of (HSO_4^-) and the impossibility of determining $\gamma_{HSO_4^-}\ \gamma_{Br^-}/\gamma_x$. In sufficiently dilute solutions these quantities might be computed from the Debye–Hückel limiting law; unfortunately, accurate rate measurements would be practically impossible in this region. The occurrence of generalized acid catalysis in this reaction might be tested by using solutions containing small concentrations of potassium bromide and a moderately weak, chemically inert acid in the presence of a high constant concentration of an inert salt, e. g., sodium perchlorate.

Other ionic reactions might be expected to show a similar effect; for example, the oxidation of hydriodic acid by chloric acid,[5] or the basic hydrolysis of the nitrourethan ion.[6]

[5] Bray, J. Phys. Chem., 7, 92 (1903).

[6] Brönsted and Delbanco, Z. anorg. allgem. Chem., 144, 248 (1925).

The Entropy of Bromine from Spectroscopic Data

BY WELDON G. BROWN*

A recent fine structure analysis of the visible absorption bands of bromine by the writer[1] has provided data from which accurate values of the thermodynamic constants of bromine may be calculated. These calculations involve nothing essentially new, although certain consequences of a rather unique isotope situation become emphasized. In this note the entropy calculated from band spectrum data is to be compared with a less accurate value obtained from experimental measurements of the specific heat.

There are two isotopes of bromine, 78.92 and 80.92, which, according to Aston's measurements,[2] are equally abundant. These give rise to three kinds of molecules, Br_2^{79}, $Br_2^{79,81}$ and Br_2^{81}, in the proportions $1:2:1$, respectively. A slight difference in the molecular constants of the Br_2^{79} and Br_2^{81} molecules leads to slightly different entropies, but because of their equal abundance this becomes smoothed out when, in calculations of thermodynamic constants, one uses the data for the $Br_2^{79,81}$ molecule. There is an additional effect due to the lack of symmetry which results in the entropy of $Br_2^{79,81}$ being greater than the entropy of either of the symmetrical species by $R \ln 2$ per mole, or $1/2\, R \ln 2$ per mole of the actual mixture since this species constitutes one-half of ordinary bromine.

The moment of inertia of bromine is sufficiently large and the centrifugal

[1] Brown, Phys. Rev., 39, 777 (1932).

[2] Aston, Proc. Roy. Soc. (London), 115, 487 (1927); 132, 489 (1931).

deformation sufficiently small to make applicable the approximation in summation of the rotational energy terms used by Gibson and Heitler, and by Giauque,[3] in the case of iodine, namely

$$Q_{rot.} = \sum_i p_i e^{-\epsilon_i/kT} = \frac{4\pi^2 IkT}{h^2} = \frac{T}{2c_2 B}$$

where c_2 is the second radiation constant, and B is the fine structure constant obtainable directly from the spectral data. This expression applies to a symmetrical molecule. The entropy is then obtained by the well-known formula[4]

$$S^\circ = R\left[\ln Q + T\cdot\frac{d\ln Q}{dT}\right]$$

The band spectrum constants for the normal electronic state of $Br_2^{79\,81}$ are as follows. The subscripts refer to the zero vibrational state.

$$B_0 = 0.08077 \qquad\qquad \omega_0 = 322.2$$
$$\alpha = 0.00027 \qquad\qquad \omega_0 x_0 = 1.07$$

In the following table the molal entropies (ideal gas, pressure one atmosphere, at 298.1°K.), calculated as indicated above, are given for each of the three molecular species, together with the entropy of the 1:2:1 mixture exclusive of the entropy of mixing. It is to be noted that the entropy of the mixture, 59.32 E. U., is equal to the entropy of $Br_2^{79,81}$ minus $\frac{1}{2} R \ln 2$.

