[CONTRIBUTION FROM THE THERMAL LABORATORY, THE DOW CHEMICAL COMPANY]

Bromine: The Heat Capacity and Thermodynamic Properties from 15 to 300°K.

BY D. L. HILDENBRAND, W. R. KRAMER, R. A. MCDONALD AND D. R. STULL

RECEIVED JANUARY 20, 1958

The heat capacity of bromine has been measured in an automatic adiabatic calorimeter from 15 to 310°K., using a magnesium alloy sample container. The heat of fusion is 2527 cal. mole^{-1} at the melting point, 265.90°K. The heat of vaporization at 298.15°K. was found to be 7387 cal. mole^{-1}. At 298.15°K., the entropy obtained from the Third Law of Thermodynamics is 58.62 cal. deg.$^{-1}$ mole^{-1}, while a value of 58.65 cal. deg.$^{-1}$ mole^{-1} is obtained from molecular data. Free energy, heat content, entropy and heat capacity functions have been tabulated to 300°K.

Bromine is one of the few common diatomic gases that have not been thoroughly studied by modern calorimetric techniques. Thus far a comparison of the entropies obtained from the Third Law of Thermodynamics and from statistical calculations based on molecular data has not been possible. The only published liquid heat capacity[1] and heat of fusion[2] data are over one hundred years old. Heat capacity data for solid bromine have been reported by Latimer and Hoenshel[3] and by Surhmann and von Lude,[4] but only the former results can be considered reliable, and even those show considerable scatter. For the above reasons, and because of the industrial importance of the material the present investigation of the thermodynamic properties of bromine was undertaken.

Lack of a suitable sample container to withstand attack by the bromine has been the principal reason that a detailed thermodynamic investigation has not been carried out earlier. In the present study, the use of a magnesium alloy sample container proved highly satisfactory, as evidenced by the calorimetric purity determination given below.

Calorimetric Apparatus.—The low temperature adiabatic calorimeter and the mechanics of its automatic operation have been described in detail.[5] Briefly, the essential features are as follows: The calorimetric assembly is of conventional design and is similar to that described by Ruehrwein and Huffman.[6] Automatic operation of the adiabatic shield control was provided by feeding the output of a twelve-junction thermel (made of Chromel-P and Constantan), which indicates the temperature difference between shield and sample container, to a servoamplifier. A motor, fed by the servoamplifier, was used to operate a microswitch that controlled the shield heating current. Excellent shield control was obtained over the entire temperature range. The temperature of the shield environment was controlled in a similar fashion. The sample temperature, indicated by a calibrated platinum resistance thermometer, was recorded continuously on a Leeds and Northrup "High Precision" resistance recorder. This has the considerable advantage of providing a complete record of the thermal history of the sample. Electrical power input to the sample heater was obtained by recording on a Brown Electronik voltage recorder the potential drops across the sample heater and across calibrated standard resistances. The accuracy of the temperature measurement was such that above 60°K., the temperature rise could be determined to better than 0.05%, while at 30°K. the accuracy was about 0.2%. Electrical power measurements were accurate to better than 0.1%. A pendulum operated clock, monitored by a quartz crystal controlled oscillator, and periodically checked against the signal from radio station WWV, automatically timed the duration of the electrical heat inputs. Even for the shortest inputs, these time intervals were known to better than 0.01%. This master clock also was used to operate a program unit which furnished the necessary switching to give the desired alternating sequences of heating and equilibration periods. A number of different programs were available, so that by changing programs or by varying the voltage drop across the sample heater, any desired temperature rise could be obtained. The program unit operated continuously and, above 40°K., required changing perhaps once a day as the sample heating requirements increased.

A further refinement of the adiabatic shield control recently incorporated was the use of a servo motor to adjust automatically the output voltage of an autotransformer feeding the shield heating circuit as the heating load changed.

Several changes in the adiabatic shield assembly also have been made since the description of ref. 5. The shield was fabricated so that the side and bottom unit could be removed for direct access to the sample container. The control thermocouple junctions were insulated with mica strips and fastened to the outside of the shield with copper lugs so as to give more intimate contact. The top, side and bottom of the shield each had four junctions, placed in separate positions. Each pair of thermocouple leads was given several turns around the shield and lacquered in place with G.E. No. 7031 adhesive, after which the outer surface of the shield was covered with a layer of aluminum foil. A terminal ring was attached to the inside top of the shield to accommodate the resistance thermometer, heater and control thermocouple wires. The copper band containing the sample control junctions, and which was clamped around the middle of the sample container, was suspended from three linen threads attached to the terminal ring.

