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Vapour pressure and standard enthalpy of sublimation of KBF_4 by a TG based transpiration technique

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Abstract

A horizontal thermobalance was adapted as a transpiration apparatus for the measurement of the vapour pressure of KBF_4 (s). Attainment of equilibrium was ascertained by the invariance of the measured values of the vapour pressures over a range of flows under isothermal conditions. Measured values of the vapour pressures could be represented by the least-squares expressions: $\log(p/\mathrm{Pa}) = 8.16(\pm 0.01) - 4892(\pm 248)/T(\mathrm{K})$ (538–560 K), $\log(p/\mathrm{Pa}) = 6.85(\pm 0.06) - 4158(\pm 240)/T(\mathrm{K})$ (576–660 K), which correspond to the equilibria of orthorhombic and cubic KBF_4 vapours, respectively. From these expressions the temperature of transformation of the orthorhombic to the cubic phase was identified to be 561 K. From the slopes of the above equations, the enthalpies of sublimation of the orthorhombic and cubic phases were found to be (93.7 ± 4.7) and (79.6 ± 4.6) $\mathrm{kJ\,mol^{-1}}$, respectively. These values differ by 14.1 $\mathrm{kJ\,mol^{-1}}$ which could be ascribed to the enthalpy of the orthorhombic to cubic phase transition of KBF_4. Third-law analysis of the vapour pressure data yielded a value of (104.6 ± 1.0) $\mathrm{kJ\,mol^{-1}}$ for $\Delta H^{\circ}_{\mathrm{sub}}$ of KBF_4 (s) at 298.15 K.

1. Introduction

Boron carbide containing boron enriched in ^{10}B isotope is used as a neutron absorber in fast reactors due to its desirable neutron absorption characteristics [1]. One of the important methods for the production of high purity boron carbide is the direct reaction between elemental boron and graphite at high temperature [2]. Elemental boron can be obtained by electrolysis of KBF_4 in a fused salt medium. In this process, KBF_4 dissolved in a molten mixture of potassium chloride and potassium fluoride is electrolysed at 1073 K. Boron is electrodeposited at the cathode and chlorine is liberated at the anode. The chlorine gas is removed continuously by flowing high purity argon gas. It is instructive to know if the potassium fluoroborate would be lost due to vapourization during electro-winning. Experimental data on the vapour pressure of potassium fluoroborate would be useful for predicting and preventing the loss of the precious enriched boron during this process. However, no systematic study has so far been reported on the temperature dependent vapourization behaviour of KBF_4 in the literature. Therefore, the vapour pressure of this compound was measured in the temperature range 538–660 K in this study using the transpiration technique.

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2. Experimental

2.1. Materials

Reagent grade KBF_4 of purity better than 99.9% (supplied by M/s Ranbaxy, Mumbai, India) was used for the transpiration experiments. The purity of the compound was established by X-ray powder diffraction and chemical characterization.

2.2. Transpiration apparatus

A horizontal thermal analysis system (Model–Seiko 320, Japan) was adapted as a transpiration apparatus for carrying out the vapour pressure measurements. The horizontal design of the thermal analysis system minimizes errors arising in weight measurement due to convection while the location of the sample and reference pan in the same uniform temperature zone of the furnace eliminates errors arising from buoyancy and thermal expansion of the beam. A Pt–13%Rh/Pt thermocouple, which formed an arm of the balance was used for measuring the temperature of the sample as well as the temperature differential. High purity helium was used as the carrier gas. To facilitate the saturation of the carrier gas with the vapourizing species, the sample was spread over the entire area on a flat platinum crucible. The flow rates were monitored by a capillary type glass flow meter. This capillary flow meter was in turn calibrated by a soap bubble displacement method [3]. A wet test meter (M/s Toshniwal, India) was used for total volume measurement at the outlet and was in turn calibrated with a capillary flow meter. The precision in the values of the flow rate measured by the capillary flow meter was ±0.5%, which resulted in an overall precision in the integral volume flow of ±1% of the total volume of the carrier gas. The reliability of this experimental technique was established by carrying out similar measurements on materials such as CsI and C_{60}, which are well characterized with respect to their vapour pressure [4]. The block diagram of the thermal analyzer, details of modifications made in it to suit the transpiration experiments and the details of the corrections made for apparent loss of weight during isothermal experiments are described elsewhere [4–6].

