

*Citation:*

Siertsema, L.H., Measurements on the magnetic rotatory dispersion of gases, in:  
KNAW, Proceedings, 1, 1898-1899, Amsterdam, 1899, pp. 296-304

Physics. — „Measurements on the magnetic rotatory dispersion of gases.” By Dr. L. H. SIERTSEMA. (Communication N<sup>o</sup>. 46 from the Physical Laboratory at Leiden by Prof. H. KAMERLINGH ONNES.)

(Read in the meeting of December 24<sup>th</sup> 1898.)

1. *Description of the apparatus.* The figures given here are intended to complete and to illustrate the description <sup>1)</sup> of the apparatus used in the investigation.

Fig. 1 shows a general view of the whole apparatus and of the different electric circuits, fig. 2—5 show the two nicolbearers in section. For the description of these I refer to the communication of March 1896, for the coils to that of June 1893, for the optical apparatus and several other details to that of January 1895. The description of the mirror-reading of which fig. 6 gives a general view, and fig. 7 and 8 represent some details, may also be found in the latter communication. Fig. 9 represents the high-pressure tubes with the manometer, fig. 10 shows one of the high-pressure stopcocks that have been used. Fig. 11 represents a section of the system of tubes for the circulation of water together with the thermometers.

#### EXPLANATION OF THE FIGURES.

Fig. 1. *General arrangement of the apparatus.* *A* collimator, *B* smaller nicol-bearer, *C* and *D* coils, *E* greater nicol-bearer, *FF* experimental tube, *G* screw for the rotation of the smaller nicol-bearer, which is connected with it by the steel wire *HH*, guided by the pulley *O*; *I* weight for pulling back the nicol-bearer. *L* vertical graduated glass scale on which the rotation of the mirror *N* is read in the telescope *K* by means of the intermediate mirror *M*, *P* prism and *Q* telescope of the spectrometer, *X* switchboard where the currents are supplied,  $\gamma$  arc-lamp, the motor of which is fed through a thinner wire originating from terminal  $\beta$ ,  $\alpha$  resistance and  $\beta$  amperemeter in the arclamp-circuit,  $\epsilon$  switch for transferring the current from the coils to the resistance *Y* or for breaking the current,  $\delta$  commutator for reversing the current in the coils, *Z* switch by means of which the whole apparatus can be switched out except the shunt *T*, which sends a derived current to the galvanometer *V* with the stop-commutator *U*.

Fig. 2—5. *Section of the two nicol-bearers.* *a* nicol, mounted in a cylinder *q*, and kept in its place in the nicol-bearer *m* by means of a ring *b* with adjusting screws, *f* experimental-tube, on to which the tube with flange *u* has been soldered and which is fastened to the nicol-bearer by the nut *g* with the stuffing ring *t*, *e* connecting nut for the high-pressure conduit, *h* level, *o* flange with six bolts and nuts *p*, *c* glass plate with nut *d* and leaden-stuffing ring *r*, which is prevented from being forced out by small rings *s*, *u* handle to which the steel wire *h* (comp. *H* fig. 1) is fastened.

<sup>1)</sup> Verslag Kon. Akad. 1893/94, p. 31; 1894/95 p. 230; 1895/96 p. 291, 317; 1896/97 p. 131, 132; Comm. Phys. Lab. Leiden N<sup>o</sup>. 7, 15, 24, 31.

