

**Chemistry.** — *The influence of the solvent on the optical rotation dispersion.* By A. L. TH. MOESVELD. (Communicated by Prof. ERNST COHEN.)

(Communicated at the meeting of October 27, 1928).

1. In a communication "on the influence of pressure on the reaction velocity and the function of the medium" A. L. TH. MOESVELD and WILHELMA A. T. DE MEESTER<sup>1)</sup> have directed attention to a statement of LANDOLT's<sup>2)</sup> concerning the influence of solvents on the rotation of dissolved active compounds, and the latter has enlarged on this subject in her thesis<sup>3)</sup>. The conception about the mutual influence of solvent and dissolved substance, given in the two papers just mentioned, enabled us to explain well-known facts about the function of pressure during the process of chemical reactions, while new inferences could be confirmed by experiments. In this conception the medium has no longer exactly the same composition throughout; the composition of the environment of a molecule of the dissolved substance differs from the gross composition of the solvent. At the same time a deformation appears in the molecule of the dissolved substance. The conception of LANDOLT about the function of the solvent with respect to the rotation of a dissolved optically active substance appears best from his own words:

"Erscheinungen solcher Art (the change of the rotation by dissolving in another solvent) lassen sich vielleicht durch die Vorstellung erklären, dass, wenn zwischen die Moleküle einer aktiven Substanz (Terpentinöl) andere Moleküle (Alkohol) treten, dadurch eine gewisse Modification in der Struktur der ersteren hervorgebracht wird, und zwar in der Weise, dass in jedem Molekül der gegenseitige Abstand der Atome, ihre Anordnung im Raume, sowie die Art der Atombewegungen, sich etwas ändert. Dies wird in um so stärkerem Grade der Fall sein, je grösser die Zahl der inaktiven Teilchen ist."

In greater support of the views developed, it seemed to us of special importance to trace in how far changes of rotation occur, when bornylacetate to different concentrations is dissolved in mixtures of water and alcohol of different composition. Various reasons made it impossible to complete this investigation in this direction, the more so as from preliminary

<sup>1)</sup> Verslagen der Kon. Akad. v. Wet. Amsterdam, 36, 827 (1927), see p. 831, note 1. Proc. 30. 1039 (1928) esp. p. 1043, footnote 1.

<sup>2)</sup> Das optische Drehungsvermögen. Braunschweig 1898, p. 210.

<sup>3)</sup> The influence of pressure on the reaction velocity and the function of the medium. Thesis, Utrecht, 1928, specially chapter X, p. 115.

investigations appeared that the accuracy would have to be considerably raised in order to draw definite conclusions. The investigation described hereafter, which is on a more or less modified plan, has given results which are in complete agreement with the views mentioned above.

2. This modification concerns what follows: Though, of course the exposition in the last paragraph on page 116 of the thesis mentioned above, about the advantages of the study of a physical constant which refers to only one of the components of the solution, holds good in every respect. yet the choice of the optical rotation for a definite colour is somewhat arbitrary. When for a definite colour the rotation changes from solvent to solvent, it may also be expected that the dispersion will every time have a different value. That is to say that for every colour another relation of the optical rotations for two different solvents will be found, so that the optical rotation alone can never be a measure for a contingent deformation. It is however possible to deduce a constant from the optical rotations for different colours, which is in close relation to the deformation caused by the solvent.

3. This constant is given by the equation of DRUDE <sup>1)</sup>, which for an optically active substance indicates the connection between optical rotation and the wavelength of the light for which the rotation obtains. It can be written in the form:

$$\alpha_{\lambda} = \Sigma \frac{k_a}{\lambda^2 - \lambda_a^2}$$

in which equation  $\alpha_{\lambda}$  represents the rotation for light of the wavelength  $\lambda$ , while  $k_a$  and  $\lambda_a$  represent constants. The constants are controlled by the place of the absorptionbands, and the constants are connected with the forces which resist a displacement of the position of equilibrium of the vibrating system in the molecule which undergoes the influence of the passing light.

For DRUDE, who applied this equation to a few instances, a summation of two terms was sufficient. Afterwards the equation has pretty well fallen into disuse, until LOWRY <sup>2)</sup>, in co-operation with many co-workers, pointed out the importance of this equation in a long series of papers. In a great number of cases a single term is sufficient, even for rotations for light from the extreme ultra violet to the infra red, but moreover he made an important application of this equation for the classification of cases of anomalous rotary dispersion, in which at least two terms of DRUDE's equation are necessary in order to be able to represent the measurements.