2.3. Differential scanning calorimetry (DSC)

A heat flux type differential scanning calorimeter (model DSC 821 e/700, M/s Mettler Toledo GmbH, Switzerland) was used for the measurement of the transition enthalpy of KBF_4. All these experiments were carried out at a heating rate of $0.17\,K\,s^{-1}$ and with a flow of $50\,ml\,min^{-1}$ of high purity argon. This equipment was calibrated using the melting temperatures of In, Pb, Zn and Sb. These calibration experiments revealed that the measured values of the temperature conform to the scale prescribed by ITS-90 [7] within ±1 K. The values of the enthalpies of these transitions were in agreement (within ±1 kJ) with those cited in the literature [8].

3. Results and discussion

3.1. Non-isothermal TG

A non-isothermal TG experiment was carried out with solid KBF_4 at a linear heating rate of $0.17\,K\,s^{-1}$ using the simultaneous TG/DTA thermal analyzer, the results of which are given in Fig. 1. The purpose of this experiment was to identify the weight loss steps besides identifying the transition temperature and decomposition/melting temperature of KBF_4. Fig. 1 reveals that about 10% (cumulative) weight loss due to vapourization occurs in a single step up to 873 K. The initial weight of the sample is in the range of 50–55 mg and the accuracy of the weight measurement is ±1 μg. The DTA recorded simultaneously revealed that the phase transition temperature of KBF_4 from orthorhombic to cubic occurs at 560 K which is in very good agreement with the values reported in the literature [9–11] as well as with those obtained using DSC (Fig. 2) and transpiration technique, in the present study.

3.2. Vapour pressure measurements

If W is the mass loss of the sample at temperature T, due to evaporation and if this is transported by a carrier gas of volume V_c (dm^3), then the apparent vapour pressure, p^{app}, can be calculated using Eq. (1), which is derived using Dalton's law of partial pressure for a mixture of ideal gases.

$$p^{app} = WRT/MV_c, \quad (1)$$

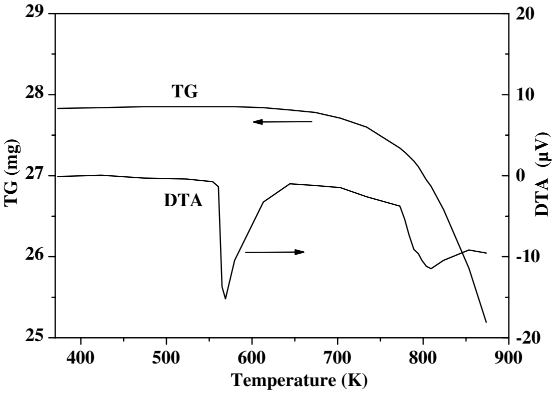

Fig. 1. TG and DTA curves of KBF_4.

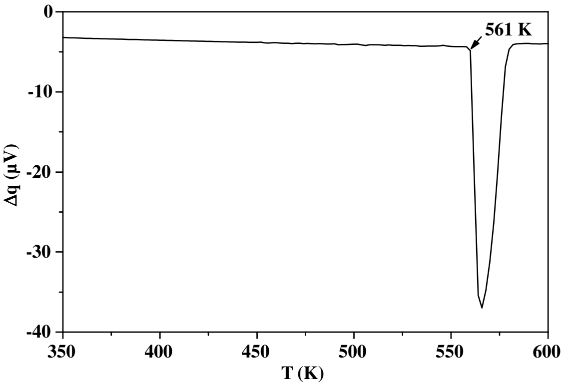

Fig. 2. DSC trace corresponding to the phase transition in KBF_4.

where M is the molecular weight of the sample and R is the universal gas constant. When Eq. (1) is used, it is implied that only one species is present in the vapour phase. It is evident from the literature [9,10] that the vapour phase, in equilibrium with solid KBF_4, contains only the monomeric KBF_4.

Attainment of equilibrium conditions was ascertained by a chair-shaped curve, which is characteristic of isothermal equilibrium vapourization in a transpiration experiment. Such a plot at 623 K is shown in Fig. 3. It is seen from this plot that the carrier gas is saturated with the vapour in the flow rate region ranging between 11 and 15 dm^3/h. Hence, in the present study, the vapour pressure measurements were carried out at a flow rate of 11–15 dm^3/h over the temperature range 560–660 K.

