

*Citation:*

A.F. Holleman, On the nitration of ortho- and metadibromobenzene, in:  
KNAW, Proceedings, 8 II, 1905-1906, Amsterdam, 1906, pp. 678-680

the radiation emitted by the photosphere ; so it stops almost  $\frac{2}{3}$ , and only a small fraction of this absorbed energy leaves the Sun in the form of radiation, emitted by the atmosphere itself. After all, more than half of the radiation coming from the photosphere is retained by the absorbing layer, and we cannot suppose it to go back to the interior without violating the second law of thermodynamics. As long as it has not been shown how the solar atmosphere may get rid of that immense quantity of energy continually supplied and never radiated, similar considerations will remain very unsatisfactory.

Our problem appears to be much less intricate when viewed from the stand-point taken by SCHMIDT <sup>1)</sup>, though the mathematical treatment will not be easy. A uniformly luminous sphere surrounded by a concentric, perfectly transparent refracting envelope, will offer the aspect of a disk the brightness of which diminishes towards the limb. This has been established approximately by SCHMIDT for the case of a homogeneous, sharply limited envelope. It is easily understood that a similar result must be obtained when assuming a transparent atmosphere of gradually decreasing density and refractive power ; but then, of course, the rate at which the luminosity varies on the disk will depend on the law of density variation. We may proceed a little farther, and accept SCHMIDT's hypothesis that the incandescent core of the Sun is *not* a sphere with a sharp boundary, but a gaseous body the density and radiating power of which are smoothly diminishing along the radius. In this way, I think, we dispose of premises from which it seems possible to derive an explanation of the general aspect of the solar disk without involving into such serious difficulties as were hitherto encountered.

**Chemistry.** — "*On the nitration of ortho- and metadibromobenzene.*"  
By Prof. A. F. HOLLEMAN.

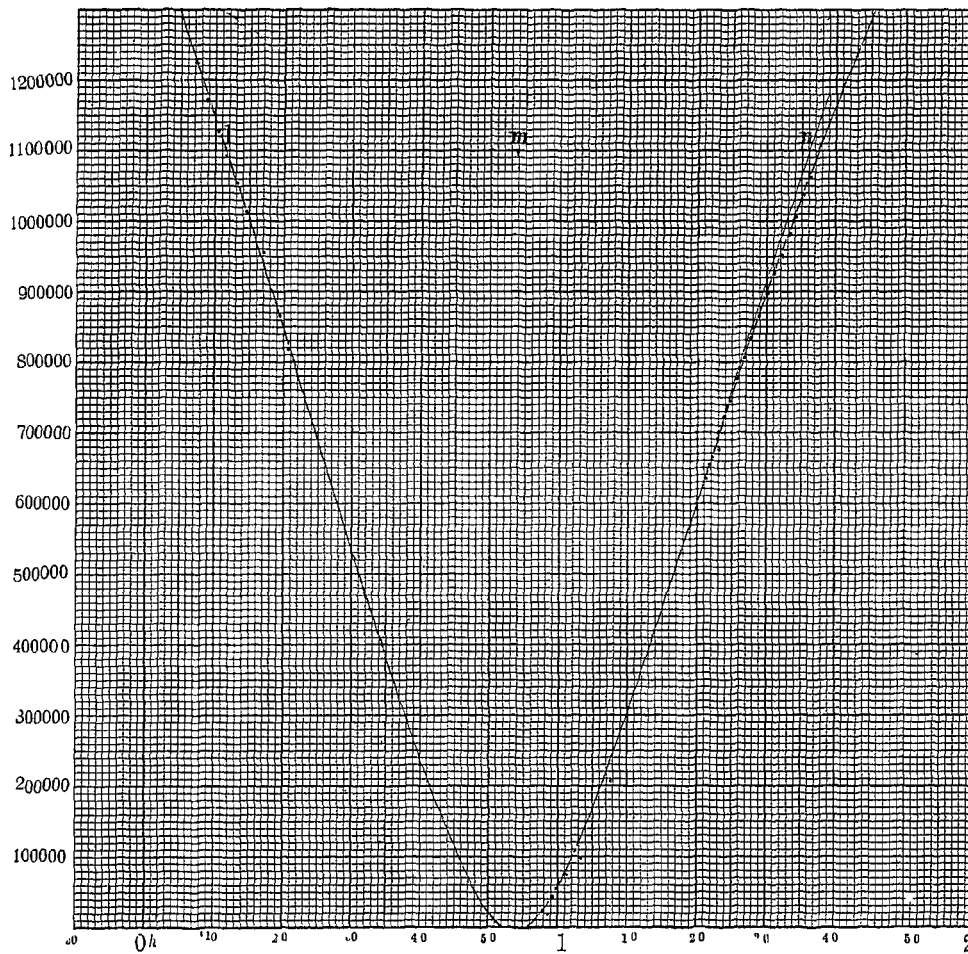
(Communicated in the meeting of January 27, 1906).

After the disturbing influence which the halogen atoms exercise on each other's directing influence in regard to the nitro-group, had been noticed in the nitration of the dichlorobenzenes, it was necessary to extend this research to the nitration of the dibromobenzenes so as to be able to find the connection between the results with the dichloro- and dibromocompounds and to compare the same with the result of the nitration of the corresponding monohalogen benzenes.

