Shull and Rundle[20] have shown by neutron diffraction measurements that the ordering in UH_3 or UD_3 is ferromagnetic with all the atoms having approximately the same orientation and moment. These measurements as well as the measurements of magnetization as a function of field and temperature[5,8,21] indicate that the magnetism arises from a single electron spin per molecule. One would expect, then, an entropy contribution of $R \ln 2 = 1.38$ cal. deg.$^{-1}$ mole^{-1} from the magnetic transition.

The disagreement between the expected theoretical value, $R \ln 2$, and the calculated values, 1.19 and 1.18, is not at all unusual for ferromagnetics. It may arise from the persistence of short range order above the Curie temperature, so that C_m does not vanish as we assumed. On the other hand it should be pointed out that Stoner's collective electron treatment[22] permits any value of the entropy up to $R \ln 2$ to be obtained.

In the temperature range 5–85°K. the experimental values of the heat capacity for UH_3 and UD_3 differ by at most 2% and the values of C_m are nearly identical as would be expected from the values of T_c. However Henry's measurements[5] of the magnetization of UH_3 and UD_3 as a function of temperature would imply a greater difference than actually has been observed. Further the values of $3RD_H$ and $3RD_D$ would indicate that even in the neighborhood of the Curie temperature the spontaneous magnetization and magnetic heat capacity of UH_3 and UD_3 are almost identical, which would lead one to expect similar values for the magneto-caloric effect in contradiction to the results reported by Karchevskii.[7] It would appear from this work that the thermal and magnetic measurements are in disagreement.

Acknowledgment.—We wish to thank Dr. T. Usui whose present address is Inst. of Phys. University of Tokyo, Tokyo, Japan, for many helpful discussions and for suggesting the method of analyzing the heat capacity data.

LEMONT, ILLINOIS

---

[20] M. K. Wilkinson, C. G. Shull and R. E. Rundle, *Phys. Rev.*, **99**, 627 (1955), Abstract.

[21] D. M. Gruen, *J. Chem. Phys.*, **23**, 1708 (1955).

[22] E. C. Stoner, *J. phys. radium*, **12**, 372 (1951); *Proc. Roy. Soc. (London)*, **A165**, 372 (1938).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE UNIVERSITY OF WASHINGTON]

The Heat of Sublimation and the Condensation Coefficient of Bromine

BY M. B. FREY AND N. W. GREGORY

RECEIVED AUGUST 19, 1959

From an effusion study, the heat of sublimation of bromine is found to be 10,680 ± 100 cal. mole^{-1} at 185°K. The condensation coefficient appears larger than 0.3.

The entropies of solid[1] and gaseous[2] bromine are well established; the heat of sublimation may be predicted from measured heats of vaporization (liquid) and fusion and heat capacities, but insufficient low temperature vapor pressure data for the solid have been reported to provide a good basis for an independent experimental determination. Several investigators, using either a direct manometric method or the measured quantity of vapor in a known volume, have reported vapor pressures for the solid close to its melting point.[3–5] Only one measurement in the low temperature range has been reported (Henglein, *et al.*, at 178°K., by the swinging quartz fiber method).

We have made an effusion study of the vapor pressure above solid bromine between 170 and 196°K. from which, together with calculated entropies, the heat of sublimation has been evaluated. The study also was designed to determine the magnitude of the condensation coefficient of solid bromine by comparison of effusion steady state pressures in various cells, as described in an earlier paper on iodine.[6]

Experimental Part

An effusion cell was constructed by rounding off the end of the inner part of a 20/35 ST Pyrex ball joint 4.3 cm. from the top of the ball. A piece of 0.001″ nickel foil was annealed and trimmed so as to overlap the inside opening uniformly by about one mm. With the foil in place a seal to the outer part of the joint was completed by lubrication with Spectrovac stopcock grease and clamping the two parts together. The joint was found leak-tight at room temperature and below; at the low temperatures of the vapor pressure measurements no perceptible reaction of bromine with the lubricant was observed.

