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THE SUBLIMATION OF SOME METAL FLUORIDE COMPLEXES AT ELEVATED PRESSURES *

N. SATO and A. KIGOSHI

Research Institute of Mineral Dressing and Metallurgy, Tohoku University, Sendai 980 (Japan)

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ABSTRACT

The sublimation of $NONbF_6$, $NOTaF_6$, $NOBF_4$, $NOGeF_5$, $NOPF_6$ and $NOSbF_6$ was measured by DSC at various pressures up to 50 atm. The relationship between temperature and equilibrium vapor pressure was obtained for each compound by the Clapeyron—Clausius plot. At the same time, the apparent molecular weights of the compounds could be estimated by using the enthalpies which were reported previously.

INTRODUCTION

The DSC measurements at 1 atm pressure [1—4] indicated that the majority of the NOF-acceptor fluoride adducts are stable salts which sublimate without decomposition on heating. The enthalpies and temperatures of these sublimation reactions were also estimated. The results obtained have been applied to the investigation of separating and refining the metallic components from their resources [5]. However, since more detailed kinetic constants, such as the relationship between temperature and equilibrium vapor pressure, are necessary for further study, more fundamental experiments on these are being carried out.

The relationship between temperature and equilibrium vapor pressure is given by the familiar Clapeyron—Clausius equation

$$\ln P = \frac{\Delta H_v}{RT} + C \tag{1}$$

where P is the vapor pressure at temperature T, ΔH_v is the enthalpy of the reaction, and C is a constant. A convenient way of determining this relationship is to measure the temperature shift of the sublimation endotherm by DSC at various pressures. From the results obtained the free energy change and the apparent molecular weight can also be estimated, i.e., from eqn. (1), the free energy is given by

$$\Delta G = -RT \ln P \tag{2}$$

* This paper is taken in part from the Dr. Eng. dissertation of N. Sato.

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because the sublimation reaction appears to involve only one gaseous component. The apparent molecular weight is introduced by comparing the ΔH_v which is given by eqn. (1) with the enthalpy obtained by the DSC measurement at 1 atm pressure [1—4].

The purpose of this paper is to report the sublimation reactions of certain metal fluoride complexes at pressures up to 50 atm using DSC tecchniques.

MATERIALS AND EXPERIMENTAL

The fluoride complexes, $NONbF_6$, $NOTaF_6$, $NOBF_4$, $NOGeF_5$, $NOPF_6$ and $NOSbF_6$, were prepared and analyzed as previously described [1—4].

The modified instrument used in this study consisted of a Rigaku Denki Standard DSC cell enclosed in a steel pressure chamber capable of operating at a maximum pressure of 150 atm. The operation was carried out by placing the sample and reference material on their respective platforms and sealing the pressure chamber. The pans used were hermetically sealed, provided with a pin-hole in the cover, and were made of aluminum or platinum. Argon gas was allowed to flow at 100 ml min^{-1} through the whole system at a predetermined pressure by adjusting the inlet and outlet valves. Once the system was stabilized, the heating cycle was started. The overall operation, including the determination of the sublimation temperature, was identical to that of the DSC measurement at 1 atm pressure [1].

In order to test the validity of the equipment, the relationship between log P and $1/T$ of H_2O was measured for values of P from 1 to 50 atm. Between 5 and 8 mg of H_2O were employed at a heating rate of 10°C min^{-1}. The data are plotted in Fig. 1. The remarkable straight line of the log P vs. $1/T$ plot yields the following equation

