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Heat Capacities of Antimony Trichloride and Tribromide

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Heat capacities of liquid antimony trichloride and tribromide saturated with their respective vapors were determined with an adiabatic calorimeter as follows: 35.2 cal K^{-1} mol^{-1} in the range, 90—210°C, for trichloride, and 34.6 cal $K^{-1}mol^{-1}$ in the range, 130—270°C, for tribromide.

For thermodynamic consideration on vaporization of antimony trichloride ($SbCl_3$) and tribromide ($SbBr_3$) at moderately high temperature, heat capacities of both halides in liquid state, which have never been determined, were required to be known, and the present authors measured them with an adiabatic calorimeter. Measurements were carried out for $SbCl_3$ in the range, 90—210°C, and for $SbBr_3$, 130—270°C, respectively.

Experimental

Apparatus and Procedure of Measurement. The calorimetric apparatus is shown schematically in Fig. 1. A capsule made of fused quartz, 5—6 cm^3 in volume, 0.8 mm in wall thickness, 5—6 g in weight, and provided with a well for an internal heater at its center was used as a sample container. Two alumel-chromel thermocouples, one for measuring the temperature of a capsule and another for adiabatic control, were fastened tightly with fine alumel wire at the middle part of the outside wall of the capsule to make a junction point of each couple touch surely to the wall surface. For measurements on $SbCl_3$, a thermocouple of 0.3 mm in diameter, and on $SbBr_3$, another of 0.2 mm in diameter were used. Calibration of each thermocouple was made by measuring the ice-point and melting points of In,[1] Sn,[2] and Pb[2] metals, the nominal purities of these metals being higher than 99.99%.

On heat capacity measurements, the pressure of argon gas filled in a nickel ball enveloping a capsule was kept at about 50 mmHg. Each sample was heated at a rate of 1°C/min with an internal heater to which practically constant wattage, the fluctuation being within ±0.5%, was supplied by a watt-stabilizer. Adiabatic control was made to make the temperature of the nickel ball equal to the temperature of the outer surface of the capsule with a heater equipped outside of the nickel ball. The heater was controlled by a proportional, integral, and differential heating device. The control fluctuation indicated by thermal emf of the alumel-chromel thermocouple was within $\pm 1\mu V$. Time required to elevate the temperature of a capsule containing a sample by 10°C was measured by a stop watch or a timer in error of less than 0.2%.

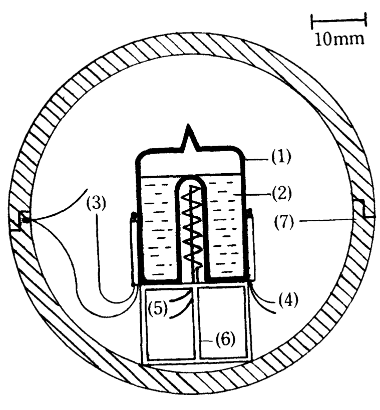

Fig. 1. The calorimetric apparatus
(1): Quartz capsule, (2): Sample, (3): Thermocouple for adiabatic control, (4): Thermocouple for measuring temperature of a capsule, (5): Internal heater, (6): Quartz stand, (7): Nickel ball.

Each sample in a reservoir was heated at a temperature between 100 and 150°C for several tens of minutes in reduced pressure (10^{-2}–10^{-3} mmHg) to remove any dissolved gas and volatile impurities prior to a distillation of the sample into a capsule through a vacuum line connecting the reservoir and the top of the capsule. The amount of the sample in the capsule was 4—5 cm^3. When the distillation was finished, the vacuum line was disconnected from the capsule by fusion. After heat capacity measurements were over, the top of the capsule was cut off to make the sample evaporate out of the capsule. After washed and dried, the empty capsule together with the cut tip was weighed. By subtracting the weight from that of the capsule containing the sample, a net weight of the sample was obtained. Buoyancy correction, less than 0.1% of total weight, was made for that purpose.