<sup>1)</sup> Lehrbuch der Optik, Leipzig 1900.

<sup>2)</sup> J. Chem. Soc. **103**, 1062, 1067, 1322 (1913); **105**, 81, 94 (1914); **107**, 1173, 1187, 1195 (1915); **115**, 300 (1919); **121**, 532 (1922); **125**, 1465, 1593, 2511 (1924); **127**, 238, 604 (1925); C. R. **181**, 909 (1925).

If the rotations satisfy a relation, consisting of one term of DRUDE's equation, when therefore

$$a_{\lambda} = \frac{k}{\lambda^2 - \lambda_0^2},$$

there is a linear relation between  $\frac{1}{a_{\lambda}}$  and  $\lambda^2$ , so that, either graphically or by calculation, one can, in a certain case quickly ascertain, whether one term will suffice. If this proves indeed to be the case, the values of the constants  $k$  and  $\lambda_0$  can be determined with rather great accuracy. If, however, there is not such a linear relation, it is pretty well impossible to deduce, with any accuracy, values for the four constants  $k_a$ ,  $k_b$ ,  $\lambda_a$  and  $\lambda_b$ , which are then necessary, seeing that it is always possible to deduce numerous groups of values of the constants, which offer as close a connection to the data obtained by experiment.

When it appeared that the rotations for pure bornylacetate as function of the light used, could very well be represented by an equation as follows :

$$a_{\lambda} = \frac{k}{\lambda^2 - \lambda_0^2},$$

we have made it our first object to execute measurements of the rotatory dispersion with the bornylacetate, while this substance was dissolved in different media and in mixtures of them. From these measurements, which could all be represented by equations of one term, we then deduced the values of  $k$ , and we have attached our views to the changes which this constant undergoes when the solvent is modified.

4. Though endeavours have not been wanting to calculate the magnitude of the rotation by a theoretical method, at least in a simple case, the result is not very satisfactory. So it is to be understood that the change which a solvent brings about in the rotation cannot be predicted either. When, however, the value of the rotation for a number of colours can be well represented by an equation of DRUDE with only one term, it is possible to say something about the influence of mixed solvents on the magnitude of  $k$ . Seeing that this constant is connected with the firmness with which the vibrating system is bound to its position of equilibrium, deformations of the molecule must be reflected in the value of the constant. It is very well possible that the normally appearing deformations have such a slight effect on the value of  $k$ , that the accuracy of the polarimetric measurements is insufficient to show those changes with certainty, but we can in the first place expect greater changes in  $k$  in those cases in which the choice of the solvent makes a maximal deformation possible. In agreement with our previous views, we shall have to choose a solvent consisting of two components with divergent properties, so that the atmosphere of a molecule of bornylacetate differs in its composition according to the side of the

molecule which we examine ; then deformation appears very sharply in consequence of the forces which are called into being by the inclination to restore equilibrium in the composition of the solvent by diffusion.

Each of the four groups which are ranged round the asymmetrical C-atom is therefore under the influence of a differently composed atmosphere, so that the electric moment of these groups is also changed in different ways, with consequently a modification in the elasticity of the vibrating system. When complications do not occur, as chemical binding of the solvent, we may, moreover, expect that the direction of change of  $k$  is the same, whatever the antagonistic components of the solvent may be, because the cause of the deformation, mentioned in the preceding paragraph, always acts in the same way.

5. In the preliminary investigations, in which, however, we discussed only the influence on the rotation, not on the dispersion constant, the solvent consisted of water and alcohol. In this case the composition of the medium can be changed only to a certain extent, because, when the amount of water is too great, the ester molecules flee from the medium altogether, and combine to drops. For our actual investigation we have made a somewhat different choice. We decidedly favour the opportunity for deformation when the molecules of bornylacetate must act as link between the component parts of the medium. If they are not completely miscible, while addition of bornylacetate brings about complete miscibility, it is obvious that we can picture the molecule of bornylacetate as the link between atmospheres of strongly divergent composition. A maximal deformation would m.m. occur, when the quantity of bornylacetate was just large enough to bring about complete miscibility. In connection with the small quantity of ester which, in the systems investigated up to this time, was sufficient to bring about the perfect miscibility, which is of course contingent with a slighter rotation of the solutions, we have provisionally let this point rest, and have, in the first place, occupied ourselves with measurements in different solvents and in mixtures of them.