The non-isothermal TG/DTA and DSC studies carried out in this study indicated that the solid compound KBF_4 exhibits a polymorphic transformation at around 560 K before melting. Hence, the vapour pressure measurements were made below and above this phase transition temperature, viz., 538–660 K. The mass loss, T and p^{app} calculated using the expression (1) for the weight losses observed on KBF_4 are listed in Table 1. The temperature dependence of p could be represented by the following least squares expressions for the temperature ranges below and above 560 K, the phase transition temperature of KBF_4.

$$\log(p/\mathrm{Pa}) = 8.16(\pm 0.01)–4892(\pm 248)/T(\mathrm{K})\ (538–560\ \mathrm{K}), \quad (2)$$

$$\log(p/\mathrm{Pa}) = 6.85(\pm 0.06)–4158(\pm 240)/T(\mathrm{K})\ (576–660\ \mathrm{K}). \quad (3)$$

A plot of $\log p$ versus $1/T$ is shown in Fig. 4. By solving Eqs. (2) and (3) a value of 561 K was obtained for the temperature of transformation of the orthorhombic phase of KBF_4 to its cubic modification. This value is in excellent agreement with the values of 560 K and 561 K obtained by DTA and DSC, respectively, from the present study as well as with the value of 556 K reported in Refs. [9–11]. The slopes obtained from the linear regression analysis of the temperature dependence of the vapour pressure data are (93.7 ± 4.7) and (79.6 ± 4.6) kJ mol^{-1} for the orthorhombic and cubic phases, respectively. These values correspond to the standard enthalpy of sublimation of these phases at the mean temperature of these measurements. The difference in the

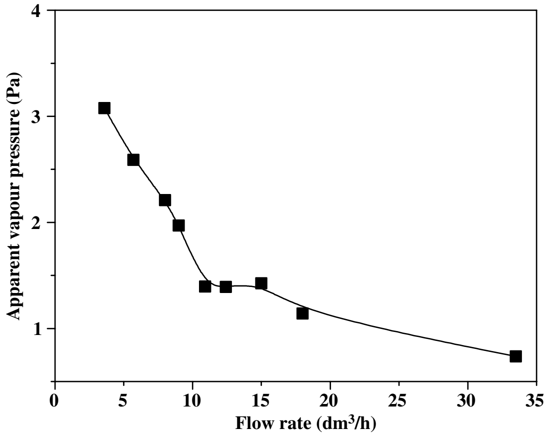

Fig. 3. Apparent vapour pressure versus flow rate of KBF_4 at 623 K.

Table 1
Vapour pressure of KBF_4 by the TG transpiration technique

Experiment number	T (K)	Mass loss (μg) (cumulative)	V_C (dm^3)	Pressure (MPa)
1	538.2	20	5.71	124.5
2	543.7	31	8.0	140.1
3	544.2	32	8.0	143.8
4	552.7	60	10.909	200.8
5	560.2	80	10.909	271.3
6	575.8	120	10.909	418.3
7	591.7	200	10.909	716.4
8	591.7	153	10.909	548.1
9	601.4	300	12.414	1092.2
10	601.6	340	12.414	1088.2
11	609.8	320	12.414	1038.1
12	612.6	280	10.909	1038.6
13	617.8	350	12.414	1150.3
14	622.7	420	12.414	1391.4
15	622.7	370	10.909	1394.8
16	622.7	470	15.0	1425.7
17	622.7	520	15.0	1288.6
18	633.2	570	10.909	2185.0
19	643.4	640	10.909	2493.3
20	653.8	840	10.909	3324.8
21	659.5	870	10.909	3473.6

Initial weight of the sample: 50 mg.

