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SUBLIMATION CALORIMETRIC STUDIES USING A CALVET MICROCALORIMETER[†]

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ABSTRACT

Sublimation enthalpy at 298.15 K derived by linear regression analysis of sublimation calorimetric data at higher temperatures is presented for acetylurea, *N*,*N*-dimethyluracil, trimethyl isocyanurate, trimethyl cyanurate, acetylacetonates of Be(II), Cu(II), Fe(III), Cr(III), Zn(II) and Co(II), $Be_4O(O_2CC_2H_5)_6$, $Be_4O(O_2NO)_6$ and $Cu(NO_3)_2$. Limitation of the present strategy for deriving $\Delta_{sub}H°$ (298) and possible future improvements are discussed.

INTRODUCTION

The use of a Calvet microcalorimeter in combination with Knudsen cell type sample containers was first reported by Chastel *et al.*(ref.1) in 1969. Since then, similar sublimation calorimetric systems have been reported by Malaspina *et al.*(refs.2-4), Sabbah *et al.*(refs.5,6) and the present authors(ref.7). Another technique, vacuum sublimation drop calorimetric method, was employed by Skinner *et al.*(ref.8).

In this paper, sublimation calorimetric studies carried out in our laboratory are reviewed, some unpublished results are briefly presented, and limitation and possible future improvements of the present strategy for deriving standard enthalpy of sublimation at 298.15 K are discussed.

Vapor pressure of a solid substance is usually lower than that of the same substance in the liquid state. This results in low vapor effusion rate from a Knudsen cell type sample container placed in an evacuated space, which in turn lowers heat absorption per unit time and also increases time required for the sublimation of a least amount of sample. The adoption of a Calvet microcalorimeter is a suitable choice owing to its high sensitivity and long-term stability. Furthermore, a wide working temperature range enables us to measure sublimation enthalpy of a substance which is at ordinary temperatures barely volatile, at higher temperatures where vapor pressure is sufficiently high. In addition, measurements at various temperatures allow us to reduce observed enthalpies to 298.15 K by extrapolation.

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EXPERIMENTAL

The present apparatus and procedure for sublimation calorimetry using a Calvet microcalorimeter, ambient to 473 K type, were described in detail elsewhere(ref. 7). The features of the present apparatus are that it can be used for substances that are unstable in air in virtue of a stopper seal, which is removed under vacuum to start vapor effusion from the sample container, and that it can be used for corrosive substances, *e.g.*, $Cu(NO_3)_2$, by employing a version of sample container in which a sample is only in contact with polytetrafluoroethylene and stainless steel. The least amount of sample sublimed is 10 mg, the shortest time spent for vapor effusion in a run is 2 hours and the least measured heat is 10 J. Vapor pressure ranges from 0.7 to 420 Pa. Calibration by electric energy is carried out during a period when output signal from the calorimeter is kept constant while vapor is effusing out of the sample container. The simultaneous calibration is requisite, since otherwise heat capacity of the calorimeter proper changes by the contribution from the stopper seal, which is placed on the sample container after and before a sublimation run. As vapor pressure of a sample is usually low enough, experimental results are identified with standard enthalpies of sublimation at the temperatures within the extent of uncertainty.

RESULTS

Testing of the system(ref.7)

The present sublimation calorimetric system was tested by using naphthalene, which had been recommended from IUPAC(ref.9) as a test substance for sublimation enthalpy measurement. Sublimation enthalpies measured at various temperatures were reduced to 298.15 K by the equation:

$$\Delta_{\mathrm{sub}}H^\circ(298) = \Delta_{\mathrm{sub}}H^\circ(T) - [H^\circ(\mathrm{g},T) - H^\circ(\mathrm{g},298)] + [H^\circ(\mathrm{c},T) - H^\circ(\mathrm{c},298)]. \qquad (1)$$

Enthalpy data for gaseous and crystalline states were taken from literature(refs. 10,11). Derived values were (72.52 ± 0.33), (72.47 ± 0.34) and (72.30 ± 0.40) kJ mol^{-1} for three different sublimation apparatus, which were in good agreement with the IUPAC recommended value of (72.5 ± 0.25) kJ mol^{-1}. Experimental results obtained for anthraquinone, which is much less volatile than naphthalene, agree with the calorimetric values of Malaspina *et al.*(ref.12).

