., 8 (1975) 45.
4 A. Kaddouri, R. Del Rosso, C. Mazzocchia, P. Grounchi and D. Fumagalli, J. Therm. Anal. Cal., 66 (2001) 63.
5 P. Forzatti, N. Kotzev, L. Gencheva, I. Pasquon, D. Shopov and P. L. Villa, J. Catal., 65 (1980) 369.
6 F. Trifiro, G. Caputo and P. L. Villa, J. Less-Common Metals, 36 (1974) 305.
7 H. Kleykamp, J. Nucl. Mater., 131 (1985) 221.
8 P. N. Namboodiri and S. N. Tripathi, J. Phase Equilib., 23 (2002) 339.
9 J. Berkowitz, M. Inghram and W. A. Chupka, J. Chem. Phys., 26 (1957) 842.
10 Y. Ikeda, H. Ito, T. Mizuno, K. Amioka and G. Matsumoto, High Temp. Sci., 16 (1983) 1.
11 R. Mishra, M. Ali, S. R. Bharadwaj and D. Das, J. Nucl. Mater., 321 (2003) 318.
12 Kubaschewski, C. B. Alcock and P. J. Spencer, Metallurgical Thermochemistry, 6th Edition, Pergamon Press, Oxford 1993.
13 Ivtanthermo 'Database on thermodynamic properties of individual substances and related software' Version 3, 1992–2000 Glushko Thermocentre of Res.
14 L. Brewer, R. H. Lamoreaux, R. Ferro, R. Marazza and K. Girgis, in Molybdenum: Physico-Chemical Properties of its Compounds and Alloys, IAEA review, special issue no. 7, Ed. L. Brewer (IAEA, Vienna 1980).
15 I. Barin, 'Thermochemical Data of pure substances', Vol. II and I (3rd Edition), VCH Publishers, New York 1995.
16 O. Knacke, O. Kubaschewski and K. Hesselman, Thermochemical Properties of Inorganic Substances, 1991.

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