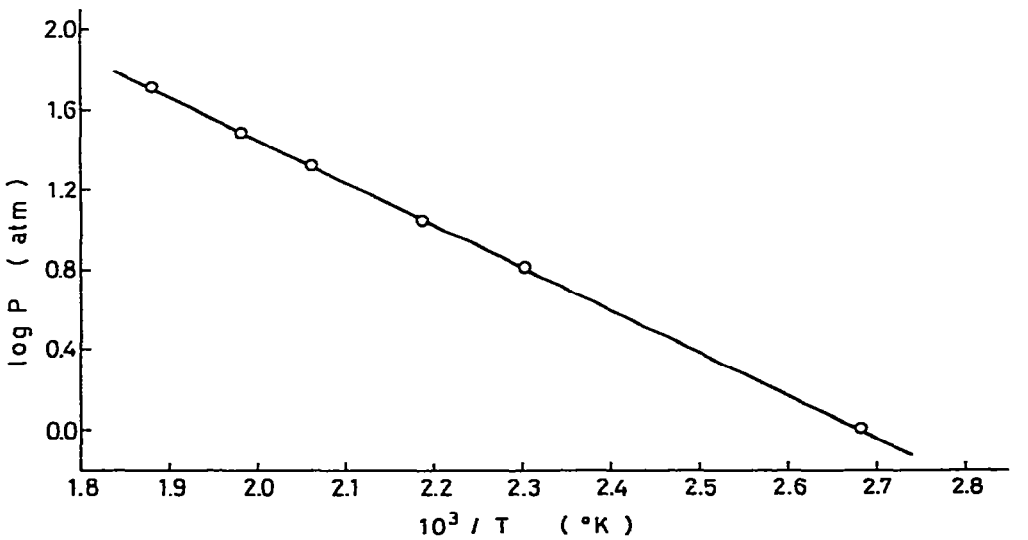

Fig. 1. Clapeyron—Clausius plot for H_2O.

$$\log P = -\frac{2141}{T} + 5.74 \quad (3)$$

From this and eqn. (1), ΔH_v is given as

$$\Delta H_v = 2.303R \times 2141 = \lambda v M$$

where M is the molecular weight of H_2O. This relationship provides a value of 544 cal g^{-1} for the latent heat of vaporization of water, λv, which is in good agreement with the accepted value of 539 cal g^{-1}.

RESULTS AND DISCUSSION

The DSC curves at elevated pressures indicated that the behavior of the fluoride complexes studied was intrinsically the same as that at 1 atm pressure. The transition endotherms which were observed for $NONbF_6$, $NOTaF_6$, $NOBF_4$ and $NOSbF_6$ at 1 atm pressure appeared at the same respective temperatures for all pressures studied, while the sublimation temperatures at elevated pressures were, as expected, markedly shifted depending upon pressure. The sublimation temperatures measured at 1 atm pressure [1—4] were readily available for all $\log P$ vs. $1/T$ plots in the present study.

Sublimation of $NONbF_6$

The relationship between $\log P$ and $1/T$ obtained from the DSC curves is shown in Fig. 2. The following equation is deduced from this linear relationship

$$\log P = -\frac{6970}{T} + 11.6 \quad (4)$$

and according to eqn. (2), the free energy is given by

$$\Delta G = 31\,870 - 53.0T \quad (5)$$

The value of enthalpy represented by the first term of eqn. (5) is 1.16 times as large as that of 27 400 cal/$NONbF_6$ reported previously [1]. This fact can be explained by a partial association (or dissociation) of the fluoride complex molecule on sublimation because the deviation greatly exceeded the limit of both experimental errors. Of the compounds studied, the degree of deviation detected was 0.48—7.45, as described later. In the case of $NONbF_6$, the apparent molecular weight considered corresponds to $(NONbF_6)_{1.16}$.

Sublimation of $NOTaF_5$

The results obtained are summarized in Fig. 3. From this linear relationship, the following equation is obtained

$$\log P = -\frac{15\,940}{T} + 24.7 \quad (6)$$

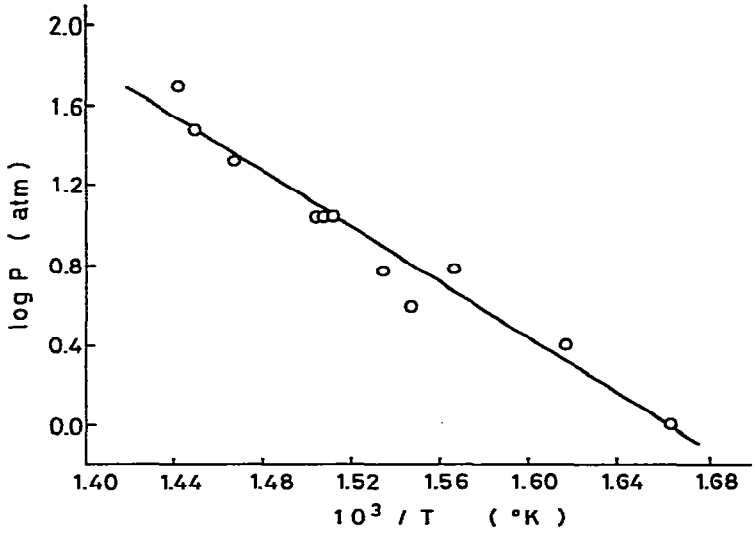

Fig. 2. Clapeyron—Clausius plot for $NONbF_6$.

therefore

$$\Delta G = 72\,900 - 113.0T \qquad (7)$$

As known from this equation, the value of enthalpy for the sublimation of $NOTaF_6$ is 4.14 times as large as that of 17 600 cal/$NOTaF_6$ reported previously [1]. Accordingly, the apparent molecular weight considered corresponds to $[NOTaF_6]_{4.14}$.