The sample container was fabricated from a magnesium[7] alloy having the composition, Mg, 96%, Al, 3% and Zn, 1%, and had a volume of about 65 cm.^{3}. A central re-entrant well was provided for the platinum resistance thermometer, around which were clustered ten re-entrant wells for replaceable heaters. The heaters were made up of glass insulated constantan wire encased in a copper tube of 3 m.m. o.d., and had a resistance of 10 ohms each. A light coating of silicone grease on the thermometer and heaters ensured good thermal contact. Twenty horizontal heat distributing discs were bonded to the heater wells, but not to the thermometer well or container wall. The container parts were joined by heliarc welding. Closure was provided by means of a threaded nickel plug fitted with a thin Teflon gasket. A nickel plug fitted with a female standard tapered joint was used in attaching the sample container to a vacuum line for filling.

The platinum resistance thermometer (R_0 = 91 ohms) was constructed as described by Southard and Milner[8] and Meyers,[9] and was calibrated by comparing it at 43 points between 11 and 300°K. with a platinum resistance thermometer calibrated by the National Bureau of Standards. The ice point was taken to be 273.15°K. and one defined calorie was taken as 4.1840 absolute joules.

Refrigeration was provided by mounting the calorimetric

---

[1] T. Andrews, *Quart. J. Chem. Soc.* (*London*), **1**, 18 (1849); *Pogg. Ann.*, **75**, 335 (1848).

[2] V. Regnault, *Ann. chim. phys.*, [3] **26**, 268 (1849).

[3] W. M. Latimer and H. D. Hoenshel, THIS JOURNAL, **48**, 19 (1926).

[4] R. Surhmann and K. von Lude, *Z. Physik.*, **29**, 71 (1924).

[5] D. R. Stull, *Anal. Chim. Acta*, **17**, 133 (1957).

[6] R. A. Ruehrwein and H. M. Huffman, THIS JOURNAL, **65**, 1620 (1943).

[7] J. W. Mellor ("A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., New York, N. Y., Vol. II, 1922, p. 92) has stated "Magnesium foil is not attacked after lying for 5 years in contact with bromine."

[8] J. C. Southard and R. T. Milner, THIS JOURNAL, **55**, 4384 (1933).

[9] C. H. Meyers, *J. Research Natl. Bur. Standards*, **9**, 807 (1932).

assembly in the experimental cavity of a Collins Helium Cryostat.

Reliability of the Apparatus.—As a check on the operation of the automatic calorimeter, the heat capacity of *n*-heptane was measured between 15 and 300°K. and compared with the results of both the National Bureau of Standards[10] and the Bureau of Mines.[11] The heat capacity measurements were made with a platinum sample container, identical in construction to the magnesium container described above, with the exception that a short platinum tube was gold soldered to the container top and a soft glass tube sealed on for filling and closure. Otherwise the calorimetric apparatus and operation of the equipment are the same as used for the measurements on bromine. Two complete runs were made on a *n*-heptane sample of 99.97 mole % purity (these are more recent measurements than those reported in ref. 5) and the individual points were compared with the smooth values of Ginnings and Furukawa.[10] Except for the region below 50°K., the agreement is within 0.2 to 0.3%. Below 50°K., our results are higher, some by as much as 1.5%. When compared with the results of the Bureau of Mines,[11] the agreement below 50°K. is better, although our results are still higher; above 50°K., the agreement is again within 0.2 to 0.3%. The reason for the discrepancy below 50°K. is not clear, but it is felt that two factors are involved (1) decreasing sensitivity of the temperature measurement, and (2) temperature scale error, since some difficulty was encountered during calibration of the thermometers in this region (a leak in the standard thermometer and subsequent loss of the helium exchange gas was indicated).

A comparison of the entropy summaries from the three different laboratories, is indicative of the type of data obtained with the automatic calorimeter. The comparison is given in Table I.