L. H. SIERTSEMA: „Measurements on the magnetic rotatory dispersion in gases.”

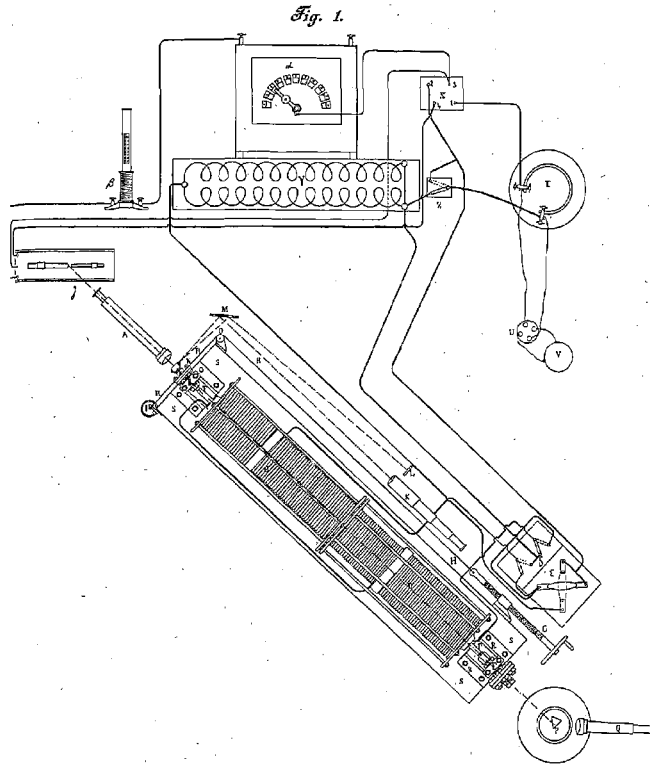


Fig. 1.

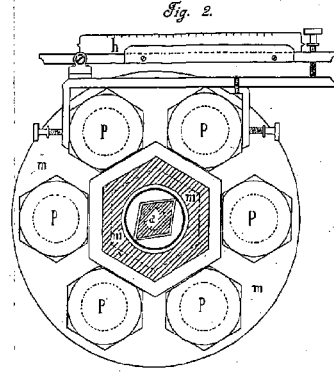


Fig. 2.

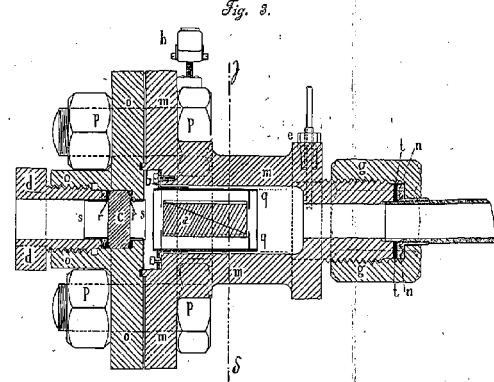


Fig. 3.

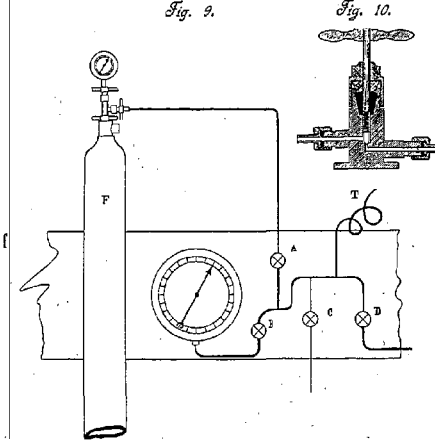


Fig. 9.

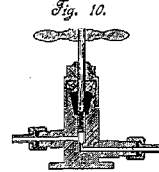


Fig. 10.

Fig. 4.

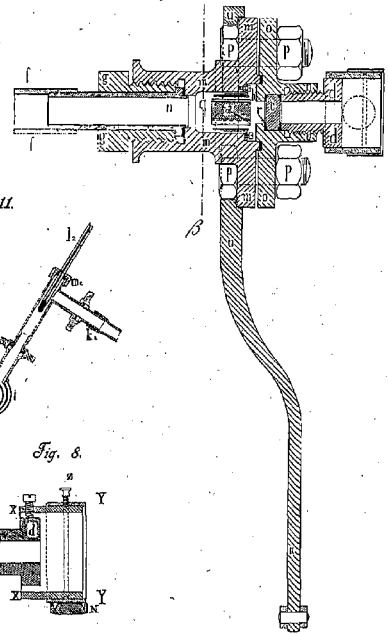


Fig. 5.

