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KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday May 27th, 1899.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 27 Mei 1899 Dl. VIII).

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The following papers were read:

Chemistry. — "*On the system: water, phenol, acetone.*" By Dr. F. A. H. SCHREINEMAKERS. (Communicated by Prof. J. M. VAN BEMMELEN.)

Two cases may, in general, be distinguished in which plaitpoints appear or disappear on the ζ-surface (by the ζ-surface without further qualification, is meant, both here and in what follows, that area of the ζ-surface which relates to the liquid state).

1. The plaitpoint appears at the margin of the ζ-surface.
2. The plaitpoint appears, on the ζ-surface itself and not at its margin.

Mr. SCHREINEMAKERS has already found experimentally various examples of the first case; for example, in the equilibria between water, succinonitrile and sodium chloride salt or ethylic-alcohol and also in the systems formed from water, and phenol with common salt or aniline or ethylic-alcohol.

The second case, viz. the appearance or disappearance of a plaitpoint on the area of the ζ-surface itself and not on its border, may arise in different ways.

It occurs, for example, when a plait divides into two other plaits so that it also occurs with the connodal line which represents the equilibrium between the two liquid phases. According to the researches of Mr. SCHREINEMAKERS this case occurs, most probably, in the system: [water – alcohol – succinonitrile] at about 4°.

There is however, another case which Mr. SCHREINEMAKERS has now discovered experimentally. Let us suppose that at a certain temperature T the ζ-surface is at every point convex from below. On changing the temperature a plaitpoint may now appear on the ζ-surface, which, on a further change of temperature, may develop into a plait in such a way that connodal lines with two plaitpoints are produced. We then have the case that at this temperature the three components, taken in pairs, are completely miscible, but that ternary mixtures exist for which this is not the case.

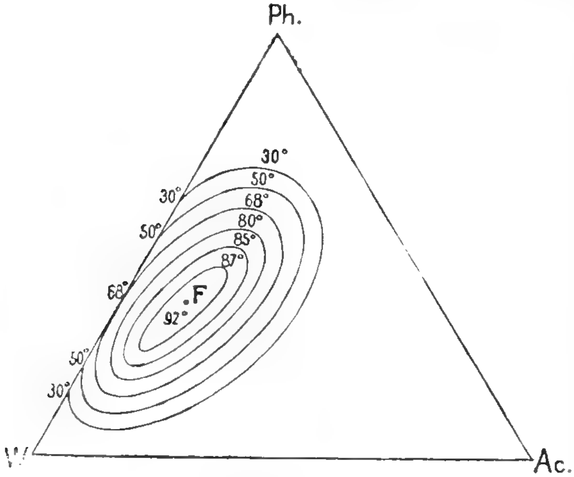

Fig. I

Mr. SCHREINEMAKERS has realised this in the system: [water (W) – phenol (Ph) – acetone (Ac)] for which the connodal lines for 30°, 50°, 68°, 80°, 85° and 87° are diagrammatically represented in figure 1. Their exact positions can be found by means of the following tables.

Composition of the solutions on the connodal line at 30°.

$^0/_0$ W	92	92.3	91	88.4	81	70.9	62.1	51.6	39.8	28.9	21.8
$^0/_0$ Ac	0	1.7	4	7.6	15	23.1	28.9	34.9	40.2	43.1	40.2
$^0/_0$ Ph	8	6	5	4	4	6	9	13.5	20	28	38
$^0/_0$ W	18.4	17.2	17.9	19.1	21.1	22.6	25.2	27.1	28.7	30	31
$^0/_0$ Ac	34.1	25.8	81.1	12.9	9.9	7.4	4.6	2.3	1.3	0.5	0
$^0/_0$ Ph	47.5	57	64	68	69	70	70.2	70.6	70	69.5	69

Composition of the solutions on the connodal line at 50°.

$^0/_0$ W	89	90.3	90	87.5	83.8	69.4	60	49.3	37.8	23.3
$^0/_0$ Ac	0	1.7	4	7.5	10.7	22.6	28	33.2	38.2	34.7
$^0/_0$ Ph	11	8	6	5	5.5	8	12	17.5	24	42

$^0/_0$ W	20.9	22.7	24.6	26.4	29.1	32.2	34.4	36.3	38
$^0/_0$ Ac	21.1	15.3	11.4	8.6	5.4	2.8	1.6	0.7	0
$^0/_0$ Ph	58	62	64	65	65.5	65	64	63	62

Composition of the solutions on the connodal line at 68°.

$^0/_0$ W	66	50.1	45	39.6	34.6	31	28.6	26.9	26.4
$^0/_0$ Ac	0	0.9	2	3.4	6.4	10	13.4	18.1	26.6
$^0/_0$ Ph	34	49	53	57	59	59	58	55	47

$^0/_0$ W	33.9	46	56.6	66.5	77.6	84.7	87.6	86.4	66
$^0/_0$ Ac	34.1	31	26.4	21.5	14.4	7.3	3.9	1.6	0
$^0/_0$ Ph	32	23	17	12	8	8	8.5	12	34

Composition of the solutions on the connodal line at 80°.

$^0/_0$ W	83.3	82.9	74.7	61.8	52.5	40.6	32.2	33.4	35.4
$^0/_0$ Ac	3.7	7.1	13.8	20.2	24.5	27.4	21.8	15.6	11.6
$^0/_0$ Ph	13	10	11.5	18	23	32	46	51	53

$^0/_0$ W	40.5	49.7	62.7
$^0/_0$ Ac	7.5	4.3	2.8
$^0/_0$ Ph	52	46	34.5

Composition of the solutions on the connodal line at 85°.

$^0/_0$ W	80.1	71.7	58.4	49.1	37.2	39.2	44.3	58.9
$^0/_0$ Ac	9.9	13.3	19.1	22.9	17.3	12.8	8.2	5.1
$^0/_0$ Ph	13	15	22.5	28	45.5	48	47.5	36

Composition of the solutions on the connodal line at 87°.

$^0/_0$ W	78.3	70.1	56.5	44.3	41.5	46.4	64.5
$^0/_0$ Ac	6.7	12.9	18.5	20.7	13.5	8.6	5.5
$^0/_0$ Ph	15	17	25	35	45	45	30

The preceding tables are obtained by interpolation. Varying quantities of phenol are added to mixtures of water and acetone containing 1.83, 4.24, 7.94, 15.6, 24.6, 31.8, 40.4, 50.2, 59.9 and 64.9 percent of acetone, and the temperature was determined at which the two liquid phases which form are converted into a single phase.

Let us now examine the different connodal lines in figure 1. Below 68° they terminate in two points on the side W–Ph. of the triangle; these two points represent two binary solutions which are in equilibrium with each other. The positions of the conjugate points on the connodal line itself is still unknown. At 68° the connodal line touches the side W. Ph. in a point, at which the two liquid phases of the binary system W. Ph. become identical. As is shown in the figure at 80°, 85° and 87°, the connodal lines at higher temperatures lie wholly within the triangle and approach each other as the temperature rises, disappearing finally at about 92° in the point F. The composition at the point F is approximately 59 $^0/_0$ of water, 12 $^0/_0$ of acetone and 29 $^0/_0$ of phenol.

Above 92° the ζ-surface is convex at every point when regarded from below; as the temperature falls a double plaitpoint therefore appears at the point F, when this temperature of 92° is reached. On further depression of the temperature the point F develops into a plait with two plaitpoints, of which one moves towards the side W. Ph. where it disappears at 68° in the point at which the connodal line of 68° touches the side W. Ph.; at still lower temperatures therefore one point of folding alone remains.

A further investigation will show whether it is possible in some measure te learn the course of the plaitpointcurve.

Mr. SCHREINEMAKERS has thus shown experimentally that connodal lines with two, one or no plaitpoints may appear on the ζ-surface. The first example with two plaitpoints has been communicated in the preceding paper; in previous investigations connodal lines with one and with no plaitpoint were referred to.

Chemistry. — "*On the nitration of benzoic acid and its methylic and ethylic salts.*" By Prof. A. F. HOLLEMAN. (Communicated by Prof. C. A. LOBRY DE BRUYN.)

Some time ago (Recueil 17.335) I described a process for the quantitative determination of the three isomeric mononitrobenzoic acids in mixtures of them. This process has been simplified and improved so that the results obtained by it now attain an accuracy of about 1 %; by this means an answer to the following questions is obtainable:

1. To what extent does the proportion in which the acids are formed in the nitration of benzoic acid depend on the temperature at which this takes place?

2. How do the methylic and ethylic salts of benzoic acid behave in this respect?

These two questions being answered we find at once, (3). How this proportion is modified by the replacement of the hydrogen of the carboxylgroup by methyl or ethyl.

This appears from the following table:

Nitration at		— 30°	0°	+ 30°
Benzoic acid	o	14.4	18.5	22.3
	m	85.0	80.2	76.5
	p	0.6	1.3	1.2
Methylic benzoate.	o	23.6		25.7
	m	74.4		69.8
	p	2.0		4.5
		—40°		
Ethylic benzoate.	o	25.5	28.3	27.7
	m	73.2	68.4	66.4
	p	1.3	3.3	5.9

From this it is obvious that the characteristic of the process of nitration, the preponderant formation of the meta-acid, is retained throughout the interval of temperature of 60° and is unaffected by the substitution in the carboxyl group, but that the quantity of secondary products is considerably increased both by raising the temperature and by the substitution.

The details of this investigation will shortly be published in the "Recueil".

Groningen, May, 1899.

Astronomy. — „*The system of Sirius according to the latest observations*". By Mr. H. J. Zwiers. (Communicated by Prof. H. G. van de Sande Bakhuyzen).

In N⁰. 3336 of the „*Astr. Nachr.*" I have deduced the system of elements of the companion of Sirius so as to have an example for the application of my new method of computing the orbits of double stars. I have found :

Elements I.

$$T = 1893.759$$

$$\mu = -7^\circ.04486 \text{ (Period} = 51.101 \text{ year)}$$

$$e = 0.6131$$

$$i = 44^\circ\ 36'.0$$

$$\Omega = 37\quad 3.6 \text{ (1900.0)}$$

$$\lambda = \pi - \Omega = 223\quad 36.6$$

$$a = 7''.77$$

The observations which served as a basis for this orbit, extend from 1862 till the spring of 1890, when the companion was seen for the last time at Lick-Observatory by Burnham. For about six years it then disappeared in the rays of the principal star, till, towards the end of 1896, new measurements could be obtained again at Mount Hamilton. The absolute positions of Sirius, as observed in the meridian of Leyden, were reduced to the centre of gravity of the system by aid of the elements just given, combined preliminarily with the distance of the principal star to this centre, as found by Auwers. In pursuance of the same object I immediately after the reappearance of the component took the computation once more in hand. For the computation of the final values I thought it advisable however to await a few further oppositions. As soon as Messrs. Keeler and Aitken of Lick-Observatory had kindly communicated to me by letter, in February and March of this year, the results of their measurements in the recent winter, I have derived the final equations [1]. The error of my ephemeris amounting

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[1] An observation received in the beginning of May from Prof. Hussey arrived too late to be included in the computation.

in the winter of 1896—97 to over 4° and decreasing the following winter to somewhat over 2°, now proved to be reduced to 0° in the last opposition [1]). A total of 16 serviceable measurements after the periastronpassage seemed sufficient to venture on a correction of the elements of this interesting system.

The space not allowing me to enumerate here all the separate measurements, I must refer to the *Astr. Nachr.* 3084—85, for the observations up to 1890, where Prof. AUWERS communicates them in extenso. Here and there only do the positions used by me differ a little from his on account of assigning slightly different weights to the results of the separate nights. Just as Prof. AUWERS I had formerly been obliged to derive a measurement of HALL in 1888 from the compilation given by Prof. BURNHAM in *Monthly Notices* lviii 6 without knowing its source. In the 2nd part issued since then of the *Observations of double Stars, made at the U. S. Naval Observatory by* ASAPH HALL, I find: 1888.248 $p =$ 23°27; $s =$ 5″777, with remarks as *faint*, *very faint*, *extremely faint* for the separate nights. Not being able however to make the angle of position agree in any way with the surrounding measurements I have now also excluded this measurement. Farthermore Mr. HALL gives a few yearly means differing slightly from his previous statements in *M. N.*, *A. N.*, and *A. J.* I considered the last values the best and have modified the previous data accordingly.

The communication of the separate measurements after the periastron-passage would demand too much space; I therefore restrict myself to the following table of the mean numbers for each observer [2]).

The observed angles of position have already all been reduced to the meridian of 1900.0 by applying the correction for precession.

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[1]) It may be mentioned here that the orbit of Prof. AUWERS leaves the following deviations (*Obs.* — *Comp.*): + 15°.24; + 13°.87; + 11° 53. These are indeed greater, but they also indicate that the assumed time of revolution is nearer the truth than mine.

[2]) As a rule all the observations of one and the same observer during one opposition are contracted into a single mean. With the relatively great changes in r however, the motion of the angle in this part of the orbit is far from regular and the 2nd differences (with an ephemeris from year to year) amount to several degrees. I have therefore not dared to join into means the observations 5 and 11, 7 and 12, 13 and 15, 14 and 16; in every case the difference in time amounts to half a year nearly.

(*In passing the proofs through the press*). In *M. N.* lviii 6 is still communicated the following measurement of LEWIS at Greenwich with the 28-inch: 1898.214, $\theta =$ 179°2, $r =$ 4″68 (1 night). This had been overlooked but would have received at all events the weight 0, the deviation in the angle of position amounting almost to 10°, *i. e.* to more than 0″5 in arc of the great circle (according to elements II: $\Delta\theta = +$ 9°93; $\Delta r = +$ 0″63).

N⁰.	Date.	Observer.	Observation.		Number of nights.	n	Δ_1		Δ_2	
			$\mathfrak{p}$	r			$\mathfrak{p}$	r	$\mathfrak{p}$	r
1	1896.920	Schaeberle [1]	189°20	3″73	4	3	+4°60	−0″35	−0°27	−0″06
2	97.017	Aitken [2]	187.03	3.84	8 : 5	4	+3.81	−0.27	−0.83	+0.03
3	.206	Hussey [3]	186.62	3.78	1	1	+6.04	−0.39	+1.84	−0.06
4	.216	Brenner [4]	189.07	3.68	2	0	+8.63	−0.49	+4.46	−0.16
5	1897.802	See [5]	173.89	4.63	4	3	+1.19	+0.29	−1.52	+0.67
6	.818	Aitken [6]	174.78	4.03	4 : 3	3	+2.28	−0.32	−0.38	+0.07
7	.828	Boothroyd [7]	173.66	4.95	2	2	+1.29	+0.60	−1.35	+0.99
8	.839	Schaeberle [8]	175.18	3.95	3	2	+2.91	−0.40	+0.31	−0.02
9	.940	Hussey [9]	175.04	4.01	3 : 2	2	+4.07	−0.37	+1.72	+0.02
10	1898.151	Aitken [10]	170.82	4.22	2	2	+2.44	−0.22	+0.63	+0.18
11	.273	See [11]	168.93	4.79	3	2	+2.02	+0.31	+0.52	+0.73
12	.276	Boothroyd [11]	170.74	4.86	3	2	+3.87	+0.38	+2.37	+0.79
13	1898.737	Aitken [10]	161.68	4.22	3	2	+0.14	−0.40	−0.21	+0.04
14	.785	Hussey [10]	162.10	4.18	2	2	+1.10	−0.45	+0.86	−0.02
15	1899.177	Aitken [10]	154.30	4.55	1	1	−2.44	−0.20	−1.76	+0.24
16	.286	Hussey [10]	154.63	4.40	3	2	−0.96	−0.38	−0.04	+0.06

[1] A. J. 394; mean having regard to the weights. — [2] A. N. 3465; 1st, 7th and 8th nights weight 2. — [3] A. J. 427. — [4] A. N. 3421; excluded for unreliability of the method — [5] A. N. 3469; every night weight 1. — [6] A. J. 424 and 429; mean having regard to the weights. — [7] A. N. 3469; the two nights equal weight. — [8] A. J. 420. — [9] A. J. 427; every night weight 1. — [10] Received in M S.; mean having regard to the weights. — [11] M. N., lviii 7; all the nights weight 1.

The manner in which the weights n have been deduced shall be stated farther on; in both columns Δ_1 are contained the differences from my elements of A. N. 3336 in the sense *Obs.* — *Comp.*

My first work was to investigate anew the personal errors of the observers. These attaining considerable amounts especially in the distances I resolved to found the correction of the orbit exclusively on the angles of position. With the exclusion of the evidently unsuccessful measurements the means were taken of the differences *Obs.* — *Comp.* for every opposition, a diagram of these was made, the points being connected by a curve in the best way possible. According to the method of Prof. AUWERS I also assigned weights of the form $q = mn$, where m depends on the telescope and n on the number of nights. I assumed preliminarily:

$m = 2$ for: Dearborn Obs. (β, Hough), Mt. Hamilton (both refractors), Princeton (23-inch), Virginia Univ., and the 26-inch of Washington.

$m = 1.5$ for: Cambridge (Mass.), Cincinnati, Glasgow (Mo.), Malta, Rutherford & Wakely, Perrotin, Bigourdan, $O\Sigma$, Russell and the small refractor at Washington.

$m = 1$ for all the other observers at refractors of at least 9-inch or reflectors of at least 20-inch aperture.

Farthermore:

$n = 4$ for more than 6 nights.
$n = 3$ for 4, 5 or 6 nights.
$n = 2$ for 2 or 3 nights.
$n = 1$ for 1 night.

Σq was multiplied for every yearly mean by the (computed) distance r in order to reduce to arcs of the great circle and so to obtain comparable weights. Finally to every yearly mean *Obs.— Comp.* a weight $p = \frac{r\,\Sigma\,q}{100}$, rounded off to tenths, was assigned. Observations deviating more than 0″5 (in arc of the great circle) were always excluded.

By comparing *Obs.—Comp.* for every observer with the corresponding ordinate of the curve, corrections were deduced whose mean furnished the following personal corrections (the weights, according to the number of nights, being taken into consideration).

Observer.	$\Delta\theta$	Weight.	Observer.	$\Delta\theta$	Weight.	Observer.	$\Delta\theta$	Weight.
Bigourdan	+0°77	3	Hall	—0°33	2 and 4	Stone	+1°79	3
Bond	—0.09	3	Holden	+1.12	4	Struve	—0.53	3
Burnham	—0.28	4	Hough	+0.24	4	Wilson	+1.10	3
Dunér	+0.16	2	Howe	+0.07	3	Winlock	+0.56	3
Engelmann	—0.45	2	Newcomb	+0.09	2 and 4	Young	—0.15	2 and 4
Foerster	+0.05	2	Peirce	—0.94	3			
Frisby	—0.96	4	Pritchett (C.W.)	—0.71	3			

The measurement of Struve at Rome gets the weight 2. Burnham's measurement in 1881.85 at the 12-inch at Mt. Hamilton is united to his measurements at Dearborn Obs.; likewise the measurements of Engelmann at the 7½-inch and the 8-inch at Leipzig and those of Newcomb at the small and the great refractor at Washington. For Young and Hall the corrections obtained for the small refractor were united with half weight to those for the great one. Wherever in the last column two weights are given, the former refers to the smaller instrument.

Observers whose personal corrections could not be deduced received as a rule a weight that was 1 smaller than otherwise would have been their due with a view to the nature of the instrument. A weight 3 was assigned to LEAVENWORTH, PERROTIN, PETERS and WATSON; 2 to CHACORNAC, FUSS, LASSELL, MARTH, H. S. PRITCHETT, RUTHERFORD & WAKELY, SEARLE, UPTON and WINNECKE; the others received a weight 1.

After applying these corrections we could pass to the formation of the definitive yearly means *Obs.—Comp.* The assigned weights were again of the form *gn*, where *n* was assumed as before.

