

# The Vapor Pressure and Enthalpy of Vaporization of Molten Aluminum Bromide to the Critical Point<sup>1</sup>

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The vapor pressure of molten aluminum bromide has been measured by an inverted capillary technique from 536°K and 1.18 atm to 761°K and 28.3 atm. The data are represented by the relation  $\log P(\text{atm}) = 4.6688 - 2451.9/T^\circ\text{K}$  from 639 to 761°K with an average deviation of 0.70% for the 14 experimental points. Extrapolation to the critical temperature ( $763 \pm 2^\circ\text{K}$ ) gives a critical pressure of  $28.5 \pm 0.6$  atm. From 536 to 639°K the Antoine vapor pressure relation,  $\log P(\text{atm}) = 4.1893 - 1876.8/(T - 80)$  fits the data with an average deviation of 0.57% for the 15 experimental points. The enthalpy of vaporization has been calculated from 528°K (1 atm) to 761°K.

## Introduction

The preceding paper<sup>2</sup> reported data for the co-existence and critical temperature of aluminum bromide. Fischer, Rahlfs, and Benze<sup>3</sup> have determined the vapor pressure up to the normal boiling point (528°K), but experimental data above 1 atm are not available in the literature. This is a report of an investigation of the vapor pressure from the boiling point to temperatures just below the liquid-vapor critical point, and, together with our preceding paper, it characterizes the thermodynamics of vaporization to the critical point.

## Experimental Section

The semimicro boiling point method employed for the vapor pressure measurements on bismuth chloride<sup>4</sup> and mercuric chloride<sup>5</sup> was used in this work. The apparatus has been described in detail elsewhere.<sup>6</sup> The aluminum bromide used in this investigation was a part of the material prepared for the critical temperature and orthobaric density measurements.<sup>2</sup> The bromine content, determined by precipitation as silver bromide, was found to be 89.95% compared to a theoretical bromine content of 89.88%.

## Results and Discussion

The vapor pressure of molten aluminum bromide was determined at 28 points over a temperature interval of 536–761°K and a pressure range of 1.18–28.3 atm. The experimental data are presented in Table I and Figure 1. The recorded temperatures are corrected for the temperature gradient between the position of the thermocouple and the liquid surface. These corrections varied from 2 to 3° depending on the temperature. Below 17 atm the observed pressures were corrected by the addition of 0.01 atm for the static head of aluminum bromide. Vapor pressure measurements above 17 atm are recorded to the nearest 0.1 atm, and the correction was negligible.

Two runs were made using different charges of aluminum bromide as indicated in Table I. There is no evidence of systematic deviation between the individual runs. It was found that the data could be fitted by the relation

$$\log P(\text{atm}) = 4.6688 - 2451.9/T^\circ\text{K} \quad (1)$$

from 760.8 to 639.5°K with an average deviation of 0.70% for the 14 experimental points. From 639.5 to 535.8°K the data are represented by the Antoine vapor pressure equation

$$\log P(\text{atm}) = 4.1893 - 1876.8/(T - 80) \quad (2)$$

with an average deviation of 0.57% for the 15 experimental points. As shown in Table I, the pressures calculated by eq 1 and 2 are identical at 639.5°K and the same is true for the calculated values of  $(dP/dT)$  at this temperature.

The critical pressure calculated by eq 1 is  $28.5 \pm 0.6$  atm using the critical temperature of  $763 \pm 2^\circ\text{K}$  reported previously<sup>2</sup> for aluminum bromide.

Figure 1 presents the experimental data on a  $\log P$  vs.  $1/T$  plot. The open circles represent the experimental data points obtained in this investigation and the solid circles are used for the experimental data of Fischer, Rahlfs, and Benze.<sup>3</sup> The curve is calculated by eq 1 from 760.8 to 639.5°K and by eq 2 from

(1) This work was made possible by the support of the Research Division of the U. S. Atomic Energy Commission under Contract No. AT(04-3)-106.

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**Table I:** Experimental Vapor Pressures of Aluminum Bromide