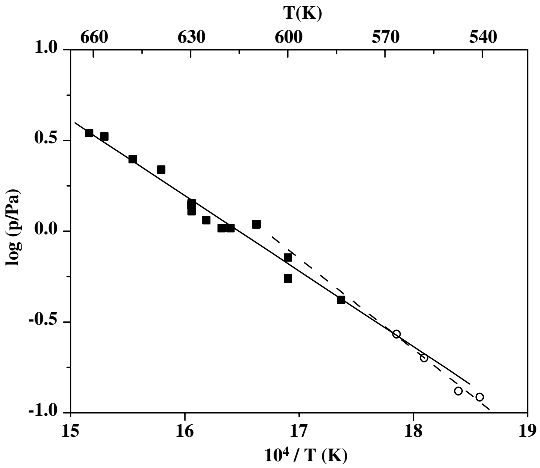

Fig. 4. Temperature dependence of equilibrium vapour pressure of KBF_4.

enthalpies of sublimation of these two phases is 14.1 kJ mol^{-1}. This difference is equal in magnitude to the enthalpy of phase transitions and is in excellent agreement with the value recommended by Knacke et al. [9], by Dworkin and Bredig [11] and that of 14.5 kJ mol^{-1} obtained using DSC measurements as well as with the value of 16.8 kJ mol^{-1} cited in Ref. [10]. The values of the phase transition temperature and enthalpy of transition are compared in Table 2.

3.3. ΔH^o_{sub} of KBF_4 at 298 K by the third-law method

In order to assess the temperature dependent errors in the vapour pressure measurements, a third-law analysis of the vapour pressure data was carried out. The differential Gibbs energy function (Δfef) for the vapourization reaction was calculated using the Gibbs energy functions of each participating member of this reaction, in the temperature range 400–700 K. These values were obtained from Ref. [10]. The enthalpy of sublimation at 298 K was then derived using Eq. (4).

$$\Delta H^{\circ}_{sub}(KBF_4) = \Delta G^{\circ}_{vap} - T \cdot \Delta \mathrm{fef}. \quad (4)$$

For the vapourization process, values of ΔH°_{sub} of KBF_4 (s) were calculated for the experimental data given in Table 1. A plot of ΔH°_{sub} of KBF_4 (s) against experimental temperatures is shown in Fig. 5. The mean value of ΔH°_{sub} at 298 K was found to be (104.6 ± 1.0) kJ mol^{-1}. The random scatter values of ΔH°_{sub} at 298 K around the mean value indicate the absence of any significant temperature dependent errors in the vapour pressure measurements.

Table 2
Comparison of ΔH°_{trans} and T_{trans} of KBF_4

ΔH°_{trans} (kJ mol^{-1})	T_{trans} (K)	Reference
14.1	556	[9,11]
16.8	556	[10]
14.1	561	This work – TG transpiration
14.5	561	This work – DSC
–	560	This work – DTA

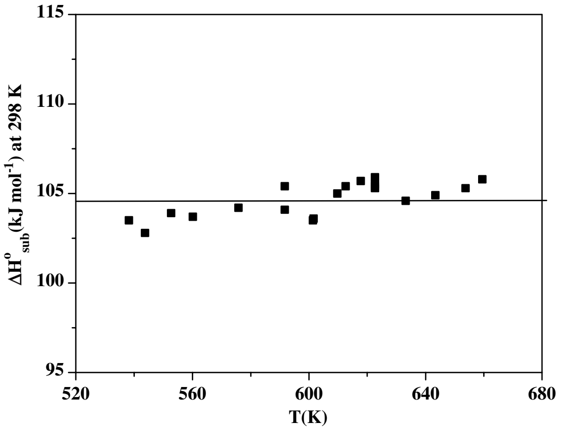

Fig. 5. Temperature dependence of ΔH°_{sub} at 298 K obtained from the third law analysis of the vapour pressure data.

4. Conclusion

A horizontal dual arm single furnace thermal analysis system was adapted as a transpiration apparatus for reliable vapour pressure measurements. The equilibrium nature of volatilization was established by a plateau in the plot of apparent isothermal vapour pressure against flow rate of the carrier gas. The plot of log p against $1/T$ exhibited a break at 561 K for the phase transition of KBF_4, which is in excellent agreement with the values of 560 K and 561 K obtained by DTA and DSC techniques, respectively, as well as with the literature value of 556 K. The standard enthalpies of sublimation were derived to be (93.7 ± 4.7) and (79.6 ± 4.6) kJ mol^{-1} for the orthorhombic and cubic phases of KBF_4, respectively, at the mean temperature of the measurements, which in turn led to a value of 14.1 kJ mol^{-1} for the standard enthalpy of transition. Third-law analysis of the experimental data yielded a value of (104.6 ± 1.0) kJ mol^{-1} for the standard enthalpy of sublimation of KBF_4 at 298 K.

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