6. Our provisional measurements had shown us that we should have to carry accuracy to the highest standard possible ; we have succeeded in the way described hereafter, to determine rotations, also for red and for violet light, which are accurate to within two or three hundredths of a degree.

We obtained light of different colours with the help of the monochromator of VAN CITTERT ; in order to get sufficient intensity, especially for red and for violet light, we took as source of light a self regulating arc lamp (of LEITZ, current 4 Amp.). With very closely adjusted slits sufficient light is retained ; the narrow spectrum region which is isolated in this way, combined with a half shadow angle of  $2^\circ$ , made a very sensitive adjustment possible.

As instrument we used the polarisation apparatus according to LANDOLT-LIPPICH with triple field of vision. By means of a vernier hundredths of a degree could be read. The polarimeter tube, provided with a double jacket, had a length between the cover glasses of 22.00<sup>5</sup> cm. at 30°.0 C. With the help of a hot-air motor, provided with a little pump, it was possible to pass through the jacket water of constant temperature, coming from a thermostate, which was regulated at 30°.4 C. In the polarimeter tube was then a temperature of 30°.0 C. The measurements have always been made for seven colours, pretty regularly distributed over the visible spectrum. In order to facilitate in some cases the comparison with other investigators, we have, as accurately as possible, chosen wavelengths agreeing with strong spectrum lines, so that, when a monochromator is wanting, and sources of light are used which give a line spectrum, combined with prisms "à vision directe", in order to remove the lines that are not wanted, our colours can be reproduced. The correct value of the wavelength of the light used was always checked by measuring the rotation of a standardized plate of quartz; a graduated drum, on which the displacement of the movable slit of the monochromator could be read, made the first rough adjustment of the sort of light, which was wanted, possible; then we corrected this adjustment, until the rotation found, which held good for the plate of quartz, agreed with the calculated value.

We calculated these rotations with the help of an equation for the dispersion of quartz, deduced by LOWRY <sup>1)</sup> out of a huge number of very accurate measurements which stretch far beyond the region of visibility. If the wavelength  $\lambda$  is expressed in microns, the rotation of a plate of quartz, per mm of thickness, is given by :

$$\alpha = \frac{9.5639}{\lambda^2 - 0.0127493} - \frac{2.3113}{\lambda^2 - 0.000974} - 0.1905.$$

Almost perfectly equal results are obtained by the equation :

$$\alpha = \frac{11.6064}{\lambda^2 - 0.010627} + \frac{13.42}{\lambda^2 - 78.22} - \frac{4.3685}{\lambda^2}$$

which LOWRY <sup>2)</sup> had previously deduced from his measurements. Table I gives the wavelengths of the kinds of light chosen, and the corresponding rotations of the normal plate of quartz used.

TABLE I.  
Calculated rotation of quartzplate A for some kinds of light.

7065	6362	5893	5351	4922	4607	4358 Å.
23°.69	29°.51 <sup>5</sup>	34°.69 <sup>5</sup>	42°.59 <sup>5</sup>	50°.95	58°.78	66°.36

<sup>1)</sup> Philos. Trans. (A) 226, 391 (1927).

<sup>2)</sup> Philos. Trans. (A) 212, 261 (1913).

7. The *d*-bornylacetate used came from POLAK's Frutal Works at Amersfoort, and was already pretty pure. When a quantity of about 3 kg had been melted and then crystallized at room temperature a couple of times, until only a small part had remained liquid, we further purified the preparate by letting it, after melting, crystallize at constant temperature in a thermostate. After repeating this process a sufficient number of times, always at slightly higher temperatures, it was possible in this way to obtain at last rather more than 2 L. of bornylacetate, which at 27°.7 still solidified completely.

For the specific volume at 30°.00 C. we found in two determinations: 1.02338, and 1.02340 ( $d_4^{30} = 0.97715$ , and 0.97714); at 26°.50 C. the specific volume amounted to: 1.02129 ( $d_4^{30}$  0.97915 respectively 0.97915).

