A microthermogravimetric system for the measurement of vapour pressure by a transpiration method

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Abstract

A novel automatic recording microthermogravimetric system for the measurement of vapour pressures at high temperatures by transpiration method was designed and fabricated. The performance of the system was checked by measuring the vapour pressure of anhydrous cadmium chloride in flowing dry argon in the temperature range 713–833 K. The vapour pressure of cadmium chloride in this range could be expressed as

$$\ln(P/\text{Pa}) = -(20\,109.10 \pm 262.32)/T + (29.46 \pm 0.344)$$

The enthalpy of sublimation of $CdCl_2$ derived from this equation at the mean temperature of investigation was found to be 167.2 ± 2.2 kJ mol^{-1} and compared very well with the value of 166.5 ± 4.7 kJ mol^{-1} reported by Skudlarski et al. (J. Chem. Thermodyn., 19 (1987) 857) from their recent Knudsen effusion mass spectrometric measurements.

The present system can be used for measurement of vapour pressures up to 1425 K and is the first of its kind in which the mass loss due to vaporization is monitored continuously during the conventional transpiration experiment. The system described in this paper effects considerable saving of time in the experiment and minimizes the errors associated with mass measurements in the conventional transpiration method currently in use.

INTRODUCTION

A transpiration technique designed primarily to measure the vapour pressures of liquids and solutions at normal laboratory temperatures by Regnault [1] in the first half of the nineteenth century has been adopted successfully in recent years in the measurement of vapour pressures of materials up to temperatures as high as 2500 K [2]. Vapour pressures between 10^{-3} Pa and 10 kPa can be measured by this technique in the controlled reactive or inert gaseous environment [3]. The experimental method currently in use is, however, quite cumbersome and time

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consuming. We describe in this paper a simple system built in our laboratory, employing an automatic recording microthermogravimetric system. The instrument is not only simple to operate but also yields the most reliable data in the shortest possible time.

The performance of this apparatus was tested by measuring the vapour pressure of pure anhydrous cadmium chloride in the temperature range 713–833 K. Cadmium chloride is known to vaporize congruently in this range, giving predominantly $CdCl_2(g)$ as the cadmium bearing species in the vapour phase [4, 5]. The vapour pressure and the enthalpy of sublimation of $CdCl_2$ at the mean temperature derived from the data of the present study are in excellent agreement with those reported recently from Knudsen effusion mass spectrometric studies [5].

PRINCIPLE OF THE TECHNIQUE

A detailed account of the transpiration technique, including the theory, can be found in several excellent reviews [3, 6]. In this technique the mass loss of the sample maintained at a constant temperature in the uniform temperature zone of the furnace is measured in the presence of a gas (generally termed the carrier gas) flowing over it at a constant rate. The flow rate of the carrier gas is chosen so that the thermodynamic equilibrium between the vapour and the vaporizing material is virtually undisturbed. This is established experimentally (see measurement of vapour pressure of $CdCl_2$). The vapour pressure p of the material under investigation is then calculated from the relation

$$p = n_v RT/V_c = (W_v/M_v)RT/V_c \tag{1}$$

where n_v is the number of moles of the vapour transported by V_c litres of the carrier gas swept over the sample, T is the ambient temperature at which the volume of the carrier gas swept over the sample is collected, W_v is the mass loss of the sample, M_v is the molecular weight of the vapour species and R is the gas constant.

Equation (1) is based on the following assumptions.

(a) The vapour behaves ideally.

(b) The thermodynamic equilibrium between the vapour and the vapourizing material is undisturbed by the flow of the carrier gas.

(c) All the vapour is transported by the carrier gas alone.