Materials. *$SbCl_3$*: $SbCl_3$,[3] the nominal purity being, higher than 99%, was purified with five times' vacuum distillation. $SbCl_3$ thus prepared was analyzed chemically; obsd. Sb, 53.36; Cl, 46.55 wt% calcd. Sb, 53.37; Cl, 46.63 wt%. Any impurities were not found by the emission spectrophotometric analysis. Mp 73.4°C.

$SbBr_3$: $SbBr_3$ was prepared at 250°C by direct reaction of metallic Sb,[1] the nominal purity six nines, with bromine,[4] the nominal purity higher than 99.5%. The reaction product thus prepared was then distilled five times in vacuum. The chemical composition of the purified $SbBr_3$ is: obsd. Sb, 33.70; Br, 66.19 wt% calcd. Sb, 33.68; Br, 66.32 wt%. The emission spectrophotometric analysis indicated very weak spectrum lines of Cu and Si on the purified $SbBr_3$. Mp 96.4°C. Liquid densities observed in the range, 100—250°C, by the pycnometric method were estimated to be: $3.95-2.67\times10^{-3}t$ (g/cm^3), where t is °C.

Hg: Hg,[5] the nominal purity being higher than 99.9%, was washed with dilute aqueous HNO_3, and then distilled five times in vacuum. Any impurities were not found by the emission spectrophotometric analysis on Hg thus purified.

Phenylether: Phenylether of special grade[6] was once distilled in reduced pressure of 7 mmHg, and then purified with five times' fractional recrystallization and two times' vacuum distillation. Any impurities were not found on phenylether thus prepared by the gaschromatographic technique. Mp 26.9°C.

Heat Capacity Determination. Heat capacity is deter-

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[1] Osaka Asahi metal.
[2] Nihon Kinzoku.
[3] Yotsuhata Kagaku, GR.
[4] Merck, GR.
[5] Junsei Kagaku, EP.
[6] Tokyo Kasei, GR.

mined according to the following equation:

$$P = (m_c/M_c)C_c + (m_s/M_s)C_s + E \qquad (1)$$

where P is the input energy required to elevate the temperature of a calorimeter by 1°C, m weight in gram, M molecular weight in gram, C heat capacity per mole and E the sum of energies for thermocouples, protective tubes, an internal heater, a stand for a capsule and small heat exchange between the capsule containing a sample and the surroundings. c refers to a capsule and s to a sample. The amount of heat exchange varies depending on the stray emf of a thermocouple used for adiabatic control, on the heating rate, on the amount of a sample and on its thermal properties defining the extent of heat transfer. Except for thermal properties of a sample used, it is possible to keep all experimental conditions almost invariable in every heat capacity measurement. Therefore, when E, which is determined by measuring known heat capacity of a material chosen as a standard in strictly the same condition as in measurements on a sample, heat capacity of which is unknown, is used for determining heat capacity of the sample, the systematic error of heat capacity thus determined is caused principally by the difference in thermal properties between the standard and the sample.

The authors determined E on Hg, heat capacity of which is well-established,[7] for heat capacity calculation on antimony halides. To estimate the accuracy of heat capacity thus determined, heat capacity of phenylether determined by Furukawa *et al.*[8] with the probable error of ±0.25% was chosen as a relative standard, and was compared with that measured by the present authors in the same way as described above. Difference between the two would indicate the upper limit of accuracy of heat capacity on halides; thermal conductivity of a molten salt is, in general, smaller than that of Hg and larger than that of phenylether, hence, its heat capacity can be measured more accurately than that of phenylether by the adiabatic calorimetric technique.