The following table contains in the first column the mean date, in the second the preliminary means *Obs.—Comp.* which have served for the construction of the curve of the errors referred to before, in the third the definitive means corrected for personal error. The last column furnishes in the same way as before the value of

$$\frac{1}{100} r \Sigma (g\, n) ,$$

Date.	$\Delta_1 \delta$	$\Delta_2 \delta$	p	Date.	$\Delta_1 \delta$	$\Delta_2 \delta$	p
1862.21	+0°57	+0°49	2.1	1878.12	−0°02	+0°12	6.8
1863.22	+0.13	+0.33	1.7	1879.13	−0.16	0.00	6.8
1864.20	−0.74	−0.93	2.8	1880.16	+0.28	+0.38	8.8
1865.21	−0.21	−0.14	2.3	1881.17	+0.18	+0.04	9.0
1866.21	−0.02	+0.10	2.3	1882.21	−0.27	−0.07	10.1
1867.20	+0.23	+0.21	2.8	1883.15	−0.14	−0.32	7.5
1868.19	−0.42	−0.54	3.6	1884.18	−0.46	−0.43	7.2
1869.19	0.00	−0.26	2.2	1885.19	−0.21	−0.15	4.4
1870.17	−0.65	−0.73	3.7	1886.14	−0.32	−0.23	4.0
1871.22	−0.70	−1.12	1.3	1887.19	−1.12	−1.07	2.8
1872.18	−0.03	−0.55	3.0	1888.970	……	−0.16	0.6
1873.22	−0.74	−0.92	1.4	1890.275	……	−1.44	0.3
1874.18	−0.49	−0.47	4.2	1897.004	……	+4.38	1.3
1875.22	−1.14	−0.89	4.7	1897.971	……	+2.43	3.2
1876.14	−0.48	−0.19	4.0	1898.844	……	+0.01	0.9
1877.19	−0.44	−0.22	4.4				

For the last position the measurement of HUSSEY in April 1899 could not be taken into account. Of all the measurements after 1888.0 the means are taken without regard to personal correction, this not being independently deducible and the use of the value deduced above for BURNHAM being prohibited on account of the entirely different appearance of the system.

That the number of the normal positions might not be unnecessarily great I formed normal places by uniting the yearly means two by two according to their weights for the whole of the period 1862—1880 when the changes in distance were still very slight and the motion of the angle therefore pretty regular and moreover very small. An exception was only made for the first three, of which only one position was formed. In order to simplify still further the following computations, the value of *log* $\sqrt{p}$ was rounded off to tenths; these modified values are indicated by *log* $\sqrt{p'}$ to distinguish them from the preceding. In this manner the following 21 normal deviations were obtained:

N⁰.	Date	$\Delta\theta$	$l.\sqrt{p'}$	N⁰.	Date	$\Delta\theta$	$l.\sqrt{p'}$	N⁰.	Date	$\Delta\theta$	$l.\sqrt{p'}$
1	1863.31	−0°154	0.4	8	1877.75	−0°014	0.5	15	1886.14	−0°23	0.3
2	1865.71	−0.020	0.3	9	1879.84	+0.217	0.6	16	1887.19	−1.07	0.2
3	1867.76	−0.212	0.4	10	1881.17	+0.04	0.5	17	1888.970	−0.16	9.9
4	1869.80	−0.555	0.4	11	1882.11	−0.07	0.5	18	1890.275	−1.44	9.7
5	1871.89	−0.722	0.3	12	1883.15	−0.32	0.4	19	1897.004	+4.38	0.1
6	1873.94	−0.582	0.4	13	1884.18	−0.43	0.4	20	1897.971	+2.43	0.3
7	1875.64	−0.568	0.5	14	1885.19	−0.15	0.3	21	1898.844	+0.01	0.0

As has already been stated the observations after the periastron-passage could not be treated in the same way as the previous ones, because for that part of the orbit the data are far from sufficient for a satisfactory deduction of the personal corrections. This statement however does not imply that the corrections found *before* 1888 are not at all subject to doubt. Whoever's task it was to investigate the critical problem of these corrections will immediately admit, that in a part of the orbit where e. g. two of the observers have a predominating influence, there can be no question about a complete elimination of the personal errors, even apart from the fact that the accidental errors are often many times greater than the constant ones. Hence the determination of the latter may be very uncertain.

Moreover it is a fact that the personal error often varies greatly with the angle of position itself, especially when the latter, as is the case with Sirius, gradually falls from 90° to 0°, so that the connecting line passes from the horizontal to the vertical position. However I did not feel at liberty to pass over the entire question; the indications of systematic differences were often too clear for doing so.

With regard to the last three normal positions I have still to remark that to the 24-inch refractor of Lowell Observatory the same weight 4 is assigned as to the 36-inch of Mt. Hamilton. The differences $\Delta\,\theta$ have been laid down in the following diagram and have been joined by right lines.

That the remaining errors might vanish as nearly as possible the differential relations were derived between the differences in the angle of position θ and the several elements. Without difficulty we find:

$$\Delta\,\theta = \Delta\,\text{☊} - \frac{\sin i}{\cot w + tg\, w \cos^2 i}\,\Delta\, i + \left(\frac{R}{r}\right)^2 \cos i\,\Delta\,\lambda +$$

$$+ \left(\frac{a}{r}\right)^2 \sin E \cos i\,(2 - e^2 - e\cos E)\,\Delta\,\varphi + \left(\frac{a}{r}\right)^2 \cos i \cos \varphi\,\Delta\, M_0 +$$

$$+ \left(\frac{a}{r}\right)^2 \cos i \cos \varphi\,(t - T_0)\,\Delta\,\mu\ .$$

In this expression
- w indicates the distance from the node, measured in the plane of the orbit,
- E the excentric anomaly,
- r the apparent, and R the true distance of the companion,
- φ the angle of excentricity.

The epoch T_0, for which M_0 stands, may be chosen arbitrarily; I have placed it somewhere in the middle of the period of observation namely at 1880.0.

The equations of errors obtained were treated in the well known manner according to the rules of the method of the least squares; to make the coefficients less unequal the following substitutions were made (logarithmically):

$$x = 0.6\,\Delta\,\text{☊}\,; \qquad y = 0.0\,\Delta\, i\,; \qquad z = 0.7\,\Delta\,\varphi\,; \qquad u = 1.8\,\Delta\,\mu\,;$$

$$v = 0.4\,\Delta^{\lambda} \qquad w = 0.5\,\Delta\, M_0\,; \qquad n = 0.7 \text{ degrees.}$$

For the sake of brevity I state only the normal equations found (numerical coefficients)

$$
\begin{array}{llllllll}
+7.54570\,x & -\ 5.39749\,y & +2.20722\,z & +0.63518\,u & +\ 9.67691\,v & +4.10538\,w & = -0.39532 \\
-5.39749\,x & +10.82040\,y & -2.44634\,z & +2.60262\,u & -\ 7.12051\,v & -0.31135\,w & = +2.69237 \\
+2.20722\,x & -\ 2.44634\,y & +3.76221\,z & -1.35865\,u & +\ 2.10846\,v & -0.23716\,w & = -2.15710 \\
+0.63518\,x & +\ 2.60262\,y & -1.35865\,z & +1.89029\,u & +\ 1.00294\,v & +1.96012\,w & = +1.73341 \\
+9.67691\,x & -\ 7.12051\,y & +2.10846\,z & +1.00294\,u & +12.66065\,v & +5.51165\,w & = -0.26101 \\
+4.10538\,x & -\ 0.31135\,y & -0.23716\,z & +1.96012\,u & +\ 5.51165\,v & +3.73403\,w & = +1.34712
\end{array}
$$

These equations furnished the following values (logarithmically):

$$
\begin{array}{lll}
x = 0.820019 & z = 0.330168_n & v = 0.790540_n \\
y = 9.055875 & u = 0.615761_n & w = 0.628364
\end{array}
$$

from which were deduced:

$$
\text{System I}^a \left\{
\begin{array}{lll}
\Omega = 45^\circ\ 22'.7 & \mu = -\ 7^\circ.37278 & \\
i = 45^\circ\ 10'.2 & M_0 = 103^\circ.6656 & (T = 1894.0696) \\
e = 0.5832 & \lambda = 211^\circ\ 17'.5 &
\end{array}
\right.
$$

I thought it more advisable however to deduce the two elements μ and T directly from the observations, rather than from the above values. With the corrected elements Ω, i, e and λ the mean anomalies were deduced from the first and the last three angles of position; these were then united with suitable weights into 2 mean numbers, from which was easily deduced:

I^b. $\mu = -\ 7^\circ.314775$ $T = 1894.0367$

With these elements the following errors were left in the normal positions:

1 : −0°.131
2 : +0 .169
3 : +0 .025
4 : −0 .319
5 : −0 .513
6 : −0 .409
7 : −0°.422
8 : +0 .114
9 : +0 .362
10 : +0 .224
11 : +0 .163
12 : −0 .006
13 : +0°.003
14 : +0 .451
15 : +0 .597
16 : +0 .119
17 : +2 .103
18 : +2 .550
19 : −0°.207
20 : +0 .151
21 : −0 .220

These errors are also represented in the lower diagram and connected by interrupted lines. Especially the last two positions before the periastron are now badly represented, a fact not to be wondered at, considering the large amount of the corrections of the elements. Although these positions have but the weights 0.6 and 0.3 I have yet proceeded to a second approximation. For the new 2nd members of the normal equations I found :

+0.32052 +0.66856 +0.51950 +0.20554 +0.30590 +0.37168.

After a new solution of the normal equations μ and T were again determined as above; the system of elements obtained is:

$$\text{System II.}\left\{\begin{array}{ll} T = 1894.0900 & i = 46^\circ\ 1'9 \\ \mu = -7^\circ.37069 & \text{☊} = 44\ 30.2 \quad (1900.0) \\ e = 0.5875 & \lambda = 212\ \ 6.4 \end{array}\right.$$

The deviations left by this system in the normal positions are as follows. They have been connected by dotted lines in the diagram.

1 : —0°.203
2 : +0 .209
3 : +0 .082
4 : —0 .250
5 : —0 .455
6 : —0 .380
7 : —0°.433
8 : +0 .034
9 : +0 .182
10 : —0 .032
11 : —0 .161
12 : —0 .420
13 : —0°.521
14 : —0 .205
15 : —0 .218
16 : — 0 .925
17 : +0 .773
18 : +0 .098
19 : —0°.300
20 : +0 .158
21 : —0 .087

The outstanding errors are unimportant, but a certain regularity is unmistakable. The characteristic curvature in the original curve of errors before the periastron, is found back all but unchanged in the diagram of systems I^b and II. The cause may be sought in a perturbation by a third (invisible) member of the system ; the supposition however that not entirely eliminated personal errors have been at work seems to me more plausible. A third possibility remains : the not perfect accuracy of the coefficients of the equations of errors in the 2nd approximation might be the cause. Strictly speaking these ought to have been recalculated with the elements of system I^b.

But this supposition is already very inprobable *a priori*. To arrive at certainty on this subject without an entirely new and prolix computation, I made use of the method of **Klinkerfues** based on six angles of position. The ratio of the planes of triangles in the apparent orbit to those in the true orbit being always as $\cos i : 1$ we have

$$\frac{\sin(v_2 - v_1)\sin(v_3 - v_6)}{\sin(v_3 - v_1)\sin(v_2 - v_6)} = \frac{\sin(\theta_2 - \theta_1)\sin(\theta_3 - \theta_6)}{\sin(\theta_3 - \theta_1)\sin(\theta_2 - \theta_6)}$$

and two other similar equations in which the indices 4 and 5 are successively to be substituted for the index 3. For the epochs of the normal positions 2, 6, 10, 14, 17 and 20 the deviations of these normal positions were united with those of the two neighbouring ones according to the weights. We thus obtained :

$$\theta_1 = 76^\circ.219 \qquad \theta_2 = 59^\circ.650 \qquad \theta_3 = 45^\circ.476$$

$$\theta_4 = 33^\circ.573 \qquad \theta_5 = 13^\circ.213 \qquad \theta_6 = 173^\circ.079.$$

The second members of the equations may be denoted by α, β and γ:

$$\alpha = +0.481680 \qquad \beta = +0.297904 \qquad \gamma = +0.120061$$

I started successively from 4 hypotheses : 1° system II ; 2° $\Delta M_0 = +1^\circ$; 3° $\Delta \mu = +0^\circ.03$; 4° $\Delta e = +0.01$.

From the three anomalies deduced from these I computed :

	1st hypothesis.	2nd hypothesis.	3rd hypothesis.	4th hypothesis.
α	+ 0.468089	+ 0.465082	+ 0.464792	+ 0.474842
β	+ 0.294009	+ 0.290553	+ 0.290125	+ 0.304140
γ	+ 0.119778	+ 0.117508	+ 0.116272	+ 0.135123^5

from which the following equations ensued :

$$-0.003007\,\Delta M_0 \quad -0.003297\,\Delta\mu \quad +0.006753\,\Delta e \quad = +0.013591$$

$$-0.003456\,\Delta M_0 \quad -0.003884\,\Delta\mu \quad +0.010131\,\Delta e \quad = +0.003895$$

$$-0.002270\,\Delta M_0 \quad -0.003506\,\Delta\mu \quad +0.015316\,\Delta e \quad = +0.000283$$

The solution of these equations furnished the following entirely improbable values:

$$\Delta M_0 = +\,51^\circ.8590 \qquad \Delta \mu = -\,2^\circ.011252 \qquad \Delta e = -\,0.07627$$

The question of course remained in how far these values might be brought within admissible limits by small allowable modifications in the assumed angles of position. Moreover, on account of their being arithmetical means, the corrections assumed for the six epochs were not exactly situated on the curve which connects the deviations in the best way possible. I have constructed therefore the curve of errors for the Elements II on a relatively large scale and I have deduced by its aid, for the same epochs as above, the following angles of position:

$$\theta_1 = 76^\circ.281 \qquad \theta_2 = 59^\circ.581 \qquad \theta_3 = 45^\circ.446$$

$$\theta_4 = 33^\circ.503 \qquad \theta_5 = 13^\circ.029 \qquad \theta_6 = 172^\circ.924$$

From these I computed:

$$\alpha = +\,0.484570 \qquad \beta = +\,0.299769 \qquad \gamma = +\,0.120475.$$

The solution of the equations now led to:

$$\Delta M_0 = +\,57^\circ.0261 \qquad \Delta \mu = -\,2^\circ.23501 \qquad \Delta e = -\,0.0854$$

It seemed to me that this proved sufficiently how impossible it is to cause the disappearance of the observed systematic course by a purely elliptic motion and I therefore stopped at System II, taking this to be the best which can be deduced for the present from the observations.

Finally I have determined the semi-axis of the orbit for each observer who had given more than three measurements of distance. As a rule measurements leaving a greater error than $0''.5$ were excluded. This fate befell, besides one unsuccessful observation of SECCHI in 1863, only 5 other measurements of *OΣ*. This is not to be wondered at, if we consider the low position of Sirius at Pulkowa. The results obtained are compiled alphabetically in the following table where the column n gives the number of measurements from which a is deduced.

Observer.	a	n	Observer.	a	n
Aitken	7''.805	5	Hussey	7''.594	4
Bigourdan	7 .507	5	Newcomb	7 .747	4
Burnham	7 .404	10	Peirce	7 .576	4
Dunér	7 .417	5	Pritchett (C.W.)	7 .668	5
Frisby	7 .776	4	Stone	7 .423	5
Hall	7 .533	18	Struve	7 .812	14
Holden	7 .911	7	Wilson	7 .314	4
Hough	7 .358	8	Young	7 .579	7

From all the measurements of the above observers I find in the mean 7''594 for the semi-major axis. The complete system of elements by the side of which I introduce for the sake of comparison the one found by Prof. AUWERS in 1892, runs as follows:

	System II. ZWIERS	_System V*._ AUWERS
T	1894.0900	1893.615
μ	−7°37069	−7°2877
P	48.8421 year	49.399 year
e	0.5875	0.6292
i	46° 1'9	42° 25'6
☊	44 30.2 (1900.0)	37 30.7 [1] (1850.0)
π—☊	212 6.4	219 56.5
a	7''594	7''568

I have also investigated for systematic deviations the *distances* found in the various years. To each observer of the above table the weight 1 was given (with the exception of the 6 measurements, mentionned above), the remaining ones were given the weight ½, evident failures being excluded. After the periastron-passage the observations of SEE and BOOTHROYD were omitted. As appears from the table

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[1] Reduction to 1900.0 + 16'.9.

on page 8 where in the columns Δ_2 the various values of *Obs.—Comp.*, as resulting from a comparison of the observations with System II, have been given already, these observations deviate in distance from 0″67 to 0″99 (in the same direction) from the computed ones, whereas the other distances, measured at Mt. Hamilton, fairly oscillate round them. The following consideration proves *a priori* that the latter must come nearer to the truth. The area of the sector traversed yearly is already known with great approximation from the first part of the orbit. So in each new orbit $r_1 r_2\, arc\, (O_1—O_2)$ must have about the same value as in the old one. Now $O_1—O_2$ is equal to 27°424 as appears from the normal positions 19 and 21, and equal to 23°052 according to the old orbit. Half the difference of the logarithms is 9.96229 = *log.* 0.9168, so that the old distances must be diminished on an average by 8.32%. This gives for 1897.0, 1898.0 and 1899.0 respectively 3″8, 4″0 and 4″3 (compare the ephemeris below), whilst the observations at Lowell Observatory gave much greater values.

The following table gives the yearly means obtained for a with their weights. It is easy to understand that from 1887 an error in r must appear magnified in a.

1862	8″33	(1½)	1873	7″33	(4)	1884	7″50	(7½)
1863	7.65	(2)	1874	7.63	(3½)	1885	7.42	(4)
1864	7.81	(2)	1875	7.49	(5)	1886	7.47	(5)
1865	7.49	(2½)	1876	7.75	(4½)	1887	7.62	(3)
1866	7.69	(6½)	1877	7.64	(4)	1888	7.47	(2)
1867	7.57	(3)	1878	7.66	(5)	1890	7.74	(1)
1868	7.58	(4½)	1879	7.61	(7½)	1897	7.58	(5)
1869	7.53	(4½)	1880	7.49	(8)	1898	7.72	(3)
1870	7.69	(3)	1881	7.53	(10½)	1899	7.85	(2)
1871	7.65	(4)	1882	7.51	(8)			
1872	7.67	(5½)	1883	7.62	(6)			

In the upper figure of the diagram accompanying this paper these values are laid down for the middle of the year and have been connected by right lines. One can see that the deviations are but relatively very small (the weight of the value found for 1862 is in fact about zero) and that the values continually oscillate round the horizontal line of 7″59. Sixteen times the latter is intersected by the connecting lines, fourteen times this is not the case. There is no indication of systematical errors of any importance and I believe I am justified in declaring that system II satisfies all just claims.

For a comparison with future observations I have deduced an ephemeris, an extract of which follows in the subjoined table:

Date	θ	r	Date	θ	r	Date	θ	r
1896.0	205°53	3″60	1900.5	140°64	4″77	1905.0	107°17	6″80
.5	196.61	3.71	1901.0	135.60	4.97	.5	104.67	7.03
1897.0	188.14	3.80	.5	130.97	5.18	1906.0	102.34	7.26
.5	180.08	3.90	1902.0	126.71	5.40	.5	100.14	7.49
1898.0	172.42	4.00	.5	122.78	5.63	1907.0	98.07	7.71
.5	165.17	4.12	1903.0	119.16	5.86	.5	96.12	7.93
1899.0	158.36	4.26	.5	115.82	6.09	1908.0	94.27	8.14
.5	152.00	4.41	1904.0	112.72	6.33	.5	92.52	8.35
1900.0	146.10	4.58	.5	109.85	6.56	1909.0	90.85	8.56

The parallax of Sirius has been determined very accurately by the heliometer measurements of GILL and ELKIN at the Cape in the years 1881—83 and 1888—89. If we take with GILL 0″374 ± 0″006 for the mean according to the weights (M. N., Jan. 1898, p. 81), we shall find for the sum of the masses of the two stars 3.51 times that of the sun, of which, according to AUWERS (l. c. page 231) somewhat over $^2/_3$ is due to Sirius itself.

Physics. — "*Measurements on the magnetic rotation of the plane of polarisation in oxygen at different pressures.*" By Dr. L. H. SIERTSEMA. (Communication N°. 49 from the Physical Laboratory at Leiden, by Prof. KAMERLINGH ONNES).

The results of my measurements on the magnetic rotation of the plane of polarisation in some gases, made at a pressure of about 100 atm., agreed fairly well with those made by KUNDT and RÖNTGEN [1]).