Transpiration experiments are generally performed at a total pressure of one atmosphere, for which the ideal gas equation can be assumed to be valid. Experiments are also designed to meet closely the criteria in assumptions (b) and (c) by choosing appropriate flow rates of the carrier gas swept over the sample. The range of flow rates is such that the relative contribution to the mass loss of the sample due to other processes such as diffusion is insignificant compared to the mass loss caused by the vapour
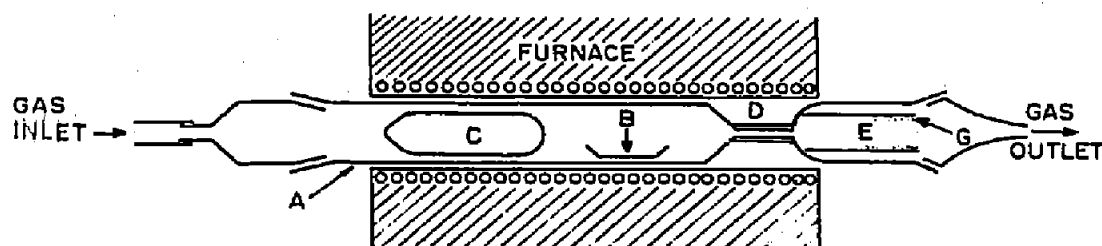
Fig. 1. Schematic of transpiration apparatus: A, ceramic tube; B, sample boat; C, ceramic block; D, capillary; E, detachable condenser tube; G, condensed vapour.

transported by the carrier gas. Moreover, it is ensured that the flow rates chosen are not too fast to disturb the thermodynamic equilibrium between the sample and the vapour. That these conditions are met in the experiment is deduced from the plateau in the plot of the apparent pressure versus the flow rate of the carrier gas (see measurement of vapour pressure of $CdCl_2$).

TRANSPIRATION APPARATUS

The conventional transpiration apparatus (Fig. 1) consists essentially of the ceramic tube A heated by a resistance wound furnace. The sample under investigation is kept in the uniform temperature zone. The sample boat B is located between the ceramic block C and the capillary D. The carrier gas preheated by contact with the ceramic block sweeps the vapour through the capillary and the vapour condenses in the temperature gradient region downstream. A detachable condenser tube E is generally placed immediately after the capillary so that the vapour leaving the capillary condenses in this tube at G. The ceramic block improves the temperature uniformity in the reaction zone.

EXPERIMENTAL PROCEDURE

The transpiration experiment consists of the following two parts.
(1) Determination of the plateau in the plot of the apparent pressure versus the flow rate of the carrier gas at the suitable temperature (preferably the mean) in the range of measurements and;
(2) Determination of equilibrium vapour pressures at various temperatures from which the mean enthalpy of vaporization is derived.

The experimental quantities measured to obtain the above information are as follows.
(a) The mass loss W_v of the sample due to the vapour transported away from it by the carrier gas;
(b) the rate of flow of the carrier gas over the sample and the total time for which it is passed, from which the total volume of the gas swept over the sample V_c is calculated;
(c) the temperature at which the experiment is performed;

(d) the ambient temperature T at which the volume of the carrier gas is measured.

The accuracy of the results obtained depends on the accuracy with which these quantities are measured.

Measurement of mass loss

The mass loss of the sample contained in the boat ranges from a few milligrams to hundreds of micrograms and is monitored by any one of:

(1) weighing the sample with the boat before and after the experiment [7];

(2) in the experiments in which the saturated vapour is carried into the condenser and deposited (see Transpiration apparatus), weighing the condenser before and after the experiment to give the mass of the vapour transported into it during the experiment and hence the mass loss of the sample;

(3) analysing the vapour deposited in the condenser chemically, employing sensitive analytical techniques [8].

Of the above three methods the chemical analysis of the condensate in the condenser provides the most accurate information, but is quite time-consuming. In the first of these methods there is an inevitable error due to vaporization of the sample during attainment of the temperature of the experiment, which can be minimized only by increasing the total time of the experiment. Moreover, the total weight of the sample with the boat is too large compared to the mass loss of the sample involved in the experiment. The determination of the mass loss from the vapour deposited in the condenser by weighing it before and after the experiment also gives results of poor accuracy because of the relatively small increase in the weight of the collector compared to its total weight. Further, there can also be considerable weighing error caused by the sample's characteristics (e.g. it may be hygroscopic) if adequate care is not exercised during cooling of the sample.

