## Huygens Institute - Royal Netherlands Academy of Arts and Sciences (KNAW)

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Calculating however with the same value of x the proportion of the nitro-m-chlorotoluenes formed by the nitration of m-chlorotoluene, there is no such gratifying concordance. This is due to the fact, that in this case the two substituents act no longer independently of each other, but that both methyl and chlorine al direct the entering nitro group to the places 2, 4, and 6. Now we must not simply add the figures for the isomers, but we must take the resultant of their action, as is indicated in the scheme below, in which it is assumed that the benzene nucleus is a regular hexagon.



If we calculate in this way the proportion of the isomers, we find indeed a gratifying concordance between calculation and experiment:



Amsterdam, org. chem. lab. of the Univ.

October 1912.

**Physics.** — "On the polarisation impressed upon light by traversing the slit of a spectroscope and some errors resulting therefrom." By Prof. P. ZEEMAN.

In a communication "The intensities of the components of spectral lines divided by magnetism"<sup>1</sup>), I drew attention to the fact that by the polarizing action of the grating the ratio of the observed intensities of the components of a triplet differs considerably from

<sup>1</sup>) These Proceedings, October 26 1907.

the ratio present in the light as it is emitted by the source. In some cases the observer sees only a faint central component and two intense outer components, whereas the true ratio is just the reverse. In order to obtain in the image the true ratio of the intensities I suggested to introduce before the slit of the spectroscope a quartz plate of such a thickness, that the incident light is rotated through an angle of  $45^{\circ}$ .<sup>1</sup>)

Besides the mentioned polarizing effect of the grating there is a second cause tending to make the ratio of the intensities of components of different direction of vibration in the image different from that corresponding to the constitution of the emitted light. I mean the polarization impressed upon light which traverses fine slits. Since FIZEAU<sup>2</sup>) this effect is well-known, but the errors which may ensue from it in investigating spectral lines magnetically resolved have not yet been pointed out.

The following simple experiment is easily made. A vacuum tube charged with mercury is placed in a horizontal magnetic field. The emitted light is analysed by means of a spectroscope-securing great illumination and high resolving power. The slit must be under the control of the observer at the eye-piece. The two yellow mercury lines, which are resolved into triplets or the green mercury line, which splits into three groups each of three lines may be observed. If the slit is rather wide then the central components of the yellow triplets may have twice the intensities of the outer ones; the three groups of the green mercury line have about the same integral intensity if not wholly resolved. If the slit (made of platinoid) be narrowed gradually, the intensity of all components decreases, but that of the central component or group more than that of the outer ones. At last the central components of the triplets and even the middle group of the brilliant green line can be made to disappear entirely<sup>\*</sup>), whereas the outer components remain visible. From these observations we cannot but conclude that the vibrations perpendicular to the slit at last hardly traverse the narrow slit.

The correctness of this explanation may be inferred from the fact that the *ratio* of the intensities changes gradually during the narrowing of the slit.

The view may be controlled by the following observations. If a

<sup>8</sup>) This extreme case involves the use of an exceptionally narrow slit rarely employed in practice.

<sup>&</sup>lt;sup>1</sup>) l. c. p. 291.

<sup>&</sup>lt;sup>2</sup>) FIZEAU. Ann. de Chim. et de Phys. Vol. 63 p. 385. 1861.

quartz plate, rotating the plane of polarisation through 90° be introduced before the slit of the spectroscope, then only the outer components of the resolved spectral line can be made to disappear.

A second observation was made with the slit only of the spectroscope. The lens of the collimator being removed the slit of the spectroscope could be seen distinctly while viewing along the axis of the spectroscope. Looking through a calcspar rhomb the slit appears double. With a wide slit, illuminated by the radiating tube, the two images exhibit the same intensity; a narrowing of the slit gradually makes the image due to the vertical vibrations more brilliant than the other one.

I will mention two cases in which errors may be introduced by the polarization impressed by the narrow slit. This happens in the first place in the case mentioned above of the comparison of the intensities of resolved components vibrating in different planes. In the second place when the resolution of lines originally diffuse toward one side of the spectrum is investigated, *apparent* shifts and dissymmetrical separations may result. Is the original spectral line diffuse toward the red then a decrease of the intensity of the central line of a triplet will cause an apparent shift relatively to the outer components toward the violet. The reverse will be the case if the original line is diffuse toward the violet.

The apparent shift now under consideration has had no influence in the experiments concerning a change of wavelength by magnetic forces of the line Hg 5791, which the author<sup>1</sup>) and (independently) GMELIN<sup>2</sup>) discovered at the same time. Its existence could be demonstrated also by the method of FABRY and PEROT, a method not dependent upon the use of a narrow slit.

It is a favourable circumstance that a quartz plate introduced before the slit of the spectroscope and giving a rotation of the plane of polarization of  $45^{\circ}$ , eliminates at the same time as well errors due to the polarising action of the grating as those caused by the narrowness of the slit.

<sup>&</sup>lt;sup>1</sup>) ZEEMAN, Change of wavelength of the middle line of triplets. These Preceedings February 29, 1908, in print in the Dutch edition March 12, 1908, in the English March 29, 1908.

<sup>&</sup>lt;sup>2</sup>) P. GMELIN. Über die unsymmetrische Zerlegung der gelben Quecksilberlinie 5790 im magnetischen Felde. Physik. Zeitschr. p. 212 (eingegangen 24 Febr. 1908) appeared April 1, 1908.

## **Physics.** — "Contribution to the theory of binary systems. XXI. The condition for the existence of minimum critical temperature." By Prof. J. D. VAN DER WAALS.

Already in the theory of binary systems concerning perfectly miscible substances we repeatedly found the case of a minimum critical temperature, and already in my "Théorie moléculaire" I derived the condition for the existence of such a minimum, and expressed it in the form:

$$\frac{a_{12}}{b_{13}} < \frac{a_1}{b_1} \text{ and } \frac{a_{12}}{b_{12}} < \frac{a_2}{b_2} \cdot$$

In my investigations of recent times, in which I chiefly intended to ascertain the conditions for the only partial miscibility, my attention was again directed to the possibility of the existence of a minimum  $(T_{k,x})$ , and I have come to the conclusion that there is also question of such a minimum  $(T_k)_x$  for the mixture ether-water, but that the value of x for  $T_k$  minimum lies very close to the ether side. If as second component we always take the substance with the greater value for the size of the molecules, so ether in the case under consideration, the value of x is 1 or nearly 1. In the experimental investigation by Dr. SCHEFFER my expectations have proved to be correct, and he has even succeeded in observing the course of the p, T-line for given value of x up to a certain distance from the ether side, and found it in perfect harmony with the course predicted by theory for completely miscible substances. He has even succeeded in reaching the value of x at which the plaitpoint entirely coincides with the critical circumstances for such a mixture taken as homogeneous. According to this experimental investigation, of which I express my sincere admiration, the value of x at which the minimum value of  $(T_k)_c$  occurs, is so close to the ether side that we may put this value =1, and the second value mentioned of x is at a distance of more than 0,3 from the ether side, so that we may put it smaller than 0,7. For smaller value of x the non-miscibility, as a new circumstance occurring in this system, prevents the observation of the course of the ordinary plaitpoint line.

In my investigation of the causes of imperfect miscibility and of the different forms which can occur for only partial miscibility, I was led to apply a simplification in the theory, which I thought that though certainly of influence on the quantitative accuracy, would be of little or no influence on the qualitative course of the pheno-