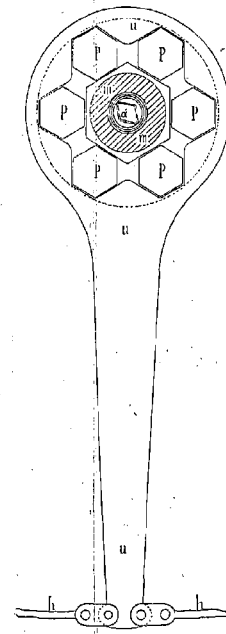


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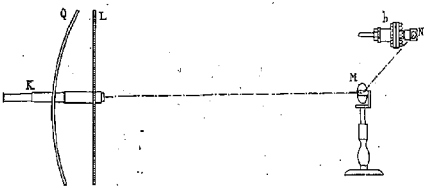


Fig. 11.

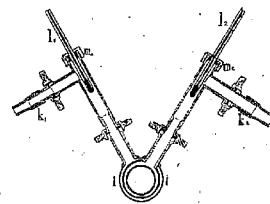


Fig. 7.

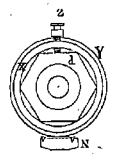


Fig. 8.

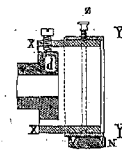
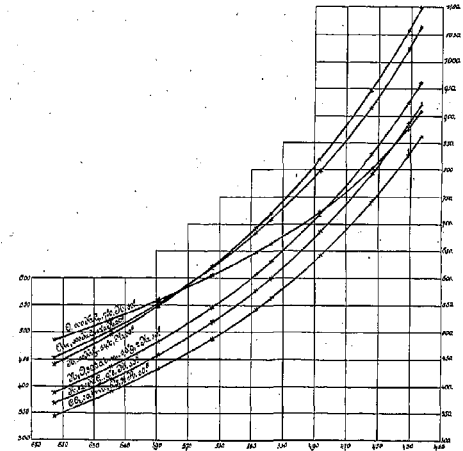


Fig. 12.



- Fig. 6. *General arrangement of the mirror-reading.* *K* telescope, *L* graduated glass scale, illuminated by the mirror-strips *Q*, *M* intermediate mirror, *N* reading mirror.
- Fig. 7 and 8. *Mounting of the mirror on the nut in the flange of the smaller nicol-beaver.* *d* nut, *X* and *Y* two rings, *Z* fastening-screws, *N* reading-mirror.
- Fig. 9. *High-pressure conduit.* *F* cylinder with compressed gas, *A* high-pressure stopcock for closing the former, *B* stopcock for closing the manometer, *C* and *D* stopcocks for drawing off the gas, *T* connection with the experimental tube.
- Fig. 10. *High-pressure stopcock.* See *A*, *B*, *C* and *D* of the preceding figure.
- Fig. 11. *Sections of the tubes for the circulation of water together with thermometers.* *i i* tubes in sections, *k*<sub>1</sub> supply, *k*<sub>2</sub> outlet, *l*<sub>1</sub> and *l*<sub>2</sub> thermometers, *n*<sub>1</sub> and *n*<sub>2</sub> nuts.
- Fig. 12. *Curves of the rotatory constants.* See further on.