The experiment in the conventional transpiration method suffers from the inherent mass errors described above. It is also very cumbersome and must be stopped to obtain the mass loss data at each temperature and flow rate.

Measurement of the flow rate and the total volume of the carrier gas swept over the sample

The measurement of the volume of the gas swept over the sample is relatively simple and involves much less error. The flow rate and hence the total volume of the carrier gas swept over the sample is regulated and monitored using a flowmeter calibrated by the soap film technique

described elsewhere [9]. The flow rate at the exit of the system was measured by a rotameter calibrated against the capillary flow meter.

Measurement of temperature

The accurate measurement of temperature is done by using thermocouples calibrated at the melting points of pure metals as recommended in ref. 10. The details of calibration are described in ref. 11. The Pt–Pt13%Rh thermocouple was used in the present system.

SPECIAL FEATURES OF THE PRESENT APPARATUS

The novelty of the present apparatus lies in the automatic recording of the temperature and the mass change in the sample under investigation. The other features, however, are identical to those found in most of the transpiration systems used by other investigators [12]. The advantages of automatic recording of the mass loss are discussed at the end of this paper.

Details of design and construction

In the present system (Fig. 2) the sample A under investigation (spread uniformly) is contained in a tiered sample holder B comprising three pans 10 mm in diameter and 2 mm deep. The pans are made of platinum foil and stacked one above the other, leaving a gap of about 1 mm between each pan. The three tiered sample holder is suspended on one arm of an electronic recording type microbalance C (Sartorius model 4411) with the help of a 0.2 mm diameter hangdown wire D made of platinum–platinum/13% rhodium alloys. The other arm of the balance carries a silica pan E for taring the weight of the sample and the container located in the furnace. The 0.2 mm diameter hangdown wire carrying the tiered sample pan passes through a 4 mm internal diameter (ID) silica tube F. F serves two purposes: supporting the thermocouple