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[1]) Arch. Néerl. (2) 2, p. 378 (1899); Comm. Phys. Lab. Suppl. 1.

If we want to compare them with those made by H. Becquerel, who has worked at a pressure of 1 atm. we must make use of a supposition on the relation of the rotatory constants at 100° and at 1 atm. The simplest supposition already made in the treatise mentioned is, that the rotation is proportional to the density of the gas [1]. But then differences will be found between Becquerel's results and mine, which in the case of oxygen amount to over 10 % and even more than that in the case of other gases. These differences might make us doubt the validity of our supposition [2], and this caused me to make some measurements on the rotatory constants in oxygen at different pressures, in order thus to put to the test the proportionality of rotation and density.

Till now the pressures were read on a metal-manometer, the corrections of which had been previously determined [3]. In order to obtain also a sufficient precision especially for lower pressures, the pressure was measured with the hydrogen manometer, used by Verschaffelt in his investigations on the isothermals of mixtures of CO_2 and H_2 [4]. I used this manometer in the same way as he did when he compared its indications with those of the standard open manometer [5]. The copper connecting-tube mentioned there was now fixed to my apparatus. Mr. Hartman kindly took upon him to take the readings of the manometer.

The d'Arsonval galvanometer [6] has now been clamped in a stand suspended as invented by Julius, to protect it against vibrations [7], so that the readings could be taken with greater accuracy. For the rest, everything was used in the same way as before.

The observations are made with commercial oxygen at four pressures, at each of which three or two sets of adjustments have been made, in the same order as before [8]. The calculation [9] then yields for each a number proportional to $\frac{\omega}{d}$, where ω is the rotatory constant and d the density, borrowed from Amagat's [10] observations. These numbers are:

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[1] l. c. p. 328.
[2] l. c. p. 379.
[3] l. c. p. 300.
[4] Thesis for the doctorate, Leyden 1899, p. 15. Comm. Phys. Lab. No. 45 and 47.
[5] Thesis for the doctorate, p. 17.
[6] Arch. Néerl. p. 305.
[7] Wied. Ann. 56, p. 151 (1895).
[8] l. c. p.320.
[9] l. c. p. 325—330.
[10] Ann. de Ch. et de Ph. (5) 19 p. 375 (1880).

Pressure in atm.	$\frac{\omega}{d} \times$ const.	means.
97.38	1565	
96.68	1560	1559
96.13	1553	
73.04	1571	
72.82	1548	1555
72.50	1545	
49.33	1555	1555
49.15	1557	
38.47	1546	
38.44	1545	1550
38.12	1558	

All measurements are made at a wave-length of 0.608 μ.

The means can be esteemed equal, because the differences lie within the errors of observation [1]), and we find our supposition confirmed for pressures ranging from 100 to 38 atm. If at 1 atm. variations of 10 % would appear, we could expect them to be perceptible at least at 38 atm. This not being the case, we shall have to look elsewhere for the cause of the difference between BECQUEREL's results and mine.

With N_2O and with CO_2 the differences [2]) alluded to are much greater and it might be possible that with these gases, which diverge more from an ideal gas than oxygen, deviations from the proportionality in question would be perceptible.

Therefore I intend to make the same measurements on the magnetic rotation of one of these gases also.

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[1]) l. c. p. 371.

[2]) l. c. p. 379.

(June 20th, 1899.)

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday June 24th, 1899.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 24 Juni 1899 Dl. VIII).

CONTENTS: "On the influence of water upon the rapidity of the formation of ether from methyliodide and ethyliodide and from sodiummethylate and sodiumethylate." By Prof. C. A. LOBRY DE BRUYN and Dr. A. STEGER, p. 23. — "On an instance of conversion of mixture-crystals in a compound." By Prof. H. W. BAKHUIS ROOZEBOOM, p. 23. — "On the enantiotropy of tin." By Dr. ERNST COHEN and Dr. C. VAN EYK. (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM). p. 23. — „The continuation of a one valued function represented by a double series." By Prof. J. C. KLUYVER, p. 24. — "On standard gas-manometers" (With 2 plates). By Prof. H. KAMERLINGH ONNES). p. 29. — "The determination of isothermals for mixtures of HCl and C_2H_6." (With one plate). By Mr. N QUINT GZN. (Communicated by Prof. J. D. VAN DER WAALS, p. 40. — „The elementary Theory of the ZEEMAN-effect. Reply to an objection of POINCARÉ." By Prof. H. A LORENTZ, p. 52. — „On the finding back of the comet of HOLMES according to the computations of Mr. H. J. ZWIERS." By Prof. H. G. VAN DE SANDE BAKHUYZEN, p. 69.

The following papers were read:

Chemistry. — „*On the influence of water upon the rapidity of the formation of ether from methyliodide and ethyliodide and from sodiummethylate and sodiumethylate*". By Prof. C A LOBRY DE BRUYN and Dr. A. STEGER.

(Will be published in the Proceedings of the next meeting.)

Chemistry. — „*On an instance of conversion of mixture crystals in a compound*". By Prof. H. W. BAKHUIS ROOZEBOOM.

(Will be published in the Proceedings of the next meeting.)

Chemistry. — „*On the enantiotropy of Tin*". By Dr. ERNST COHEN and Dr. C. VAN EYK (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

(Will be published in the Proceedings of the next meeting.)

Mathematics. — *"The continuation of a one-valued function, represented by a double series."* By Prof. J. C. Kluyver.

In his paper „Ueber die Entwickelungscoefficienten der lemniscatischen Functionen" (Math. Ann., Bd. 51, p. 181) Mr. Hurwitz called attention to the perfect analogy between the Bernoullian numbers B_n and another class of rational numbers E_n occurring as coefficients in the expansion of the particular elliptic function pu, whose fundamental parallelogram of periods is a square.

It is possible to carry still somewhat further this analogy. In fact, the numbers B_n are closely connected with the values of the integral transcendental function $(1 + e^{-\pi i z})\,\zeta(z)$, which correspond to positive integer values of z, and we will show that the numbers of Hurwitz admit of a similar interpretation.

If we consider the doubly infinite series

$$\sum{}' \frac{1}{(m\omega + m'\omega')^n}\,,$$

$$\left.\begin{matrix} \pm m \\ \pm m' \end{matrix}\right\} = 0,\ 1,\ 2,\ \ldots\ldots$$

the ratio ω'/ω being a complex quantity the imaginary part of which we assume to be positive, it is known that this series converges absolutely as soon as the integer $n > 2$. Changing the integer n into an arbitrary real number $a > 2$ the series is still convergent, a determinate value however cannot be attached to its sum, until the amplitude of each separate term is fixed in some way or other. In order to define this amplitude without ambiguity we draw across the plane, containing the network with the vertices $m\omega + m'\omega'$, a straight line or barrier leading from the point 0 to ∞ and passing through the points ω, 2ω, 3ω, ... Then, having fixed once for all the amplitude θ of the stroke ω, we agree to understand by the amplitude of $m\omega + m'\omega'$ the angle θ, augmented by the angle through which the barrier is to be turned in a positive direction till it coincides with the stroke $m\omega + m'\omega'$. According to this agreement to every real value of $a > 2$ belongs a determinate value of the sum of the series, moreover it is easily inferred that its convergence and its one-valuedness are not impaired when the real exponent a is replaced by a complex quantity $z = x + i\,y$, provided we have $x > 2$.

Hence we may put

$$Z(z;\, \omega, \omega') = Z(z) = \Sigma' (m\omega + m'\omega')^{-z} \ ,$$

and we have thereby arrived at a one-valued function $Z(z)$, as yet merely existing in that part of the z-plane where $x > 2$.

It will be at once noticed, that the agregate of values through which the thus defined function $Z(z)$ can be made to pass, essentially depends upon the convention made concerning the amplitude of $m\omega + m'\omega'$. It is only when z acquires positive integer values > 2, that this convention becomes wholly immaterial.

The question now arises whether the function $Z(z)$ can be continued across the limit of the domain in which it is originally defined by means of the double series. This question may be answered in the affirmative, indeed, it will be found that by converting the double series into a definite integral the required continuation readily presents itself.

Let 2ω and $2\omega'$ denote a pair of primitive periods of an elliptic function $\wp u$ and let us put

$$\psi(u) = \wp u - \frac{\pi^2}{4\,\omega^2} \cdot \frac{1}{\sin^2 \dfrac{\pi\, u}{2\,\omega}} \ .$$

Then, we consider the integral

$$I = \frac{1}{2\,\pi\, i} \int\limits_L \frac{\psi(u)}{u^{z-1}}\, du$$

and take it along a loop L beginning and ending at $u = \infty$, going positively round the point $u = 0$ and enclosing the points ω, $2\,\omega$, $3\,\omega$, ... its double linear part being drawn as closely as possible along the right line 0, ω, $2\,\omega$ ... Under the restriction that the real part of $z > 2$ it follows from the application of CAUCHY's theorem, that the integral I is simply equal to the negative sum of the residues corresponding to the poles β of $\psi(u)$. For these poles constitute the system of singular points that the subject of integration possesses in the region outside the loop.

Thus, as we have in general

$$\begin{aligned} \beta &= 2\,m\omega + 2\,m'\omega' \ , \\ \pm\, m &= 0,\ 1,\ 2,\ \ldots \\ \pm\, m' &= 1,\ 2,\ \ldots \end{aligned}$$

we must conclude

$$I = -\frac{1}{2\pi i}\sum_{\beta}\int\frac{\psi(u)}{u^{z-1}}\,du = -\frac{1}{2\pi i}\sum_{\beta}\int\frac{du}{u^{z-1}(u-\beta)^2} =$$

$$= (z-1)\sum_{\beta}\frac{1}{\beta^z} = \frac{1}{2^z}(z-1)\Sigma'(m\omega + m'\omega')^{-z} .$$

$$\pm m = 0,\ 1,\ 2,\ \ldots$$

$$\pm m' = 1,\ 2,\ \ldots$$

The above double series still differs from that which served to define $Z(z)$ because it does not include the terms of the simple series

$$\Sigma'(m\omega)^{-z} .$$

$$\pm m = 1,\ 2,\ \ldots$$

Hence replacing this series by the equivalent expression $(1 + e^{-\pi i z})\,\omega^{-z}\,\zeta(z)$ there results

$$I = \frac{1}{2^z}(z-1)\left[Z(z\,;\,\omega,\omega') - (1 + e^{-\pi i z})\,\omega^{-z}\,\zeta(z)\right] .$$

We will now seek to express the integral I in a different way, The function $\psi(u)$ can be expanded in a trigonometric series. By a known formula we have

$$\psi(u) = -\frac{\eta}{\omega} - \frac{2\pi^2}{\omega^2}\sum_k \frac{kq^{2k}}{1-q^{2k}}\cos\frac{\pi uk}{\omega} ,$$

$$\left(q = e^{\frac{\pi i \omega'}{\omega}}\right)$$

and owing to the fact that along the path of integration the ratio u/ω remains real, we are at liberty to substitute in the integral I the cosine-series for the function $\psi(u)$. So we are led to a series of integrals, each of which of the form

$$J_k = \frac{1}{2\pi i}\int_L \frac{1}{u^{z-1}}\cos\frac{\pi u k}{\omega}\,du .$$

Always supposing the real part of $z > 2$, we find by the usual methods of integration

$$J_k = - e^{-\pi i z} \cos\frac{\pi z}{2} \, \frac{1}{\Gamma(z-1)} \left(\frac{\pi k}{\omega}\right)^{z-2},$$

whence it follows that

$$I = 2 e^{-\pi i z} \cos\frac{\pi z}{2} \left(\frac{\pi}{\omega}\right)^{z} \frac{1}{\Gamma(z-1)} \sum_k \frac{q^{2k}}{1-q^{2k}} k^{z-1}$$

Combining this equation with the one we got before, we finally have

$$Z(z;\, \omega, \omega') = (1 + e^{-\pi i z})\, \omega^{-z} \zeta(z) +$$

$$+ \frac{2}{\Gamma(z)} \left(\frac{2\pi}{\omega}\right)^{z} e^{-\pi i z} \cos\frac{\pi z}{2} \sum_k \frac{q^{2k}}{1-q^{2k}} k^{z-1}.$$

Now, in deducing this equation we postulated that the real part of z was greater than 2, but as the right hand side defines a one-valued function of z, holomorph all over the z-plane, we may regard this equation as the proper definition of $Z(z)$, thus establishing the existence of an integral transcendental function that is only partially represented by the doubly infinite series. The resemblance between the functions $Z(z)$ and $(1 + e^{-\pi i z})\, \omega^{-z} \zeta(z)$ is manifest. The former is evolved from the doubly infinite system $m\omega + m'\omega'$, the latter arose entirely in the same way from the simply infinite system $m\omega$. Therefore we may conceive $Z(z)$ as an extension of the function $(1+e^{-\pi i z})\, \omega^{-z} \zeta(z)$, the relation between these functions finding its analogue in the relation between the elliptic functions and the simply periodic ones.

Seeking for the values of $Z(z)$ corresponding to integer values of its argument, we find in the first place that $Z(z)$, therein behaving as $(1 + e^{-\pi i z})\, \omega^{-z} \zeta(z)$, vanishes whenever z is either a positive odd or a negative integer > 1. For $z = 0$, we get

$$Z(0) = 2\zeta(0) = -1,$$

for $z = 1$ there results

$$Z(1) = \lim_{\delta = 0} (1 - e^{-\pi i \delta})\, \omega^{-1} \zeta(1 + \delta) = \frac{\pi i}{\omega}.$$

As for positive and even integer values of z we have

$$Z(2n) = 2\omega^{-2n} \zeta(2n) + \frac{2}{\Gamma(2n)} \left(\frac{2\pi}{\omega}\right)^{2n} (-1)^n \sum_k \frac{q^{2k}}{1-q^{2k}} k^{2n-1},$$

and from this formula for $n = 1$

$$Z(2) = \frac{\pi^2}{3\omega^2} + 4\,\psi(0) + \frac{4\,\eta}{\omega} = \frac{4\,\eta}{\omega}\,,$$

whereas for larger values of n we can write in general

$$Z(2n) = 2\,\omega^{-2n}\,\zeta(2n) + \frac{2^{2n}}{\Gamma(2n)}\,\psi^{(2n-2)}(0)\,.$$

Now considering the expansion

$$pu = \frac{1}{u^2} + \sum_n \frac{\lambda_n}{2\,n} \cdot \frac{u^{2n-2}}{(2\,n-2)!}\,,$$

where the leading coefficient λ_1 is zero and the other λ's stand for certain known polynomials in the invariants g_2 and g_3, we deduce from it

$$\psi(u) = \sum_n u^{2n-2} \left[\frac{\lambda_n}{2\,n} \cdot \frac{1}{(2n-2)!} - 2\,\zeta(2n)\,\frac{2n-1}{(2\omega)^{2n}} \right]$$

and

$$\psi^{(2n-2)}(0) = \frac{\lambda_n}{2n} - \frac{2}{(2\omega)^{2n}}\,\Gamma(2n)\,\zeta(2n)\,,$$

so that we find

$$Z(2n) = \frac{2^{2n}\,\lambda_n}{(2n)!}$$

provided n be greater than 1.

In order to obtain an expression of the numbers E_n of HURWITZ we take

$$\omega = 1,\ \omega' = i,\ \alpha = 2\int_1^\infty \frac{d\,s}{\sqrt{4\,s^3 - 4\,s}} = 2{,}622057....\,,\ g_2 = 4\alpha^4,\ g_3 = 0\,.$$

In this special case we have

$$\lambda_{2n+1} = 0\,, \qquad \lambda_{2n} = \alpha^{4n}\,E_n\,,$$

where E_n is a rational and positive number, obeying the relation

$$E_n = \frac{(4n)!}{(2\alpha)^{4n}}\,Z(4n\,;\,1,\,i)\,,$$

this relation obviously being the analogue of the well known formula for the Bernoullian numbers

$$B_n = \frac{(2n)!}{(2\pi)^{2n}}\,(1 + e^{-2n\pi i})\,\zeta(2n)\,.$$

Physics. — Communication N⁰. 50 from the Physical Laboratory at Leiden by Dr. H. Kamerlingh Onnes: "*Standard Gas-manometers.*" (Precision-piezometers with variable volume for gases.)

§ 1. *Purpose.* Further progress in the knowledge of the laws from which we derive the equation of condition for the gaseous and the liquid state, depends for a great deal on accurate determinations with perfectly pure gases and their mixtures in proportions exactly known. In these determinations the principal thing is to measure the pressure and volume of a precisely known quantity of gas at constant temperatures. The standard open manometer [1] of reduced height formerly described offers us a means of attaining great accuracy in measuring the pressure. In the following pages I intend to describe piezometers in which (at temperatures above the freezing-point of mercury) the volume of a gas, shut off by mercury and compressed to different pressures, in proportion to the volume which it would occupy at 0° and 760 m.m. (the *normal volume*) can also be read with great accuracy. These apparatus enable us to determine the isothermal lines for gases to within $\frac{1}{5000}$, at temperatures (above the limit mentioned) which can be kept sufficiently constant to allow measurements with the standard open manometer of reduced height.

If the piezometer-tubes are filled with a standard gas, of which the equation of condition for ordinary temperatures has been determined by means of the open manometer, or if their indications have been compared immediately with the open manometer indepently from a determination of constants, they can also conversely be used to replace the open manometer when the measurements have to be made in a shorter time than is required for reading the standard open manometer of reduced height at high pressures.

This method has been followed by me in an investigation taken up a long time ago on the isothermal lines of hydrogen (now to be extended of course to the since discovered argon and helium) together with those of different mixtures of gases at low temperatures (for the obtaining and keeping constant of which the cryogenic laboratory was devised [2])).

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[1] Comm. from the Physical Laboratory at Leiden N⁰. 44.

[2] Comm. Phys. Lab. Leiden N⁰. 14; the means for the accurate measuring of the low temperatures are treated of in Zitt. Versl. 30 Mei and 27 Juni 1896. Comm. Phys. Lab. Leiden N⁰. 27.

It would be very difficult to keep the temperatures at which those isothermals are to be determined so constant that during the time required for a determination with the open standard manometer no variations can occur which would influence the pressure to be measured more than the errors of adjustment. The best thing to be done seemed to measure the pressure in the piezometers of constant volume filled with gas at a low temperature (a following communication will treat of its construction and use) by means of gas-gauges which have themselves been compared with the open manometer of reduced height, and to construct these closed manometers so that they are not much inferior either in sensibility or reliability to the standard open manometer.

In order to render the indications of the piezometers or manometers as reliable as possible the glass tubes in which the gas is compressed have been taken so wide as appeared to be compatible with a sufficient power of resistance and would not render too difficult the handling. The chance that a perceptible quantity of the gas, albeit in extremely small bubbles, should adhere to the walls when the mercury rises, as well as the influence of a deviating behaviour of the gas-layers at the surface of the glass, becomes less as the tube is wider. Moreover the more regular shape of the meniscus renders the determination of the volume more accurate and diminishes the influence of capillary disturbances on the measurement of the pressure.

The manometer-tubes may be cleaned and refilled without invalidating the determination of constants once made. This is of great importance, also because it enables us to apply a differential method when comparing the isothermals of two gases or mixtures of gases. For if we dispose of two manometers of the kind to be described, we can compress these gases simultaneously under the same pressure, and *interchange* them in the two sets; so the errors which the apparatus might still show, are eliminated for the greater part.

For the rest the closed manometers are so constructed that the normal volume can be very accurately determined not only at the beginning of the measurements made under pressure, but at any time we should want to. In order to do so the manometer-tube filled with gas may be taken from the apparatus, placed in a space of constant temperature, — where the difference between the pressure of the enclosed gas and the atmosphere can be measured, taking into account the capillary depression —, and may be replaced in the apparatus being still as clean as before while the quantity of enclosed gas does not undergo the least change during this operation. The data for the necessary corrections can also be determined with great accuracy.

Lastly care has been taken that the mercury in the apparatus does not come into contact with anything but carefully cleaned glass or iron and cork or solidified cement. Accordingly the menisci in the manometer-tubes remain perfect. All this entitles us to call the apparatus described in the following pages when used as gasmanometer, a standard manometer.