2. *Formulae for interpolation of different forms.* It has been stated in a previous communication<sup>1)</sup> that the different theories of the magnetic rotation lead to two forms of formulae for the rotatory constants of  $\omega$ , viz.

$$\omega = \frac{C_1}{\lambda} + \frac{C_3}{\lambda^3} + \dots \dots \dots \text{(I)}$$

$$\omega = \frac{C_2}{\lambda^2} + \frac{C_4}{\lambda^4} + \dots \dots \dots \text{(II)}$$

With a view to the fact that in the case of oxygen we obtained with the first form a better accordance with the rotatory constants observed than with the second form<sup>2)</sup>, we have published in the later communications only formulae for interpolation of the form (I) with two terms. In the meantime the continuation of the calculations showed that for nearly all gases the form (II) with two terms was more satisfactory. The contrary proved to hold only for oxygen and for the mixtures of oxygen and nitrogen, among which we may mention in the first place air, further a mixture with 87.8 percent oxygen, on which some observations have been made in the be-

<sup>1)</sup> Versl. Kon. Akad 1894/95 p. 237; Comm. Phys. Lab. at Leiden N<sup>o</sup>. 15, p. 27.

<sup>2)</sup> " " " " p. 238; " " " " N<sup>o</sup>. 15, p. 28.

gining<sup>1)</sup>, and a mixture with 26.0 percent, on which only a few observations have been made not published hitherto. For these mixtures form (II) required three terms, as was the case with oxygen.

For judging of the accordance of the formulae we have always calculated the probable error of an observation of the weight one, according to the rules of the method of least squares. In the two first columns of the following table these probable errors are to be found. They are computed by taking three terms in the form II for oxygen and mixtures containing oxygen as said above, and two terms for the other gases, and belong to the rotatory constants expressed in minutes, multiplied by  $10^6$  and for the pressure and the temperature mentioned in the observations.

## P R O B A B L E E R R O R S.

Form of formula for interpolation:	I	II	III
Oxygen	5.8	5.4	5.0
Mixture with 87.8 percent O	6.9	7.8	
"    "    26.0    "    O	3.9	3.0	
Air	3.2	2.7	4.4
Nitrogen	9.3	7.4	7.7
Hydrogen	8.9	4.7	4.2
Carbonic acid I	0.147	0.122	0.106
"    "    II <sup>2)</sup>	0.184	0.081	0.047
Nitrogen monoxide	5.4	3.0	2.2

An investigation of the errors, which are to be anticipated in the different adjustments and readings, always yielded for the error to be expected in the rotatory constant numbers larger than those of the table given above, e. g. for oxygen 11 in the violet and 6 in the red. With a view to this fact the accordance for all formulae mentioned may be considered satisfactory. Yet in the gases without oxygen the errors of the form (II) with two terms are always smaller than those of (I), so that if in choosing between the two forms we had to consider this only, we should prefer for these gases the form (II). But it is not excluded that other forms of formulae for interpolation should yield a still smaller error. This appeared to be the case with the form

<sup>1)</sup> Versl. Kon. Akad. 1894/95, p. 236. Comm. Phys. Lab. at Leiden N<sup>o</sup>. 15, p. 26.

<sup>2)</sup> Observations with gas from two cylinders of unequal purity.

$$\omega = a + \frac{b}{\lambda^2} \dots \dots \dots \text{(III)}$$

which gave the errors given in the third column of the table.

3. *Law of mixtures.* When we wish to apply the corrections for impurities in the gases investigated, we have to assume a law, from which the magnetic rotatory constant of a mixture can be calculated from the constants of its constituents. In a former communication <sup>1)</sup> a simple law has been assumed, without any consideration of its theoretical basis.

We can deduce this law from the supposition that the magnetic rotation is an additive property, and that the rotatory constant of a mixture is therefore equal to the sum of a number of terms, to which each molecule contributes one. Let the condition of the mixture be determined by the pressure  $p$ , by the temperature  $t$  and for the rest by assuming that in the unit of volume  $\mu N$  grammoles of one component are mixed with  $(1 - \mu) N$  of the other. Let  $q'_{p,t,\mu}$  be the amount which a grammoles of the first component contributes to the rotatory constant, and  $q''_{p,t,1-\mu}$  the same for the other component and let  $Nq_{p,t,\mu}$  be the rotatory constant of the mixture, then we find that