G with the tip located near the sample pan; carrying the gas entering from the rear port H in the balance housing to the sample site after getting preheated to the temperature of the sample on passing through the temperature gradient along its path. The centre tube F also facilitates location of the baffles I in a position which helps to improve the temperature uniformity in the sample region and also to minimize the diffusion contribution to the total mass loss of the sample. Of the three baffles located in the uniform temperature region of the reaction tube, the first is made of Pt–20%Rh alloy and the other two of
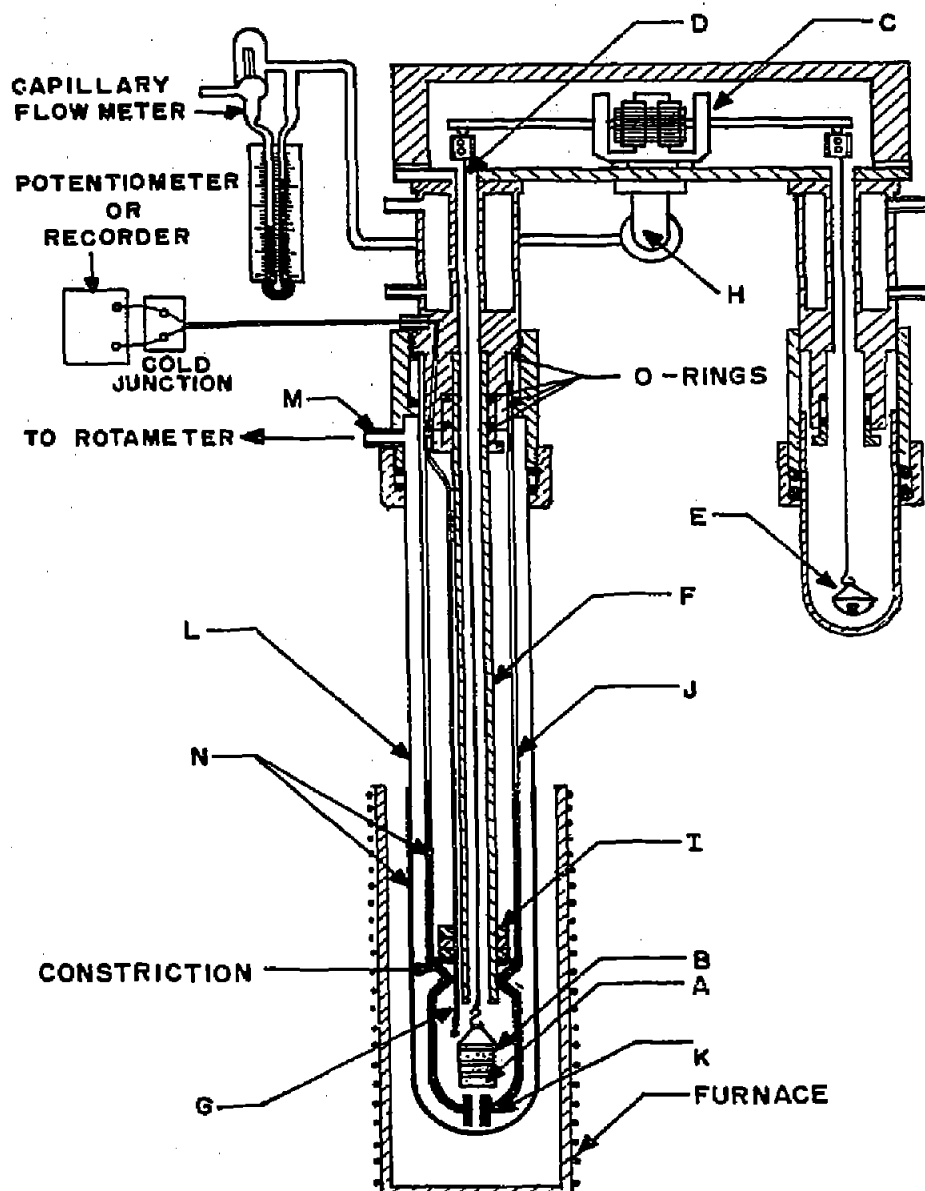
Fig. 2. Diagram of the transpiration apparatus incorporating the microthermogravimetric system: A, sample; B, tiered sample holder; C, electronic recording-type microbalance; D, hangdown wire (0.2 mm in diameter); E, silica pan for weight taring; F, 4 mm internal diameter (ID) silica tube; G, thermocouple; H, rear port in the balance housing; I, baffles made of (i) Pt–20%Rh plate and (ii) alumina discs; J, 14 mm ID silica tube; K, capillary (1.5 mm diameter hole); L, 28 mm ID silica tube; M, 8 mm diameter hole; N, layers of platinum coating.

recrystallized alumina. These baffles have a 3 mm diameter side hole, which guides the thermocouple sleeve and facilitates the location of the thermocouple near the sample.

The sample pan is surrounded by the 14 mm ID silica tube J. This tube is constricted about 2.5 cm from its closed end. The constriction acts as a support to the baffles, which can slide freely over the central 4 mm ID silica

tube and the thermocouple sleeve fixed on its side. The baffles sitting on the constricted part improve the uniform temperature in the sample region and also minimize the diffusion of the vapour in the upward direction because these virtually isolate the sample region from the rest of the reaction tube. The closed end of the 14 mm diameter silica tube is provided with a 1.5 mm diameter hole K. The carrier gas entering the reaction chamber through the 4 mm ID central tube sweeps the vapour out through this hole, which then condenses on the inner and outer surfaces respectively of the 28 and 14 mm ID silica tubes in the annular space, in the temperature gradient.