TABLE I

COMPARISON OF *n*-HEPTANE ENTROPY SUMMARIES, CAL. MOLE^{-1} DEG.$^{-1}$

	Dow	N.B.S.[10]	Bu. Mines[11]
S, 0°K. to m.p.	35.748	35.655	35.733
Fusion	$\frac{3359}{182.56} = 18.399$	$\frac{3351}{182.56} = 18.355$	$\frac{3355}{182.56} = 18.378$
M.p. to 298.15°K.	24.322	24.379	24.397
S, liq. at 298.15°K.	78.469	78.389	78.508

The summary of Table I shows that, as stated above, both the results of this research and that of the Bureau of Mines are higher than that of the Bureau of Standards in the region below the melting point. This is primarily due to the differences arising from extrapolation of the heat capacity data to 0°K. Based on our experimental points from 15 to 30°K., we have used a Debye function with $\Theta = 125°$ and 6 degrees freedom, giving $S_{15°\text{K.}} = 0.522$ e.u. The Bureau of Mines[11] has used a Debye function with $\Theta = 121.7°$ and 5.5 degrees freedom, giving $S_{15°\text{K.}} = 0.518$ e.u., whereas the Bureau of Standards[10] uses $\Theta = 138.2°$ and approximately 7.2 degrees freedom to give $S_{15°\text{K.}} = 0.470$ e.u. Other small differences arise in the entropies of fusion.

While it is understood that the automatic calorimeter, in its present stage of development, is not capable of attaining the ultimate high accuracy of a manually operated precision calorimeter, it is believed that the apparatus described herein will be useful in most Third Law work. The advantages of the automatic operation are obvious.

Purification of Bromine.–Approximately one liter of commercial bromine (purity about 99.6 mole %) was refluxed for an hour from a mixture of 16 g. of chromic oxide dissolved in 200 ml. of concentrated sulfuric acid in order to remove organic material. The bromine then was distilled into a clean, dry, glass-stoppered bottle. Chlorine was removed by dissolving about 25 g. of freshly fused cesium bromide in 500 ml. of the freshly distilled bromine and allowing the solution to stand overnight. The bromine was then further treated to remove hydrobromic acid and water by distillation back and forth through a train containing alternate tubes of magnesium oxide and phosphorus pentoxide. In filling the calorimeter, the purified bromine was distilled in under its own vapor pressure from an all-glass vacuum system. A sample weighing 185.558 g. (1.1610 moles) was used in the heat capacity measurements. The molecular weight of bromine was taken to be 159.83.

The inert nature of the magnesium alloy container to attack by bromine can be shown by the purity determination. The first melting curve was obtained during the initial low temperature run, after the bromine had been in the sample container at room temperature for two days. An impurity of less than 0.001 mole % was indicated. Following this first run, some repairs were made to the liquefier and the bromine was allowed to stand at room temperature in the magnesium container for 14 days before the final purity determination was made during the third low temperature run. This second analysis of the reciprocal fraction melted *versus* equilibrium temperature indicated an impurity of less than 0.0015 mole %; evidently only a negligible amount of corrosion had occurred. The heat of vaporization measurements were made on a portion of the calorimetric sample after the low temperature measurements were completed.

Heat Capacity Data.—Three low temperature runs were made covering the range 15 to 310°K. The temperature rise was approximately 10% of the absolute temperature below 50°K. and 5 to 6° between 50°K. and room temperature. Tables of the observed heat capacity data are available on microfilm.[12] Smoothed heat capacities at even temperatures, taken from a plot of the data, are given in Table VI. The majority of the experimental points deviate from the smooth curve by less than 0.2%. No heat capacity anomalies were observed.

A comparison of the present results with those of Latimer and Hoenshel[3] for the solid shows that the latter's results are 7% high at 15°K., 1 to 3% low from 20 to 50°K., 2 to 4% high from 50 to 90°K. and shows essentially a random scatter of ±1% from 90°K. to the melting point. The larger scatter below 90°K. probably results from L. and H.'s use of an estimated temperature scale in this region.

The Melting Point Data.—The melting point of bromine was determined by adding increments of electrical energy to the solid near the melting point and noting the ensuing equilibrium temperature. The automatic shield control was kept in operation throughout this period, so that the heat of fusion also could be evaluated. The data obtained in this fashion are given in Table II.

TABLE II

MELTING POINT OF BROMINE

% Melted	Equilibrium temp., °K.
20	265.893
32	265.895
45	265.895
58	265.895
96	265.896
Accepted value	265.90 ± 0.05

Heat of Fusion.—The heat of fusion of bromine was measured in two different ways—by the incremental method described above and by continuous heating starting below the melting point and end-

---

[10] (a) D. C. Ginnings and G. T. Furukawa, THIS JOURNAL, **75**, 522 (1953); (b) T. B. Douglas, G. T. Furukawa, R. E. McCoskey and A. F. Ball, *J. Research Natl. Bur. Standards*, **53**, 139 (1954).

[11] U. S. Bureau of Mines, Petroleum Experiment Station, Bartlesville, Oklahoma, private communication.

[12] Document No. 5543, A.D.I. Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. Photoprints or 35 mm. microfilm copies available for $1.25 each.