Interchangeable foils with two different orifice sizes were prepared, giving the equivalent of two cells. A third all-glass cell, No. 5 described in the earlier paper on iodine,[6] also was used. Geometric characteristics of the cells are summarized in Table I.

TABLE I

Cell	Orifice area, $A_0 \times 10^3$ cm.^{2}	$A_0/A_s \times 10^4$ [a]	K [b]
2	3.58	2.85	0.96
3	28.2	22.4	.99
5	16.7	135	.98

[a] A_s cell cross-section area. [b] Orifice Clausing factor.[7]

Bromine was produced directly in the vacuum system by heating a sample of anhydrous copper(II) bromide (the sample could be isolated from the effusion system by a fluorocarbon lubricated stopcock). The released bromine was condensed directly in the effusion cell, entering through the orifice, by cooling the bottom with liquid nitrogen. The cell then was brought to the desired temperature for each vapor pressure measurement by immersing it in a Dewar flask filled with one of these described slush baths:

---

[1] D. L. Hildenbrand, W. R. Kramer, R. A. McDonald and D. R. Stull, THIS JOURNAL, **80**, 4129 (1958).

[2] W. H. Evans, T. R. Munson and D. D. Wagman, *J. Research, Natl. Bur. Standards*, **55**, 147 (1955); R. P. 2614.

[3] W. Ramsey and S. Young, *J. Chem. Soc.*, **49**, 453 (1886).

[4] T. Isnardi, *Ann. Physik*, **61**, 264 (1920).

[5] F. A. Henglein, G. von Rosenberg and A. Muchlinski, *Z. Physik*, **11**, 1 (1922).

[6] J. H. Stern and N. W. Gregory, *J. Phys. Chem.*, **61**, 1226 (1957).

[7] S. Dushman, "Vacuum Technique," John Wiley and Sons, Inc., New York, N. Y., 1949, Chap. 2.

170°K., cyclohexene; 177°K., hexane; 182°K., *n*-butyl alcohol; 189°K., ethyl acetate; 194.8°K., powdered Dry Ice (heated, no liquid). During a run (times ranged between 5 and 150 minutes) the effused bromine was collected on a liquid oxygen cooled Pyrex finger, 3.0 cm. o.d., inserted in a 5.0 cm. o.d. Pyrex tube attached as closely as possible to the outer part of the ball joint. The bottom of the cold finger was *ca.* 5 cm. above the orifice. At the end of each run the apparatus was filled with dry nitrogen, the finger quickly exchanged with a clean duplicate and the system re-evacuated. The bromine sample was then carefully dissolved in potassium iodide solution and the liberated iodine determined by the amperometric "dead-stop" method.[6,8]

Results and Discussion

Vapor pressures were calculated from the Knudsen equation $P_{\text{mm.}} = \dfrac{17.14\ n(MT)^{1/2}}{A_0 tK}$ and are shown graphically in Fig. 1. Data from cells 2 and 3 are in very close agreement and lie only slightly above those from cell 5. The close correspondence of the latter to equilibrium values indicates a much larger condensation coefficient than observed for iodine in the same pressure range.[6] From the equation $P_e/P_s = 1 - A_0/A_s\alpha$, which is difficult to apply because of the small difference of P_e and P_s relative to experimental error, α (the condensation coefficient) appears to be *ca.* 0.3 when A_s is assumed equal to the cell cross-sectional area.

To test the effect of the form of the solid, several runs were made in which the sublimed bromine, which condensed originally in well-formed crystals on the side and bottom of the effusion cell, was allowed to melt in the cell and then refrozen. A difference in pressure above the frozen liquid (as compared with the original sublimed crystals) was observed only at the highest temperatures (−78°) in the cell with the largest orifice, cell 3. This point, indicated by the solid symbol, Fig. 1, is above the pressure observed with the original crystals, perhaps because of an increased effective surface area or a change in the condensation coefficient. At lower temperatures, no difference in pressures was observed.