The 28 mm ID tube L surrounding the 14 mm ID tube is closed at one end and provided with an 8 mm diameter hole M about 15 mm from its open end. The two tubes are fixed to the balance housing through appropriate metal collars and O-ring fittings. The carrier gas transporting the vapour through the 1.5 mm diameter hole located at the closed end of the 14 mm diameter silica tube comes out through the 8 mm diameter side hole M in the 28 mm ID tube and passes through the rotameter connected at the outlet. The outer surfaces of both the 14 and 28 mm ID tubes are coated with a platinum layer near their closed ends. The metallic layer on the 28 mm ID tube is earthed to avoid accumulation of static charge caused by the gases rubbing on the silica surfaces.

MEASUREMENT OF VAPOUR PRESSURE OF $CdCl_2$

To check the performance of the present system the vapour pressure of anhydrous cadmium chloride ⟨$CdCl_2$⟩ was measured in the temperature range 713–833 K in flowing pure argon gas dried by passing over anhydrous magnesium perchlorate. $CdCl_2$ is known to vaporize congruently, giving predominantly a single molecular species $CdCl_2(g)$ in the vapour phase [4, 5].

In the present experiments anhydrous $CdCl_2$ (AnalaR grade) (obtained by dehydration of the hydrate and stored in a magnesium perchlorate dessicator before use) was heated to the desired temperature in flowing dry argon. The temperature was maintained constant to ±1 K with the help of a proportional-type temperature programmer (Indotherm Model MPC-500). At zero time after the thermal equilibrium was established the total mass loss indicated on the LED monitor of the control unit of the electronic balance was tared and the continuous monitoring of the mass loss was started as a function of time. A typical mass loss record for $CdCl_2$ at 762 K is shown in Fig. 3. The isothermal rate of mass loss was found to be independent of time at each temperature; this is typical of the vaporization process.

Figure 4 shows a plot of the apparent pressure of $CdCl_2$ as a function of flow rate at 773 K. The vapour pressures were calculated from eqn. (1). The various quantities measured and the final values of the computed pressures are listed in Tables 1 and 2. It can be seen from Fig. 4 that the apparent
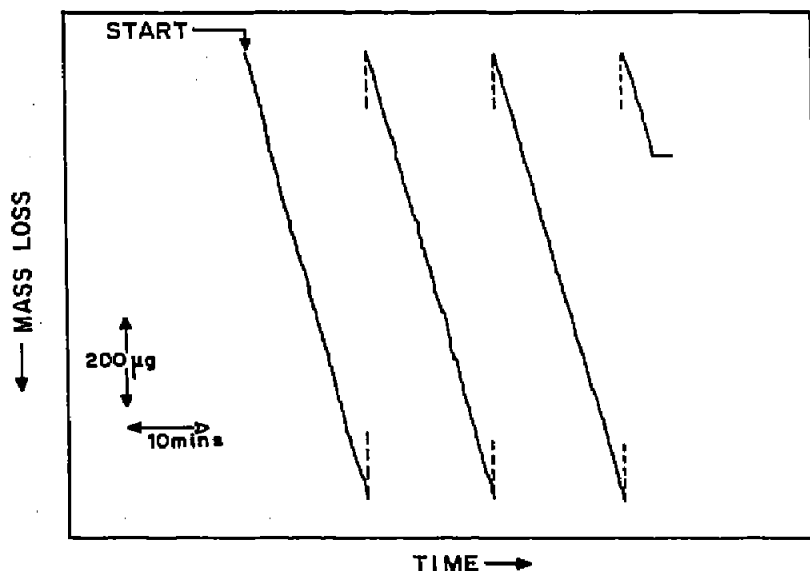
Fig. 3. A typical mass loss vs. time trace recorded at 762 K (flow rate 2490 ml hr^{-1}).

vapour pressure of $CdCl_2$ is virtually independent of the flow rate in the region 1700–2600 ml hr^{-1}, implying that the equilibrium between the vapour and the solid is maintained in this flow rate region [3]. The experiments at other temperatures were performed at the flow rates of 2100 ml/hr^{-1}. Figure 5 shows a plot of $\ln(P/\text{Pa})$ vs. $1/T$ for the vaporization of $CdCl_2$. The vapour pressure of $CdCl_2$ as a function of temperature could be expressed in this range by the equation