Run no.	T, °K	Pressure, atm		% dev	dP/dT × 10 <sup>3</sup>
		Obsd	Caled, eq 2		
2	535.8	1.18	1.18	0	24.54
2	542.4	1.35	1.35	0	27.29
2	550.7	1.59	1.59	0	31.01
1	552.0	1.63	1.63	0	31.62
1	553.1	1.66	1.67	0.60	32.24
2	566.3	2.12	2.14	0.94	39.11
1	566.9	2.13	2.16	1.41	39.37
1	576.4	2.54	2.56	0.79	44.90
1	584.3	2.94	2.93	-0.34	49.79
1	596.2	3.54	3.58	1.13	58.06
2	597.5	3.66	3.65	-0.27	58.90
2	606.6	4.17	4.22	1.20	65.76
1	615.4	4.88	4.83	-1.02	67.76
2	621.0	5.25	5.25	0	77.52
2	639.5	6.78	6.84	0.88	94.43
Av ±0.57%					
		Caled, eq 1			
2	639.5	6.78	6.84	0.88	94.43
1	647.6	7.70	7.64	-0.78	102.85
2	652.7	8.12	8.17	0.62	108.27
2	664.2	9.41	9.49	0.85	121.41
2	672.2	10.53	10.51	-0.19	131.32
2	693.6	13.52	13.61	0.66	159.72
2	703.9	15.47	15.33	-0.90	174.68
1	709.5	16.29	16.34	0.30	183.26
2	726.5	20.0	19.7	-1.60	210.51
2	746.0	23.9	24.1	0.92	244.59
1	748.3	24.6	24.6	0	249.71
1	756.8	26.8	26.8	0	264.77
2	758.2	27.0	27.2	0.74	267.52
1	760.8	28.3	27.9	-1.31	272.52
C.P.	763.0	...	28.5	...	(276.77)
Av ±0.70%					

639.5 to 391.5°K. Fischer, *et al.*, reported the normal boiling point of aluminum bromide to be 528°K and our eq 2 also gives a value of 528°K. This is somewhat lower than the values 529.5°K selected by Kelley<sup>7</sup> and 530°K given in the JANAF tables.<sup>8</sup>

Table II compares the experimental pressures of Fischer, Rahlfs, and Benze<sup>3</sup> with those calculated by eq 2. Included in the table are the values of the pressures calculated by the free energy of vaporization relation developed by Kelley<sup>7</sup> from the same data. While eq 2 is empirical, it reproduces the experimental points somewhat better than the theoretically based equation developed by Kelley. This is probably due to the choice of -25 cal/mole deg as the constant difference in the heat capacities of liquid and gaseous aluminum bromide. A value of -18, as derived from the enthalpies of vaporization given by ref 3 (13.9 and 12.1 kcal/mole at 410 and 510°K, respectively) would have given a better representation.

**Table II:** Comparison of Observed and Calculated Vapor Pressure of Aluminum Bromide below 1 Atm

Temp, °K	Pressure, atm			Caled - obsd (atm)	Kelley
	Obsd, ref 3	Caled, eq 2	Caled, Kelley		
522.7	0.887	0.891	0.888	0.004	0.001
519.3	0.834	0.826	0.828	-0.008	-0.006
518.0	0.806	0.802	0.806	-0.004	0
500.0	0.526	0.526	0.540	0	0.014
495.2	0.468	0.467	0.482	-0.001	0.014
493.5	0.455	0.447	0.462	-0.008	0.007
493.5	0.453	0.447	0.462	-0.006	0.009
493.1	0.442	0.443	0.458	0.001	0.016
493.0	0.439	0.442	0.457	0.003	0.016
483.1	0.344	0.342	0.356	-0.002	0.012
465.5	0.212	0.209	0.219	-0.003	0.007
462.0	0.192	0.189	0.198	-0.003	0.006
461.8	0.191	0.188	0.196	-0.003	0.005
437.6	0.086	0.087	0.090	0.001	0.004
436.2	0.085	0.084	0.086	-0.001	0.001
430.2	0.067	0.067	0.069	0	0.002
422.0	0.049	0.050	0.051	0.001	0.002
414.4	0.038	0.038	0.038	0	0
413.7	0.036	0.037	0.037	0.001	0.001
Av dev				0.97%	2.42%
404.0	(0.026)	0.025	0.024	-0.001	-0.002
401.0	(0.022)	0.023	0.021	0.001	-0.001
400.5	(0.021)	0.021	0.021	0	0
391.5	(0.013)	0.015	0.014	0.002	0.001
Av dev 4 pts.				5.94%	4.98%

The enthalpy of vaporization of aluminum bromide may be calculated from the present data using the Clapeyron relation

$$\Delta H_{\text{vap}} = \frac{T(V_g - V_l)(dP/dT)}{41,300} \quad (3)$$

where  $V_g$  and  $V_l$  represent the orthobaric molar volumes of vapor and liquid,  $(dP/dT)$  is the rate of change of vapor pressure with respect to temperature, and the numerical factor converts the value to kilocalories per mole. Fischer, *et al.*,<sup>3</sup> reported that aluminum bromide vapor consisted almost entirely of  $\text{Al}_2\text{Br}_6$  molecules; therefore, our calculations of  $(V_g - V_l)$  and the enthalpy of vaporization refer to a mole of  $\text{Al}_2\text{Br}_6$ .