Dimerization of benzoic acid in the saturated vapor above crystal(ref.13)

This substance was also recommended as a test substance for sublimation enthalpy measurement in the 1974 IUPAC recommendation(ref.9). It is well-known that lower members of alkanoic acids dimerize to a considerable extent in the saturated vapor above the crystal. Since benzoic acid molecules dimerize completely in the crystal, dimerization in the saturated vapor above the crystal is suspected.

Sublimation enthalpies of benzoic acid measured at various temperatures were reduced to 298.15 K, by assuming that the saturated vapor consisted solely of monomeric species. Derived values agreed well with each other. This shows that the degree of dimerization in the saturated vapor above crystal is not significantly high and its effect on experimental results would be neglegible within the extent of the present accuracy of sublimation calorimetry(0.3 %). However, the adoption of this substance as a test substance is not recommended, since sublimation enthalpy is determined by various methods and the dimerization would influence experimental results differently for different methods.

Linear regression analysis of experimental data

Frequently, it is impossible to use equation (1) for the reduction of experimental data to 298.15 K owing to the lack of enthalpy data for crystalline and/or gaseous states. In such cases, linear regression analysis was applied for sublimation enthalpy and temperature. Uncertainty for the regression estimate at T K was calculated as the one at a 95 per cent confidence level:

$$s_f \cdot t\{1 + \frac{1}{n} + \frac{(T - \overline{T})^2}{\Sigma_i (T_i - \overline{T})^2}\}^{1/2}, \qquad (2)$$

where n is the number of runs, T_i is the temperature of the i-th run, $\overline{T}$ is the mean temperature, t is the statistical t value, and s_f is the standard deviation from the fit. Four examples of the linear regression analysis are shown in Fig. 1. The upper and lower curves in each figure show the 95 per cent confidence limits as a function of temperature. Standard enthalpies of sublimation obtained by this method are presented for organic compounds and metal complexes in Table 1. Although Zn(acac)$_2$, Co(acac)$_2$ and Ni(acac)$_2$ are oligomeric in the crystals, $\Delta_{sub}H°(298)$ given in the table are those for 1 mol of the momomeric species. Ni(acac)$_2$ evidently decomposed in the sample container. Sublimation enthalpy was measured also for 2,4,6-triisopropylbenzophenone and its photo-isomer(ref.16) and malondiamide(ref.17).

DISCUSSION

As seen in expression (2), the magnitude of uncertainty for a regression estimate depends on the imprecision of experimental data[s_f], the extent of temperature range where measurements were performed[$\Sigma(T_i - \overline{T})^2$], the extent of extrapolation[$(T - \overline{T})$], and the number of runs[n and t]. For rather volatile substances, *e.g.*, those shown in Fig. 1, no seriously large uncertainty would be introduced to $\Delta_{sub}H°(298)$ by the application of the linear regression analysis. However, situation is different for less volatile substances. Measurements at high temperatures are required for these substances so as to increase the effusion rate of vapor. On the other hand, extension of experimental temperature range to higher temperatures is often limited by melting and/or thermal decomposition of the substance. Large uncertainties found for some of metal complexes given in Table 1 was brought about not by the imprecision of experimental data but by the narrow temperature range and long extrapolation. Another practical problem is the long time required for a series of runs.