Sublimation of $NOBF_4$

The log P vs. $1/T$ plot for $NOBF_4$ consisted of two linear relationships as shown in Fig. 4. From the results, the following equations were obtained

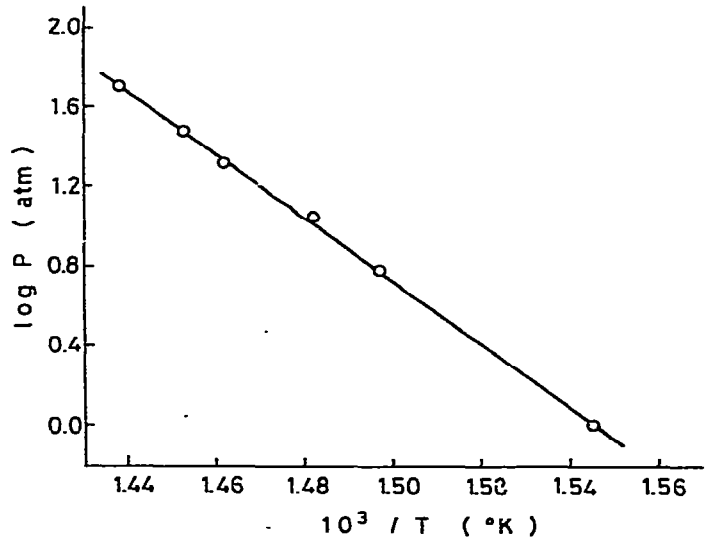

Fig. 3. Clapeyron—Clausius plot for $NOTaF_6$.

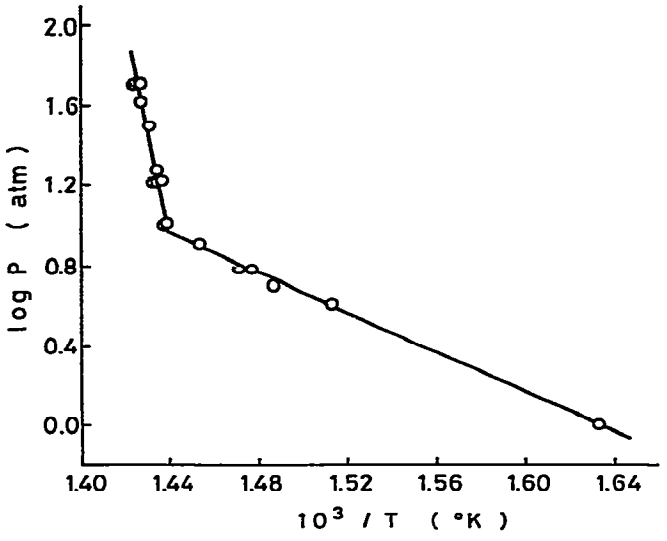

Fig. 4. Clapeyron—Clausius plot for $NOBF_4$.

lower than 422°C, 9.2 atm

$$\log P = -\frac{4960}{T} + 8.11 \quad (8)$$

$$\Delta G = 22\,700 - 37.1T \quad (9)$$

higher than the above conditions

$$\log P = -\frac{54\,200}{T} + 78.9 \quad (10)$$

$$\Delta G = 247\,700 - 360T \quad (11)$$

The apparent molecular weights calculated from eqns. (9) and (11) correspond to $(NOBF_4)_{0.68}$ and $(NOBF_4)_{7.45}$, respectively, because the enthalpy for 1 atm pressure is 33 270 cal/$NOBF_4$ [3].

Sublimation of $NOGeF_5$

The $\log P$ vs. $1/T$ plot for this compound is shown in Fig. 5. The following equations are deduced from this linear relationship

$$\log P = -\frac{3860}{T} + 8.42 \quad (12)$$

$$\Delta G = 17\,650 - 38.5T \quad (13)$$

Since the enthalpy for 1 atm pressure is 36 470 cal/$NOGeF_5$ [4], the apparent molecular weight considered corresponds to $(NOGeF_5)_{0.48}$.