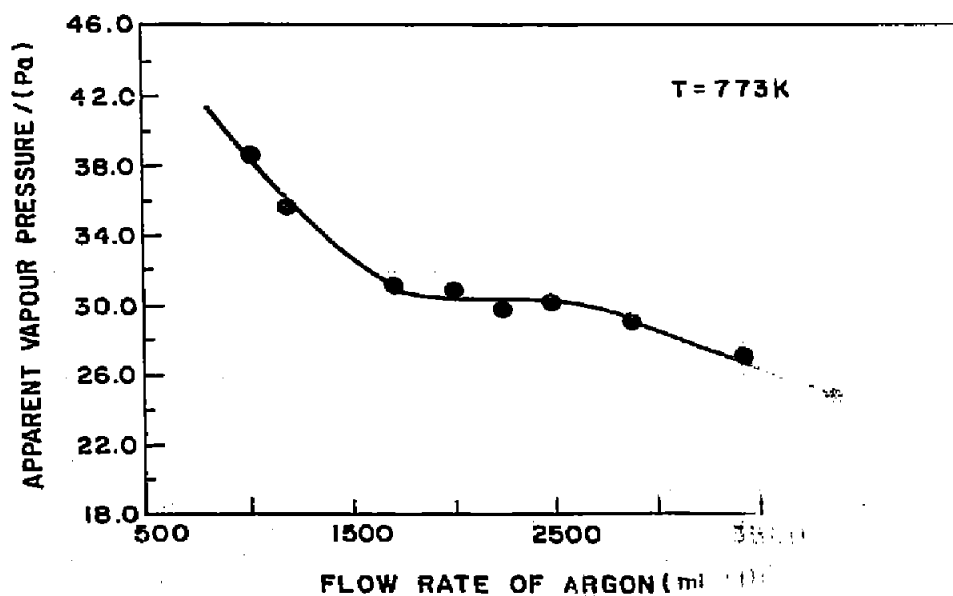$$\ln(P/\text{Pa}) = \frac{-(20\,109.10 \pm 262.32)}{T} + (29.46 \pm 0.344)$$

Fig. 4. A plot of apparent pressure vs. ⁖

TABLE 1

Apparent pressure of $CdCl_2(g)$ as a function of flow rate of argon at 773 K

Flow rate of argon (ml hr^{-1})	Volume of argon gas swept (ml)	Mass loss of $CdCl_2$ per litre of argon (mg l^{-1})	Apparent pressure (Pa)
1040	1080	2.87	38.5
1310	1420	2.66	35.7
1720	2220	2.31	31.0
2010	2010	2.30	30.9
2280	2590	2.22	29.8
2520	3180	2.25	30.2
2890	4180	2.15	28.8
3430	4890	1.98	26.6
3890	6320	1.83	24.6
4080	6950	1.78	23.8

The enthalpy of sublimation of $CdCl_2$ derived from this plot at the mean temperature of measurements is 167.2 ± 2.2 kJ mol^{-1}. This is in excellent agreement with the value of 166.5 ± 4.7 kJ mol^{-1} obtained by Skudlarski et al. [5] in their recent Knudsen effusion mass spectrometric measurements in the temperature interval about 100°C below that in the present study. The third law value of the enthalpy of sublimation $\Delta H^\circ_{298(sub)}$ obtained in the present work from the vapour pressures measured at different temperatures