Table III presents the results of these calculations. The enthalpy of vaporization,  $\Delta H_{\text{vap}}$ , is very sensitive to the accuracy of the vapor density data, particularly at low vapor densities. Therefore, the experimental values of the density were used from ref 2 instead of the

(7) K. K. Kelley, U. S. Department of the Interior, Bureau of Mines, Bulletin No. 383, U. S. Government Printing Office, Washington, D. C., 1935.

(8) "JANAF Thermochemical Tables," The Dow Chemical Co., Midland, Mich.

Table III: Vaporization Data for Aluminum Bromide

$T$ , °K <sup>a</sup>	Vapor, pressure, atm	$(V_g - V_l)$ , cc/mole of $\text{Al}_2\text{Br}_6$	$T(dP/dT)$ , atm	$\Delta H_{\text{vap}}$ , kcal/mole of $\text{Al}_2\text{Br}_6$	$\Delta H_{\text{vap}}$ , calcd eq 5	Dev, %
760.3	27.80	413	206.43	2.06	2.07	0.48
759.8	27.67	452	205.60	2.25	2.21	-1.78
758.4	27.29	518	203.15	2.55	2.55	0
754.9	26.36	652	197.14	3.11	3.19	2.57
754.4	26.23	687	196.30	3.26	3.26	0
748.9	24.83	873	187.19	3.96	3.97	0.25
742.6	23.29	1,072	177.04	4.60	4.59	-0.22
734.4	21.40	1,318	164.51	5.25	5.24	-0.19
733.2	21.13	1,393	162.70	5.49	5.32	-3.10
732.1	20.89	1,421	161.08	5.54	5.40	-2.53
726.2	19.62	1,596	152.53	5.89	5.78	-1.87
714.1	17.20	1,961	135.98	6.46	6.46	0
700.8	14.80	2,543	119.230	7.34	7.11	-3.13
683.0	12.00	3,253	99.193	7.81	7.84	0.38
658.1	8.78	4,808	75.322	8.77	8.73	-0.46
626.3	5.67	7,751	51.421	9.65	9.68	0.31
609.8	4.43	10,014	41.588	10.08	10.13	0.50
591.0	3.28	13,493	32.081	10.48	10.60	1.14
543.5	1.38	30,954	15.087	11.31	11.66	3.09
528.0	1.00	(42,100) <sup>c</sup>	11.370	(11.59)	11.98	3.36
410 <sup>3</sup>	...	...	...	13.9	14.06	1.15
510 <sup>3</sup>	...	...	...	12.1	12.33	1.90
528 <sup>3</sup>	...	...	...	12.0	11.98	-0.17
529.5 <sup>7</sup>	...	...	...	10.92	11.95	9.43 <sup>b</sup>
530 <sup>3</sup>	...	...	...	12.00	11.94	-0.50

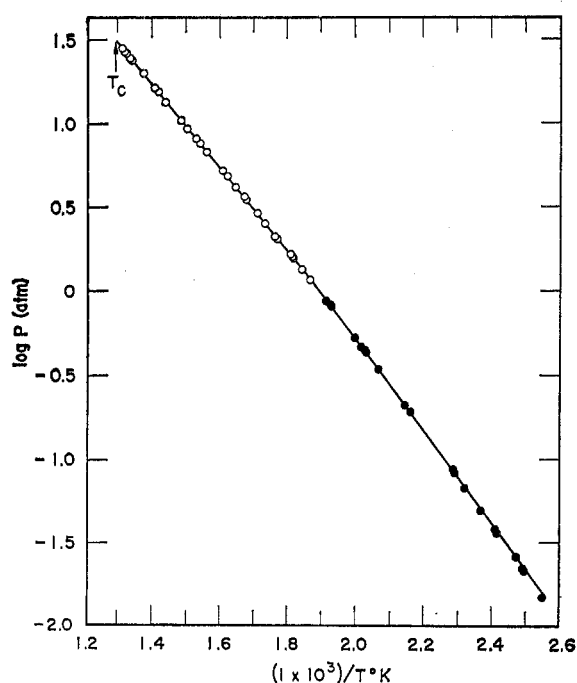
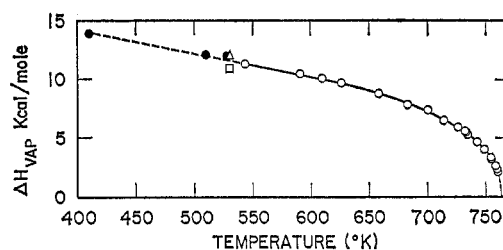
Av dev %  $\pm 1.21$ <sup>a</sup> Superscripts 3, 7, and 8 refer to literature sources. <sup>b</sup> Not included in average. <sup>c</sup> Calculated from extrapolated vapor density values.

