of Br_2 as a third body for Br atom recombination fall close to the curve of Russell and Simons[3] for the plot of log of the recombination rate constant *vs.* boiling point suggests that the intermolecular attractions which halogen molecules exert on halogen atoms are not of a highly specific chemical type.

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The Entropy of Iodine. Heat Capacity from 13 to 327 K. Heat of Sublimation[1]

BY D. A. SHIRLEY AND W. F. GIAUQUE

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The heat capacity of iodine has been measured from 13 to 327°K. The thermodynamic properties, C_p, S^0, $-(F^0 - H_0^0)/T$ and $(H^0 - H_0^0)/T$ have been tabulated to 330°K. The entropy of the solid at 298.15°K. = 27.76 cal. deg.$^{-1}$ mole^{-1}, the heat of sublimation at 0°K., $\Delta H_0^0 = 15658$ cal. mole^{-1} and the heat of sublimation at 298.15°K. was found to be 14922 cal. mole^{-1}.

The generally accepted value 27.9 cal. deg.$^{-1}$ mole^{-1} for the entropy of solid iodine at 298.15°K. rests less on the rather inadequate heat capacity measurements from which it was calculated, than on its successful use in a calculation[2] of the heat of sublimation of iodine from the vapor pressure data over a temperature range of nearly one hundred degrees. A value based on sufficiently complete heat capacity data will have a greater reliability and the present work was done to provide these data.

Experimental Procedure and Iodine Sample.—Undoubtedly the reason why more complete calorimetric data on the important substance iodine have not become available long ago is that it will react with typical low temperature calorimeters. To avoid this difficulty a special calorimeter was constructed from a 90-cc. Pyrex bottle, blown to fit approximately into a copper cylindrical shell with a diameter of 4.4 cm. and length 9.5 cm. The bottle had a small glass stoppered neck which extended slightly above a small monel neck and collar at the top of the copper shell. The final closure was by means of a copper cap which could be soldered to the monel collar. Monel was used to prevent excessive heat conduction to the calorimeter during the soldering process. As usual, the interior of the calorimeter was filled with helium to improve heat conduction. As would be expected the glass bottle increased the time required for thermal equilibrium and thus caused some increase in the magnitude of the corrections for heat transfer between the calorimeter and its surroundings; however, this involved only a minor decrease in accuracy. In general the calorimetric equipment was similar to that described previously.[3] A gold resistance thermometer–heater was used for high precision temperature measurements and Laboratory Standard Thermocouple No. 105 was used as a temperature reference. The thermocouple was checked for reliability during this work with the following results: 0.02° high at both the triple point (13.94°K.) and the boiling point (20.36°K.) of hydrogen; 0.01° high at the triple point (63.15°K.) and 0.06° high at the boiling point (77.34°K.) of nitrogen.

The sample of iodine was taken from Baker and Adamson Lot No. LO98 (resublimed) and the maximum limits of impurities given were: non-volatile, 0.010% and Cl and Br, 0.005%.

An amount of 253.271 g. *in vacuo* was used for the measurements. 0°C. was taken as 273.15°K. and 1 defined calorie was taken equal to 4.1840 absolute joules.

The Heat Capacity and Thermodynamic Properties of Iodine.—The experimental data are given in Table I and the derived thermodynamic functions are given for C_p, S^0, $(F^0-H_0^0)/T$ and $(H^0-H_0^0)/T$ at even temperature intervals in Table II.

TABLE I

HEAT CAPACITY OF IODINE, CAL. DEG.$^{-1}$ MOLE^{-1}

Cal. deg.$^{-1}$ mole^{-1}			Mol. wt. = 126.91		
T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
13.62	2.143	78.18	10.30	192.96	12.27
15.71	2.644	84.61	10.51	202.06	12.34
18.04	3.322	90.99	10.73	209.66	12.44
20.55	4.018	97.27	10.88	216.84	12.47[a]
23.33	4.754	104.01	11.05	223.32	12.64
26.16	5.359	110.99	11.21	231.05	12.67
29.24	6.051	118.43	11.37	239.68	12.67
32.30	6.510	126.10	11.60	248.58	12.73
36.13	7.051	133.48	11.64	256.85	12.75
39.93	7.549	140.90	11.72	264.96	12.83
44.24	8.043	148.36	11.83	273.32	12.73
49.26	8.520	155.65	11.99	282.02	12.86
54.52	8.891	162.71	12.00	291.14	12.88
60.05	9.361	170.04	12.07	301.22	13.12
65.79	9.757	177.56	12.15	311.19	13.15
71.87	10.044	185.21	12.20	321.93	13.33

[a] This result is uncertain by ±1% due to water vapor in the apparatus and is thus given no weight.

The data of Lange[4] cover the range 9 to 52° K. His measurements deviate from the present work by ± 1% near and somewhat above the boiling point of hydrogen and above 30°K. they are 2 to 4% high.

A Debye extrapolation below 10°K. gives 0.350 cal. deg.$^{-1}$ mole^{-1} as the entropy less the nuclear spin effect at that temperature.

The thermodynamic functions for iodine gas have been given in the Bureau of Standards Tables.[5] We have applied a small correction to convert these values to 0°C. = 273.15°K. instead of 273.16° K. and have also altered the values given for 0 and 25° slightly in addition since these values appear to have been interpolated in the main series without complete accuracy. The only satisfactory method of interpolating such values to 0.001 appears to be a difference plot with a function correspond-

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[1] This work was supported in part by the National Science Foundation.

[2] W. F. Giauque, THIS JOURNAL, **53**, 507 (1931).

[3] W. F. Giauque and C. J. Egan, *J. Chem. Phys.*, **5**, 45 (1937).