§ 2. *General arrangement.* The apparatus now used in the Leiden Laboratory is designed for measurements with 4 piezometers ranging from 4 to 64 atmospheres. In the construction of the apparatus, I have successively been ably assisted by Dr. LEBRET and especially by Mr. SCHALKWIJK, both assistants and Messrs. CURVERS and FLIM, instrumentmakers, to all of whom I render thanks. It contains, when used for measurements of pressure, and as represented in Plate I, four closed manometers placed in a row, on each of which a definite range of pressure is read, viz. 4—8, 8—16, 16—32, 32—64 atm.; each following manometer has a small range of pressure in common with the preceding, through which proper continuity and mutual testing are obtained. The piezometer-tubes are placed in compression-cylinders, each of which can be connected separately with the apparatus in which the pressure is to be measured, while all can be connected mutually.

The whole apparatus is mounted usually in a definite place. The pressure is transferred from the apparatus, in which we want to measure it, to the manometer through a narrow tube filled with compressed gas. This method offers many advantages in a research laboratory like that at Leiden.

The choice of the stages of pressure agrees with the division into pieces for 4 atmospheres of the standard open manometer which ranges as far as 60 atm., and with which the closed manometer is used as an auxiliary apparatus in order to attain a pressure higher than 60 atm., in the way described in Comm. n⁰. 44.

As the closed manometer for the next stage made after the same principle is not yet ready (it requires a compression tube with a thicker wall and greater volume than those existing) we use for pressures above 64 atm. closed manometers of simpler construction [1]).

The mutual testing of the various closed manometers will be described when the observations made with the apparatus are com-

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[1]) Comp. VERSCHAFFELT, Thesis for the doctorate, Leiden 1899.

municated, together with the measurements made in order to test the accuracy of the standard open manometer of reduced height by dividing it into two parts, which are equilibrated with each other or simultaneously with one or two closed manometers.

§ 3. *The piezometer- or manometertubes.* These are made of Jena normal glass and recall in so far as the general form is concerned the type used by CAILLETET (comp. fig. 3 and 4). On to the upper end of the stem a wider reservoir has been blown of about the same volume as the divided stem in order that on each manometer the range of the pressures extends only so far that the highest pressure at which an adjustment in that tube can be made is twice the lowest. In this way we ensure the sensibility to be about the same at the different parts of the graduated scale.

The diameters of the reading-tubes (comp. fig. 3 and 4) are for the four manometer-tubes 8, 6, 4 and 3 mm. respectively. The diameters of the upper reservoirs and the thickness of the reading tubes and of the upper reservoirs have been chosen so as to be in accordance with these (comp. fig. 6).

A very accurate determination of the volume of the enclosed gas when compressed is rendered possible by fixing a very fine capillary tube of known volume (diameter about 0.3 mm.) on to the upper reservoir just as with AMAGATS's piezometer (e_3 comp. fig. 6).

After sealing off we can, by measuring the length of that part of the capillary tube that has remained unchanged and by estimating the volume of the conical part formed by the sealing off, compute its whole volume from a definite mark. The error thus remaining may be entirely neglected.

A wider capillary e' (fig. 7) carrying a small cock has formerly been welded on to the capillary tube at the place where it will be sealed off. By means of this cock we can connect the tube with the vacuum pump, suck up liquids in the manometer-tube, supply dry air, etc.; moreover it is useful in calibrating.

The tube, dried and ready to be filled is sealed off at the place where the wider capillary tube has been welded on to the narrow one. If the tube has afterwards to be cleaned again, which can not but imperfectly be done without opening it and sucking liquid through, or if the tube has to be calibrated anew, the fine point is filed off and at that place a new tube resembling the one sealed off is joined on. In this way we lose in each operation only a few mm. of the capillary tube e and we can use the same manometer for numerous sets of measurements before it is necessary to weld on a new capillary to the upper part of the reservoirs. If this happens to be the case we can no longer calculate the new volume of the reservoir from the old one by means of an insignificant and perfectly sure correction, which is possible as long as we preserve the same capillary tube.

The graduated stem *c* is made from a carefully selected perfectly straight and almost cylindrical tube. The graduation extends from 0 to 50 cm., continued on either side over some cm. in order to make sure that the diameter of the tube in the neighbourhood of 0 and 50 does not show any particular change. It did not seem desirable to make the graduation extend over more than 50 cm. as it is necessary to keep the whole length at a constant temperature. The divisions are at distances of 1 mm. and the readings are taken by means of a kathetometer.

It is of great importance that the whole tube should be perfectly vertical. Therefore care is taken that the stem and the cylinders of the manometer-tubes are well centred, and that the tube is truly centred in the steel tube with flange *O* (fig. 3. Pl. I) the whole apparatus being placed vertical by means of the plummet (compare also § 5).

The reading tube is connected with the lower reservoir *a* by means of a wider tube, *b* fig. 3. By means of this wider part the manometer-tube is cemented ¹) in the flange *O*, which for this purpose must be made so that it can be pushed over the upper reservoir. The outer diameter and the thickness of the wider part are taken a little larger than those of the upper reservoir, and the bore of the flange belonging to it so much larger that between the glass and the flange space remains for a thin layer of cement (about 0.5 mm.).

The lower cylinder *a* is thin, as in the manometers of the type used by CAILLETET and AMAGAT. At its lower end however the manometer-tube terminates differently; it is provided with a *U*-shaped tube placed under the lower reservoir, of which the branch *f* connected with the reservoir is graduated. The purpose of this tube is to enable us to determine accurately the normal volume or to test it (as has been mentioned in § 1) at any time we should wish. Before we proceed to the filling with gas we, in the manner in-

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¹) In some cases, when for instance we should want to heat the piezometer-tube, it may be desirable not to cement the piezometer but to enclose it in the flange by packing. But as we have principally in view its use as gasmanometer we need not dwell on this particular.

dicated by CAILLETET, introduce in the lower reservoir, held in a sloping position, a quantity of mercury sufficient to fill this *U*-tube. After the manometer has been filled with gas in the said position, we cause the mercury to enter the *U*-tube by turning the manometer into the vertical position. Then by reading the position of the surface of the mercury in the divided and calibrated branch *f*, after the manometer-tube is detached from the filling apparatus, we can determine the volume of the enclosed gas, while the difference in level with the other branch *g* indicates the excess ot pressure, above the pressure indicated by the barometer. And this determination can be made with great accuracy because we could allow the diameter of both the branches of the small manometer to be 8 mm., so that the correction for the capillary depression can be determined with sufficient accuracy from the form of the menisci.

The length of the *U*-tube warrants that the gas remains shut off even when changes of temperature and atmospheric pressure occur.

The peculiar position of the *U*-tube with regard to the manometer-tube leaves room under the lower reservoir for the tube *h*, which acts a very important part in different operations, viz. the exhausting with the mercury-pump, the filling with pure gas and the shutting off of a definite quantity of gas. This tube *h* is bent downwards slantingly and backwards and carries at the end a ground tap which fits in a ground cap, welded on to the glass conduit of the mercury-pump and the gas-generating apparatus (Comm. N°. 27 p. 15).

After the piezometer-tube is cleaned and dried, the capillary end at the top of its upper reservoir has been sealed off, and the wider part of its stem has been cemented in the flange, it can be successively exhausted and filled with gas by means of this tube *h*. Then by revolving the piezometer-tube round the axis of the joint we can admit the mercury from the lower reservoir into the *U*-tube and so shut off the gas perfectly sure, after which the tube may be separated from the gas-generating apparatus. It needs no comment that the operation described must be done with great care in order to prevent that the tube *h* breaks off, as the manometer is already burdened with the heavy flange.

In order to facilitate any repairs to be made in the *U*-tube, its branches are connected by a narrower tube that can easily be straightened in the flame and after the repair is finished can be bent again into the original form without any damage to the calibrated tube.

§ 4. *The compression-cylinders and stopcocks.* (Pl. I, fig. 1, 2, 3.) The manometer-tubes filled with gas and closed by the mercury in the *U*-tubes are introduced into the compression-cylinders A previously filled to the rim with mercury. In order to prevent the air from getting into the *U*-tube, care is taken that the mercury is flowing out of the tube (by heating the manometer reservoir) at the moment that its opening is immersed below the mercury surface in the compression-cylinders. When the compression-cylinder is closed by the flange in which the manometer is cemented, the mercury pushed up by that part of the flange which fits in the compression-cylinder, drives the air out. The superfluous mercury escapes until by firmly screwing on the nut *N* we obtain a tight fit on the washer *p*. Then the reservoir of the manometer-tube is contained in a space wholly and exclusively filled with mercury.

By means of this contrivance we can take the manometer-tube from the apparatus without its coming in contact with any liquid but mercury, and avoid the great number of difficulties which always arise when we transfer, as usualy is done, the pressure by another fluid on the mercury in the compression-cylinder.

It is desirable that we should have at hand a greater number of manometer-tubes with flanges in order that we may successively place several piezometers previously prepared into the compression-cylinders. The 4 compression-cylinders of the apparatus on Pl. I consist of well-drawn iron tubes, carrying taps welded on at both ends[1]). They are mounted together on a stand *V*, in the notches of which they fit in with the parts of the two taps that are filed sexangularly; they are shut up by a counter plate, in which likewise notches have been filed. These notches together with those in the stand hold the sexangular taps, as clearly shown in fig. 1 Pl. II.

Thus it is easy to place into and to take out of the apparatus each of the compression-cylinders separately, while the tubes with the stand form a whole and are kept as it were in a large wrench, which can be held firmly so as not to meet with the difficulty, which else so often occurs, whenever we want to screw the nut of a compression-cylinder tightly by means of a wrench with a long lever.

The whole stand is placed in a wooden receptacle for the mercury that might flow out.

The compression-cylinders can be opened on both sides. In

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[1]) The boring of a bar is very expensive and it is difficult to get smaller pieces of tubing with walls sufficiently thick to be provided with screw-thread and a sexangular tap.

cleaning the inner surface we therefore do not meet with the difficulty, which generally is occasioned by the bottom part. At their lower ends the compression cylinders are closed by nuts L, similar to those at the upper ends; through these they are coupled to steel tubes l_1, l_2, l_3, l_4 bent rectangularly, terminating in the stopcocks k_1, k_2, k_3, k_4 [1]) which serve to couple each manometer (sometimes two) to the pressure-conduit or to disconnect them according as to whether or no the pressure to be measured is within the range of the manometer.

These stopcocks are below the upper rim of the compression cylinders so as to allow us to fill without difficulty the compression-cylinder and the tube entirely with mercury; as they are provided with cork stuffing the mercury cannot become dirty by streaming along, in or out.

The pressure is transferred on to the mercury in the compression-cylinders by means of mercury in the tubes s_1. The stopcocks of the different compression tubes are mounted on a board, screwed on to the stand V (see Pl. I fig. 1 and 2) together with a system of supply-tubes. These supply-tubes filled entirely with mercury connect the compression-cylinders with:

1°. a mercury-reservoir R_1, serving to supply mercury and to guarantee that, when the apparatus is not watched there still remains in case of change of temperature and atmospheric pressure a sufficient excess of pressure in the apparatus even if the stopcocks were open. This reservoir is always closed by the iron stopcock k_5 when determinations of pressure are being made.

2°. the principal tube s_3 through which the pressure is transferred on to the mercury in the tubes, and which may be closed by an iron stopcock k_6 [2]).

The tubes s_1 are entirely filled with mercury by exhausting them and then admitting mercury from R_1; the stopcocks, like the other ones are provided with cork stuffing.

Through the supply-tube s_3, immersed in the mercury down to the bottom of the reservoir R_2 we supply from the mercury in R_2 as much as is required to compress the gas in the manometer tubes. The pressure to be measured is transferred on to the mercury in the reservoir by means of compressed gas. In order to apply the

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[1]) The construction of steelwork of this kind is described in Comm. N°. 27 and 44.

[2]) These stopcocks did not require the same great care as bestowed on the steel stopcocks of the single manometers (which must be perfectly reliable) as not all manometer-tubes may be exposed to the highest pressure.

correction resulting from the difference in level between the surface on which the pressure to be measured is applied, β, and the top of the meniscus of the mercury in one of the manometer-tubes δ_4, it is necessary to know the level of the mercury in the reservoir R_2. This is indicated by the gauge-glass P, beside the reservoir R_2. It consists of a thick-walled tube, drawn out on both ends and provided with steel caps and steel capillary tubes t_1, t_2, as described in Comm. n°. 44, which form at the higher and lower ends the connection with the mercury-reservoir R_2 (or what comes to the same with the siphon tube s_3). The stopcock k_7 serves to close the gauge-glass when the reservoir has been exhausted and we want to let mercury flow into it through the tube s_3.

The correction just mentioned for the vertical distance between the level of the mercury in the reservoir (as indicated by the gauge-glass) and the meniscus in the manometer where the reading is taken, which in the case of many manometrical measurements could but very roughly be applied, is accurately determined here with a kathetometer.

A divided scale on which we can immediately transfer the readings is placed at the side of the gauge-glass. With the aid of the kathetometer we compare the level of the graduations with the level of the graduations on the manometer-tubes to be read. This is done before and after they have been provided with the waterjackets m_1, m_2, m_3 and m_4. To protect the observer the gauge-glass is provided at the back and on the sides with iron plates and in front with a thick plate-glass.

On a board near R_2 stopcocks and tubings are fastened which are represented in Pl. I fig. 1 and 2 require no separate description. By means of these we can:

1°. close (by means of k_9) the conduit s_7 through which the pressure is transferred [1]) by means of compressed gas;

2°. read the pressure (k_8 being shut) transferred through this conduit, on an auxiliary manometer M, before the compressed gas is allowed to transfer the pressure into the measuring apparatus, in order to get to know, which manometer is to be connected;

3°. make and break arbitrarily the connection with the auxiliary manometer, whenever this seems desirable, while making the measurements of pressure;

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[1]) As for instance a tube which forms a connection with an apparatus like that of Dr. SIERTSEMA's Comm. N°. 49, or a tube, which connects the manometers with the piezometer for gases compressed at low temparatures, mounted in another room.

4°. exhaust the conduits (through k_9 and k_{11} before the connecting of s_7 and s_8) and to fill the reservoir R_2 with mercury through k_6 and k_5);

5°. To connect the apparatus with the standard open manometer (through k_{11}).

When the apparatus is used as a manometer the bottoms of the waterjackets on to which the glass waterjackets are fastened with india-rubber, are screwed on to the flanges O at λ (seefig. 3). The temperature is kept constant by means of circulating water [1]) and of the stirring rods r_1, r_2, r_3, r_4, while thermometers (not represented in the figure) enable to read the temperature at differents heights. The stirring rods are suspended from the stand S_1, which is constructed so that it can easily be removed.

§ 5. *Some remarks on cleaning, cementing and filling.* The cleaning of the tubes is of great importance. Only when this is done with the greatest care, it is possible that the menisci remain perfect. As for the precautions to ensure this, I refer to Comm. N°. 27. Attention must be drawn however to the fact that, without particular precautions it would be impossible to clean the tubes by boiling for instance with nitric acid. In the first place different parts of the walls are very thick; moreover they are very long and terminate on one end in a comparatively narrow tube, on the other end in an extremely narrow capillary tube, which almost closes them. The difficulty arising from this, was removed by placing the tubes, as shown in Pl. II fig. 2, in expressely made boiling-tubes of ordinary size in which the cleansing-liquid is poured also filling the manometer-tube (being not entirely shut on both sides), and is heated until the liquid begins to boil within the manometer-tube.

Round the manometer-tube a platinum wire is slung, which prevents contact between manometer-tube and boiling-tube, and serves to take the manometer-tube out of the boiling-tube.

In cementing the manometer-tubes in the flanges, we must take care that the axes of the two coincide. Therefore it seemed desirable to make special moulds in which the tube and the flange are fastened. (Compare fig. 3 Pl. II).

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[1]) I shall not dwell on this circulation. When the piezometers are used at temperatures much differing from that of the room we must surround them with liquid- or vapour-jackets (or liquid-jackets enclosed in vapour-jackets).

On to the part λ of the flange provided with a screw-thread, we screw a brass tube in which two openings e have been cut, and in which the stem of the manometer-tube may be fastened by means of the wooden stopper h cut in two. Over the wider lower-part of the flange, we slide the tube consisting of a narrow and a wide piece in which openings have been cut at b, d and also at e, and which fits at λ round the former tube. By means of a tight ring at f the two tubes are kept in a coaxial position. In the wide end of the second tube the lower cylinder of the manometer-tube may be fastened at a by means of a wooden stopper likewise cut in two.

The cementing is done in the following way: the manometer-tube is heated to a little above the melting-point of the cement, a thin layer of which is spread on the tube. In the meantime the steel piece with the brass tube screwed on to it is heated also to about the same temperature. Then the manometer-tube (in the reversed position of fig. 3) is slid into the steel piece, over this the second tube is slid and then the halves of the wooden stopper are put in their places. In this way the manometer-tube is truly centred and the space between manometer-tube and flange is entirely filled up with cement. Through the openings we may pour in additional cement. After this is solidified we turn the apparatus upside down (position of fig. 3) so that the glass-reservoir rests on the collar c of cement oozed out.

The superfluous cement is washed away with benzine.

For the filling with pure hydrogen I refer to Comm. N⁰. 27; for the revolving of the manometer-tube round the axis of the tube h, in order to shut off the gas by means of mercury admitted beforehand into the reservoir, I refer to § 3 of this paper.

§ 6. *Calibration, determination of the volume of the tube and measurements of the normal volume of the enclosed gas.* In order to calibrate the graduated tubes and to determine the volumes of the reservoirs, we weld a wider tube with a glass stopcock on to the capillary tube where the manometer-tube is to be sealed off. On the other side of the stopcock, this wider tube terminates in a fine point.

After being cleaned and dried the manometer-tube is entirely filled with mercury. The calibration and gauging is done by weighing the mercury which we let flow out. I will not dwell on these operations and the corrections they require as they can better be treated of when the observations made are communicated, but here I will only mention that in these operations much time was saved and the degree of accuracy was greatly increased by placing the tube in a double walled copper box lined with thick felt, the inner and the outer wall being provided with plate-glass windows in order to enable us to take readings along the whole scale of the tube (comp. Pl. II fig. 4). The space between the two walls was filled with water and the constancy of the temperature was promoted by stirring.

The tube to be calibrated rests on a wooden ring and the lengthening-piece with stopcock, welded on to the upper-reservoir, passes through an india rubber stopper cut in two. The point of the manometer-tube through which the mercury flows is protected from variations of temperature by a copper felt-lined cap fastened to the box by a bayonet-adjustment; this cap can easily be removed (for a short time) whenever we want to let a quantity of mercury flow out from the tube.

The readings for determining the normal volume are made while the manometer-tube is placed in a double-walled box as described above, (comp. Pl. II fig. 5) but in which the windows were only small, as we wanted to read only the position of the mercury in the *U*-tubes and of the thermometer. These readings and that of the standard barometer (the box communicating with the atmosphere by a small tube) yield a perfectly accurate determination of the normal volume, which is of the greatest importance for the investigation of the isothermal lines.

Physics. — Prof. VAN DER WAALS presents on behalf of Mr. N. QUINT GZN. a paper on: „*The determination of isothermals for mixtures of* HCl *and* C_2H_6."

Introduction.

At the commencement of this investigation there were but few observations made, which might be used for testing Prof. VAN DER WAALS's theory on the behaviour of mixtures of two substances. At that time Mr. KUENEN was the only one who had examined some mixtures and his observations agreed with that theory. In order to add to the material on this subject (to which also Mr. VAN DER LEE, Mr. VERSCHAFFELT, Mr. HARTMAN have since contributed), I have examined mixtures of HCl and C_2H_6. The results of the determinations of the isothermals and a short description of the experiments follow; I hope soon to publish some further details and a calculation of volume-contraction etc.

The substances.

From the theory follows that some mixtures, when being condensed at a certain temperature will show the phenomenon, indicated as retrograde condensation second type. Mr. KUENEN had not been able to observe this phenomenon; therefore it was desirable to select substances, in which at least theoretically, the phenomenon of r. c. II was to be found.

As Mr. KUENEN states in Phys. Soc. (13) 10, 1895, this is the case with some mixtures, if the component that has the higher vapour-pressures, has also the higher critical temperature. We settled therefore on HCl and C_2H_6, because each of these substances has also a critical pressure which may be easily attained.

