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The Free Energy, Entropy and Heat Capacity of Bromine and of Hydrogen Bromide from Spectroscopic Data

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The free energy, entropy and heat capacity of gaseous bromine and of hydrogen bromide have been computed for the temperature range 200–1600°K. The equilibrium constants for the reaction $\text{Br}_2 = 2 \text{ Br}$, obtained from these numbers and the spectroscopic heat of dissociation, differ from Bodenstein's values by more than his apparent

experimental error. Calculations for the dissociation of hydrogen bromide give results which agree with the e.m.f. measurements of Bodenstein and Geiger, but are in definite disagreement with the experiments of von Falckenstein when the latter are corrected for the dissociation of bromine.

IN A recent paper,¹ Brown, who had effected the rotational analysis of the bromine spectrum,² reported that a calculation of the equilibrium constant for the dissociation of diatomic into monatomic bromine "by the Gibson and Heitler equation" leads to values of $\log K$ which were uniformly about 0.15 less than the experimental results of Bodenstein.³ This discrepancy was so surprising in view of the excellent agreement found by Gibson and Heitler⁴ in the case of the iodine dissociation that it seemed worth while to recompute the equilibrium. Brown gave no details of his calculation, but presumably treated the rotational-vibrational levels of the bromine molecule as those of a rigid rotator combined with a harmonic oscillator; it did not seem likely that the error introduced by this simplification could account for the serious discrepancy (0.7 cal./deg. in $R \ln K$) which he reported, but we have nevertheless computed the free energy, entropy and heat capacity for the temperature range 200–1600°K, taking account of the interaction and stretching terms in the formula for the energy levels. Since the dissociation of hydrogen bromide into hydrogen and bromine has been measured by von Falckenstein,⁵ we have also carried out similar calculations for hydrogen bromide.

Brown² gives for $\text{Br}^{79} - \text{Br}^{81}$, $\epsilon_v = 323.2(v + \frac{1}{2}) - 1.07(v + \frac{1}{2})^2$, $B_v = 0.08077 - 0.000275v$, $D = -2.03 \times 10^{-8}$. Owing to the existence of the two isotopes of bromine in almost equal proportions (0.505 : 0.495), the three diatomic varieties will exist at high temperatures in the proportions 0.255 of 79–79, 0.500 of 79–81, 0.245 of 81–81. As far as the calculation of thermodynamic reaction quantities is concerned, it has been shown⁶ that it is permissible to calculate the free energy and entropy as if the substance were non-isotopic, provided that this procedure is adopted for each of the reactants and products, and that the spectroscopic constants used in the computation are averages, the result of properly weighting the constants for each of the isotopic varieties. Calculation shows that such effective constants for bromine are (within the limits of experimental error) just those for 79–81 and the calculation can thus be carried out with these constants as if for a non-isotopic bromine of molecular weight 159.83; it is necessary, of course, to add the usual symmetry correction for a homonuclear diatomic molecule, $-R \ln 2$, in spite of the fact that all rotational levels are present in 79–81 with full statistical weight.

The free energy, entropy and heat capacity entered in Table I⁷ were obtained from Gordon

¹ W. G. Brown, *J. Am. Chem. Soc.* **54**, 2394 (1932).

² W. G. Brown, *Phys. Rev.* **39**, 777 (1932).

³ Bodenstein, *Zeits. f. Elektrochemie* **22**, 327 (1916).

⁴ Gibson and Heitler, *Zeits. f. Physik* **49**, 465 (1928).

⁵ von Falckenstein, *Zeits. f. physik. Chemie* **68**, 270 (1909).

⁶ Giauque and Overstreet, *J. Am. Chem. Soc.* **54**, 1731 (1932); see also Gordon and Barnes, *J. Phys. Chem.* **36**, 2292 (1932) and reference 1.

⁷ In the calculations, the values of the universal constants are those given in *Int. Crit. Tab.*, Vol. I.

