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LETTERS TO THE EDITOR

Prompt publication of brief reports of important discoveries in physics may be secured by addressing them to this department. Closing dates for this department are, for the first issue of the month, the twentieth of the preceding month; for the second issue, the fifth of the month. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents.

Resonance Spectrum of Bromine

It has been found possible to excite a resonance spectrum of nine terms in bromine vapor at very low pressure. The λ5461 line of the mercury arc was used in the excitation of the fluorescence. Two types of light furnace were used. In the first type a large mercury arc was constructed concentrically about a tube 70 cm in length containing the bromine vapor. In the second type two powerful mercury arcs, vertical and operated in series at 5 to 10 amperes, were mounted inside an elliptical reflector with the bromine tube. Each arc was connected to the vacuum line and was equipped with a third 10,000 volt electrode to facilitate starting.

The bromine resonance tube was connected to the high vacuum line as well as to a reservoir in which solid bromine was maintained at −63°C, by immersion in melting chloroform. The bromine vapor pressure was accordingly about 0.2 mm. Plates were obtainable in 3 hours on a Steinheil three prism spectrograph. Wave-length measurements were made from microphotometer traces.

Insofar as could be determined on the low dispersion plates, each line was actually a doublet of wave number separation equal to 22. All of the terms were included fairly accurately by the series formula:

$$1/\lambda_n = 18{,}307.6 - 326n + 2n^2.$$

In this expression, n represents the positive order of the line, with the use of Wood's resonance spectrum notation, and λ_n is the wave-length of the short wave-length component of the doublet of n^{th} order. The wave-lengths of the shorter components of all but one of the nine orders are given in Table I.

TABLE I.

Order	Wave-length	Order	Wave-length
1	5559.8A	5	5975.5A
2	5659.9	6	6089.0
3	(masked by the yellow lines of mercury)	7	6199.5
		8	6316.0
		9	6437.0
4	5863.5		

It is of interest to compare the iodine resonance spectra found by Wood with the bromine series. In the case of iodine with excitation by λ5461 the series is expressed by:

$$1/\lambda_n = 18{,}307.6 - 213n + 0.6n^2.$$

The separation of the doublets for iodine is 5 wave numbers. The bromine resonance spectrum is exceedingly less intense than the iodine spectrum.

It is not certain that the true bromine rotation doublets have been resolved. The presumable long wave components are much weaker than the short wave components and in some cases seem to be absent entirely.

HAROLD PLUMLEY
Physics Department,
University of Chicago,
February 22, 1933.

On the Statistical Foundation of Debye's Theory of Electrolytes

Professor V. K. La Mer has recently drawn my attention to some paradoxical inconsistencies in the thermodynamic evaluation of the free energy of electrolytes if expressions for the ionic potentials are used which have been derived by a consistent application of the well-known Debye-method. These difficulties though pointed out six years ago in a paper by Gronwall, La Mer and Sandved have not hitherto found a satisfactory explanation. They can be summarized in the statement that the free energy of an electrolytic solution seems to depend on the way in which the ions are assumed to be charged (either simultaneously or successively) while the initial and final state are kept constant. This would mean that the free energy at constant temperature is no longer a function of the instantaneous state alone but also of its previous history—in contradiction to the principles of thermodynamics.

As a result of a closer investigation it has been found that the Debye-method *in general* leads to expressions which do not obey the integrability relations of thermodynamics. More specifically, it can be stated that the limiting law (without ionic diameters) satisfies the thermodynamic requirements. Expressions which contain individual ionic diameters as well as all higher approximations for ions of nonsymmetrical valence-type do not conform to the integrability conditions. This explains also the paradox mentioned above.

A more detailed publication will follow soon.

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February 27, 1933.