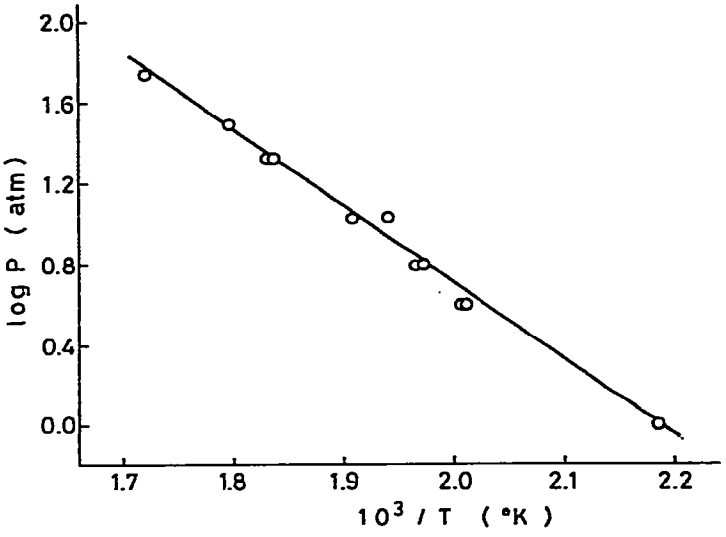

Fig. 5. Clapeyron—Clausius plot for $NOGeF_5$.

Sublimation of $NOPF_6$

As in the case of $NOGeF_5$, the results for $NOPF_6$ are summarized in Fig. 6 and the following equations are obtained

$$\log P = -\frac{3900}{T} + 6.76 \tag{14}$$

$$\Delta G = 17\,820 - 30.9T \tag{15}$$

The apparent molecular weight considered corresponds to $(NOPF_6)_{0.50}$ because the enthalpy for 1 atm pressure is 35 700 cal/$NOPF_6$ [2].

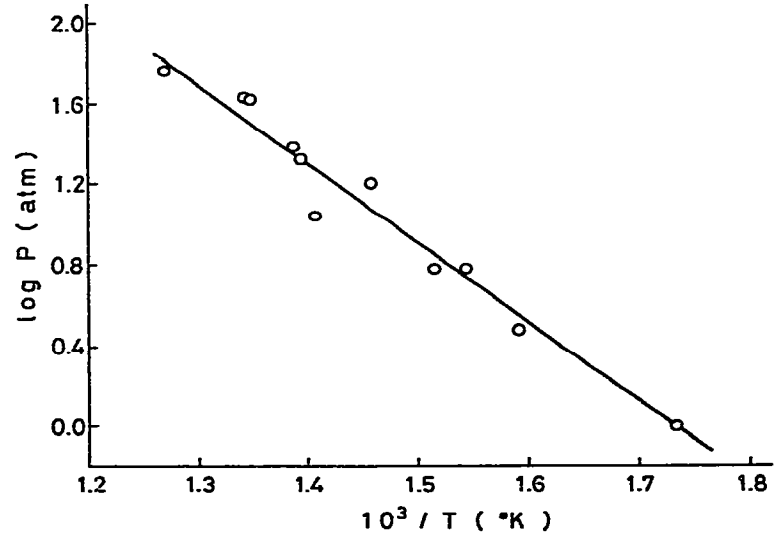

Fig. 6. Clapeyron—Clausius plot for $NOPF_6$.