HCl was obtained by adding drops of concentrated sulphurous acid to pure HCl, to which some Fe_2SO_4 had been added. When the gas obtained in this way, was dried, it was very pure, as appeared from the slight increase of pressure (at 12° about 0,2 atm.), when condensed and from the agreement of the critical data with those found by ANSDELL.

In order to obtain ethane, acetate of sodium was subjected to electrolysis; the gas which was developed, was condensed at a low temperature (about —50°), the vapourphasis was removed, and from the liquid phasis a quantity of gas had been collected. Though this method is the same as had furnished good results to Mr. KUENEN, I have not succeeded in making the gas as pure; this C_2H_6 presented in being condensed at 21°, an increase of pressure of 1,4 atm. As however the values for the critical data as found by me (crit. temp. 31°,88; crit. pressure 48,94 atm.) did not differ much from those found by Mr. KUENEN for his ethane (crit. temp. 31,95 à 32,2; crit. press. 48,64 à 48,91) and as moreover it is difficult to obtain perfectly pure ethane, as clearly appears from the observations of others (DEWAR, OLSZEWSKY and HAENLEN found resp. for crit. temp. 35°, 34° and 34°,5 and for crit. press. 45,2; 50,2 and 50 atm.) I resolved to continue the observations with the ethane I had obtained.

The Method.

The compressibility of the two substances mentioned and also that of four mixtures (prepared in a mixing-apparatus made completely of glass), was compared with that of dry air, free from carbonic acid, at temperatures which were the same for the two substances and for the mixtures. The gas was compressed in a calibrated tube of CAILLETET, on which the mm. were marked, and the thickwalled part of which was placed in a waterbath of about 35 L. After this water had reached the desired temperature, the temperature was kept constant by means of an alternating current, which passed through two tubes filled with a solution of NH_4Cl, which were placed in the bath. Moreover in this bath were found the coil, serving to move the electro-magnetic stirrer in the CAILLETET-tube, and a stirrer, kept in motion by the flow of water.

The temperatures between 15° and 35° were read from a thermometer, which was divided in $^1/_{20}$°; the others from thermometers with a division of $^1/_{10}$°; now and then the thermometers were tested by means of a normal thermometer, which had been compared with an air thermometer at the Reichsanstalt.

The pressures were calculated by making use of the table which Mr. AMAGAT gives for the compressibility of air in Ann. de Ch. et de Phys. 6e série 1898.

The Results.

It appeared already in the observation of the first mixture, that I, no more than Mr. KUENEN, should succeed in observing the retrograde condensation 2nd type. For the critical temperature of the point of tangency and of the plaitpointcurve were so near each other, that I could scarcely state a difference between these temperatures. Moreover, also in these mixtures the phenomenon of a maximum pressure and a minimum critical temperature appeared, which made the region, where r. c. II was possible, still more limited. (See KUENEN, experiments on mixtures of N_2O and C_2H_6 etc. Zeitschr. für phys. Chem. XXIV, 4, 1897).

This maximum pressure occurs when $x = 0.44$ and this minimum critical temperature when $x=0,62$ (ethane is considered as the solved substance, N_2O as the solving substance), as appears from the graphical representation, in which the course of the plaitpointcurve, of the curves of the vapour pressure of the simple substances and the border-curves of the mixtures are indicated. This diagram, drawn up according to the initial and final points of condensation, occurring in the tables, is founded on the following tables.

H Cl

t	p_a
14,55	38,03
21,3	44,25
30,23	53,82
41,45	68,47
51,3	84,13

C_2H_6

t	p_a
13,2	32,21
21,3	38,75
25,4	42,19
30,23	46,92
31,88	48,94

Mixture I. $x = 0,1388$

t	p_a	p_b
13,7	40,42	42,33
21,3	48,11	49,97
25,4	52,74	54,48
30,23	58,36	59,93
41,45	74,37	75.26
43,1	77,51	

Mixture II. $x=0,4035$

t	p_a	p_b
14,1	45,72	46,94
21,2	53,36	54,25
25,4	58,42	59,19
30,23	64,80	65,11
30,43		65,30
30,53	65,42	

Mixture III. $x=0,6167$

t	p_a	p_b
14	43,96	45,83
21,3	51,64	53,18
25,4	56,55	57,57
27,25	59,15	
27,25	59,30	

Mixture IV. $x=0,7141$

t	p_a	p_b
14,5	42,18	44,60
21,3	49,08	51,10
25,4	53,87	55,25
27,33	56,49	56,92
27,37	56,84	

The results of the determinations of the isothermals are represented in the tables from A to F. The following remarks may be added:

The values represent the observations, so that the corrections, which might be drawn from the graphical representation, have not been applied.

The isothermal of 25°,4 for HCl and that of 52°,5 for mixtures II are not given, as the former was most likely not reliable, and as the latter could not be determined, because the Cailletet-tube was broken.

When the substance was divided into heterogeneous phases, the vapour-volumes then present were also repeatedly measured; they are, however, less accurate than the total volumes on account of the uncertainty of the correction, which is to be made for the meniscus. All volumes are expressed in the theoretical normal volume (i. e. the volume at 0° and 1 atm. multiplied with $(1+a)\ (1-b)$) as unity; moreover the volumes, at which for the first time liquid is to be observed, are underlined, and those at which the vapour phasis disappears, are doubly underlined.

The pressures are expressed in atmospheres, the error will seldom exceed $^1/_{1000}$, at least for the lower pressures.

A. Hydrochloric acid. $V_0 = 54{,}348$ cM³.

Temp.	Tot. Vol 0,0	Vapour Vol. 0,0	Pressure.
14°,55	1890		38,03
	1738	1717	38,09
	1615	1584	38,09
	0902	0796	38,09
	0420	0258	38,14
	0190		38,21
	0189		38,25
21°,30	2157		37,18
	2149		37,25
	2122		37,58
	2105		37,81
	2086		38,01
	2065		38,23
	2043		38,46
	2023		38,69
	1897		40,24
	1885		40,38
	1804		41,45
	1792		41,64
	1780		41,81
	1710		42,74
	1686		43,07
	1615		44.
	44,16		1663
	44,25		1566
	44,47		0194
30°,23	2318		37,44
	2269		37,96
	2220		38,50

Temp.	Tot. Vol. 0,0	Pressure.
30°,23 (contin.)	2170	39,08
	2112	39,81
	2077	40,29
	2041	40,74
	1990	41,36
	1930	42,16
	1820	43,84
	1733	45,20
	1628	46,85
	1505	48,94
	1402	50,75
	1230?	53,82
	0219	53,95
	0207	54,10
41°,45	2347	39,32
	2200	41,14
	2069	43,05
	1951	44,78
	1840	46,64
	1712	48,88
	1581	51,17
	1431	54,64
	1261	58,47
	1148	61,20
	1027	64,18
	0913	66,96
	0830	68,47
	0239	68,63

Temp.	Tot. Vol. 0,0	Pressure.	Temp.	Tot. Vol. 0,0	Pressure.
51°,3 crit. point	0414	84,13	52°,5	1986	47,05
52°,5	2706	37,22	(contin.)	1807	50,34
	2546	39,08		1638	53,72
	2358	41,45		1450	58,28
	2168	44,14		1260	63,42
				1075	68,88

B. Ethane. $V_0 = 54,491$ cM³.

Temp.	Tot. Vol. 0,0	Vapour Vol. 0,0	Pressure.	Temp.	Tot. Vol. 0,0	Vapour Vol. 0,0	Pressure.
13°,2	1968		32,21	25°,4	1822		37,02
	1818	1781	32,29		1599		39,19
	1599	1521	32,36		1414		40,88
	1321	1178	32,48		1265		42,10
	1032	0822	32,72		1255		42,19
	0725	0443	33,05		0880	0696	42,56
	0434	0072	33,53		0665	0362	42,89
	0387		33,71		0477	0067	43,29
	0368		33,89		0430		43,54
21°,3	1876		35,26	30°,23	1785		38,86
	1785		36,05		1599		40,86
	1692		36,91		1414		42,88
	1599		37,70		1228		44,88
	1506		38,38		1042		46,39
	1488		38,59		0949		46,90
	1479		38,66		0940		46,92
	1469		38,72		0930		46,94
	1464		38,75		0498		47,76
	0526	0173	39,76				
	0404		40,13				

Temp.	Tot. Vol. 0,0	Pressure.
31°,38	0759	48,26
31°,63	$\underline{0759}$	48,79
31°,63	$\underline{\underline{0563}}$	49,06
31°,83	0669	48,95
31°,86	0697	48,93
31°,88 crit. point.	0688	48,94
33°,73	0473	54,41
41°,45	1785	42,13
	1767	42,34
	1748	42,63
	1730	42,83
	1711	43,10
	1526	45,74
	1507	45,99
	1489	46,23
	1470	46,52
	1228	50,12
41°,45 (contin.)	1210	50,48
	1191	50,73
	1172	51,05
52°,5	1786	45,45
	1767	45,64
	1749	45,87
	1730	46,14
	1711	46,50
	1526	49,73
	1507	50,02
	1489	50,26
	1470	50,68
	1228	55,47
	1210	55,81
	1191	56,11
	1173	56,65

C. Mixture I. $V_0 = 54,989$ cM^3.

$x = 0,1388$.

Temp.	Tot. Vol. 0,0	Vapour Vol. 0,0	Pressure.
13°,7	2019		37,20
	1957		37,85
	1897		38,54
	1840		39,22
	1783		39,91
	$\underline{1725}$		40,41
	1704		40,42
	1548	1529	40,60
	1367	1324	40,72
13°,7 (contin.)	1110	1031	40,96
	0868	0759	41,21
	0617	0465	41,51
	0348	0015	41,90
	0217		42,13
	$\underline{\underline{0213}}$		42,33
21°,3	2132		37,84
	2020		39,20
	1897		40,74

Temp.	Tot. Vol. 0,0	Vapour Vol. 0,0	Pressure.
21°,3	1783		42,27
(contin.)	1655		44,11
	1548		45,66
	1428		47,48
	1382		48,11
	1061		48,48
	0760	0642	48,86
	0450	0274	49,52
	0227		49,97
25°,4	2270		37,19
	2145		38,63
	2020		40,27
	1893		41,94
	1773		43,65
	1655		45,43
	1540		47,29
	1419		49,34
	1300		51,41
	1212		52,74
	0961	0907	53,10
	0643	0515	53,57
	0408	0216	53,96
	0236		54,48
30°,23	2369		37,10
	2232		38,71
	2045		40,98
	1863		43,54
	1707		45,99
	1569		48,34
	1404		51,35
	1257		54,25
	1255		54,28
30°,32	1032		58,36
(contin.)	0808	0742	58,78
	0479	0312	59,38
	0259		59,93
41°,45	2559		37,10
	2406		38,79
	2221		41,20
	2031		43,88
	1854		46,71
	1675		50,07
	1511		53,36
	1316		57,81
	1136		62,25
	0953		67,09
	0853		69,93
	0613		74,37
	0515		74,72
	0425		74,95
	0313		75,26
43°,1 pl. p. t.	0420		77,51
52°,5	2735		37,15
	2690		37,62
	2531		39,48
	2342		41,96
	2146		44,78
	1959		47,92
	1769		51,63
	1585		55,55
	1406		60,11
	1234		65,06
	1049		71,03
	0878		77,04

D. Mixture II. $V_0 = 55{,}887$ cM^3.

$x = 0{,}4035$.

Temp.	Tot. Vol. 0,0	Vapour Vol. 0,0	Pressure.
14°,1	2116		36,29
	1918		38,51
	1745		40,63
	1573		42,84
	1398		45,11
	$\underline{1345}$		45,72
	0949	0847	45,86
	0609	0404	46,10
	$\underline{\underline{0282}}$		46,94
21°,2	2241		36,55
	2056		38,67
	1867		41,03
	1697		43,41
	1523		45,98
	1340		48,95
	1161		51,79
	$\underline{1045}$		53,36
	0839	0667	53,57
	0489	0254	53,76
	$\underline{\underline{0306}}$		54,25
25°,4	2294		36,83
	2098		39,16
	1914		41,60
	1754		43,87
	1583		46,59
	1401		49,73
	1208		53,18
	1039		56,18
	$\underline{0877}$		58,42
	0732	0647	58,48
25°,4	0511	0288	58,72
(contin.)	$\underline{\underline{0332}}$		59,19
30°,23	2414		36,52
	2235		38,56
	2059		40,83
	1867		43,50
	1698		46,21
	1528		49,20
	1341		52,80
	1162		56,46
	0865		62,20
	$\underline{0610}$		64,80
	0528	0378	64,99
	0465	0178	65,10
	$\underline{\underline{0417}}$		65,11
30°,43	$\underline{\underline{0439}}$		65,30
30°,53 plaitp.	0471		65,42
30°,58	0488		65,45
41°,45	2537		37,29
	2355		39,46
	2173		41,83
	1976		44,75
	1799		47,70
	1641		50,80
	1461		54,60
	1292		58,58
	1105		63,49
	0872		70,24
	0582		78,02

E. Mixture III. $V_0 = 54{,}207$ cM^3.

$x = 0{,}6167.$

Temp.	Tot. Vol. 0,0	Vapour Vol. 0,0	Pressure.
14°	2015		36,53
	1854		38,28
	1651		40,61
	1490		42,56
	1355		43,96
	1177	1121	44,17
	0969	0850	44,43
	0775	0588	44,70
	0531	0266	45,13
	0327		45,83
	0317		54,33
	0305		66,94
21°,3	2160		36,69
	1974		38,81
	1786		41,18
	1612		43,53
	1422		46,18
	1243		48,73
	1015		51,64
	0857	0768	51,92
	0662	0459	52,27
	0484	0184	52,75
	0365		53,18
	0337		63,01
	0326		69,15
25°,4	2245		36,72
	2034		39,14
25°,4 (contin.)	1778		42,50
	1550		45,83
	1306		49,65
	1122		52,66
	0926		55,39
	0799		56,55
	0662	0517	56,87
	0520	0216	57,17
	0416		57,57
	0361		64,38
27°,25	2271		36,79
	2152		38,16
	1928		40,96
	1734		43,61
	1554		46,40
	1336		49,97
	1119		53,65
	0893		57,14
	0772		58,35
	0714		58,68
	0684		58,88
	0666		58,91
	0629		59,10
	0612		59,15
	0583	0525	59,19
	0562	0460	59,23
	0546	0296	59,28
pl. p.	0540	0296?	59,30

Temp.	Tot. Vol. 0,0	Pressure.
27°,25	0498	59,34
(contin.)	0469	59,54
	0439	60,06
	0406	61,56
	0384	63,98
	0366	67,80
27°,30	0587	59,21
	0564	59,25
30°,23	2337	36,73
	2188	38,42
	2174	38,60
	1984	40,96
	1795	43,63
	1618	46,35
	1432	49,60
	1256	52,70
	1057	56,41
	0796	60,57
	0493	63,64
	0365	74,91
41°,45	2518	36,89
	2285	39,63
41°,45	2113	41,85
(contin.)	1920	44,70
	1740	47,67
	1553	51,26
	1372	54,99
	1192	59,26
	1185	59,40
	1045	62,97
	0814	69,11
	0579	76,07
	0469	81,32
52°,5	2665	37,20
	2445	39,80
	2195	43,18
	2006	46,07
	1830	49,13
	1817	49,42
	1624	53,38
	1391	58,90
	1192	64,42
	1017	70,19
	0854	76,19

F. Mixture IV. $V_0 = 54,305$ cM³.

$x = 0,7141.$

Temp.	Tot. Vol. 0,0	Vapour Vol. 0,0	Pressure.
14°,5	1895		37,13
	1735		38,81
	1598		40,31
	1451		41,92
	1448		41,96
	1422		42,18
	1153	1072	42,64
	0882	0710	43,15
	0611	0347	43,77
	0606	0339	43,78
	0347		44,60
21°,3	2066		37,15
	1905		38,85
	1709		41,26
	1539		43,43
	1357		45,81
	1079		49,08
	0838	0705	49,62
	0582	0300	50,44
	0385		51,10
25°,4	2142		37,24
	1974		39,17
	1774		41,69
	1589		44,20
25°,4	1426		46,54
(contin.)	1237		49,35
	1052		51,84
	0853		53,87
	0709	0574	54,26
	0586	0310	54,72
	0434		55,25
27°,33	0530		56,92
27°,34	0677		56,49
27°,35	0814		55,69
27°,37	0576	0271?	56,84
pl. p. 27°,39	0664		56,62
	0645		56,68
	0621		56,75
	0590		56,87
27°,40	0617		56,83
30°,23	2266		37,03
	2095		38,90
	1913		41,20
	1714		43,96
	1542		46,56
	1361		49,51

Temp.	Tot. Vol. 0,0	Pressure.	Temp.	Tot. Vol. 0,0	Pressure.
30°,23	1182	52,51	41°,45	1179	58,10
(contin.)	0993	55,61	(contin.)	0993	62,47
	0797	58,24		0800	67,27
	0560	60,48		0571	73,93
	0399	68,04	52°,5	2613	37,40
41°,45	2445	37,29		2428	39,59
	2285	39,42		2168	43,03
	2100	41,48		1921	46,90
	1910	44,18		1662	51,70
	1727	47,04		1187	63,13
	1545	50,42		0936	71,12
	1362	54,08		0758	77,77

Physics. — "*The elementary theory of the* ZEEMAN-*effect. Reply to an objection of* POINCARÉ." By Prof. H. A. LORENTZ.

§ 1. In a recent article in L'Éclairage Électrique [1]) POINCARÉ comes to the conclusion that the well known theory of ZEEMAN's phenomenon, according to which every luminous particle contains either a single movable ion, or a certain number of such ions whose vibrations are mutually independent, can account for the doublet which is seen along the lines of force, but is unable to explain the triplet which one observes in a direction perpendicular to these lines. This result is obtained by treating, not the emission but the absorption in the magnetic field, and it is curious that the same mode of reasoning has led VOIGT [2]) to formulae implying the existence of the triplet. I believe this discrepancy to be due to POINCARÉ's erroneously omitting the term

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[1]) POINCARÉ, La théorie de LORENTZ et le phénomène de ZEEMAN, Éclairage Électrique, T. 19, p. 5, 1899.

[2]) VOIGT, Ueber den Zusammenhang zwischen dem ZEEMAN'schen und dem FARADAY'schen Phänomen, Göttinger Nachrichten, 1898, Heft 4, p. 1.

$$\varepsilon_k \, a \, \frac{d Z_k}{dt}$$

in his equation (6) on page 8.

In order to explain this, I shall in the first place compare the different formulae that may be applied to the propagation of light in an absorbing gaseous body, placed in a magnetic field.

§ 2. The equations of VOIGT contain the following quantities:

1⁰. The components u, v, w of a vector (the vector of NEUMANN) which comes into play in all media, the aether itself included, which are traversed by light-waves.

2⁰. The components ξ, η, ζ of a second vector (the vector of FRESNEL), which is related to the former in the way expressed by the equations

$$\xi = \frac{\partial w}{\partial y} - \frac{\partial v}{\partial z}, \quad \eta = \frac{\partial u}{\partial z} - \frac{\partial w}{\partial x}, \quad \zeta = \frac{\partial v}{\partial x} - \frac{\partial u}{\partial y} \quad . \quad . \quad . \quad (1)$$

3⁰. A certain number of vectors P_1, P_2, P_3, ..., serving to determine the state of the ponderable molecules, and each of them corresponding to one of the principal modes of vibration of a molecule. The components of the vector P_h are denoted by U_h, V_h, W_h, and the index h is likewise affixed to the constant coefficients belonging to these different vectors.

4⁰. A vector (Ξ, H, Z), which is defined as follows:

$$\Xi = \mathrm{v}^2 \xi + \Sigma \varepsilon_h U_h, \quad H = \mathrm{v}^2 \eta + \Sigma \varepsilon_h V_h, \quad Z = \mathrm{v}^2 \zeta + \Sigma \varepsilon_h W_h \,. \quad (2)$$

Here, the coefficients ε are constants, and v is the velocity of light in the aether [1]).

