THE DIELECTRIC CONSTANT AND MOLECULAR WEIGHT OF BROMINE VAPOR

By Linus Pauling*

Abstract

It is shown that the conclusion reached by Bramley in a recent article that bromine has the formula $(Br_2)_6$ is inconsistent with previous results relating to the density of this substance in the gaseous state and that it is not theoretically justified by the considerations presented by the author.

In a recent paper entitled "Measurements of Velocity of the Synthesis of Hydrogen Bromide by Capacity Change" Arthur Bramley[1] has reported that his experiments lead to a value of 1.0128 (reduced to 0° and 1 atm.) for the dielectric constant of bromine vapor, from which he draws the conclusion that bromine has the formula $(Br_2)_6$. Assuming that bromine vapor consists of diatomic molecules, he calculates from Lorentz's formula $\kappa-1=C\rho$, where ρ is the density and C a constant evaluated from measurements on liquid bromine, that the dielectric constant κ should be 1.0022. Furthermore, from the index of refraction n of bromine vapor, 1.00115 (reduced to 0°C. and 1 atm.) and the equation $\kappa=n^2$, he finds a nearly equal value 1.0023. Since his observed value of $\kappa-1$ is almost six times that calculated for Br_2, he concludes that bromine vapor must have the formula $(Br_2)_6$.

This conclusion is, however, not in accord with density investigations. In an extensive series of vapor-density experiments, E. P. Perman[2] has shown that except at very high temperatures bromine vapor consists entirely of diatomic molecules. Vapor-densities (referred to that of hydrogen as unity) from one series of experiments at 14.7-15° are given in the accompanying table.

Pressure in mm.	98.65	63.70	32.10	16.65
Vapor-density	80.3	80.4	81.3	83.3

Professor Perman concludes "These results show that, on approaching the liquid state, bromine has no tendency to form molecules with more than two atoms. This agrees with the results of Paterno and Nasini[3] by Raoult's method, which indicated molecules Br_2 in aqueous and acetic acid solutions." He further states that experimental errors

* National Research Fellow in Chemistry.

[1] A. Bramley, Phys. Rev. **25**, 858 (1925).

[2] E. P. Perman, Proc. Roy. Soc. **48**, 45 (1890).

[3] Paterno and Nasini, Deutsch. Chem. Ges., Ber. **21**, 2153 (1888).

account for the apparent increase in vapor-density at very low pressures; this increase of course could not be adduced as evidence of the formation of molecules with more than two atoms, for this would contradict the principle of Le Chatelier.

The value reported by Bramley for the dielectric constant of bromine vapor is surprisingly high, in view of the fact that diatomic bromine molecules presumably do not have large electric moments. It is unfortunate that the investigator published none of his experimental data on capacity measurements and determinations of the partial pressure of bromine, which would have permitted checks on his calculations. It seems probable that the value 1.0128 is incorrect because of large experimental errors, for the capacity measurements represented in the graphs were subject to remarkably large fluctuations, amounting, in fact, in some cases to as much as fifty percent of the total change produced by the reaction. The investigator attributed these fluctuations in his measurements to variations in the amounts of bromine vapor present as Br_2 and as $(Br_2)_6$. Since $(Br_2)_6$ is probably not present this explanation is of course unsatisfactory; even if it were present, familiar statistical mechanical considerations indicate that such enormous fluctuations could not be expected to occur in a chemical equilibrium involving such a large number of molecules.[4]

This uncertainty concerning the experimental work throws doubt also on the final conclusion reached by the investigator that the specific photochemical rate for the chemical reaction considered has a negative temperature coefficient.

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[4] That such fluctuations in a chemical equilibrium do not occur is at once evident if one considers their influence for example on the pressure of the system. From Fig. 2 of Bramley's paper it is seen that the measured capacity of the cell had for a period of two minutes a value greater than the equilibrium value by an amount of over 15% of the total change corresponding to the complete combination of hydrogen and bromine to form hydrogen bromide. Since the capacity measurements are made on all the gas between the two plates in his cell, this result requires that if the volume of the gas (about 1 cc) were kept constant, the pressure would show variations due to the postulated fluctuations from the equilibrium state. As there is liquid bromine present the pressure is at least 150 mm; hence the explanation of his observations advanced by Bramley would require that pressure variations greater than 20 mm and lasting more than two minutes occur in this system. This is, however, obviously not possible; we are led to accept the alternative explanation that the variations are due to experimental error.