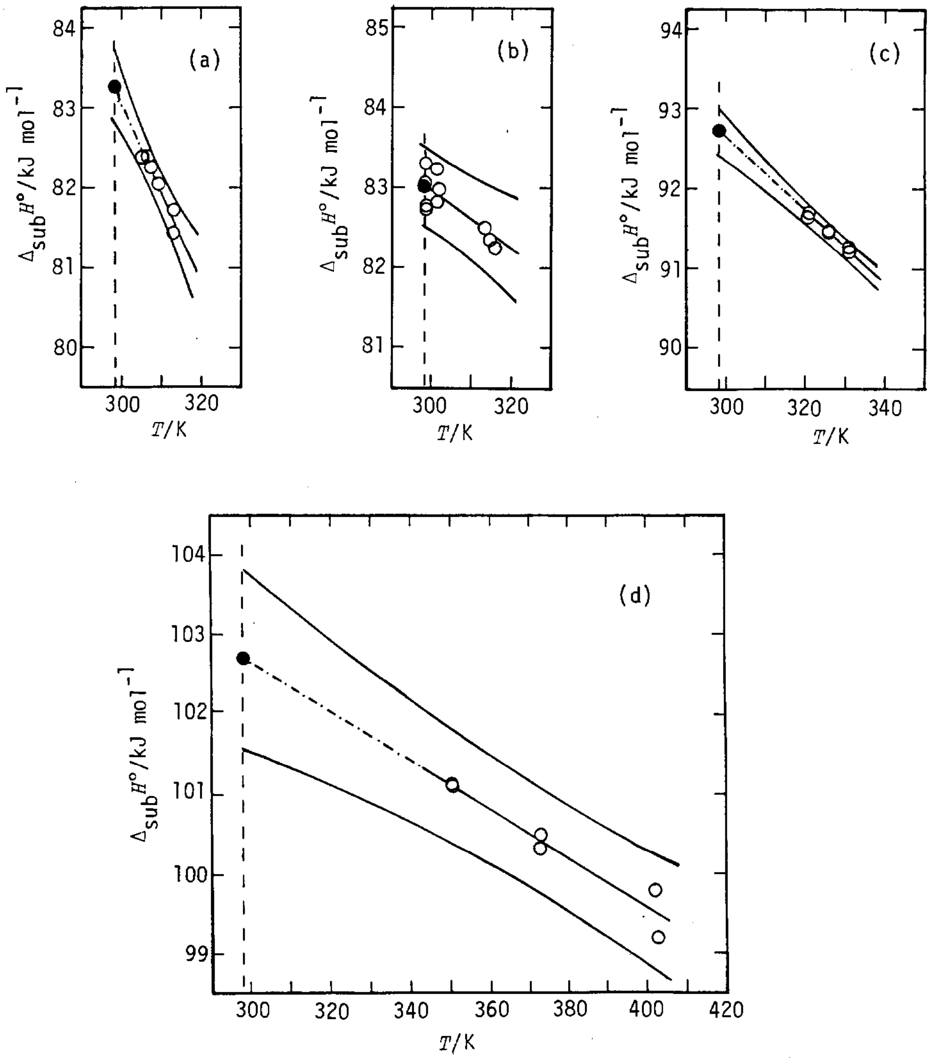

Fig. 1. Linear regression analysis of sublimation enthalpies of (a)thioacetamide, (b)tetramethylthiourea, (c)*N*,*N*-dimethyl-3-nitroaniline and (d)*N*,*N*-dimethyl-4-nitroaniline. Upper and lower curves in each figure show the 95 per cent confidence limits. Open circles are experimental data and filled circles are the regression estimates at 298.15 K.

A more essential problem , which is more serious for less volatile substances, is that the linear regression analysis is based upon the assumption that heat capacity difference between crystalline and gaseous states is independent of temperature, which is only approximately true. The magnitude of error introduced from this source to $\Delta_{\mathrm{sub}}H°(298)$ increases with the extent of extrapolation.

A solution to these problems is the direct use of equation (1). Sublimation calorimetry is carried out at a reasonably high temperature. The enthalpy change for crystal is measured readily by temperature jump(drop) calorimetry using the same Calvet microcalorimeter(refs.19,20) and that for vapor(gas) can be calculated by means of molecular vibrational analysis using spectroscopic data or a molecular orbital method together with the information on the molecular structure. Development along this line is under way in our laboratory.

Standard state pressure, $p°$, was taken to be 10^5 Pa in this paper.

TABLE 1

Standard enthalpies of sublimation at 298.15 K, derived as linear regression estimates from experimental data at higher temperatures, of (a) organic compounds and (b) metal complexes. Uncertainties are those at a 95 per cent confidence level. Parenthesized values are the numbers of runs.