Besides of the pure preparate we have also determined the rotation of two less pure fractions for yellow light (5893 Å). Whereas the rotation in a tube of 22 cm in the first case amounted to 93°.89, we found for a fraction which was crystallized at 0°.1 C. lower temperature 93°.88, and for one which had solidified at 0°.5 C. lower temperature 93°.92, values which are equal within the errors of the experiment.

8. We have now used the purest fraction in order to determine the rotation dispersion of this substance. For this purpose, after regulating the monochromator for the correct colour, we always made 14 readings for equal faintness of the three parts of the field of vision, for the rotation of the plate of quartz as well as for the preparate. From time to time the zero<sup>1)</sup> was also checked; this was found to be constant during the whole investigation. The readings were a little less certain only with the most extreme colours (7065 respectively 4358 Å); yet even then the deviations from the average were rarely greater than 0°.03. For the other colours the possibility of reproduction was much greater, unless fatigue had set in, when long series of measurements had been made.

The results of two fillings (I and II) with the pure preparate, investigated at 30°.2 C., are given in Table II.

In order to get an idea of the influence of temperature on the rotation, and to be able to reduce the figures found to those which hold good for 30°.0 C. we have also investigated preparate II at 26°.6 C. for light of wavelengths: 7065, 5893, 4922, and 4358 Å, at which for the rotations was found 63°.92, 94°.89, 142°.27, and 189°.23. The influence of temperature is therefore relatively small, viz. in the mean 1.06 % for 3°.6 C. (without indication for gradual change of this influence with the colour of the light), or 0.3 % per degree.

In the 5<sup>th</sup> column Table II contains the values of the rotation, reduced

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<sup>1)</sup> We have satisfied ourselves of the fact that the zero did not change by inserting the empty polarimetertube with coverglasses tightly screwed down.

TABLE II.

Rotation of *d*-bornylacetate at 30°.2 C; length of the tube 22.00<sup>5</sup> cm.

$\lambda$	Praeparate		Mean	$\alpha$ reduced to 30°.0 C.	$[\alpha]_{30^\circ 0}$ found	$[\alpha]_{30^\circ 0}$ calculated	cal.—found in ‰
	I	II					
4358	187°.15	187°.19	187°.17	187°.28	87°.12	87°.24	+ 1.4
4607	164.14	164.12	164.13	164.23	76.40	76.43	+ 0.4
4922	140.78	140.78	140.78	140.86	65.52 <sup>5</sup>	65.51	±
5350	116.38	116.37	116.37 <sup>5</sup>	116.44	54.16	54.15	±
5893	93.89	93.87	93.88	93.94	43.70	43.66	— 0.9
6362	79.34	79.32	79.33	79.38	36.93	36.92	±
7065	63.31	63.22	63.26 <sup>5</sup>	63.30	29.45	29.46	±

to 30°.0 C., while in column 6 the specific rotations deduced from them are inserted ( $d_4^{30^\circ 00}$  0.97714, length of tube = 2.200<sup>5</sup> dm).

9. Supposing that the specific rotation  $[\alpha]$  as function of the wavelength  $\lambda$ , can be represented by one term of DRUDE's equation, we can put down seven equations, in order to calculate the two constants appearing in it, of the form <sup>1)</sup> :

$$\lambda_0^2 + k \frac{1}{[\alpha]} = \lambda^2$$

these equations contain as unknowns  $\lambda_0^2$  and  $k$ . By solving this set of equations with the help of the method of least squares we find for  $k$  and  $\lambda_0^2$  the values 13.75 and 0.03236 respectively, so that here DRUDE's equation takes the form of :

$$[\alpha] = \frac{13.75}{\lambda^2 - 0.03236}.$$

From the value of  $\lambda_0^2$  (expressed in microns) follows for  $\lambda_0$ : 1800 Å as the place of the absorption band in the ultra violet.

Column 7 of Table II gives the values of the rotation calculated with this equation and column 8 shows how close the agreement is between the values

<sup>1)</sup> DRUDE's equation slightly transformed.

calculated and the values found. The greatest deviation occurs in the violet, where, on account of the neighbourhood of the absorptionband, the chance of greater differences <sup>1)</sup> can play a part. For the rest we must not lose sight of the fact that the error in the reading of the rotation of the plate of quartz (which shows a three times smaller rotation than the bornylacetate, see Table I) passes 3 × enlarged into the rotation of the preparate. It is seen therefore that the rotation of the bornylacetate can be perfectly represented by one term of DRUDE's equation, a result which is quite in agreement with the results for many other organic compounds investigated by LOWRY.