and Barnes,⁸ Eqs. (6), (9) and (11). For temperatures less than 700°K, the quantities $(\ln Q_v + \epsilon_0 hc/kT)$, S_v/R , C_v/R , \bar{v} , \bar{v}^2 , s_1 , s_2 , c_1 , c_2 were obtained by interpolation in their Tables I–XI; for temperatures $\geq 700^\circ\text{K}$, $\omega_e hc/kT$ lies beyond the range of the tables and therefore the calculation was carried out as shown in their Example 4, the integrations starting from $v=11$, as in that example. There is an additional small correction that contributes to the heat capacity at the highest temperatures but not to the entropy or free energy; this is due to the excited electronic states⁹ 14,734 and 15,891 cm^{-1} above the normal $^1\Sigma$ state of the molecule. The first of these excited states is unclassified and no correction can be applied as yet but the second is presumably $^3\Pi$ with $\epsilon_v' = 169.7(v' + \frac{1}{2}) - 1.913(v' + \frac{1}{2})^2$ and $B' = 0.0592$. To a good enough approximation, the resulting contribution to the heat capacity is given by

$$6R \cdot \left(\frac{Ahc}{kT} \right)^2 \cdot e^{-Ahc/kT} \cdot \left[\frac{B_0}{B_0'} \cdot \frac{\sum e^{-\epsilon_v' hc/kT}}{\sum e^{-\epsilon_v hc/kT}} \right]$$

where $A = 15,891$. The numerical value of this term is only 0.004 for 1600° and 0.002 for 1500° and is included in the numbers entered in Table I.

In the case of hydrogen bromide, the constants¹⁰ are $\epsilon_v = 2647(v + \frac{1}{2}) - 44(v + \frac{1}{2})^2$, $B_v = 8.342 - 0.225v$, $D = -0.000,325$, and the quantities necessary for the calculation can be obtained for the whole temperature range from the tables. The effect of the H² isotope of hydrogen on the effective spectroscopic constants has been ignored, since this is vanishingly small¹¹ except for artificially enriched samples.

None of the values of $-(F^\circ - E_0^\circ)/T$ and S° in Table I includes the nuclear spin contribution. For bromine (since $j_s = 3/2$) this would amount to $R \ln 16$ and must be added to the entries, as must the isotope contribution, if "absolute" values are desired; for hydrogen bromide, the spin contribution would be $R \ln 8$.

⁸ Gordon and Barnes, J. Chem. Phys. **1**, 297 (1933).

⁹ W. G. Brown, Phys. Rev. **38**, 1179 (1931), also reference 2; Weizel, *Bandenspektren*, p. 385, Leipzig (1931).

¹⁰ Czerny, Zeits. f. Physik **44**, 235 (1927); Kratzer, Zeits. f. Physik **3**, 289 (1920); Weizel, *Bandenspektren*, p. 327.

¹¹ Urey and Rittenberg, J. Chem. Phys. **1**, 137 (1933).

TABLE I.

T°K	Bromine			Hydrogen Bromide		
	$-(F^\circ - E_0^\circ)/T$	S°	C_P°	$-(F^\circ - E_0^\circ)/T$	S°	C_P°
200	47.822	55.291	8.272	37.786	44.703	6.959
250	49.509	57.162	8.486	39.330	46.256	6.961
298.1	50.868	58.667	8.618	40.550	47.481	6.964
300	50.918	58.722	8.622	40.594	47.526	6.964
350	52.130	60.058	8.713	41.663	48.599	6.970
400	53.196	61.226	8.777	42.589	49.530	6.983
450	54.146	62.263	8.824	43.407	50.354	7.006
500	55.006	63.194	8.859	44.139	51.094	7.039
550	55.789	64.040	8.888	44.802	51.767	7.085
600	56.509	64.814	8.911	45.409	52.386	7.141
650	57.176	65.528	8.931	45.968	52.960	7.204
700	57.797	66.191	8.948	46.487	53.496	7.274
750	58.377	66.809	8.963	46.971	54.001	7.350
800	58.922	67.388	8.977	47.426	54.477	7.426
850	59.437	67.932	8.989	47.854	54.930	7.503
900	59.923	68.446	9.001	48.259	55.364	7.580
950	60.384	68.933	9.011	48.644	55.773	7.656
1000	60.823	69.396	9.022	49.010	56.168	7.730
1050	61.242	69.836	9.031	49.360	56.547	7.801
1100	61.643	70.257	9.041	49.695	56.911	7.869
1150	62.026	70.659	9.050	50.016	57.263	7.934
1200	62.394	71.044	9.059	50.325	57.602	7.996
1250	62.747	71.414	9.068	50.623	57.929	8.055
1300	63.087	71.770	9.077	50.911	58.247	8.111
1400	63.732	72.443	9.094	51.456	58.851	8.214
1500	64.334	73.071	9.113	51.969	59.421	8.307
1600	64.898	73.660	9.132	52.451	59.960	8.390