Between the vectors (Ξ, H, Z) and (u, v, w) there exists a relation, expressed by

$$\frac{\partial^2 u}{\partial t^2} = \frac{\partial H}{\partial z} - \frac{\partial Z}{\partial y}, \quad \frac{\partial^2 v}{\partial t^2} = \frac{\partial Z}{\partial x} - \frac{\partial \Xi}{\partial z}, \quad \frac{\partial^2 w}{dt^2} = \frac{\partial \Xi}{\partial y} - \frac{\partial H}{\partial x} \quad . \quad . \quad (3)$$

Finally there are a certain number of equations — three for each

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[1]) In order to avoid confusion, I shall depart a little from the notation of VOIGT and from that which I myself have used on former occasions.

vector P_h — which are to be considered as the equations of motion for the ponderable matter. They are of the form

$$\frac{\partial^2 U_h}{\partial t^2} + d_h U_h + f_h \frac{\partial U_h}{\partial t} + g_h \left(B \frac{\partial W_h}{\partial t} - C \frac{\partial V_h}{\partial t} \right) + \varepsilon_h \xi = 0, \text{ etc. }^{1)} \qquad (4)$$

in which d, f and g are constants. The terms with the first coefficient depend on the elastic forces acting in the ponderable particles, the terms with f serve to introduce a resistance and consequently an absorption of light, while the terms with g are due to the forces produced by the magnetic field.

The field is supposed to be homogeneous; the components of the magnetic force in the field are A, B, C.

In the simplest case there is only one vector P. The signs of summation (in (2)) and the indices h are then to be omitted, and there will be no more than three equations (4).

§ 3. On the basis of the electromagnetic theory of light I have established the equations of motion in the following way 2).

Let there be N equal molecules per unit of volume, each of them containing a movable ion of charge e and effective mass $\varkappa$. Let x, y, z be the displacements, in the directions of the axes, of one of the ions; then $e\,\mathrm{x}$, $e\,\mathrm{y}$, $e\,\mathrm{z}$ will be the components of the electric moment of a molecule, and, if a horizontal bar over the letters is employed to indicate mean values taken for a large number of particles, the components of the electric moment per unit volume will be

$$\mathrm{M}_x = Ne\bar{\mathrm{x}}, \quad \mathrm{M}_y = Ne\bar{\mathrm{y}}, \quad \mathrm{M}_z = Ne\bar{\mathrm{z}},$$

If the ions are in a state of vibration, they will excite in the aether a certain periodic dielectric displacement and a similar magnetic force; besides these, there may exist, independently of the ions, a disturbance of the equilibrium in the aether, in which there is a dielectric displacement, say (f_0, g_0, h_0).

Now, in order to obtain the equations of motion for one of the ions, I conceived a sphere B, whose radius, though very small in comparison with the wave-length, is very much larger than the

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1) The sign "etc." will always be used to indicate two equations similar to the one that is written down and relating to the axes of y and z.

2) LORENTZ, La théorie électromagnétique de MAXWELL et son application aux corps mouvants, Leiden, BRILL 1892. Also in Arch. néerl. T. 25.

molecular distances, and the centre of which is occupied by the molecule to be considered. I denoted by

$$\mathfrak{X}', \quad \mathfrak{Y}', \quad \mathfrak{Z}'$$

the components of the electric force at the centre of the sphere, in so far as it is due to the molecules within the surface, by

$$-\mathfrak{f}\,\mathrm{x}, \quad -\mathfrak{f}\,\mathrm{y}, \quad -\mathfrak{f}\,\mathrm{z}$$

the components of the elastic force by which the ion is driven back to its position of equilibrium, and by

$$\mathfrak{M}_x\,, \quad \mathfrak{M}_y\,, \quad \mathfrak{M}_z$$

three auxiliary functions, satisfying the equations

$$\left.\begin{aligned} \left(\Delta - \frac{1}{\mathrm{V}^2}\frac{\partial^2}{\partial t^2}\right)\mathfrak{M}_x &= -4\,\pi\,\mathrm{M}_x\,, \\ \left(\Delta - \frac{1}{\mathrm{V}^2}\frac{\partial^2}{\partial t^2}\right)\mathfrak{M}_y &= -4\,\pi\,\mathrm{M}_y\,, \\ \left(\Delta - \frac{1}{\mathrm{V}^2}\frac{\partial^2}{\partial t^2}\right)\mathfrak{M}_z &= -4\,\pi\,\mathrm{M}_z\,. \end{aligned}\right\} \quad \ldots\ldots \quad (5)$$

In these the velocity of light in the aether is again represented by V. Finally, I found for the first of the three equations of motion [1])

$$\varkappa\frac{d^2\mathrm{x}}{dt^2} = -\mathfrak{f}\,\mathrm{x} + \frac{e^2}{\mathrm{V}}\frac{d^3\mathrm{x}}{dt^3} + \frac{4}{3}\pi\,\mathrm{V}^2\,e\,\mathrm{M}_x +$$

$$+\,\mathrm{V}^2\,e\left[\frac{\partial^2\mathfrak{M}_x}{\partial x^2} + \frac{\partial^2\mathfrak{M}_y}{\partial x\,\partial y} + \frac{\partial^2\mathfrak{M}_z}{\partial x\,\partial z} - \frac{1}{\mathrm{V}^2}\frac{\partial^2\mathfrak{M}_x}{\partial t^2}\right] + 4\,\pi\,\mathrm{V}^2\,e\,f_0 + e\,\mathfrak{X}' \quad . \quad . \quad (6)$$

The term

$$\frac{e^2}{\mathrm{V}}\frac{d^3\mathrm{x}}{dt^3}\,,$$

which corresponds to the damping of the vibrations by radiation, was shown to be so small that it may be neglected.

If, in (6), we replace some of the terms by their mean values, we shall find after division by e and after replacing $\mathfrak{X}'$ by M_x, multiplied by a constant,

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[1]) l. c., § 128.

$$\frac{\mathrm{v}}{q}\,\mathrm{M}_x+\frac{\varkappa}{Ne^2}\frac{\partial^2 \mathrm{M}_x}{\partial t^2}=$$
$$=\mathrm{v}^2\left[\frac{\partial^2\mathfrak{M}_x}{\partial x^2}+\frac{\partial^2\mathfrak{M}_y}{\partial x\,\partial y}+\frac{\partial^2\mathfrak{M}_z}{\partial x\,\partial z}-\frac{1}{\mathrm{v}^2}\frac{\partial^2\mathfrak{M}_x}{\partial t^2}\right]+4\pi\,\mathrm{v}^2 f_0\,,\ \text{etc.}\ \ (7)$$

where q is a constant coefficient.

If the ion experiences a resistance, proportional to the velocity, we must introduce a term

$$-c\,\frac{d\mathrm{x}}{d\,t}$$

on the right-hand side of (6), and in the case of a magnetic field with the magnetic force $(A,\ B,\ C)$, there will be a term

$$e\left(C\,\frac{d\mathrm{y}}{d\,t}-B\,\frac{d\mathrm{z}}{d\,t}\right).$$

Hence, the equations (7) will change into

$$\left.\begin{array}{l}\dfrac{\mathrm{v}}{q}\,\mathrm{M}_x+\dfrac{\varkappa}{N e^2}\dfrac{\partial^2 \mathrm{M}_x}{\partial t^2}+\dfrac{c}{N e^2}\dfrac{\partial \mathrm{M}_x}{\partial t}-\dfrac{1}{N e}\left(C\dfrac{\partial \mathrm{M}_y}{\partial t}-B\dfrac{\partial \mathrm{M}_z}{\partial t}\right)= \\ \qquad =\mathrm{v}^2\left[\dfrac{\partial^2\mathfrak{M}_x}{\partial x^2}+\dfrac{\partial^2\mathfrak{M}_y}{\partial x\,\partial y}+\dfrac{\partial^2\mathfrak{M}_z}{\partial x\,\partial z}-\dfrac{1}{\mathrm{v}^2}\dfrac{\partial^2\mathfrak{M}_x}{\partial t^2}\right]+4\pi\,\mathrm{v}^2 f_0\,,\end{array}\right\}\ (8)$$

etc.

§ 4. The above formulae may be put in a form better known in the theory of electro-magnetism and admitting of direct comparison with the equations of VOIGT. We shall arrive at it, if we observe that there will be a magnetic force $\mathfrak{H}$, which may be decomposed into two parts, the one $\mathfrak{H}_1$ being produced by the vibrations of the ions, and the other $\mathfrak{H}_2$ belonging to the same state of motion as $(f_0,\ g_0,\ h_0)$.

The components of the first of these parts are found to be [1])

$$\mathfrak{H}_{1x}=\frac{\partial^2\mathfrak{M}_z}{\partial y\partial t}-\frac{\partial^2\mathfrak{M}_y}{\partial z\partial t}\,,\ \mathfrak{H}_{1y}=\frac{\partial^2\mathfrak{M}_x}{\partial z\partial t}-\frac{\partial^2\mathfrak{M}_z}{\partial x\partial t}\,,\ \mathfrak{H}_{1z}=\frac{\partial^2\mathfrak{M}_y}{\partial x\partial t}-\frac{\partial^2\mathfrak{M}_x}{\partial y\partial t}\,,\ \ (9)$$

and those of $\mathfrak{H}_2$ satisfy the equations

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[1]) l. c., § 124.

$$\frac{\partial \mathfrak{H}_{2x}}{\partial t}=4\pi \mathrm{v}^2\left(\frac{\partial g_0}{\partial z}-\frac{\partial h_0}{\partial y}\right),\ \frac{\partial \mathfrak{H}_{2y}}{\partial t}=4\pi \mathrm{v}^2\left(\frac{\partial h_0}{\partial x}-\frac{\partial f_0}{\partial z}\right);$$

$$\frac{\partial \mathfrak{H}_{2z}}{\partial t}=4\pi \mathrm{v}^2\left(\frac{\partial f_0}{\partial y}-\frac{\partial g_0}{\partial x}\right). \quad . \quad . \quad . \quad . \quad . \qquad (10)$$

Now, if we put

$$\mathfrak{E}_x=\mathrm{v}^2\left[\frac{\partial^2 \mathfrak{M}_x}{\partial x^2}+\frac{\partial^2 \mathfrak{M}_y}{\partial x\,\partial y}+\frac{\partial^2 \mathfrak{M}_z}{\partial x\,\partial z}-\frac{1}{\mathrm{v}^2}\frac{\partial^2 \mathfrak{M}_x}{\partial t^2}\right]+4\pi \mathrm{v}^2 f_0\text{, etc.} \qquad (11)$$

we shall find

$$\frac{\partial \mathfrak{E}_y}{\partial z}-\frac{\partial \mathfrak{E}_z}{\partial y}=\frac{\partial^2}{\partial t^2}\left[\frac{\partial \mathfrak{M}_z}{\partial y}-\frac{\partial \mathfrak{M}_y}{\partial z}\right]+4\pi \mathrm{v}^2\left(\frac{\partial g_0}{\partial z}-\frac{\partial h_0}{\partial y}\right)\text{, etc.,}$$

or, by (9) and (10),

$$\frac{\partial \mathfrak{E}_y}{\partial z}-\frac{\partial \mathfrak{E}_z}{\partial y}=\frac{\partial \mathfrak{H}_x}{\partial t},\ \frac{\partial \mathfrak{E}_z}{\partial x}-\frac{\partial \mathfrak{E}_x}{\partial z}=\frac{\partial \mathfrak{H}_y}{\partial t},\ \frac{\partial \mathfrak{E}_x}{\partial y}-\frac{\partial \mathfrak{E}_y}{\partial x}=\frac{\partial \mathfrak{H}_z}{\partial t}. \qquad (3')$$

The form of these equations shows that $\mathfrak{E}$ is precisely the "electric force."

In virtue of (11) the equations (8) become

$$\frac{\mathrm{v}}{q}\mathrm{M}_x+\frac{\varkappa}{N e^2}\frac{\partial^2 \mathrm{M}_x}{\partial t^2}+\frac{c}{N e^2}\frac{\partial \mathrm{M}_x}{\partial t}-\frac{1}{N e}\left(C\frac{\partial \mathrm{M}_y}{\partial t}-B\frac{\partial \mathrm{M}_z}{\partial t}\right)=\mathfrak{E}_x\text{, etc.} \qquad (4')$$

As we see, they express the relation between the electric force and the electric moment.

Finally, from (9) we may deduce the formula

$$\frac{\partial \mathfrak{H}_{1z}}{\partial y}-\frac{\partial \mathfrak{H}_{1y}}{\partial z}=\frac{\partial}{\partial t}\left[\frac{\partial^2 \mathfrak{M}_x}{\partial x^2}+\frac{\partial^2 \mathfrak{M}_y}{\partial x\,\partial y}+\frac{\partial^2 \mathfrak{M}_z}{\partial x\,\partial z}-\Delta \mathfrak{M}_x\right],$$

or, if (11) be taken into account,

$$\frac{\partial \mathfrak{H}_{1z}}{\partial y}-\frac{\partial \mathfrak{H}_{1y}}{\partial z}=\frac{\partial}{\partial t}\left[\frac{1}{\mathrm{v}^2}\frac{\partial^2 \mathfrak{M}_x}{\partial t^2}-\Delta \mathfrak{M}_x\right]+\frac{1}{\mathrm{v}^2}\frac{\partial \mathfrak{E}_x}{\partial t}-4\pi\frac{\partial f_0}{\partial t}.$$

Combining this with

$$4\pi\frac{\partial f_0}{\partial t}=\frac{\partial \mathfrak{H}_{2z}}{\partial y}-\frac{\partial \mathfrak{H}_{2y}}{\partial z},$$

and attending to (5), we see that

$$\frac{\partial \mathfrak{H}_z}{\partial y} - \frac{\partial \mathfrak{H}_y}{\partial z} = 4\pi \frac{\partial \mathrm{M}_x}{\partial t} + \frac{1}{\mathrm{V}^2} \frac{\partial \mathfrak{E}_x}{\partial t}.$$

Now, let a new vector $\mathfrak{D}$ be defined by the equation

$$\mathfrak{D} = \mathrm{M} + \frac{\mathfrak{E}}{4\pi \mathrm{V}^2}; \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2')$$

then:

$$\frac{\partial \mathfrak{H}_z}{\partial y} - \frac{\partial \mathfrak{H}_y}{\partial z} = 4\pi \frac{\partial \mathfrak{D}_x}{\partial t}, \quad \frac{\partial \mathfrak{H}_x}{\partial z} - \frac{\partial \mathfrak{H}_z}{\partial x} = 4\pi \frac{\partial \mathfrak{D}_y}{\partial t},$$

$$\frac{\partial \mathfrak{H}_y}{\partial x} - \frac{\partial \mathfrak{H}_x}{\partial y} = 4\pi \frac{\partial \mathfrak{D}_z}{\partial t} \quad . \; . \; . \quad (1')$$

Since $\mathfrak{E}$ is the electric force, $\mathfrak{E}/4\pi \mathrm{V}^2$ will be the dielectric displacement in the aether; $\mathfrak{D}$ will therefore be the total dielectric displacement and $\dot{\mathfrak{D}}$ the displacement-current. Thus the equations (1′) are seen to contain the well known relation between the magnetic force and the electric current.

In (1′), (2′), (3′) and (4′) we have got the complete system of equations of motion. We might have obtained them also by starting from the relation between $\mathfrak{E}$ and M, which I have assumed in my „Versuch einer Theorie der electrischen und optischen Erscheinungen in bewegten Körpern"; it would only have been necessary to add the terms which arise from a resistance and from the action of a magnetic field. The above method is less simple, but it goes farther in explaining the mechanism of the phenomena.

§ 5. Now, it is easily seen that the equations of the electromagnetic theory are identical with those of VOIGT, if in these latter only one vector P is assumed.

Indeed, if, in the formulae of VOIGT, we replace

$$\frac{\partial u}{\partial t}, \; \frac{\partial v}{\partial t}, \; \frac{\partial w}{\partial t}, \; \xi, \; \eta, \; \zeta, \; U, \; V, \; W, \; \Xi, \; H, \; Z$$

by

$$\frac{\mathfrak{H}_x}{4\pi \mathrm{V}^2}, \; \frac{\mathfrak{H}_y}{4\pi \mathrm{V}^2}, \; \frac{\mathfrak{H}_z}{4\pi \mathrm{V}^2}, \; \frac{\mathfrak{D}_x}{\mathrm{V}^2}, \; \frac{\mathfrak{D}_y}{\mathrm{V}^2}, \; \frac{\mathfrak{D}_z}{\mathrm{V}^2},$$

$$-\frac{\mathrm{M}_x}{\varepsilon}, \; -\frac{\mathrm{M}_y}{\varepsilon}, \; -\frac{\mathrm{M}_z}{\varepsilon}, \; \frac{\mathfrak{E}_x}{4\pi \mathrm{V}^2}, \; \frac{\mathfrak{E}_y}{4\pi \mathrm{V}^2}, \; \frac{\mathfrak{E}_z}{4\pi \mathrm{V}^2},$$

the equations (2) and (3) change into (2′) and (3′), and the formulae (1), if first differentiated with regard to t, take the form (1′).

As to the equations of motion (4), these become

$$-\frac{1}{\varepsilon}\frac{\partial^2 \mathrm{M}_x}{\partial t^2}-\frac{d}{\varepsilon}\mathrm{M}_x-\frac{f}{\varepsilon}\frac{\partial \mathrm{M}_x}{\partial t}-\frac{g}{\varepsilon}\left(B\frac{\partial \mathrm{M}_z}{\partial t}-C\frac{\partial \mathrm{M}_y}{\partial t}\right)+\frac{\varepsilon \mathfrak{D}_x}{\mathrm{v}^2}=0,\text{ etc.}\quad(12)$$

or, if we put for $\mathfrak{D}$ the value (2′), and multiply by $\frac{4\pi \mathrm{v}^4}{\varepsilon}$,

$$4\pi \mathrm{v}^2\left(\frac{\mathrm{v}^2 d}{\varepsilon^2}-1\right)\mathrm{M}_x+\frac{4\pi \mathrm{v}^4}{\varepsilon^2}\frac{\partial^2 \mathrm{M}_x}{\partial t^2}+$$

$$+\frac{4\pi \mathrm{v}^4 f}{\varepsilon^2}\frac{\partial \mathrm{M}_x}{\partial t}-\frac{4\pi \mathrm{v}^4 g}{\varepsilon^2}\left(C\frac{\partial \mathrm{M}_y}{\partial t}-B\frac{\partial \mathrm{M}_z}{\partial t}\right)=\mathfrak{E}_x,\text{ etc.}\quad . \quad . \quad (13)$$

This agrees with (4′) [1]. At the same time we are led to the following relations between the coefficients

$$4\pi \mathrm{v}\left(\frac{\mathrm{v}^2 d}{\varepsilon^2}-1\right)=\frac{1}{q},\quad \frac{4\pi \mathrm{v}^4}{\varepsilon^2}=\frac{\varkappa}{Ne^2},$$

$$\frac{4\pi \mathrm{v}^4 f}{\varepsilon^2}=\frac{c}{Ne^2},\quad \frac{4\pi \mathrm{v}^4 g}{\varepsilon^2}=\frac{1}{Ne}.\quad . \quad . \quad . \quad . \quad . \quad (14)$$

§ 6. If we suppose a molecule to contain a certain number of ions, each of which can be displaced from its position of equilibrium, the total electric moment M may be split up into the parts $\mathrm{M}_1, \mathrm{M}_2, \ldots,$ corresponding to the displacements of the separate ions. In this case, the equations (1′), (2′) and (3′) will still hold, but instead of (4′) we shall have as many times three equations, as there are ions in the molecule. For the sake of brevity, I shall put $\mathfrak{X}'=\mathfrak{Y}'=\mathfrak{Z}'=0$ [2].

If, now, we wish to write down the equation (6) for the h^{th} ion, we have to replace x by x_h, but the term $\frac{4}{3}\pi \mathrm{v}^2 e \mathrm{M}_x$ will still contain the total moment M_x. Instead of (4′) we shall therefore get

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[1] VOIGT's formulae in Wied. Ann., Bd. 67, p. 345 are likewise of the same form.