TABLE 2

The enthalpy of sublimation of $CdCl_2$ from vapour pressure data

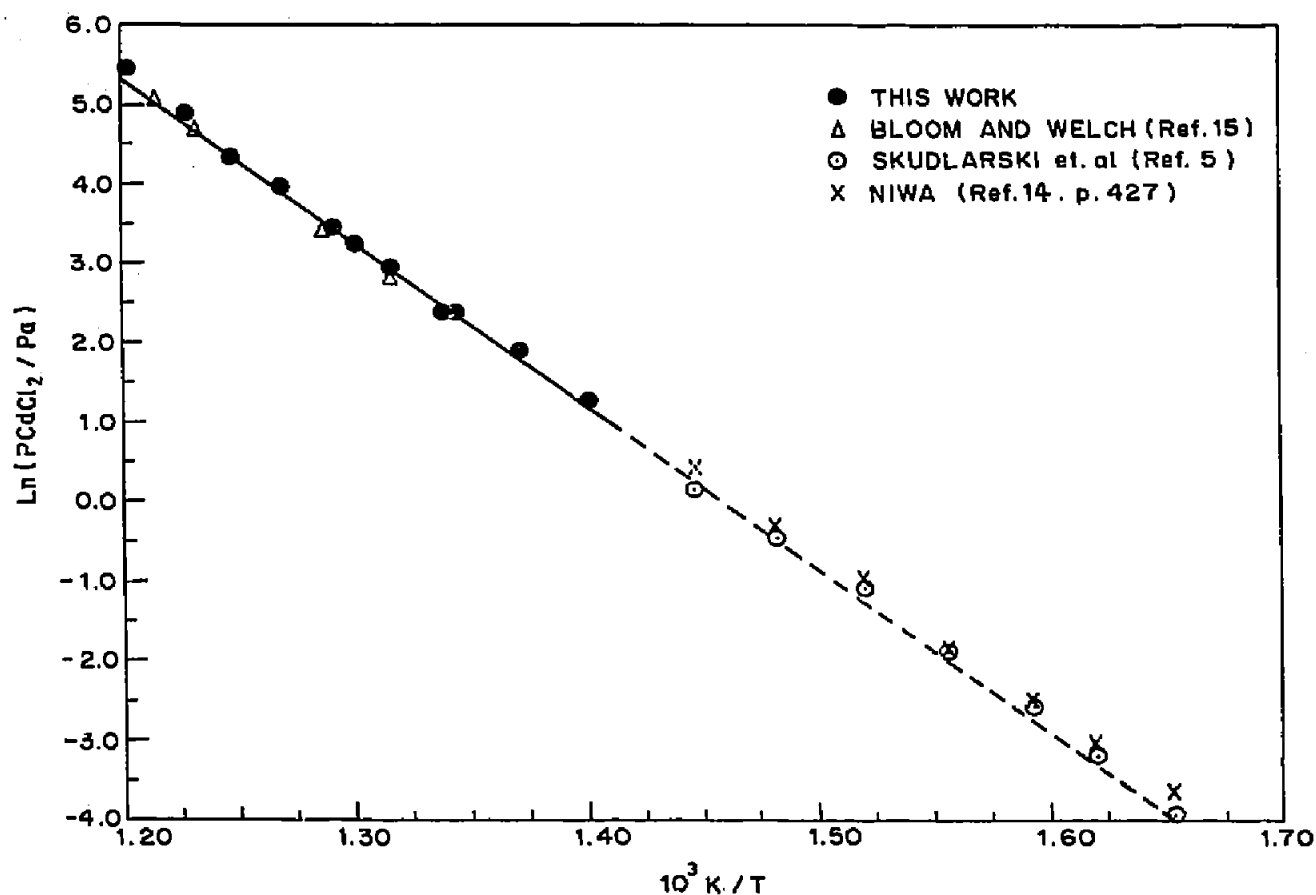| Temperature (K)	Mass transfer per litre of carrier gas (mg l^{-1})	Pressure (Pa)	$\Delta H^\circ_{298(sub)}$ (kJ mol^{-1}) (third law)
713	0.27	3.6	176.8
729	0.49	6.6	176.8
744	0.86	11.5	176.6
745	0.86	11.5	176.9
760	1.40	18.8	177.0
768	1.88	25.2	176.8
773	2.31	31.0	176.5
788	3.76	50.4	175.4
801	5.91	79.3	176.0
816	9.65	129.5	175.5
833	17.96	241.0	174.6

Average 176.4 ± 0.7

Fig. 5. A plot of ln(P/Pa) vs. $1/T$ for $CdCl_2$.