TABLE III

HEAT OF FUSION OF BROMINE

Initial temp., °K.	Final temp., °K.	ΔH, cal./mole
261.17	268.66	2527.3[a]
260.17	269.19	2526.4[b]
261.74	269.70	2528.0[a]
261.95	269.86	2527.6[b]
	Accepted value	2527 ± 2
	Regnault[3] (1849)	2580

[a] Incremental heating. [b] Continuous heating.

ing several degrees above. In the incremental method, about nine hours were required to complete melting, whereas about five hours were required for continuous heating. The results obtained by the two methods, given in Table III, are in excellent agreement. Heat capacity data were used to correct for the initial heating of the solid and the final heating of the liquid.

TABLE IV

HEAT OF VAPORIZATION OF BROMINE AT 25°

Run	Grams vaporized	Rate, g. min.$^{-1}$	Av. temp., °C.	Cor. ΔH, cal. mole^{-1}
1	13.891	4.0	25.57	7429
2	18.130	4.0	25.26	7367
3	16.867	4.2	25.31	7349
4	15.949	0.61	25.40	7412
5	16.402	.63	25.52	7402
6	15.751	.60	25.24	7361
			Accepted value	7387 ± 27

Heat of Vaporization.—The heat of vaporization of bromine at 25° was measured in order to compare the Third Law and statistical entropies of the ideal gas. The bromine was contained in a platinum vaporizer of 24 cc. volume attached to an all glass system. Bromine left the vaporizer through a spray trap and then passed through a $^1/_8$ inch o.d. heat exchange spiral approximately one foot long, which was connected to a vacuum system. The vaporizer could be loaded through a straight lead-in tube also attached to the spray trap. This assembly fitted into a copper calorimeter can containing 225 g. of water, a stirrer, heater and a platinum resistance thermometer. The calorimeter can itself was placed inside a larger copper container submerged in a thermostated water-bath. The calorimeter can was insulated from the outer copper container with micarta spacers and the surrounding layer of air. The electrical heater inside the can was used for calibration. The temperature drop produced by vaporization and the corresponding rise during the electrical calibration were measured with the calibrated platinum resistance thermometer.

TABLE V

THE ENTROPY OF BROMINE, CAL. MOLE^{-1} DEG.$^{-1}$

0–15° (extrapolation)	0.650
15–265.90°K. (graphical)	24.136
Fusion, $\frac{2527}{265.90}$	9.504
265.90–298.15°K. (graphical)	2.094
Liquid at 298.15°K.	36.384 ± 0.10
Vaporization, $\frac{7387}{298.15}$	24.776
$S^0 - S$ actual (Berthelot eq.)	0.034
Compression, $R \ln \frac{760}{208}$	−2.575
Ideal gas at 298.15°K.	58.62 ± 0.20
S^0 from mol. data, 298.15°K.	58.65

TABLE VI

THERMODYNAMIC PROPERTIES OF BROMINE, CAL. MOLE^{-1} DEG.$^{-1}$

T, °K.	S^0	$\frac{H^0 - H_0^0}{T}$	$-\frac{F^0 - H_0^0}{T}$	$C_p{}^0$
15	0.650	0.479	0.171	1.725
20	1.325	.955	.370	3.040
25	2.144	1.501	.643	4.309
30	3.027	2.059	.968	5.364
35	3.921	2.595	1.326	6.226
40	4.799	3.095	1.704	6.929
45	5.650	3.554	2.096	7.500
50	6.465	3.973	2.492	7.968
55	7.244	4.354	2.890	8.355
60	7.985	4.701	3.284	8.683
65	8.692	5.019	3.673	8.969
70	9.366	5.310	4.056	9.228
80	10.628	5.829	4.799	9.682
90	11.791	6.280	5.511	10.074
100	12.870	6.677	6.193	10.419
110	13.879	7.031	6.848	10.728
120	14.824	7.352	7.472	11.011
130	15.718	7.643	8.075	11.273
140	16.563	7.911	8.652	11.520
150	17.365	8.159	9.206	11.755
160	18.130	8.392	9.738	11.981
170	18.864	8.609	10.255	12.200
180	19.570	8.814	10.756	12.416
190	20.245	9.009	11.236	12.632
200	20.898	9.196	11.702	12.851
210	21.530	9.376	12.154	13.077
220	22.144	9.549	12.595	13.315
230	22.742	9.719	13.023	13.570
240	23.324	9.885	13.439	13.848
250	23.896	10.049	13.847	14.157
260	24.458	10.215	14.243	14.504
Solid 265.90	24.786	10.312	14.474	14.732
Liquid 265.90	34.290	19.816	14.474	18.579
270	34.573	19.796	14.777	18.487
280	35.241	19.746	15.495	18.300
290	35.881	19.693	16.188	18.164
298.15	36.384	19.651	16.733	18.089
300	36.496	19.641	16.855	18.077