It is, perhaps, of interest to note what error would have been introduced in Table I if the second order terms in the energy level formula had been ignored. If, for 1600°K, bromine had been treated as a harmonic oscillator of frequency $\omega_e(1-2x) = 321.1$ plus a rigid rotator ($B = 0.080,77$), the entries¹² in Table I would have been 64.826, 73.494 and 8.927. In the case of $-(F^\circ - E_0^\circ)/T$, neglect of the anharmonic term in x causes an error of 0.036 in the final result, neglect of the interaction terms which take account of the change in B with v , an error of 0.022 and neglect of the stretching terms involving D , an error of 0.014. In the case of the heat capacity at the same temperature, the corresponding errors are 0.112, 0.060 and 0.030, respectively, which (with the contribution 0.004 from the excited $^3\Pi$ state) just account for the difference between the value 8.927 and the entry in the table. In the case of hydrogen bromide at

¹² Using the notation of reference 8 for bromine at 1600°K, we find that $(\ln Q_v + \epsilon_0 hc/kT) = 1.4055$, $S_v/R = 2.2941$, $C_v/R = 1.0493$, $\bar{v} = 3.16$, $\bar{v}^2 = 23.9$, $s_1 = 6.98$, $s_2 = 78.9$, $c_1 = 8.20$, $c_2 = 186$; $\beta_1 = 0.003,405$, $\beta_2 = 1.16 \times 10^{-5}$, $\bar{d} = d_0(1 + 0.0068\bar{v}) = 0.00709$.

1600°, the assumption that its spectrum could be treated as that of a harmonic oscillator of frequency 2559 plus a rigid rotator with $B = 8.342$, would lead to the values 52.418, 59.884 and 8.260 instead of the numbers entered in the table.

THE THERMAL DISSOCIATION OF BROMINE

From Brown's value of the heat of dissociation,⁹ 1.962 volts, ΔE_0° for the reaction $\text{Br}_2 = 2 \text{ Br}$ is 45,230 cal. The values of $-(F^\circ - E_0^\circ)/T$ for monatomic bromine can be readily computed since the "State Sum" for monatomic bromine is simply $(4 + 2 \cdot \exp[-3685hc/kT])$ where 3685 cm^{-1} is the separation¹³ of the $^2P_{3/2}$ and $^2P_{1/2}$ states of the bromine atom. The resulting $-R \ln K_1 = R \ln (P_{\text{Br}_2})/(P_{\text{Br}})^2$ are entered in Table II and correspond to the continuous curve of Fig. 1; the figure also shows the experimental results of Bodenstein³ and of Perman and Atkinson¹⁴ as recalculated by Lewis and Randall.¹⁵ It is evident that there is still a difference of about

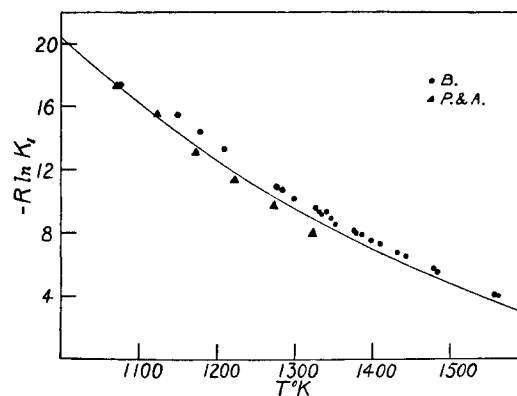


FIG. 1. The equilibrium constant for the thermal dissociation of bromine. $K_1 = (P_{\text{Br}})^2/(P_{\text{Br}_2})$.

half a calorie per degree between Bodenstein's results and the entries in Table II, and that this discrepancy is considerably larger than his apparent experimental error. This result is rather surprising, since there is no reason to distrust the spectroscopic data and Bodenstein's figures give every internal evidence of self-consistency.

THE DISSOCIATION OF HYDROGEN BROMIDE

From the entries of Table I, Giauque's data for hydrogen¹⁶ and the calorimetrically determined heat of formation of gaseous hydrogen bromide, *viz.*, 12,100 cal., it follows that $\Delta F_{298.1}^\circ$ for the reaction $\frac{1}{2}\text{H}_2 + \frac{1}{2}\text{Br}_2(g) = \text{HBr}(g)$ is -12,850 cal. and that ΔE_0° is -11,990 cal.¹⁷ The resulting values of $R \ln K_2 = R \ln (P_{\text{HBr}})/(P_{\text{H}_2})^{1/2} \cdot (P_{\text{Br}_2})^{1/2}$ and of ΔF° for the reaction are given in Table II; these numbers agree with those given by Nernst's free energy equation¹⁸ (which was based on the e.m.f. measurements of Bodenstein and Geiger)¹⁹ within about a quarter of a calorie per degree in $R \ln K_2$ up to 1500°K.