TABLE 3

The enthalpy of sublimation of $CdCl_2$ from various investigators

Method of measurement	$\Delta H^{\ominus}_{298(sub)}$ (kJ mol^{-1})		Ref.
	Second law	Third law	
Knudsen effusion	187.9 ± 14.5	177.8 ± 0.4	5
Transpiration	219.1 ± 1.6	167.5 ± 8.2	13
Knudsen effusion	191.0 ± 1.7	182.3 ± 0.8	14
Transpiration	193.1 ± 16.5	177.1 ± 1.3	15
Transpiration	130.0 ± 6.2	189.6 ± 1.9	16
Transpiration	188.6 ± 2.2	176.4 ± 0.7	This work

and employing the free energy functions used in ref. 5 was found to be 176.4 ± 0.7 kJ mol^{-1}. Similarly, the second law value for the enthalpy of sublimation of $CdCl_2$ derived from the enthalpy increment data used in ref. 5 was 188.6 ± 2.2 kJ mol^{-1}. These values are in good agreement with those compiled by Skudlarski et al. [5] from the work of various investigators (Table 3).

DISCUSSION

There have been several measurements of the vapour pressures of $CdCl_2$ employing both transpiration and Knudsen effusion techniques. The results obtained by various investigators have recently been summarized in ref. 5. The excellent agreement between our value of the enthalpy of sublimation of $CdCl_2$ (167.2 ± 2.2 kJ mol^{-1}) and the value of Skudlarski et al. [5] at the mean temperature of the two studies by independent techniques establishes the accuracy of our measurements.

The results obtained by other investigators employing transpiration [15] and Knudsen effusion techniques [5, 14] are incorporated in Fig. 5 along with our results for comparison. It can be seen that the enthalpy of sublimation obtained in the transpiration experiments is higher in some cases than that derived from Knudsen effusion measurements. This could perhaps be due to the different temperature intervals over which these measurements were made. Most of the transpiration measurements were made up to the melting point of $CdCl_2$. The vapour pressures of cadmium-bearing species near the melting point of $CdCl_2$ are well beyond the Knudsen effusion range and, furthermore, the contribution of the dimer to the total pressure is also significant. Both these factors would result in an increased slope of the plot of $\ln(P/Pa)$ vs. $1/T$ and hence the derived enthalpy of vaporization.

Although Skudlarski et al. [5] in their measurements have reported that the vapour of $CdCl_2$ consists predominantly of the monomer in their range of temperature measurement, Moss [16] has observed about 15% dimer contribution in the vapour above solid $CdCl_2$ near its melting point. In our present transpiration data there is significant difference in the mean enthalpy of vaporization derived from the $\ln(P/Pa)$ vs. $1/T$ plot if the value of the pressure derived at the highest temperature of the present measurement (833 K) is included in the linear least squares analysis of the data. The mean value for the enthalpy of sublimation under this condition works out to be 170.9 ± 3.1 kJ mol^{-1}. The dimer contribution to the total pressure at this temperature is known to be more than 10% [13, 16], so the point at 833 K was ignored in the analysis of the present data.

CONCLUSION

It is seen from the present work that the automatic recording transpiration system designed and fabricated in our laboratory yields most reliable data of a high degree of accuracy in the shortest possible time. This is the first time that the microthermobalance has been adopted in on-line monitoring of the mass loss in a conventional transpiration experiment. The design of the system is simple and with little alteration the unit can be used for normal thermogravimetric investigations. The reliability of the results

obtained with this instrument has recently been demonstrated in our studies on the vaporization of molybdenum trioxide [17]. Several investigations on the thermodynamics of transition metal molybdates are currently in progress using this system.

The temperature range of measurement in the present apparatus can be increased substantially by replacing the silica tubes by those of recrystal-d alumina. This is currently being attempted.

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