The operation of the platinum vaporizer was checked by measuring the heats of vaporization of water and benzene at 25° and comparing these with known values. Eight vaporization runs on water gave an average value of 585.3 ± 2.0 cal. g.$^{-1}$, as compared with the accepted value(13) of 583.6 cal. g.$^{-1}$. For benzene, six runs gave an average value of 103.7 ± 0.3 cal. g.$^{-1}$, compared with 103.6 cal. g.$^{-1}$ from ref. 13. In both cases, the measured values of this research agree with the accepted values within the experimental error, which is about 0.35%.

Six vaporization runs were made using 14- to 18-gram samples of bromine. Complete vaporization of the sample produced a temperature drop of about three degrees in the calorimeter can. The rate of vaporization was varied by inserting constrictions in the line. Corrections were applied for heat interchange (based on drift rates), for the amount of sample in the vapor phase at the start of a run, and for the absence of sample during the electrical calibration. All weights were corrected to vacuum. A summary of the measurements is given in Table IV. ΔC_p was used to correct the heats to 25°. There appears to be no observable dependence on rate of vaporization, although this was varied by a factor of seven. The uncertainty of 27 cal. mole^{-1}, or 0.35%, is in line with the experimental error found during the check runs on benzene and water.

The Entropy of Bromine.—The calorimetric entropy summary is given in Table V. The extrapolation below 15°K. can be handled in several ways. A Debye function with 5 degrees of freedom and $\Theta = 111°$ gives an excellent fit to the data between 15 and 30°K. and leads to an entropy at 15°K. of 0.607 e.u. However, objections have been raised to the use of a Debye function with more than 3 degrees of freedom on the basis that this violates the fundamental concepts of the Debye theory, even though the functions are being used in an empirical fashion. Such empirical use of Debye functions has become commonplace in the literature. The extrapolation also can be made using a Debye function with 3 degrees of freedom, together with the appropriate number of Einstein functions. The function adequately fits

$$3^{\circ}D\left(\frac{90}{T}\right) + 2^{\circ}E\left(\frac{111}{T}\right)$$

the data between 15 and 30°K. and gives an entropy at 15°K. of 0.650 e.u. This latter procedure has been used in evaluating the calorimetric entropy since it is perhaps more acceptable from a fundamental standpoint. The difference of 0.043 e.u. is probably not significant.

The entropy of liquid bromine at 25°, 36.38 cal. deg.$^{-1}$ mole^{-1}, can be compared with the value 36.6 ± 0.5 given by Kelley,(14) based on the data of Latimer and Hoenshel,(3) Andrews(1) and Regnault.(2)

The agreement between the calorimetric and statistical entropies in Table V is quite satisfactory and is well within experimental error. Such agreement is somewhat fortuitous, considering the uncertainty of 0.20 cal. deg.$^{-1}$ mole^{-1} in the calorimetric value. Thus it can be concluded that solid bromine retains no residual entropy at limiting low temperatures.

In calculating the entropy of compression, the data of Fischer and Bingle(15) were used to obtain the vapor pressure at 25°. The gas imperfection correction was evaluated with the aid of the Berthelot equation and the critical constants of Kobe and Lynn.(16)

The entropy of bromine in the ideal gas state has been calculated from molecular data by Evans, *et al.*(17) They have applied corrections for vibrational anharmonicity, rotational stretching and rotational–vibrational interaction. Their entropy value certainly should be good to within 0.01 e.u.

Thermodynamic Functions.—Values of the heat capacity, entropy, heat content and free energy functions for solid and liquid bromine, calculated from the experimental data, are given in Table VI.

MIDLAND, MICHIGAN

---

(13) N. S. Osborne and D. C. Ginnings, *J. Research Natl. Bur. Standards*, **39**, 453 (1947).

(14) K. K. Kelley, *U. S. Bur. Mines, Bull.*, **447**, 29 (1950).

(15) J. Fischer and J. Bingle, THIS JOURNAL, **77**, 6511 (1955).

(16) K. A. Kobe and R. E. Lynn, *Chem. Revs.*, **52**, 117 (1953).

(17) W. H. Evans, T. R. Munson and D. D. Wagman, *J. Research Natl. Bur. Standards*, **55**, 147 (1955).