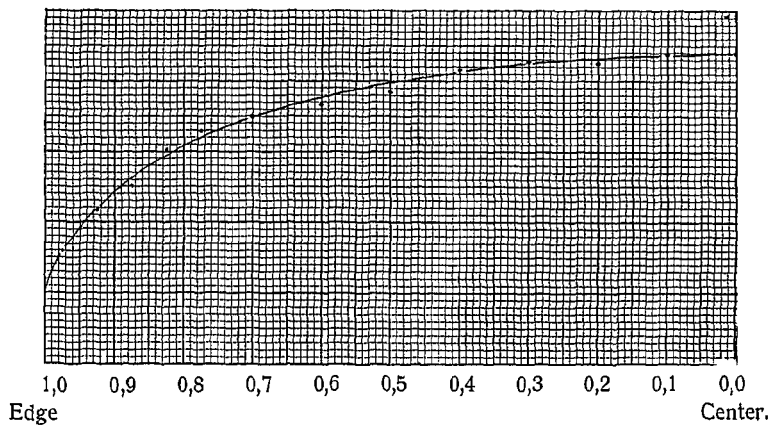
<sup>1)</sup> A. SCHMIDT, Physik. Zeitschr. 4, 282, 341, 453, 476 ; 5, 67, 528. (1903 and 1904).

W. H. JULIUS A new method for determining the rate of decrease of the radiating power from the center toward the limb of the solar disk.

Middle part of the radiation curve obtained during the solar eclipse of August 30 1905.



Radiating power across the solar disk



The necessary experiments have been considerably delayed, because it appeared that the ortho- and meta-dibromobenzenes had not as yet been obtained in a perfectly pure condition, and the search for a good method absorbed much time. We have at last succeeded in preparing *m*-dibromobenzene from perfectly pure *m*-bromoaniline by diazotation in a dilute hydrobromic acid solution, according to a direction given by ERDMANN for another purpose. *Meta*-dibromobenzene has a sp. gr. of 1.960 at 18.5°, and solidifies at — 7°. It is true that F. SCHIFF incidentally mentions (M. 11, 335) that he has met with *m*-dibromobenzene solidifying at + 1°, without saying how he has obtained the same, but there is good reason for doubting the correctness of this statement. In this case, the product obtained by me and my coadjutors (SIRKS, SLUITER) with its 8° lower solidifying point should contain about 16% of impurities. In the nitration of our *m*-dibromobenzene, however, a product is obtained having a sp. gr. such as was to be expected from a mixture of the isomers (Br<sup>1</sup> : Br<sup>3</sup> : NO<sub>2</sub><sup>4</sup>) and (Br<sup>1</sup> : Br<sup>3</sup> : NO<sub>2</sub><sup>2</sup>) brought together in the proportion indicated by the solidifying point, so that a contamination of our preparation with such a large quantity of another substance is altogether out of the question; moreover, on distillation our preparation yielded two fractions within one degree which both possessed practically the same sp. gr. and solidifying point.

*O*-dibromobenzene which was obtained in an analogous manner from *o*-bromoaniline, had a sp. gr. of 1.996 at 11° and solidified at + 6°.

The preparation of the six dibromonitrobenzenes was carried out in a manner analogous to that of the six dichloronitrobenzenes, described by me in the "Recueil" 23, 357.

The composition of the products of nitration of the dibromobenzenes was determined from their solidifying point and their sp. gr. and led to the results united in the subjoined table with the composition of the products of nitration of the dichlorobenzenes. The temperature of the nitration was 0°. (See p. 680).

In ortho-dibromobenzene the disturbance of the directing power of the one halogen atom owing to the presence of the other one is, therefore, much less than in the case of orthodichlorobenzene because in the first one 18.3 and in the second only 7.2% of by-product is formed, whilst monobromo- and monochlorobenzene yield, respectively, 29.8 and 37.6% of by-product. On the other hand, the disturbance caused by the entry of the nitro-group between the two halogen atoms in *m*-dibromobenzene is very nearly equal to that in *m*-dichlorobenzene, therefore much larger in regard to the ortho-

	Quantity of by-product in %	Quantity of by-prod. in 100 parts of main prod.
<i>o</i> -C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	7.2	7.8
<i>m</i> -C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	4.0	4.1
<i>o</i> -C <sub>6</sub> H <sub>4</sub> Br <sub>2</sub>	18.3	22.4
<i>m</i> -C <sub>6</sub> H <sub>4</sub> Br <sub>2</sub>	4.6	4.8
C <sub>6</sub> H <sub>5</sub> Cl	29.8	42.0
C <sub>6</sub> H <sub>5</sub> Br	37.6	60.5

compounds. One would feel inclined to attribute this to "steric disturbances" introduced into Organic Chemistry by V. MEIJER, were it not that the specific volume of chlorine and of bromine in the dichloro- and dibromobenzenes differs but little.

Perhaps it is rather the atomic weight of chlorine and bromine which has some connection with the above. For further particulars concerning this research the "Recueil" should be consulted.

*Amsterdam, Org. chem. Lab. of the University, January 1906.*

**Chemistry.** — "*The introduction of halogen atoms into the benzene core in the reduction of aromatic nitro-compounds*". By Dr. J. J. BLANKSMA. (Communicated by Prof. A. F. HOLLEMAN).

(Communicated in the meeting of January 27, 1906).

Some time ago I cited and communicated some experiments<sup>1)</sup> which showed that, in some cases, in the reduction of aromatic nitrocompounds, halogen atoms may be removed from the benzene core. In 1901 an article by PINNOW<sup>2)</sup> appeared in which a fairly large number of cases are mentioned, where halogen atoms are introduced into the benzene core in the reduction of aromatic nitrocompounds. PINNOW endeavours to find the conditions under which this secondary reaction is as much as possible prevented in order to prevent formation of halogenised amidocompounds as by-products, alongside the amidocompounds.

<sup>1)</sup> Proc. 30 March 1904, Recueil 24, 320.

<sup>2)</sup> Journ. für Prakt. Chem. (2) 63, 352.