$$Nq_{p,t,\mu} = N\mu q'_{p,t,\mu} + N(1 - \mu) q''_{p,t,1-\mu}$$

and therefore

$$q_{p,t,\mu} = \mu q'_{p,t,\mu} + (1 - \mu) q''_{p,t,1-\mu} .$$

The quantities  $q_{p,t,\mu}$ , introduced here, which we might call molecular rotatory power, will depend on the condition of the molecules determined by  $p, t$  and  $\mu$ . The way in which they depend on these variables cannot be deduced from the observations without the aid of a molecular theory, except in the case when  $\mu = 0$  and we have therefore to deal with simple substances.

In applying this law we assume these quantities  $q$  to be constants and then we can deduce them from those for the simple gases. Let  $r'$  and  $r''$  be the rotatory constants for the two gases at the pressure  $p$  and the temperature  $t$ . Let further  $x$  and  $y$  be the volumes of the two substances which we should have to mix in order to obtain the unit of volume of the mixture, all these volumes being measured

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<sup>1)</sup> Verslag Kon. Akad. 1894/95, p. 236. Comm. Phys. Lab. Leiden N<sup>o</sup>. 15 p. 26.

at the pressure  $p$  and the temperature  $t$ . Then we may deduce from the foregoing law that

$$r = x r' + y r''$$

which expression agrees with the one assumed before. It may be remarked that the quantities  $r$ ,  $r'$ ,  $r''$ ,  $x$  and  $y$  are taken at one and the same pressure  $p$  and one and the same temperature  $t$ , and moreover that on account of discrepancies from DALTON'S law  $x + y$  may differ from 1.

This law of mixtures deduced for gases, agrees, if the molecular rotatory power is considered to be constant, with that which has been adopted by JAHN<sup>1)</sup>, WACHSMUTH<sup>2)</sup> and others for mixtures of liquids and saline solutions.

4. *Results.* Bij applying the above-mentioned law of mixtures we can calculate the rotatory constants of the pure gases, as has been shown before. The following table gives the coefficients of the formulae

$$\omega = \frac{C_1}{\lambda} + \frac{C_3}{\lambda^3} = \frac{C_1}{\lambda} \left( 1 + \frac{d_1}{\lambda^2} \right) \dots \dots \dots \text{(I)}$$

$$\omega = \frac{C_2}{\lambda^2} + \frac{C_4}{\lambda^4} \left( + \frac{C_6}{\lambda^6} \right) = \frac{C_2}{\lambda^2} \left( 1 + \frac{d_2}{\lambda^2} \right) \dots \dots \dots \text{(II)}$$

which represent the rotatory constants  $\omega$ , expressed in minutes, and multiplied by  $10^6$ .

	pressure	temp.	$C_1$	$C_3$	$d_1$	$C_2$	$C_4$	$C_6$	$d_2$
Oxygen	100 Kg.	7° 0	272.2	19 15	0.0704	296.7	- 48.03	4 294	
mixt with 87 8% O	" "	17° 0	240.6	23.30	0.097	249.1	- 30.57	2.521	
" " 26 0 " O	" "	17° 6	200.7	40.93	0.204	210.1	- 7.71	0.805	
air	" "	13° 0	191.5	46.19	0.241	216.3	- 12.57	1.410	
nitrogen	" "	14° 0	171.2	52.86	0.309	183.6	2.27		0.0124
hydrogen	85.0 "	9° 5	138.8	45.19	0.325	151.5	2.38		0.0157
carbonic acid	1 atm.	6° 5	2.682	0.8305	0 310	2.894	0.0337		0.0116
nitrogen monoxide	30.5 atm	10° 9	75.85	22.95	0.303	81 26	0.820		0.0101

1) JAHN. Wied. Ann. 43, p. 284.

2) WACHSMUTH. Wied. Ann. 44, p. 380.