Direct measurements on this equilibrium have been carried out by von Falckenstein,⁵ the partial pressure of the hydrogen in the equilib-

T°K	Br ₂ (g) = 2Br		$\frac{1}{2}\text{H}_2 + \frac{1}{2}\text{Br}_2(g) = \text{HBr}(g)$	
	-R ln K ₁	ΔF° kcal.	R ln K ₂	$-\Delta F^\circ$ kcal.
298.1	128.92	38.43	43.12	12.85
300	127.95	38.39	42.86	12.86
350	106.09	37.13	37.09	12.98
400	89.68	35.87	32.75	13.10
450	76.89	34.60	29.36	13.21
500	66.65	33.33	26.63	13.32
550	58.26	32.04	24.40	13.42
600	51.26	30.76	22.53	13.52
650	45.33	29.47	20.94	13.61
700	40.25	28.17	19.58	13.70
750	35.83	26.87	18.39	13.79
800	31.96	25.57	17.35	13.88
850	28.55	24.27	16.43	13.97
900	25.51	22.96	15.61	14.05
950	22.78	21.64	14.88	14.13
1000	20.33	20.33	14.21	14.21
1050	18.11	19.02	13.61	14.29
1100	16.09	17.70	13.06	14.37
1150	14.24	16.38	12.57	14.45
1200	12.54	15.05	12.11	14.53
1250	10.97	13.72	11.68	14.61
1300	9.53	12.39	11.30	14.68
1400	6.94	9.72	10.60	14.84
1500	4.69	7.04	9.99	14.99
1600	2.71	4.34	9.46	15.14

¹³ Turner, Phys. Rev. **27**, 397 (1926).

¹⁴ Perman and Atkinson, Zeits. f. physik. Chemie **33**, 215, 577 (1900).

¹⁵ Lewis and Randall, *Thermodynamics*, p. 514 (1923).

¹⁶ Giauque, J. Am. Chem. Soc. **52**, 4816 (1930).

¹⁷ Datta, Zeits. f. Physik **77**, 404 (1932), gives 87,700 as the heat of dissociation of hydrogen bromide from measurements on continuous absorption. Combining this value with the heat of dissociation of hydrogen (102,900 cal., according to Richardson, Proc. Roy. Soc. A123, 466 (1929)) and of bromine, ΔE_0° is -13,600 cal. Datta's value, however, is based on a considerable extrapolation.

¹⁸ Nernst, Zeits. f. Elektrochemie **15**, 687 (1909).

¹⁹ Bodenstein and Geiger, Zeits. f. physik. Chemie **49**, 70 (1904).

rium mixture being determined by means of a semi-permeable platinum diaphragm. He found, as mean values for the forward and reverse reaction, P_{H_2} to be 1.91, 2.78 and 4.17 mm at 1297° , 1381° and 1495° , respectively,²⁰ with total pressures of 761, 764 and 777 mm. For these three temperatures, $1/K_1$ is 126, 41.5 and 11.2 from Table II, so that P_{Br_2} is 0.807, 0.830 and 0.707 mm and P_{HBr} is 756, 756 and 765 mm. The resulting $R \ln K_2$ for the three temperatures are 12.74, 12.34 and 12.11, respectively, in definite disagreement with the values found by interpolation from Table II, *viz.*, 11.32, 10.72 and 10.02. Thus the supposed agreement between

von Falckenstein's results and those of Bodenstein and Geiger comes solely from the fact that the calculations based on von Falckenstein's measurements ignored the dissociation of diatomic into monatomic bromine. It should be noted in passing that Giauque and Overstreet⁶ found a similar disagreement in the case of Löwenstein's measurements²¹ on the dissociation of hydrogen chloride. The entries in Table II are of course uncertain to the extent of the error in the calorimetrically determined heat of formation of hydrogen bromide but von Falckenstein's $R \ln K_2$, after correction for the bromine dissociation, cannot be made self-consistent by any adjustment in the heat of formation.

²⁰ The dissociation of diatomic into monatomic hydrogen is negligible at these temperatures; see reference 16.

²¹ Löwenstein, *Zeits. f. physik. Chemie* **54**, 715 (1906).