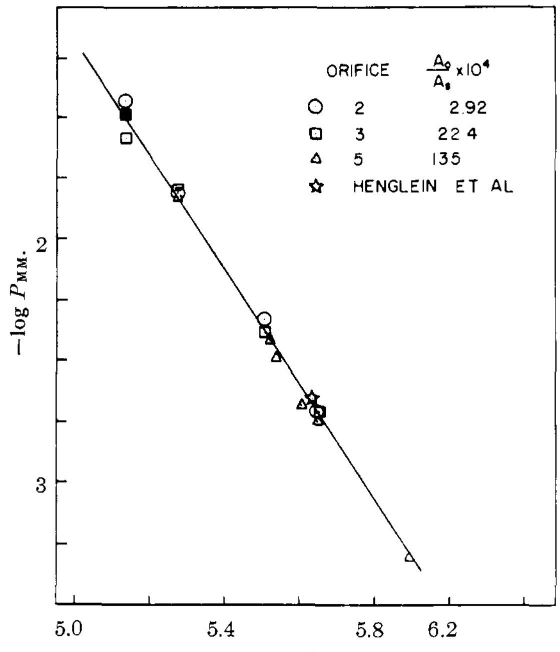

Fig. 1.—Vapor pressure of solid bromine.

TABLE II

THERMODYNAMIC DATA FOR THE SUBLIMATION OF BROMINE (BASED ON DATA FROM CELLS 2 AND 3)

T, °K.	$P_{\text{atm.}} \times 10^5$ (exptl.)	ΔF^0, ($-RT$ ln P)	ΔS^0, (ref. 1, 2)	ΔH^0, (sublim.)	$-\Delta C_p^0$, (sublim. ref. 1, 2)
194.8	4.91	3840	34.53	10570	4.72
	3.42	3981		10710	
	4.30	3891		10620	
189.5	2.03	4068	34.64	10630	4.67
	2.09	4057		10620	
181.7	0.613	4333	34.82	10680	4.61
	.538	4380		10710	
177.2	.254	4536	34.92	10720	4.60
176.7	.254	4523	34.96	10700	4.59

Data from cells 2 and 3 have been assumed to represent equilibrium vapor pressures and used to calculate the standard free energy of sublimation at each temperature. The standard entropy change for sublimation, evaluated from ref. 1 and 2, and the free energy were then combined to obtain the standard enthalpy of sublimation for each point.

Using an average value of −4.64 for ΔC_p^0 over the temperature interval 175 to 195°K., the standard heat of sublimation may be represented by the equation

$$\Delta H^0 = 11540 - 4.64T \text{ cal. mole}^{-1}$$

and the vapor pressure of the solid, as indicated by the line in Fig. 1, by the equation

$$\log P_{\text{mm.}} = -2522T^{-1} - 2.335 \log T + 16.788$$

The heat of sublimation at our mean temperature of 185°K., 10682 cal. mole^{-1}, is within experimental error of the value 10622, calculated from heat of fusion, heat of vaporization and heat capacity data.[1,2] Our heat of sublimation at 185°K., together with reported relative heat content[1,2] and heat of fusion[1] data, gives a standard heat of vaporization of liquid bromine at 25° of 7434 cal. mole^{-1}. This may be compared with the measured value of 7387 ± 27 cal. mole^{-1}, ref. 1, and 7340 cal. mole^{-1} tabulated in NBS Circular 500.[9] Our experimental uncertainty is estimated as 100 cal. mole^{-1}.

The single vapor pressure over solid bromine measured at 178°K. by Henglein, *et al.*,[5] compares favorably with our findings as shown in Fig. 1.

This work was supported by a grant from the National Science Foundation.

SEATTLE, WASHINGTON

---

[8] G. Wernimont and F. G. Hopkinson, *Ind. Eng. Chem., Anal. Ed.*, **12**, 308 (1940).

[9] Selected Values of Chemical Thermodynamic Properties, Circ. 500, National Bureau of Standards, U. S. Govt. Printing Office, 1952, Series II, Table 11-1.