	$S_{trans.}$	+	$S_{vib.}$	+	$S_{rot.}$	=	$S^\circ_{298.1}$
$Br_2^{79,79}$	41.07		1.30		16.19		58.56
$Br_2^{79,81}$	41.11		1.31		17.59		60.01
$Br_2^{81,81}$	41.15		1.32		16.23		58.70
1:2:1 mixture	$\frac{1}{4}(58.56)$		$\frac{1}{2}(60.01)$		$\frac{1}{4}(58.70)$		59.32

Comparison with specific heat measurements can be made most conveniently at the melting point temperature, 265.8°K., at which the vapor pressure, according to Henglein,[5] is 44.12 mm. From the band spectrum data we calculate $S_{265.8°}$ ($p = 44.1$ mm.) $= 61.69$ E. U., assuming a perfect gas. The specific heat measurements of Suhrmann and v. Lude[6] extend down to 20.5°K., but are few in number and somewhat erratic. From the smoothed points given by them we obtain, for the entropy of solid bromine at its melting point, 25.5 E. U., the uncertainty in which must be of the order 1.0 E. U. The entropy of vaporization at the melting point is 36.6 E. U. if we accept Henglein's value for the heat of vaporization, 9740 cal. The experimental value for the entropy of bromine gas at this temperature and pressure is then $25.5 + 36.6 = 62.1$ E. U., in good agreement with the value 61.69 calculated from spectroscopic data.

[3] Giauque, THIS JOURNAL, **53**, 507 (1931).

[4] Giauque, *ibid.*, **52**, 4808 (1930).

[5] Henglein, *Z. Physik*, **11**, 1 (1922).

[6] Suhrmann and v. Lude, *ibid.*, **29**, 71 (1924).

However, the entropy, as calculated above, cannot be used for chemical purposes without reference to the entropy of mixing of isotopes. This entropy of mixing is $^3/_2\,R$ ln 2 per mole, while for the free atoms (or for HBr, for example) it is R ln 2 per mole. If, by convention, the entropy of mixing of the atoms is to be excluded, the value for the entropy which we have calculated must be reduced by $^1/_2\,R$ ln 2. For bromine gas in its standard state this results in the value $S^{\circ}_{298.1} = 58.63$ E. U. The value is thus the same as if the additional entropy of $Br_2{}^{79,81}$ resulting from its additional states had been considered as a part of the entropy of mixing of isotopes. This places Br_2 on the same basis as HBr, the entropy of which has been calculated from band spectrum data by Giauque.[7]

The equilibrium constants for the dissociation of bromine at high temperatures, calculated by means of the Gibson and Heitler[8] equation and the band spectrum constants, are in poor agreement with the experimental values of Bodenstein.[9] The discrepancy, for which no explanation is offered, amounts to 0.15 in log K and is constant with temperature. The writer plans a further check on the entropy of bromine through the use of the experimental data for the dissociation of iodine bromide. An analysis of the iodine bromide absorption bands, which will provide the necessary spectroscopic data, is now in progress. ·

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[7] Giauque, THIS JOURNAL, **50**, 2193 (1928).

[8] Gibson and Heitler, Z. *Physik*, **49**, 465 (1928).

[9] Bodenstein, Z. *Elektrochem.*, **22**, 327 (1916).

The Recombination of Hydrogen Atoms

BY GEORGE E. KIMBALL

In a recent paper Steiner[1] has made some very interesting calculations on the rate of recombination of hydrogen atoms by triple collisions with hydrogen atoms and molecules as third bodies. He assumes that the recombination takes place in two steps: (1) the formation of an atom pair, or quasi-molecule, and (2) the stabilization of the energy-rich atom pair by collision with a third body during its lifetime τ. Throughout this work Steiner has overlooked the fact that there is another, equally probable, mechanism for the recombination. This mechanism may also be divided into two steps, but these are now: (1') collision of a hydrogen atom with a hydrogen molecule, and (2') collision of this quasi-molecule with a new hydrogen atom to form two hydrogen molecules.

Steiner finds theoretically that the diameter of a hydrogen atom in (1)

[1] Steiner, Z. *physik. Chem.*, B15, 249 (1932).