[2] l. c. § 105.

$$\left.\begin{aligned}&\frac{\mathfrak{f}_h}{Ne_h^2}\,\mathrm{M}_{hx}-\frac{4}{3}\,\pi\,\mathrm{v}^2\,\mathrm{M}_x+\frac{\varkappa_h}{Ne_h^2}\,\frac{\partial^2\mathrm{M}_{hx}}{\partial t^2}+\\&\qquad+\frac{c_h}{Ne_h^2}\,\frac{\partial\mathrm{M}_{hx}}{\partial t}-\frac{1}{Ne_h}\left(C\,\frac{\partial\mathrm{M}_{hy}}{\partial t}-B\,\frac{\partial\mathrm{M}_{hz}}{\partial t}\right)=\mathfrak{E}_x,\ \text{etc.}\end{aligned}\right\}\;.\;.\;(4'')$$

The equations (1), (2) and (3) of VOIGT, taken this time in their general form, may again be written in the form of (1'), (2') and (3'); for this purpose it will suffice to replace as before

$$\frac{\partial u}{\partial t},\quad \xi,\quad \Xi,\ \text{etc.}$$

by

$$\frac{\mathfrak{H}_x}{4\,\pi\,\mathrm{v}^2},\quad \frac{\mathfrak{D}_x}{\mathrm{v}^2},\quad \frac{\mathfrak{E}_x}{4\,\pi\,\mathrm{v}^2},\ \text{etc.}$$

and

$$U_h,\quad V_h,\quad W_h$$

by

$$-\frac{\mathrm{M}_{hx}}{\varepsilon_h},\ -\frac{\mathrm{M}_{hy}}{\varepsilon_h},\ -\frac{\mathrm{M}_{hz}}{\varepsilon_h}.$$

From (4) we shall get equations, similar to (12). They will however contain the indices h, and if we use the value

$$\mathfrak{D}=\mathrm{M}+\frac{\mathfrak{E}}{4\,\pi\,\mathrm{v}^2},$$

we obtain an equation which is only slightly different from (13). The first term in it will be

$$\frac{4\,\pi\,\mathrm{v}^4\,d_h}{\varepsilon_h^2}\,\mathrm{M}_{hx}-4\,\pi\,\mathrm{v}^2\,\mathrm{M}_x\,,$$

instead of

$$4\,\pi\,\mathrm{v}^2\left(\frac{\mathrm{v}^2\,d}{\varepsilon^2}-1\right)\mathrm{M}_x$$

in (13), and in the following terms **M** as well as the coefficients must be written with the index h.

Finally, by assuming similar relations between the coefficients as in § 5 above, this new equation will become nearly, but not quite identical with (4''), the difference consisting in this, that it will not contain

$$-\frac{4}{3}\pi \mathrm{v}^2 \mathrm{M}_x ,$$

but

$$-4\pi \mathrm{v}^2 \mathrm{M}_x .$$

For our purpose this is of no consequence. We shall confine ourselves to the case of molecules with a single movable ion or a single vector P, and even if we were to consider a more general case, our conclusions would not be materially altered.

§ 7. POINCARÉ investigates the propagation of plane waves in the direction of the axis of z. He introduces no resistance, but he assumes the existence of several ions in each molecule.

In his paper (X, Y, Z) denotes the total „dielectric polarization," (X_h, Y_h, Z_h) one of its parts, (f, g, h) the dielectric displacement. His equations, if written partly in the above notations, are

$$\lambda_h \frac{\partial^2 X_h}{\partial t^2} + \frac{X_h}{L_h} = f + \frac{1}{3} X + \varepsilon_h \left(\frac{\partial Y_h}{\partial t} C - \frac{\partial Z_h}{\partial t} B \right), \text{ etc.} \qquad (15)$$

with the constants λ_h, L_h and ε_h, and [1])

$$\left.\begin{aligned} \frac{\partial^2 f}{\partial z^2} - \frac{1}{\mathrm{v}^2}\frac{\partial^2 f}{\partial t^2} &= \frac{1}{\mathrm{v}^2}\frac{\partial^2 X}{\partial t^2}, \\ \frac{\partial^2 g}{\partial z^2} - \frac{1}{\mathrm{v}^2}\frac{\partial^2 g}{\partial t^2} &= \frac{1}{\mathrm{v}^2}\frac{\partial^2 Y}{\partial t^2}, \\ h + Z &= 0 . \end{aligned}\right\} \quad . \; . \; . \; . \; . \; . \quad (16)$$

Now, if $\mathfrak{H}$ and $\mathfrak{E}$ do not contain x and y, we shall have by our equations (1′) and (3′)

$$-\frac{\partial \mathfrak{H}_y}{\partial z} = 4\pi \frac{\partial \mathfrak{D}_x}{\partial t}, \quad \frac{\partial \mathfrak{H}_x}{\partial z} = 4\pi \frac{\partial \mathfrak{D}_y}{\partial t}, \quad 0 = \frac{\partial \mathfrak{D}_z}{\partial t} .$$

and

$$\frac{\partial \mathfrak{E}_y}{\partial z} = \frac{\partial \mathfrak{H}_x}{\partial t}, \quad -\frac{\partial \mathfrak{E}_x}{\partial z} = \frac{\partial \mathfrak{H}_y}{\partial t}, \quad 0 = \mathfrak{H}_z .$$

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[1]) By a typographical error, the formula of POINCARÉ which corresponds to the first two of the equations (16) has on the left-hand side the sign +.

Hence

$$\left.\begin{aligned} \frac{\partial^2 \mathfrak{E}_y}{\partial z^2} &= 4\pi \frac{\partial^2 \mathfrak{D}_y}{\partial t^2} , \\ \frac{\partial^2 \mathfrak{E}_x}{\partial z^2} &= 4\pi \frac{\partial^2 \mathfrak{D}_x}{\partial t^2} , \\ \mathfrak{D}_z &= 0 . \end{aligned}\right\} \quad \ldots\ldots\ldots \quad (17)$$

Let the components of the dielectric displacement in the aether be f, g, h. Then

$$\mathfrak{E}_y = 4\pi \mathrm{v}^2 g , \qquad \mathfrak{E}_z = 4\pi \mathrm{v}^2 h ,$$

and if, instead of (M_x, M_y, M_z), we write (X, Y, Z) for the electric moment per unit of volume,

$$\mathfrak{D}_x = f + X , \qquad \mathfrak{D}_y = g + Y , \qquad \mathfrak{D}_z = h + Z .$$

Putting this in (17), we are led to the equations (16), which I have just taken from POINCARÉ.

Again, if there be no resistance, our equations (4') may now be replaced by

$$\frac{\mathfrak{f}_h}{N e_h^2} X_h - \frac{4}{3}\pi \mathrm{v}^2 X + \frac{\varkappa_h}{N e_h^2}\frac{\partial^2 X_h}{\partial t^2} - \\ - \frac{1}{N e_h}\left(C \frac{\partial Y_h}{\partial t} - B \frac{\partial Z_h}{\partial t}\right) = 4\pi \mathrm{v}^2 f , \quad \text{etc.}$$

Dividing this by $4\pi \mathrm{v}^2$, and putting

$$\frac{\varkappa_h}{4\pi \mathrm{v}^2 N e_h^2} = \lambda_h ,$$

$$\frac{\mathfrak{f}_h}{4\pi \mathrm{v}^2 N e_h^2} = \frac{1}{L_h} ,$$

$$\frac{1}{4\pi \mathrm{v}^2 N e_h} = \varepsilon_h ,$$

we find the above formulae (15). POINCARÉ's equations are thus found to be identical with mine.

§ 8. In the application of the equations to the phenomena in question, I shall follow VOIGT's treatment of the case of a single vector P.

In the first place VOIGT examines the propagation of light along the lines of force, which are supposed parallel to the axis of x.

He denotes

by R the strength of the field,

by ϑ the time of vibration, divided by 2π,

by ω the velocity of propagation, and by $\varkappa$ the coefficient of absorption, in this sense, that over a distance equal to the wave-length the amplitude is diminished in ratio of 1 to $e^{-2\pi\varkappa}$.

Further he puts:

$$\varepsilon^2/d = q^2\,\mathrm{v}^2, \quad {}^1/d = \vartheta_0^{\,2}, \quad f/d = \vartheta', \quad g/d = k \text{ }^{1)} \quad . \quad . \quad (18)$$

The values of ω and $\varkappa$ for circularly polarized light are given by VOIGT's formulae (24) and (25), in which the upper signs are to be taken if the polarization is right-handed, and the lower signs if it is left-handed. To simplify these formulae, I shall put

$$\vartheta^2 \pm k\,R\,\vartheta - \vartheta_0^{\,2} = S\,;$$

we have then

$$\frac{\omega^2\,(1-\varkappa^2)}{(1+\varkappa^2)^2} = \mathrm{v}^2\left(1 - \frac{q^2\,\vartheta^2\,S}{S^2 + \vartheta'^2\,\vartheta^2}\right),$$

$$\frac{2\,\omega^2\,\varkappa}{(1+\varkappa^2)^2} = \frac{\mathrm{v}^2\,q^2\,\vartheta'\,\vartheta^3}{S^2 + \vartheta'^2\,\vartheta^2}\,.$$

Now, we may suppose that even the maximum value of $\varkappa$ is a very small fraction. The left hand members of the equations may therefore be written

$$\omega^2 \text{ and } 2\,\omega^2\,\varkappa\,;$$

hence, by division,

$$2\,\varkappa = \frac{q^2\,\vartheta'\,\vartheta^3}{S^2 - q^2\,\vartheta^2\,S + \vartheta'^2\,\vartheta^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

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¹) $2\,\pi\,\vartheta_0$ is the period of the free vibrations of which the ions are capable. As to the time ϑ', it depends on the magnitude of the resistance.

Our next question is, for what value of ϑ this will be a maximum. At all events this value will lie in the neighbourhood of ϑ_0, and if the absorption bands are narrow, it will be permitted to replace ϑ by ϑ_0 in the numerator of (19). Consequently, the denominator, for which we may write

$$\left(S-\frac{1}{2}q^2\vartheta^2\right)^2+\vartheta'^2\vartheta^2-\frac{1}{4}q^4\vartheta^4 \quad . \quad . \quad . \quad . \quad (20)$$

must become a minimum. I shall neglect the variation of the two last terms, and replace in them ϑ by ϑ_0. Then, the minimum will be reached if

$$S=\tfrac{1}{2}q^2\vartheta^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

and the maximum of absorption will be determined by

$$2\varkappa_{\text{max.}}=\frac{q^2\vartheta'\vartheta_0^3}{\vartheta'^2\vartheta_0^2-\frac{1}{4}q^4\vartheta_0^4}.$$

In order that this may be very small, I shall suppose that q^2 is greatly inferior to $\frac{\vartheta'}{\vartheta_0}$. In this case, the last term in the denominator may be neglected, so that

$$2\varkappa_{\text{max.}}=q^2\frac{\vartheta_0}{\vartheta'}.$$

At the same time we see that the last term in (20) may be neglected in comparison with the preceding one; consequently our result will be true, provided that we may neglect the variation of the second term in (20), while the first term passes through its minimum. This condition will always be fulfilled, if the absorption bands are sufficiently narrow.

The equation (21) may be replaced by

$$\vartheta^2\pm kR\vartheta-\vartheta_0^2=\tfrac{1}{2}q^2\vartheta_0^2.$$

We shall suppose ϑ' much smaller than ϑ_0. Then, from what has been said, q^2 will be much smaller than 1, and in the absence of a magnetic field, i. e. for $R=0$, the maximum of absorption will lie in the immediate neighbourhood of ϑ_0. If, moreover, $kR\vartheta_0$ be very large in comparison with $\frac{1}{2}q^2\vartheta_0^2$, we shall have approximately

$$\vartheta^2 \pm k\,R\,\vartheta - \vartheta_0^{\,2} = 0,$$

or

$$\vartheta = \vartheta_0 \mp \tfrac{1}{2}\,k\,R,$$

since $k\,R$ must be small with regard to ϑ_0.

Now, in order that a distinct doublet may be seen, the distance of the components must be large as compared with the breadth of the absorption bands.

Replacing (19) by

$$2\,\varkappa = \frac{q^2\,\vartheta'\,\vartheta_0^{\,3}}{(S - \frac{1}{2}\,q^2\,\vartheta^2)^2 + \vartheta'^2\,\vartheta_0^{\,2}}\,,$$

we see at once that for a value of ϑ, such that

$$S - \tfrac{1}{2}\,q^2\,\vartheta^2 = \pm\,\mu\,\vartheta'\,\vartheta_0$$

the value of $\varkappa$ will be

$$\frac{\varkappa_{\max}}{1 + \mu^2}\,.$$

We may therefore consider the *borders* of the absorption band to be determined by the last equation, if in it we take for μ a moderate number, say 5. Hence, the necessary condition for a distinct doublet is seen to be $k\,R > \mu\,\vartheta'$. If it is fulfilled, our above supposition as to the value of $k\,R\,\vartheta_0$ will likewise hold good. Indeed, we shall have

$$k\,R\,\vartheta_0 > \mu\,\vartheta'\,\vartheta_0\,,$$

whereas $q^2\,\vartheta_0^{\,2}$ is much smaller than $\vartheta'\,\vartheta_0$.

§ 9. We now come to the propagation of light in a direction perpendicular to the lines of force. Let the vectors P be also perpendicular to these lines, i. e. in the language of the electromagnetic theory of light, let the electric vibrations take place at a right angle to the direction of the field. Then, according to VOIGT, the velocity of propagation ω, and the absorption $\varkappa$ will be determined by his formulae (50) and (51), or if we neglect $\varkappa^2$, by

$$\omega^2 = \mathrm{v}^2 \left[1 - \frac{\frac{1}{2}\,q^2\,\vartheta^2\,S_1}{S_1^{\,2} + \vartheta'^2\,\vartheta^2} - \frac{\frac{1}{2}\,q^2\,\vartheta^2\,S_2}{S_2^{\,2} + \vartheta'^2\,\vartheta^2}\right] \quad . \quad . \quad . \quad (22)$$

and

$$2\,\omega^2\,\varkappa = \tfrac{1}{2}\,\nu^2\,q^2\,\vartheta'\,\vartheta^3 \left[\frac{1}{S_1^2+\vartheta'^2\,\vartheta^2} + \frac{1}{S_2^2+\vartheta'^2\,\vartheta^2}\right] \quad . \qquad (23)$$

Here I have put

$$\vartheta^2 - k\,R\,\vartheta - \vartheta_0^2 = S_1$$

and

$$\vartheta^2 + k\,R\,\vartheta - \vartheta_0^2 = S_2 \, .$$

It is easily seen that, with the assumptions we have made concerning the magnitude of the different terms, the equations (22) and (23) imply the existence of *two* absorption-bands, corresponding to

$$S_1 = 0 \quad \text{and} \quad S_2 = 0.$$

These bands are precisely the outer components of the triplet, one is led to by the elementary theory of the ZEEMAN-effect.

The breadth of each of these lines will be equal to that of the original absorption-band; in virtue of our assumptions it will be much smaller than the distance of the two lines.

Now it is clear that such a thing would be impossible, if the modification of the propagation of light were so small as POINCARÉ finds, namely of the order of R^2, if R is the strength of the field. If, by the action of the magnetic field, the maximum of absorption is shifted to a place, where the absorption was originally insensible, we have to do with a finite change at this point of the spectrum.

§ 10. In order to examine this more closely, we must return to the equations of motion themselves, from which the formulae (22) and (23) have been deduced. Let the magnetic force be parallel to the axis of z ($A = B = 0$, $C = R$) and let the propagation of light take place along the axis of x. Then the complex expressions, which satisfy the equations of motion and whose real parts are the values of U, V, W, ξ, η, ζ, etc., will contain the common factor

$$e^{-\frac{\varkappa x}{\vartheta\,\omega} + i\,\frac{1}{\vartheta}\left(t - \frac{x}{\omega}\right)}.$$

There will arise no confusion, if we use the letters U, V, etc. themselves to represent these complex expressions.

Let the vector P be perpendicular to the axis of z. Then

$$W = 0, \quad \text{and} \quad Z = 0.$$

By the equations (3) we find:

$$u = 0, \quad v = 0, \quad w = -\frac{\vartheta}{\omega}(\varkappa + i)\,H,$$

by (1):

$$\xi = 0, \quad \eta = -\frac{1}{\omega^2}(\varkappa + i)^2\,H, \quad \zeta = 0,$$

and by (2):

$$\Xi = \varepsilon\,U, \quad H = -\frac{\mathrm{v}^2}{\omega^2}(\varkappa + i)^2\,H + \varepsilon\,V.$$

Hence

$$H = \frac{\varepsilon\,V}{1 + \frac{\mathrm{v}^2}{\omega^2}(\varkappa + i)^2}$$

and

$$\eta = -\frac{(\varkappa + i)^2}{\omega^2 + \mathrm{v}^2(\varkappa + i)^2}\,\varepsilon\,V.$$

Consequently, the two first of the equations (4) become

$$\left(-\frac{1}{\vartheta^2} + d + \frac{if}{\vartheta}\right) U - \frac{i\,g\,R}{\vartheta}\,V = 0$$

and

$$\left(-\frac{1}{\vartheta^2} + d + \frac{if}{\vartheta}\right) V + \frac{i\,g\,R}{\vartheta}\,U - \frac{(\varkappa + i)^2}{\omega^2 + \mathrm{v}^2(\varkappa + i)^2}\,\varepsilon^2\,V = 0,$$

or, if we introduce the quantities ϑ_0, ϑ', etc.,

$$(\vartheta^2 + i\,\vartheta\,\vartheta' - \vartheta_0^2)\,U - i\,k\,R\,\vartheta\,V = 0 \quad . \quad . \quad . \quad (24)$$

$$(\vartheta^2 + i\,\vartheta\,\vartheta' - \vartheta_0^2)\,V + i\,k\,R\,\vartheta\,U - \frac{(\varkappa + i)^2}{\omega^2 + \mathrm{v}^2(\varkappa + i)^2}\,q^2\,\vartheta^2\,\mathrm{v}^2\,V = 0 \quad (25)$$

These equations correspond to the two last of POINCARÉ's formulae (6), and if we were to follow his mode of reasoning, we should say that, in virtue of (24), U must be a small quantity of the order R so that the second term in (25) becomes of the order of R^2. We should then omit this last term; all influence of the magnetic field would thereby disappear from (25).

There is however an error in this reasoning, because, as I shall now show, the coefficient of U in (24) may become of the same order as that of V.

We saw already that the place of the absorption-lines is determined by the conditions

$$S_1 = 0 \qquad \text{and} \qquad S_2 = 0\,,$$

i. e. by

$$\vartheta^2 - \vartheta_0^{\,2} = \pm\, k\, R\, \vartheta\ .$$

We have further assumed that $k\, R\, \vartheta$ is much larger than $\vartheta\, \vartheta'$ Hence, in the equation (24), the coefficient of U is approximately $\pm\, k\, R\, \vartheta$, so that

$$U = \pm\, i\, V \,.\; .\; .\; .\; .\; .\; .\; .\; .\; .\; . \qquad (26)$$

On the other hand, we may neglect in (25) the last term, at least if ϑ has a value for which the absorption is a maximum. For, neglecting $\varkappa^2$, we find for that term

$$\frac{1 - 2\, i\, \varkappa}{(\omega^2 - \text{v}^2) + 2\, \text{v}^2\, i\, \varkappa}\, q^2\, \vartheta^2\, \text{v}^2\, V. \;.\; .\; .\; .\; .\; . \qquad (27)$$

The equations (22) and (23) show that, in the middle of one of the absorption-bands, $\omega^2 - \text{v}^2$ is much smaller than $2\, \text{v}^2\, \varkappa$. We may therefore neglect the first term in the denominator. Omitting likewise in the numerator the second term, which by our assumption, lies far beneath 1, we find for (27)

$$\frac{q^2\, \vartheta_0^{\,2}\, \text{v}^2\, V}{2\, \text{v}^2\, i\, \varkappa} = -\, \frac{i\, q^2\, \vartheta_0^{\,2}}{2\, \varkappa}\, V\,,$$

But, according to (23), the maximal absorption is given by

$$2\, \varkappa = \tfrac{1}{2}\, \frac{q^2\, \vartheta_0}{\vartheta'}\,;$$

(27) may therefore be finally replaced by

$$-\, 2\, i\, \vartheta'\, \vartheta_0\, V\,,$$

a quantity that may be omitted in (25) as well as $i\, \vartheta\, \vartheta'\, V$ in the first term of that equation. In this way (25) reduces to

$$V = \mp\, i\, U\,,$$

which agrees with (26).