10. When in this way the constants were therefore determined of pure bornylacetate, we have investigated the preparation in different solvents and have always introduced into the polarimeter-tube solutions which contain 20 grammes of ester (weighed in vacuo) per 100 cc of solution. The rotations, directly measured, then lie between 12° and 42° for red and for violet light respectively. In all the cases investigated it was possible to represent the rotation by one term of DRUDE's equation. The deviations between values found and values calculated rarely surpassed 2 <sup>o</sup>/<sub>100</sub>.

Solution in absolute alcohol. The absolute alcohol was prepared by distilling alcohol with quicklime, and contained less than 0.1 % of water

For a solution of 20 % the specific rotations observed can be represented by the equation :

$$[\alpha] = \frac{14.17}{\lambda^2 - 0.03383} \quad (\lambda_0 = 1839 \text{ \AA}).$$

The change in  $k$  is therefore very marked, also the change, in  $\lambda_0^2$ , but we shall not take the latter into further consideration, also because slight variations in the values of  $[\alpha]$  can cause relatively great changes in  $\lambda_0^2$ . Graphically speaking  $\lambda_0^2$  indicates the place where the straight line  $\left(\frac{1}{[\alpha]}, \lambda^2\right)$ , after considerable extrapolation, intersects the axis. A slight change of the coefficient of direction of the line causes a great shifting of this point of intersection.

It may now be expected that the change in  $k$  will become greater when more diluted solutions are investigated, because then the molecules of bornylacetate, each for itself, have a greater number of molecules of alcohol at their disposal, or in other words, that their atmospheres do not overlap so much. This proves indeed to be the case ; for a solution of 5 %  $k$  rises to 14.86, and for a solution of 1 % to 15.32. These figures however become much less certain on account of the much smaller rotations, so that for the other solvents we have provisionally restricted ourselves to solutions of 20 %.

Now when a solution is prepared which, next to alcohol, contains so

<sup>1)</sup> From the equation follows  $[\alpha] = \infty$  for light which is maximally absorbed, as damping is not allowed for.

much water, that at  $30^{\circ}.0$  C. this mixture can contain 20 grammes of ester per 100 cc of solution<sup>1)</sup>, we have here again a possibility for greater deformation and partial splitting up of the components of the solution at the place of different groups of the estermolecule. Quite in agreement with this is the value of  $k$ , which has mounted to 14.58, while for alcohol  $k$  is 14.17, and for the pure ester  $k$  is 13.75. The solution contained 38.5 % of water (and 61.5 % of alcohol).

11. For a number of solvents and combinations of them Table 3 contains the values of  $k$ , which have always been deduced from seven specific rotations for the colours mentioned above. As regards the solvents used we wish to observe :

Pure acetic acid was obtained from glacial acetic acid to which a smaller quantity of acetic anhydride was added than corresponded with the water content, calculated from the initial freezing point. After boiling this for a couple of hours, using a reflux condensor, we again determined the freezing point, which proved to have mounted considerably, and then prepared by fractional freezing an almost pure acetic acid. (Freezing-point  $16^{\circ}.6$  C.)

Out of common gasolene two fractions were distilled, one passing between  $91^{\circ}$  and  $108^{\circ}$  C. (called "heptane" in the Table), the other of  $140^{\circ}$ — $150^{\circ}$  C. (nonane).

Benzene, free from thiophene, was distilled twice from  $P_2O_5$ ; the specific volume at  $30^{\circ}.00$  C. was 1.15284; boiling point  $80^{\circ}.1$ — $80^{\circ}.2$  C.

We used a commercial preparate decalene, of which a great quantity was kept in stock, which was no further purified; neither was this done with benzyl alcohol.

After investigating the rotation in pure solvents, we have also dissolved bornylacetate in mixtures of them, and always in the proportion of 1 : 1. When in these mixed media the rotation is a linear function of the composition, the composition must be expressed in mol. percents. The values of  $k$  calculated for mixtures which contain equal weights of the two components, are also based on the composition in mol. percents.