(a) Organic compounds

Substance	$\Delta_{\mathrm{sub}}H°(298)$ / kJ mol^{-1}
thioacetamide(ref.14)	83.25 ± 0.42(7)
tetramethylthiourea(ref.14)	83.04 ± 0.52(10)
N,*N*-dimethyl-3-nitroaniline(ref.15)	92.73 ± 0.29(8)
N,*N*-dimethyl-4-nitroaniline(ref.15)	102.7 ± 1.1(6)
acetylurea(ref.17)	103.05 ± 0.74(12)
N,*N*-dimethyluracil(ref.17)	96.4 ± 1.4(12)
trimethyl isocyanurate(ref.17)	88.2 ± 1.3(11)
trimethyl cyanurate(ref.17)	90.3 ± 1.0(15)

(b) Metal complexes(ref.18)

Substance	$\Delta_{\mathrm{sub}}H°(298)$ / kJ mol^{-1}	Substance	$\Delta_{\mathrm{sub}}H°(298)$ / kJ mol^{-1}
Be(acac)$_2$	91.0 ± 1.4(9)	Co(acac)$_2$	118.7 ± 2.2(10)
Cu(acac)$_2$	127.5 ± 3.2(8)	Ni(acac)$_2$*	155 ± 80(7)
Fe(acac)$_3$	138.4 ± 5.2(7)	$Be_4O(O_2CC_2H_5)_6$	140.8 ± 6.7(6)
Cr(acac)$_3$	132.1 ± 1.9(9)	$Be_4O(O_2NO)_6$	133 ± 20(5)
Zn(acac)$_2$	132.6 ± 8.3(7)	$Cu(NO_3)_2$	139.4 ± 4.7(5)

* Thermal decomposition was observed.
acac: acetylacetonato.

REFERENCES

1 R. Chastel, F. Steckel and H. Tachoire, Proc. 1-st Int. Conf. Calorimetry and Thermodynamics, Warsaw, 31 August to 4 September, 1969.
2 L. Malaspina, R. Gigli and G. Bardi, J. Chem. Thermodyn., 3 (1971) 827-35.
3 L. Malaspina, R. Gigli and G. Bardi, J. Chem. Phys., 59 (1973) 387-94.
4 L. Malaspina, R. Gigli and G. Bardi, J. Chem. Thermodyn., 6 (1974) 1053-64.
5 R. Sabbah, R. Chastel and M. Laffitte, Thermochim. Acta, 5 (1972) 117-27.
6 R. Sabbah, R. Chastel and M. Laffitte, Can. J. Chem., 52 (1974) 2201-5.
7 S. Murata, M. Sakiyama and S. Seki, J. Chem. Thermodyn., 14 (1982) 707-21.
8 F.A. Adedeji, D.L.S. Brown, J.A. Connor, M. Leug, M.I. Paz-Andrade and H.A. Skinner, J. Organometall. Chem., 97 (1975) 221-8.
9 J.D. Cox(Collator), Pure Appl. Chem., 40 (1974) 393-450.
10 D.R. Stull, E.F. Westrum, Jr. and G.C. Sinke, The Chemical Thermodynamics of Organic Compounds, Wiley, New York, pp. 865.
11 J. P. McCullough, H.L. Finke, J.F. Messerly, S.S. Todd. T.C. Kincheroe and G. Waddington, J. Phys. Chem., 61 (1957) 1105-16.
12 G. Bardi, R. Gigli, L. Malaspina and V. Piacente, J. Chem. Eng. Data, 18 (1973) 126-30.
13 S. Murata, M. Sakiyama and S. Seki, J. Chem. Thermodyn., 14 (1982) 723-31.
14 S. Inagaki, S, Murata and M. Sakiyama, Bull. Chem. Soc. Jpn., 55 (1982) 2808-13.
15 J. Furukawa, S. Murata, M. Sakiyama and S. Seki, Bull. Chem. Soc. Jpn., 57 (1984) 3058-61.
16 S. Inagaki, S. Murata, M. Sakiyama, Y. Ito, Y. Umehara, T. Hijiya and T. Matsuura, Bull. Chem. Soc. Jpn., 55 (1982) 2803-7.
17 A. Imamura, S. Murata and M. Sakiyama, to be published.
18 S. Murata, M. Sakiyama and S. Seki, to be published.
19 M. Naruse and M. Sakiyama, to be published.
20 T. Yamane and M. Sakiyama, to be published.