[4] E. Lange, *Z. physik. Chem.*, **110**, 343 (1924).

[5] "National Bureau of Standards," Series III, June 30, 1948; March 1, 1954.

TABLE II

THERMODYNAMIC PROPERTIES OF SOLID IODINE

	Cal. deg.$^{-1}$ mole^{-1}		0°C. = 273.15°K.	
T, °K.	C_p	S^0	$-(F^0 - H_0^0)/T$	$(H^0 - H_0^0)/T$
10	0.963	0.350	0.090	0.260
15	2.450	1.010	0.277	0.733
20	3.866	1.912	0.570	1.342
25	5.140	2.916	0.938	1.978
30	6.156	3.948	1.354	2.594
35	6.909	4.955	1.797	3.158
40	7.557	5.921	2.252	3.699
45	8.110	6.844	2.711	4.133
50	8.571	7.724	3.169	4.555
55	8.972	8.560	3.621	4.939
60	9.343	9.356	4.066	5.290
70	9.955	10.846	4.930	5.916
80	10.353	12.202	5.755	6.447
90	10.693	13.441	6.541	6.900
100	10.911	14.581	7.289	7.292
110	11.199	15.636	8.001	7.635
120	11.407	16.620	8.679	7.941
130	11.587	17.540	9.326	8.214
140	11.716	18.404	9.943	8.461
150	11.853	19.216	10.535	8.681
160	11.966	19.985	11.102	8.883
170	12.068	20.713	11.646	9.067
180	12.158	21.406	12.170	9.236
190	12.243	22.066	12.673	9.393
200	12.325	22.696	13.159	9.537
210	12.441	23.300	13.627	9.673
220	12.539	23.879	14.080	9.799
230	12.617	24.438	14.518	9.920
240	12.678	24.977	14.943	10.034
250	12.726	25.495	15.355	10.140
260	12.767	25.995	15.754	10.241
270	12.813	26.478	16.143	10.335
280	12.873	26.945	16.520	10.425
290	12.941	27.397	16.887	10.510
298.15	13.011	27.758	17.180	10.579
300	13.027	27.838	17.245	10.593
310	13.145	28.266	17.594	10.672
320	13.313	28.686	17.934	10.752
325	13.404	28.892	18.100	10.792
330	(13.488)	(29.098)	(18.266)	(10.832)

ing to a rigid rotator and harmonic oscillator. Convenient functions for the latter have been given by Johnston, Savedoff and Belzer.[6] We find at 250, 273.15, 298.15, 300, 400 and 500°K. the values 52.759, 53.469, 54.176, 54.227, 56.588 and 58.455, respectively, for $-(F^0 - H_0^0)/T$ of $I_2(g)$. All intermediate values needed were interpolated as mentioned above. At 298.15°K., S^0 for $I_2(g) = 54.176$ cal. deg.$^{-1}$ mole^{-1}.

The heat of sublimation of iodine at the absolute zero may now be calculated from the accurate vapor pressure measurements of Baxter, Hickey and Holmes[7] and Baxter and Grose[8] by use of the relationship

$$\Delta F^0/T = -R \ln P = \Delta(F^0 - H_0^0)/T + \Delta H_0^0/T$$

The results are given in Table III. It is evident that there is no significant drift in the values of ΔH_0^0 calculated from the data over the range 273.15 to 368.15°K.

TABLE III

HEAT OF SUBLIMATION AND VAPOR PRESSURE OF IODINE

	Inter. mm.		Cal. mole^{-1}		
T, °K.	$P_{\text{expt.}}$	$P_{\text{calcd.}}$	ΔH_0^0 from $P_{\text{expt.}}$	ΔH_T^0 calcd.	Ref.
273.15	0.030	0.03051	15667	15025	7
288.15	.131	.1286	15647	14964	7
298.15	.305	.3080	15664	14922	7
303.15	.469	.4669	15655	14901	7
308.15	.699	.6971	15656	14880	7
313.15	1.025	1.028	15659	14858	7
318.15	1.498	1.494	15657	14836	7
323.15	2.154	2.147	15656	14814	7
323.15	2.154	2.147	15656	14814	8
328.15	3.084	3.052	15651	14791	7
328.15	3.069	3.052	15654	14791	8
333.15	4.285	4.293	15659	14768	8
338.15	5.962	5.969	15658	14744	8
343.15	8.196	8.216	15659	14720	8
348.15	11.21	11.22	15656	14696	8
353.15	15.09	15.15	15659	14672	8
358.15	20.21	20.28	15660	14647	8
363.15	26.78	26.95	15663	14619	8
368.15	35.24	35.52	15663	14575	8
		Av.	15658 ± 3		

The equivalent calculation made earlier by Giauque[2] with less accurate data was used to show that the entropy of the solid approaches the entropy due to the nuclear spin multiplicity and unlike hydrogen it does not deviate in a specific manner due to the *ortho* and *para* states which are well-known in the gas. The present more reliable data confirm the earlier result. While an additional decrease in the entropy due to spin states will occur at extremely low temperatures, it is of course convenient to delete this effect from the entropy values used in ordinary thermodynamic calculations. The entropy value 27.76 cal. deg.$^{-1}$ mole^{-1} given here is the absolute value less the nuclear spin effect.

The heat of sublimation at temperature T may be calculated from $\Delta H_T = \Delta(H^0 - H_0^0)_T + \Delta H_0^0$. In columns 3 and 5 of Table III calculated values of the vapor pressure and heat of sublimation of iodine are given at the several temperatures based on the average value of $\Delta H_0^0 = 15658$ cal. mole^{-1}.

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