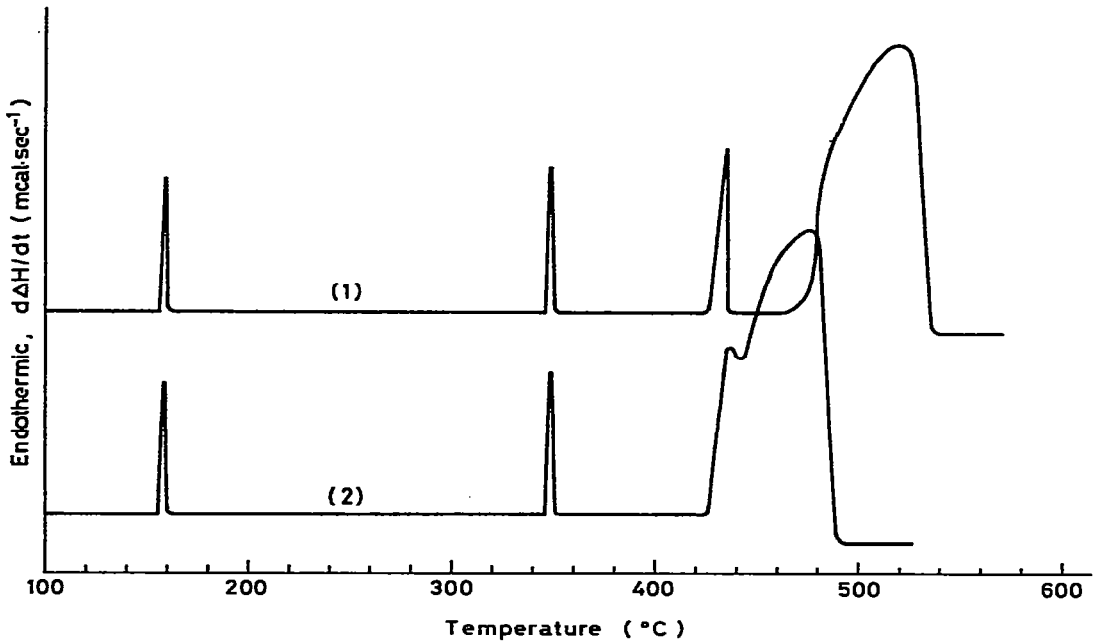

Fig. 7. Typical DSC curves for $NOSbF_6$. (1) 50 atm; (2) 1 atm.

Vaporization of $NOSbF_6$

In this case platinum cells were used because the reaction between the aluminum cell and the sample was not negligibly small. A typical DSC curve for $NOSbF_6$ at 50 atm pressure is shown in Fig. 7 (curve 1); the DSC curve at 1 atm pressure (curve 2) is also cited [2]. Comparing these two curves, it is clear that the decisive broad peak (curve 2) was derived from two overlapping reactions. The sharp peak at 426°C (curve 1) was found to originate

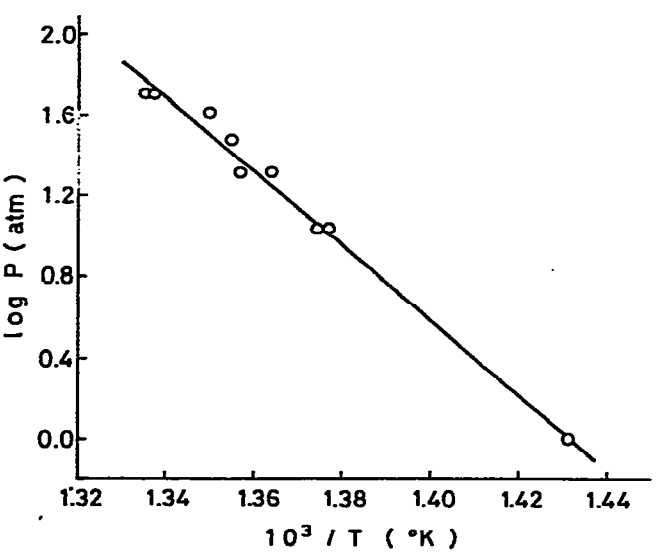

Fig. 8. Clapeyron—Clausius plot for $NOSbF_6$.

from the melting of $NOSbF_6$. Therefore, the last endotherm (curve 1) represents its vaporization which was shifted with the elevated pressure. These facts indicate that the boiling point of $NOSbF_6$ at 1 atm pressure coincides with its melting point. The enthalpy of melting estimated from the DSC curve is 2270 cal/$NOSbF_6$.

The relationship between log P and $1/T$ obtained from the vaporization endotherms is shown in Fig. 8. The following equations are deduced from this linear relationship

$$\log P = -\frac{18\,300}{T} + 26.3 \tag{16}$$

$$\Delta G = 83\,700 - 120.1T \tag{17}$$

Since the enthalpy for 1 atm pressure is calculated to be 42 300 — 2270 cal/$NOSbF_6$ [2], the apparent molecular weight considered corresponds to $(NOSbF_6)_{2.09}$.

ACKNOWLEDGEMENT

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