The numbers given differ slightly from those communicated before <sup>1)</sup> on account of a general revision of the calculations.

The law of mixtures may further be applied, as has been done before <sup>2)</sup>, to the mixtures of oxygen and nitrogen and the observed rotatory constants may be compared with those computed from the components. This comparison will prove very satisfactory in the case of air, but less so in the case of the two other mixtures.

In fig. 12 curves are given showing the relation between magnetic rotatory constant and wave-length, which are drawn by making use of the values calculated from some of the communicated formulae for interpolation. They prove clearly that the dispersion of the magnetic rotation for all gases, oxygen excepted, is pretty much the same. If we consider the large coefficient of magnetisation of oxygen, it becomes evident <sup>3)</sup> that the magnetic rotatory dispersion depends on the magnetic properties of the substance, a fact to which H. BECQUEREL has drawn the attention <sup>4)</sup>.

It is a striking fact that the order of the gases examined, when they are arranged according to the values of the coefficients  $d_1$  and  $d_2$ , should be the same as the one found for the coefficients of magnetisation. This appears from the annexed table:

	$d_1$	$d_2$	$Q \cdot 10^{10}$ <sup>2)</sup>
oxygen	0.0704	-0.056 <sup>1)</sup>	0.662
nitrogen monoxyde	0.303	+0.0101	-0.158
nitrogen	0.309	0.0124	-0.165
carbonic acid	0.310	0.0116	-0.172
hydrogen	0.325	0.0157	-0.176

<sup>1)</sup> Verslag Kon. Akad. 1896/97, p. 132. Comm. Phys. Lab. Leiden N<sup>o</sup>. 31, p. 56.

<sup>2)</sup> Verslag Kon. Akad. 1895/96, p. 301; 1896/97, p. 132; Comm. Phys. Lab. Leyden, N<sup>o</sup>. 24 p. 10, N<sup>o</sup>. 31 p. 6.

<sup>3)</sup> H. BECQUEREL. Ann. de Ch. et de Ph. (5) 12 p. 85. Comp. also Verslag Kon. Akad. 1893/94 p. 31; Comm. Phys. Lab. N<sup>o</sup>. 7 p. 9.

<sup>4)</sup> The extraordinary large dispersion, observed by BECQUEREL in substances with negative magnetic rotation drew my attention to the negative constant which QUINCKE [Wied. Ann. 24. p. 615 (1885)] found in amber. A fresh measurement with a piece of transparent, light brown amber of 1.78 cm. thickness actually showed negative rotation. Yet it appeared that the emerging ray of light, even without the action of the electro-magnet, was strongly elliptically polarized. In connection with the theoretical investigations on the magnetic rotation in doubly refracting bodies (Gouy,



The fact that  $d_1$  is almost the same for all gases with small coefficients of magnetisation seems favourable to MASCART's formula which leads to a formula for interpolation of the form (I); coefficient  $\gamma$  in this form is related in a simple way to  $d_1$ , and is according to JOUBIN's investigation <sup>3)</sup> in a high degree dependent on the coefficient of magnetisation.

If we express the rotatory constants in circular measure instead of minutes, we obtain the following coefficients

$$10^{10} \omega' = \frac{C_1'}{\lambda} + \frac{C_3'}{\lambda^3} = \frac{C_1'}{\lambda} \left( 1 + \frac{d_1}{\lambda^2} \right) \dots \dots (I)$$

$$10^{10} \omega' = \frac{C_2'}{\lambda^2} + \frac{C_4'}{\lambda^4} \left( + \frac{C_6'}{\lambda^6} \right) = \frac{C_2'}{\lambda^2} \left( 1 + \frac{d_2}{\lambda^2} \right) \dots (II)$$