Fig. 1 gives a diagram of the values found for  $k$ ; Table III gives the figures for  $k$ ,  $\lambda_0^2$  and  $\lambda_0$  in the different solvents.

12. About the dispersion and rotation in the simple media (characterized by  $k$ ) we may make the following observations. For the solution in the most normal medium we find for  $k$  : 13.79, equal to the value which holds good for the pure ester, which is quite in agreement with the conception that in such a case deforming forces do not prevail<sup>2)</sup>. The same thing holds good for the hydrogenated, aromatic hydrocarbon decalene.

<sup>1)</sup> The volume of 100 cc. holds good for  $15^{\circ}$  C.

<sup>2)</sup> At the same time it must be presumed that the mutual, deforming forces, present in pure ester, are very slight.

TABLE III.  
Values of  $k$  and  $\lambda_0^2$  in different media.

Solvent	$k$	$\lambda_0^2$	$\lambda_0$ (Å)
Bornylacetate	13.75	0.03236	1800
20 % in aethylalcohol	14.17	0.03383	1839
5 % " "	14.86	0.02195	1480
1 % " "	15.32	0.02163	1470
20 % " alcohol-water	14.58	0.02990	1730
20 % " acetic acid	14.84	0.03052	1747
" " heptane	13.79	0.03277	1810
" " acetic acid-heptane 1 : 1	14.94	0.03036	1742
" " nonane	13.82	0.03253	1804
" " acetic acid-nonane 1 : 1	14.79	0.03108	1763
" " benzene	12.72	0.03349	1830
" " benzene-acetic acid 1 : 1	14.24	0.02904	1704
" " decalene	13.80	0.03067	1751
" " decalene-acetic acid 1 : 1	14.74	0.03341	1828
" " decalene-alcohol 1 : 1	14.55	0.03154	1776
" " benzylalcohol	13.88	0.03388	1840
" " benzylalcohol-heptane 1 : 1	14.26	0.03162	1778
" " decalene-benzene 1 : 1	13.07	0.03190	1786
" " benzene-alcohol 1 : 1	13.84	0.03138	1772
" " benzylalcohol-alcohol 1 : 1	14.36	0.02735	1654
" " benzylalcohol-decalene 1 : 1	14.29	0.03163	1779
" " decalene-heptane 1 : 1	13.79	0.03145	1771
" " benzene-benzylalcohol 1 : 1	13.59	0.03419	1849
" " benzene-heptane 1 : 1	13.27	0.02855	1690

Benzene, on the contrary, lowers the value of  $k$  to 12.72, on the other hand acetic acid gives a rising to 14.84. Evidently benzene (phenylgroup) and acetic-acid act, more particularly, on different parts of the bornyl-acetate (consisting of an aromatic part and an acetate group. Aethylalcohol has an increasing influence on the value of  $k$ , while finally a slightly modified value (13.88) appears with benzylalcohol, as a consequence of the presence of a lowering phenyl- and an increasing alcohol-group.



as f.i. the combinations with acetic acid, much greater deviations of the values calculated appear; the combination acetic acid-heptane gives a value of  $k$  even greater than the value of either of the components and with a deviation of  $3\frac{1}{2}\%$  from the calculated value; in the cases investigated it is absent only in the combinations alcohol-benzene, and benzylalcohol-benzene.

Two cases deserve special attention, viz. those in which, without the presence of bornylacetate, a complete mixing of the components does not appear. These are the systems alcohol-decalene, and benzylalcohol-heptane. Here too, the deviation of the calculated value is greater than 3%, just as has been found in the system acetic acid-heptane, where, at room-temperature, we are in the immediate neighbourhood of the critical solution temperature.

Table IV gives a synopsis of the possible combinations of the six solvents, and the differences between values of  $k$  calculated and found. Finally we wish to observe that in all the cases where the deviations are not too small, the values found are greater than the values calculated.

#### *Summary.*

After having demonstrated that the rotation dispersion of bornylacetate as a liquid and in the dissolved state can always be represented by one term of DRUDE's equation, the value for the constant  $k$ , which appears in it, has been determined for six solvents, and the possible binary combinations of them. The variations in the value of  $k$  are quite in agreement with the views we have developed in a previous paper on the role of mixed media with respect to a dissolved substance.

*Utrecht, October 1928.*

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