In each work, heat capacity of two-phase system (C'), *i. e.* heat capacity of saturated vapor plus heat capacity of liquid in equilibrium with saturated vapor (C_{sat}), was observed, and C_{sat}/mol was obtained by calculation according to the following equation[9]:

$$C_{sat} = C' - \{(\Delta Hv_2 \cdot x_2 - \Delta Hv_1 \cdot x_1)/\Delta\theta - (\Delta Hv \cdot x/T)_m\} \qquad (2)$$

where $\Delta\theta$ is the difference between initial and final temperature of a capsule containing a sample, T the absolute temperature, ΔH_v the latent heat of vaporization per mole, x the mass ratio of vapor to the total sample. 1, 2, and m refer to initial, final, and intermediate stages upon rise of temperature. In Eq. (2), values of ΔH_v and x were quoted from the following references: Ref. 10 and Ref. 11 on Hg; Ref. 12 on phenylether; Ref. 11 and Ref. 13 on $SbCl_3$; ΔH_v from Ref. 14 and x from liquid densities measured here and Ref. 14 on $SbBr_3$. The vapor correction was made to be: less than 0.1% of C_{sat} at 265°C on Hg; less than 0.2% of C_{sat} at 245°C on phenylether; less than 0.3% of C_{sat} at 205°C on $SbCl_3$; less than 0.2% of C_{sat} at 265°C on $SbBr_3$.

Heat capacities[7] of Hg and quartz at constant pressure (C_p) are:

$$C_p = 6.44 + 0.19\times10^5T^{-2} \text{ (cal K}^{-1}\text{ mol}^{-1}\text{)(Hg)}:$$

$$C_p = 13.38 + 3.68\times10^{-3}T - 3.45\times10^5T^{-2} \text{ (cal K}^{-1}\text{ mol}^{-1}\text{)(quartz)}.$$

These values were used here without conversion into C_{sat}, because the difference between the two is very small on both materials in the range of temperature in which the present work was carried out.

Results

Heat capacity measurements were made three to five times on one sample at each temperature, and values of P observed were within ±1% at each temperature. In every case, P was around 3 cal K^{-1} and its 60—70% was for heat capacity of a sample.

$SbCl_3$. Heat capacity measurements were made on Hg and $SbCl_3$ alternately, then on Hg and phenylether alternately in the range, 90—210°C, at each interval of 10°C. The value of E in every case is about 1% of P in the vicinity of 100°C and about 4% of P in that of 200°C. Seven samples of $SbCl_3$ were used for measurements. Mean heat capacity obtained at each temperature is shown in Table 1 and Fig. 2. Mean error of each value, about 1% of C_{sat}, is also given in Table 1. As shown in Fig. 2, the temperature dependency of heat capacity seems to be negative. When one, however, takes mean error on the measurements into account, the dependency should be disregarded. Therefore, averaging mean heat capacity obtained at each temperature in the range, 90—210°C, 35.2 cal $K^{-1}mol^{-1}$ is determined as the heat capacity of saturated liquid $SbCl_3$.

Mean heat capacities obtained on two samples of phenylether in the range, 90—210°C, are shown in Fig. 3 and compared with those determined by Furu-

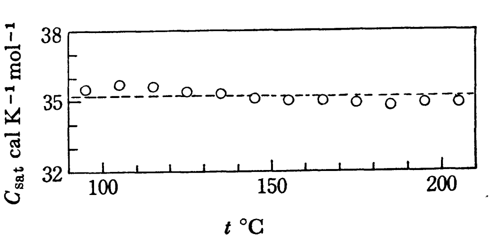

Fig. 2. Heat capacity *vs.* temperature on $SbCl_3$.

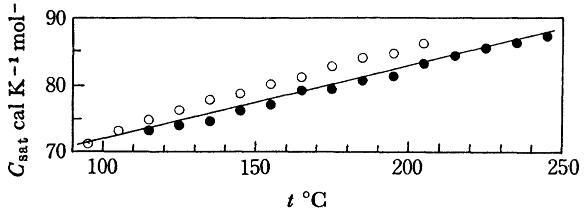

Fig. 3. Heat capacity *vs.* temperature on phenylether.
Solid line: by Furukawa *et al.*
○ and ●: by the present authors in experimental series on $SbCl_3$ and $SbBr_3$, respectively.