	pressure	temp.	$C_1'$	$C_3'$	$d_1$	$C_2'$	$C_4'$	$C_6'$	$d_2$
Oxygen	100 Kg.	7° 0	792	55.7	0.0704	563	-139.7	12.49	
mixture with 87.8% O	" "	17° 0	700	67.8	0.097	725	- 88.9	7.33	
" " 26.9 % O	" "	17° 6	584	119.1	0.204	611	- 22.43	2.342	
air	" "	13° 0	557	134.4	0.241	629	- 36.57	4.10	
nitrogen	" "	14° 0	498	153.8	0.309	534	6.60		0.0124
hydrogen	85.0 Kg.	9° 5	404	131.5	0.325	441	6.92		0.0157
carbonic acid	1 atm.	6° 5	7.80	2 416	0.310	8.42	0.0980		0.0116
nitrogen monoxide	30.5 atm	10° 9	220.6	66.8	0.303	236.4	2.385		0.0101

For practical use the following table may serve, which gives the magnetic rotatory constants for different wave-lengths, expressed in minutes and multiplied by  $10^6$ .

WIENER) this result may easily be explained without assuming a negative rotatory constant. It is not improbable that QUINCKE's result may be accounted for in a similar way.

<sup>1)</sup> According to a formula for interpolation (II) with two terms, which is not mentioned in this paper.

<sup>2)</sup> QUINCKE's constants relative to air. TÖPLER and HENNIG. Wied. Ann. 34, p. 790 (1880).

<sup>3)</sup> JOUBIN. Thèse Paris 1888, p. 24. Ann. de Ch. et de Ph. (6) 16, p. 78 (1889).

$\lambda$	oxygen	mixture with 87.8% O	mixture with 26.0% O	air	nitrogen	hydrogen	oxygen	nitrogen monoxide
pressure	100 Kg.	100 Kg.	100 Kg.	100 Kg.	100 Kg.	85.0 Kg.	1 atm.	30.5 atm.
temp.	7°.0	17°.0	17°.6	13°.0	14°.0	9°.5	6°.5	10°.9
0.423	908	877	1074	1062	1097	921	17.23	480
431	375	849	1033	1020	1054	884	16.56	461
454	799	779	930	914	944	791	14.83	413
486	721	698	812	797	818	684	12.86	359
517	663	634	720	707	719	600	11.30	315
527	646	616	694	682	691	576	10.86	303
555	604	570	628	618	620	517	9.75	272
589	559	522	561	553	548	456	8.62	241
619	523	487	510	504	495	412	7.78	218
656	484	449	457	452	439	365	6.91	193
$\frac{\rho}{f^w} =$	0.531			0.559	0.563	0.570	0.838	0.616

In the last line of this table the values of the molecular rotatory power for Na-light divided by that of water, are given according to the example of PERKIN<sup>1)</sup>. Although it appears from his investigations and those of others that the calculation of the molecular rotatory power of a chemical compound as the sum of that of its atoms does not hold good throughout, it may be interesting to compare PERKIN'S atomic rotations with those resulting from our observations. From the above-mentioned values of the molecular rotatory power follows for 1 atom:

$$O = 0.265$$

$$N = 0.281$$

$$H = 0.285.$$

PERKIN finds for oxygen 0.194 or 0.261 according to the way of composition, and for hydrogen 0.254, numbers as we see of the same order. PERKIN'S number 0.717, calculated for nitrogen in amines

<sup>1)</sup> PERKIN. J. of Chem. Soc. 45, p. 421 (1884), and following volumes.

does not agree with our number; neither is our value of  $N_2O$  to be composed from PERKIN's atomic values.

If following PERKIN we take in  $CO_2$  for 1 atom carbon 0.515, we find  $O_2 = 0.323$ , which would be more agreeable to the value 0.39, which HINRICHS<sup>1)</sup> deduced from organic acids. Taking everything together the agreement is fairly well, except for nitrogen.

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<sup>1)</sup> HINRICHS, C. R. 113, p. 500 (1891).

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(February 23<sup>d</sup> 1899.)