Figure 1. Vapor pressure of aluminum bromide: O, present work; ●, Fischer, Rahlfs, and Benze.

Figure 2. Enthalpy of vaporization of aluminum bromide: O, present work; ●, Fischer, Rahlfs, and Benze; △, JANAF tables; □, Kelley. Present data calculated per mole of  $\text{Al}_2\text{Br}_6$ . Literature values are per mole of gas. See text.

values calculated from the Guggenheim equation so as to avoid introducing a trend in the values of  $(V_g - V_l)$  at low vapor densities. The quantity  $T(dP/dT)$  was calculated from eq 1 or 2 in the appropriate temperature range.

Figure 2 shows the variation of the enthalpy of vaporization with temperature. Included in this figure are the enthalpies of vaporization reported by Fischer, Rahlfs, and Benze,<sup>3</sup> Kelley,<sup>7</sup> and the JANAF tables.<sup>8</sup> These literature values were calculated from the Clapeyron equation on the assumption that the

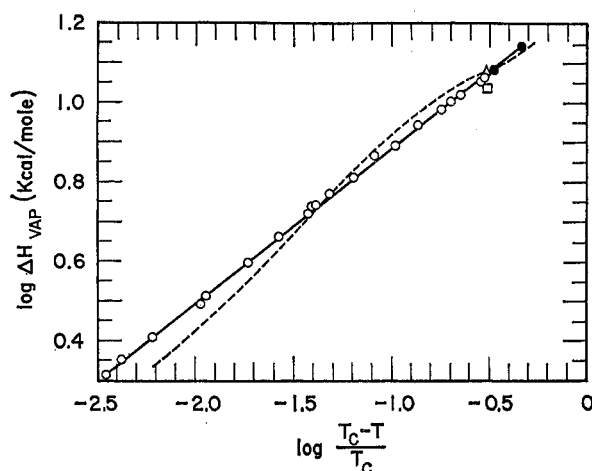


Figure 3. Log-log plot of enthalpy of vaporization vs. temperature: O, present work; ●, Fischer, Rahlfs, and Benze; Δ, JANAF tables; □, Kelley; ---, Zhuralev and Kostrova.

vapor obeyed the ideal gas law. The enthalpy of vaporization derived in that way refers to a mole of the gaseous form of the substance. That is, if  $\text{AlBr}_3$  were the only gaseous species, the  $\Delta H$  would refer to 267 g of aluminum bromide; if  $\text{Al}_2\text{Br}_6$  were the only gaseous species, the  $\Delta H$  would refer to 534 g; and for mixtures of species in the gas phase, the molecular weight would be that of the proper average of the species. Therefore, the agreement of the literature values of  $\Delta H$  near the boiling point (especially that of ref 3) with the values we obtained above, on the assumption that the molecular weight of the gas corresponded to  $\text{Al}_2\text{Br}_6$ , is a verification that this assumption is valid.

The enthalpy of vaporization and its relation to temperature has been the subject of many empirical relations. Of these the relatively simple modification of Jones and Bowden<sup>9</sup>

$$\Delta H_{\text{vap}} = l_0 \frac{(T_c - T)^n}{T_c} \quad (4)$$

was applied to the present data on aluminum bromide. In this relation,  $l_0$  and  $n$  are empirical constants. A log-log plot of the data is shown in Figure 3. The present data follow a straight line with the parameters  $l_0 = 19.03$  and  $n = 0.393$ . These values can be compared with those given by Partington<sup>10</sup> for several fluids. For  $n$  his values range from 0.3 to 0.45 and average about 0.39 for nonassociated liquids. For mercuric chloride,<sup>5</sup>  $l_0 = 18.50$  and  $n = 0.394$ . This relation also fits the enthalpy of vaporization reported by Fischer, Rahlfs, and Benze<sup>8</sup> and the value selected for the normal boiling point in the JANAF tables;<sup>8</sup> Kelley's value falls below this line. The dotted line in Figure 3 represents the tabular values of the enthalpy of vaporization listed by Zhuralev and Kostrova.<sup>11</sup> These authors extrapolated the vapor pressure curve of ref 3 up to their critical temperature of 768°K and combined these results with the orthobaric density data of Zhuralev.<sup>12</sup> Considering the vapor pressure curve was extrapolated over a temperature range of 240°, their results are surprisingly good.

The last column in Table III presents the enthalpy of vaporization of aluminum bromide according to eq 4. With the exception of the value selected by Kelley,<sup>7</sup> all of the experimental data are fitted by eq 4 with an average deviation of  $\pm 1.21\%$  and a maximum deviation of  $+3.36\%$ .

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