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TABLE 1. HEAT CAPACITIES OF $SbCl_3$ AND $SbBr_3$ (cal K^{-1} mol^{-1})

t°C	$SbCl_3$		$SbBr_3$	
	C_{sat}[a)]	ε%[b)]	C_{sat}[a)]	ε%[b)]
95	35.5	1.1		
105	35.7	1.1	—	—
115	35.6	0.9	36.3	1.0
125	35.4	1.1	35.7	0.9
135	35.3	1.2	35.1	0.9
145	35.1	1.0	35.0	1.0
155	35.0	1.1	34.7	0.9
165	35.0	1.0	34.6	0.9
175	34.9	1.1	34.4	0.8
185	34.8	1.3	34.4	1.0
195	34.9	1.2	34.4	0.8
205	34.9	1.3	34.4	1.1
215	—	—	34.4	0.8
225	—	—	34.6	0.9
235	—	—	34.8	1.0
245	—	—	34.6	0.9
255	—	—	34.7	1.1
265	—	—	34.8	0.9

a) Mean value obtained in the range $t \pm 5$°C.

b) Mean error $(\sqrt{\sum(C_{sat\ mean}-C_{sat\ obsd})^2/n(n-1)})/C_{sat}$ (%).

kawa *et al.* The present authors' are higher than Furukawa *et al.*'s, the discrepancy within 3% of C_{sat} in overall temperature range. As mentioned before, 3% is regarded as the accuracy of heat capacity on $SbCl_3$.

$SbBr_3$. Heat capacities of Hg, $SbBr_3$, and phenylether were measured alternately in the range, 110—270°C. For the measurements on $SbBr_3$, finer thermocouples, 0.2 mm in diameter, and protective tubes were used, resulting easier and more reproducible setting of the capsule and thermocouples. The value of E in every case is about -5% of P in the vicinity of 110°C and -2% of P in that of 250°C. Five samples of $SbBr_3$ were used for measurements. Mean heat capacity obtained at each temperature is shown in Table 1 and Fig. 4. Mean error of each value, about 1% of C_{sat}, is also shown in Table 1. As shown in Fig. 4, heat capacities which practically do not vary with temperature are obtained in the range, 130—270°C, however, higher values below 130°C; the reason remains unexplained. Except for those obtained below 130°C, mean heat capacity obtained at each temperature in the range, 130—270°C, was averaged, and 34.6 cal $K^{-1}mol^{-1}$ is determined as the heat capacity of saturated liquid $SbBr_3$.

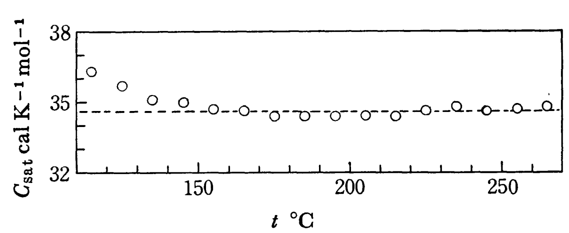

Fig. 4. Heat capacity *vs.* temperature on $SbBr_3$.

Mean heat capacities obtained in this run on three samples of phenylether in the range, 110—250°C, are also shown in Fig. 3. The present authors' agreed with Furukawa *et al.*'s within 1%, indicating that the accuracy of heat capacity on $SbBr_3$ is 1%.

Conclusion

Heat capacities of $SbCl_3$ and $SbBr_3$ saturated with their respective vapors are determined as follows:

$SbCl_3$: 35.2 cal $K^{-1}mol^{-1}$ in the range, 90—210°C.
Accuracy is 3%, mean error 1%.
$SbBr_3$: 34.6 cal $K^{-1}mol^{-1}$ in the range, 130—270°C.
Accuracy is 1%, mean error 1%.