Translated into the terms of the electromagnetic theory of light, our result becomes

$$M_x = \pm i M_y .$$

The meaning of this is that the ions move in circles perpendicular to the lines of force, the direction of this motion being opposite in the two cases, represented by the two outer lines of the absorption-triplet.

The assumptions we have found necessary in the foregoing considerations, viz. that the inequalities

$$q^2 < \frac{\vartheta'}{\vartheta_0} \quad \text{and} \quad k R > \vartheta'$$

exist in a high degree, imply that $k R$ is much larger than $q^2 \vartheta_0$.

If this is to be the case, it follows from (18) that $\frac{g}{\varepsilon^2} R \mathrm{v}^2$ must far surpass ϑ_0; in the language of the electromagnetic theory of light this means — as may be seen from (14) — that

$$\frac{R}{4 \pi \mathrm{v}^2 N e} \qquad \ldots\ldots\ldots \qquad (28)$$

must largely exceed the time ϑ_0.

Of course this condition can always be fulfilled if only the number of molecules N can be made small enough. This was to be expected because at very small densities the molecules must become independent of one another, and this is precisely what is assumed in the elementary theory.

It would be difficult to state accurately at what density the expression (28) becomes so large that distinct triplets may be seen. The preceding considerations show however that the triplets must appear in all cases where the observations along the lines of force give a good doublet.

Astronomy. — "*On the finding back of the Comet of* HOLMES *according to the computations of* Mr. H. J. ZWIERS." By Prof. H. G. VAN DE SANDE BAKHUYZEN.

In the Transactions of the Royal Academy of Sciences 1st Section Vol. III appeared a paper by Mr. H. J. ZWIERS on the orbit of the comet of HOLMES, observed from Nov. 8th 1892 till March 13th 1893. From these observations Mr. ZWIERS has deduced with great care the most probable orbit, which proved to be an ellipse, in which the comet at its greatest distance from the sun approaches

Jupiter's orbit very closely and at its shortest distance to the sun remains still outside the orbit of Mars; the period of revolution amounts to about 6 years and 11 months. In 1898 and 1899 the comet would probably again come so near to the earth, that it can be observed.

In the above-named paper Mr. ZWIERS has computed the perturbations which the comet would undergo till the end of 1898 and later on in a paper in the "Astronomische Nachrichten" Vol. 149, page 9, he has continued those computations till Sept 9th 1899. In an ephemeris added to it he has given the positions which, according to his computations, the comet would occupy on the celestial sphere.

By the aid of this ephemeris the comet has been found back as a faint nebula by PERRINE at the Lick-observatory on June 10th. Its position deviated for the computed place $22^s,2$ in right ascension and $4'17''$ in declination. Furthermore it appeared that the comet was exactly in the orbit which it had to describe according to the computations of Mr. ZWIERS, and that a perfect correspondence was obtained between the observed and the computed position by adding 0.379 days to the period of revolution. Mr. ZWIERS having taken the mean error of the period of revolution to be ± 1 day, the accuracy of the computations proves to be still greater than he had surmised.

Probably of the elements computed by Mr. ZWIERS only the period of revolution will have to be corrected a little; this cannot be stated however with certainty until more observations will have been made. For the present Mr. ZWIERS has computed a corrected ephemeris supposing only the period of revolution to be increased by 0.4 day. An ephemeris corresponding entirely with this one has been given in n⁰ 464 of the Astronomical Journal.

(August 9th, 1899.)

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday September 30th, 1899.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 30 September 1899 Dl. VIII).

CONTENTS: "On the influence of water on the velocity of the formation of ether". By Prof. C. A. LOBRY DE BRUYN and Dr. A. STEGER, p. 71. — "An example of the conversion of mixed crystals into a compound". By Prof. H. W. BAKHUIS ROOZEBOOM, p. 74. — "On the Enantiotropy of Tin". By Dr. ERNST COHEN and Dr. C. VAN EYK (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM), p. 77. — "On the Enantiotropy of Tin (II)". By Dr. ERNST COHEN and Dr. C. VAN EYK (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM). p. 81. — "The mixture crystals of $Hg J_2$ with $Hg Br_2$". By Prof. H. W. BAKHUIS ROOZEBOOM, p. 81. — "On a new kind of Transition Elements (sixth kind)". By Dr. ERNST COHEN (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM), p. 81. — "On Isodialdane". By Prof. C. A. LOBRY DE BRUYN and Mr. H. C. BYL, p. 81. — "The results of a comparative investigation concerning the palatine-, orbital- and temporal regions of the Monotreme-skull". By Dr. J. F. VAN BEMMELEN (Communicated by Prof. A. A. W. HUBRECHT), p. 81. — "On the Formation of the Resultant". By Mr. K. BES (Communicated by Prof. J. CARDINAAL), p. 85. — "Investigations with the Micromanometer". By Dr. A. SMITS (Communicated by Prof. V. A. JULIUS), p. 88. — "The determination of the refractivity as a method for the investigation of the composition of co-existing phases in mixtures of acetone and ether". By Mr. E. H. J. CUNAEUS (Communicated by Prof. J. D. VAN DER WAALS; with one plate, p. 101. — "On the Theory of LIPPMANN's Capillary Electrometer". By Prof. W. EINTHOVEN (Communicated by Prof. T. ZAAYER), p. 108. — "On the formation of Indigo from the Woad (Isatis tinctoria)". By Prof. M. W. BEIJERINCK, p. 120. — "Methods and Apparatus used in the Cryogenic Laboratory (I)". By Prof. H. KAMERLINGH ONNES (with 4 plates), p. 129. — "The dielectric constants of liquid nitrous oxide and oxygen". By Dr. FRITZ HASENOEHRL (Communicated by Prof. H. KAMERLINGH ONNES), p. 140. — "On Spasms in the Earth's magnetic force". By Dr. W. VAN BUMMELEN (Communicated by Prof. H. KAMERLINGH ONNES), p. 141. — Erratum, 141.

The following papers were read:

Chemistry. — „*On the influence of water on the velocity of the formation of ether.*" By Prof. C. A. LOBRY DE BRUYN and Dr. A. STEGER.

(Read in the meeting of June 24th 1899).

In a previous communication [1]) we drew attention to the influence of water on the velocity with which oxyethyl or oxymethyl is sub-

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[1]) Proceedings 1898 p. 166.

stituted for the nitrogroup in orthodinitrobenzene by sodium alcoholate. It appeared that the existence of constant coefficients of velocity was not at all, or very little affected by the presence of water in the methyl- or ethylalcohol, a fact which was explained by the circumstance that by far the greater part of the sodium is present as alcoholate in mixtures of water and alcohol containing even 50 % of water. The influence of the water present was however felt in the alteration of the numerical values of the constants due to the change of the medium; with ethylalcohol the change consisted of a diminution of the constants as the quantity of water present increased, with methylalcohol exactly the contrary took place.

The influence of water on the reaction under discussion could not be followed further than a 50 % mixture of water and alcohol, owing to the ever decreasing solubility of the dinitrobenzene. We pointed out therefore the desirability of finding a reaction, which would allow velocity determinations to be made, for both alcohols, from the absolute alcohol to pure water; the two different curves for the two alcohols must necessarily meet in the point corresponding to pure water, that is to the reaction with Na OH.

We have discovered such a reaction in the process of the formation of ethers from alkyliodides and alcoholates, in the special case in which methyliodide is employed; the solubility of this iodide in water being sufficient to permit of a determination of the velocity. With ethyliodide it was found that, owing to its smaller solubility, it was impossible to go further than 30% ethylalcohol (70% water) and 40 % methylalcohol (or 60 % water).

The reactions studied are thus:

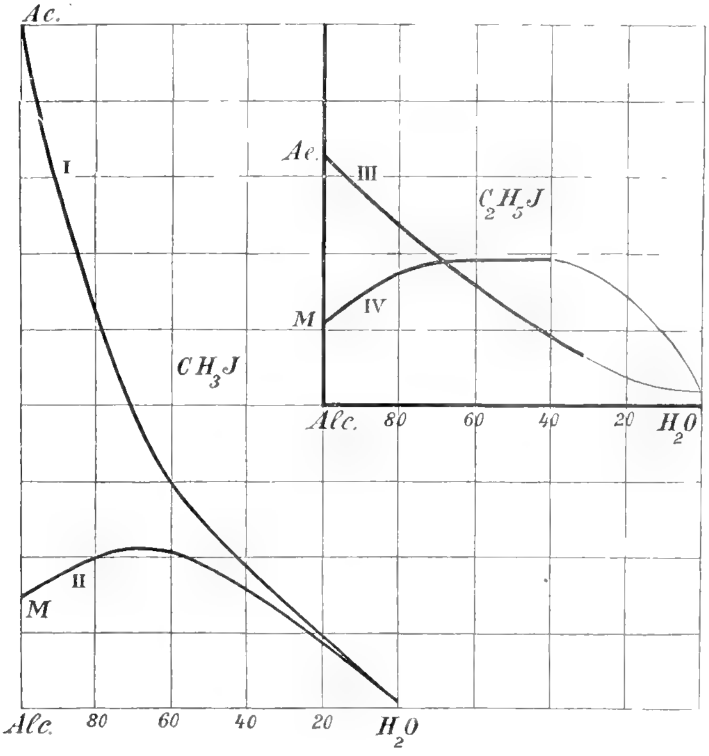
$$\text{I. } NaOC_2H_5 + CH_3I \;, \quad \text{II. } NaOCH_3 + CH_3I$$
$$\text{III. } NaOC_2H_5 + C_2H_5I \;, \quad \text{IV. } NaOCH_3 + C_2H_5I \;;$$

to which the change, $CH_3I + NaOH = CH_3ONa + NaI$, must be added.

The composition of the mixtures of water and alcohol was changed by equal steps of 10 % between absolute alcohol and water.

It was at once evident that the reaction-coefficients obtained in each experiment might be regarded as constants; with methylalcohol, the numbers are very satisfactory, less so with ethylalcohol, but still more than sufficiently so to show the change of velocity with the quantity of water present. For reaction I the numbers diminish from 0.189 for absolute alcohol to 0.0040 for water; for reaction

III, from 0,0168 to 0,005; for the reactions in methylalcohol (II and IV) an increase at first occurs with increasing content of water, for II there is a maximum at 70 % (0.032 to 0.0435) after which the numbers diminish to 0.004, for reaction IV the increase continues as far as the decomposition in 40 % alcohol (0.00525 to 0.0098) which was the extreme limit to which it was possible to go. The subjoined figure shows the change of the constants with the content of water.



It is thus evident that, as in the case of the reaction between o-dinitrobenzene and sodium alcoholate, the addition of water to ethylalcohol diminishes the velocity of the reaction, whilst with methylalcohol an increase first occurs which (reaction II) is followed by a decrease.

Attention may be drawn to some other conclusions. First, it appears that whilst for both iodides in methylalcohol there is a maximum for the mixture containing about 70 % of alcohol, the constants diminish regularly with methyliodide II, whilst with ethyliodide (IV) they remain practically constant between 40 % and 70 %. It is further seen that in the alcohol in which the electrolytic dissociation is the greater (methylalcohol) the velocity of reaction is the smaller, notwithstanding the fact that according to the researches of MENSCHUTKIN and CARRARA, methylalcohol itself accelerates similar reactions to a greater extent than ethylalcohol. It appears to us therefore that it follows from this case, as in the case of the reaction of o-dinitrobenzene and alcoholate, that reactions taking place in solvents other than water depend on circumstances which are as yet unknown, in addition to the degree of dissociation into ions.

From our earlier research we had concluded that the sodium dissolved in a 50 % mixture of alcohol and water is present mainly as alcoholate. The same conclusion may be drawn from an experiment in which a solution of 5 grams of Na in 1/2 litre of a 50 % mixture of alcohol and water was warmed to 25° for 8 days with 32 grams (1 mol.) of ethyliodide. By means of several fractional distillations about 11.5 grams of ethylether were obtained, the theoretical quantity being 15.5 grams. Considering the unavoidable losses it may therefore be said that by far the greater part of the iodide was converted into ether.

It is still necessary to examine reactions such as those here studied, in mixtures of alcohol and water containing a large proportion of water, since in these there cannot be much alcoholate.

The details of this research will shortly be published in the "Recueil des travaux chimiques."

Chemistry. — Mr. Prof. H. W. BAKHUIS ROOZEBOOM speaks on: *„An example of the conversion of mixed crystals into a compound".*

(Read in the meeting of June 24th 1899.)

In the meeting of the 25th February 1897, page 376, I gave an explanation of the solidification of mixtures of optical isomers, when the solidification results in the formation (1) of a conglomerate (2) of mixed crystals, (3) of a racemic compound.

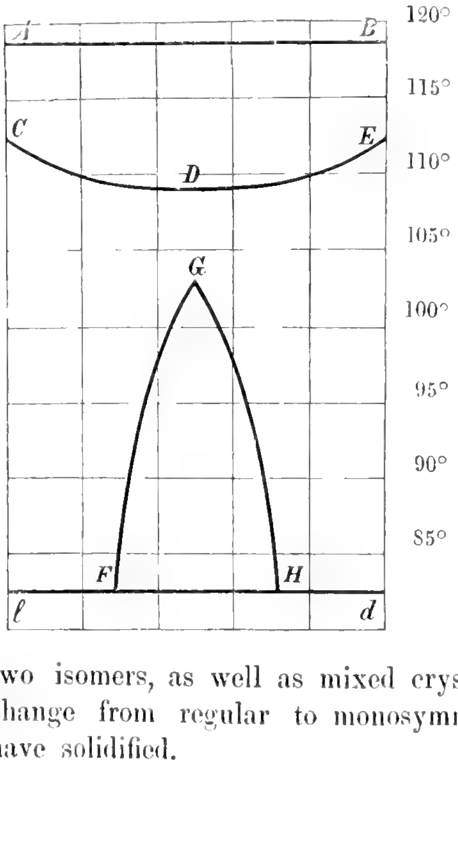
In a more complete paper, Zeitschr. phys. Chemie 28, 512, I have further developed the theory of the phenomena which must occur when these three types pass into each other when the solid mass is further cooled.

As one of the most interesting cases, Mr. ADRIANI, has at my request, studied an example of the conversion of mixed crystals into a compound below a certain temperature.

The example was camphoroxime. Mr. ADRIANI prepared the *d*-oxime; we owe the *l*-oxime to the kindness of Prof. Beckmann of Leipzig.

1. The melting points of the pure oximes and of mixtures of them were first determined. Both melt at 118°.8; the inactive mixture, containing 50% *d*- and 50% *l*-oxime melts at exactly the same temperature as also a number of mixtures containing excess of *d*- or *l*-oxime. No difference could be discovered within the limits of attainable accuracy. The accuracy here is not more than 0 °.1, because it is very difficult to determine the melting-point exactly, owing to the small difference in the refractive indices of the solid and liquid. Very satisfactory results were obtained finally by using very thin walled tubes in which a thin cylindrical ring of the solid mass was placed just above the lower end. The solid mass is, in all proportions, microscopically homogeneous and regular. Forster and Pope's view (Journ. Chem. Soc. 71.1049) that we are here concerned with mixed crystals is confirmed by the discovery of one melting-point line alone.

At the same time the existence of mixed crystals of optical isomers, the probability of which was pointed out by Kipping and Pope, is confirmed.



In the figure, the horizontal line *AB* represents the melting point line. The view that the melting points of all the mixtures would be the same is thus confirmed in this case. I have already pointed out that this is possible in no other series of mixed crystals than those containing optical isomers.

A consequence of the horizontal melting-point line is that each mixture solidifies to a homogeneous mass. The melting point line therefore represents the compositions both of the liquid and of the solid phase.

2. According to Pope the two isomers, as well as mixed crystals containing them, undergo a change from regular to monosymmetric crystals shortly after they have solidified.

The temperatures at which this change took place were however unknown. They were therefore determined.

Change from regular to monosymmetric crystals.

100 $^0/_0$ *d* or *l*	112°.6
90 $^0/_0$ „ „ „	110°.6
70 $^0/_0$ „ „ „	109°.7
50 $^0/_0$ „ „ „	109°.4

These values are shown by the line *CDE*, which is completely symmetrical and has a minimum of temperature at the transition point of the inactive mixture. Since here again only one curve is obtained for all the transition temperatures we must conclude that the regular mixed crystals change into monosymmetric mixed crystals.

When the change takes place with falling temperature it may be much delayed; in the other direction however it is very sharp. With the microscope it may be observed clearly, with the thermometer with great difficulty, and very distinctly by means of the dilatometer. With the non-racemic mixed-crystals it is possible that the transition takes place through some interval of temperature. In any case this is very small.

3. A further change takes place in the monosymmetric mixed crystals when they are cooled still more. Pope has observed this, only in the inactive mixtures, and ascribed it to the formation of a racemic compound (which may be obtained from a solution of the inactive mixture at the ordinary temperature). In that case the conversion of the mixed crystals into the compound should theoretically occur in other mixtures also but at lower temperatures.

This has been shown to be the case.

Conversion of mixed crystals into a compound.

50 $^0/_0$ *d* or *l*	103°
60 $^0/_0$ „ „ „	97°
70 $^0/_0$ „ „ „	86°

These points are indicated by the line *FGH* which has a maximum at 50 $^0/_0$.

The change occurs less readily the greater the excess of *d* or *l* which is present and proceeds very slowly. At 75 % it could not be observed even at the ordinary temperature.

The monosymmetric crystals change to a granular mass; when excess of *d* or *l* is present this is of course only partial.

The transition temperature in this case could not be detected by means of the thermometer or of the dilatometer but only by means of the microscope and then only when the temperature was rising. With 50 % the change is complete at the maximum temperature; with the other mixtures the change is gradual; the line *FGH* represents the temperatures at which the racemic compound in a given mixture has just disappeared. All points between the two branches represent conglomerates of the compound with mixed crystals.

The course of the conversion of mixed-crystals into a compound, deduced by me on theoretical grounds, is therefore completely confirmed by this first example.

Chemistry. — „*On the Enantiotropy of Tin*". By Dr. ERNST COHEN and Dr. C. VAN EYK (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

(Read in the meeting of June 24th 1899).

1. That pure tin falls into a grey powder when exposed to great cold is a phenomenon with which the tin traders of Russia especially have been long familiar. The phenomenon is, in that country, so common that a special name has been given to the tin powder which may be translated as *tin which may be scattered.*

The phenomenon has been very frequently referred to in scientific literature; the first description of it is due to ERDMANN[1]) in 1851. He is followed by FRITSCHE[2]), LEWALD[3]), RAMMELSBERG[4]), OUDEMANS[5]), WALZ[6]), PETRI[7]), SCHERTEL[8]), RAMMELSBERG[9]),

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[1]) Journ. f. pract. Chemie 52, 428 (1851).

[2]) B. B. 2, 112 en 540 (1869); Mém. de l'Académie de Pétersbourg, VII Série N^0 5 (1870).

[3]) Dinglers polytechn. Journal 196, 369. (1870).

[4]) B. B. 3, 724 (1870). Zeitschrift für Chemie 1870. 733.

[5]) Processen-Verbaal der Kon. Akad. v. Wetenschappen te Amst., vergad. 28 Oct. 1871.

[6]) WAGNER's Jahresbericht 1873, 207 uit: Deutsche Industriezeitung 1872, 468.

[7]) WILDEMANNS Ann. (2) 2, 304. (1877).

[8]) Journ. für pract. Chemie 19, 322 (1879).

[9]) Berl. Akad. Ber. 1880, 225.

MARKOWNIKOFF [1]), EMELJANOW [2]), EDV. HJELT [3]), HOEVELER [4]), STOCKMEIER [5]) and SCHAUM [6]).

The phenomenon has been observed on articles made of tin such as organ pipes, buttons of uniforms, coffee pots, medals, rings etc. and not only on blocks of pure Banca tin.

Whilst tin in the ordinary, well known condition, is silver-white, it becomes grey under certain circumstances and loses its coherence.

2. The different authors by no means agree as to the cause of the change.

Some ascribe the change to great cold, others to the combined influence of cold and vibration, whilst a third group of observers speak somewhat vaguely of an influence which the greater or smaller rate of cooling of the tin after it had been melted might exert on the occurrence of the phenomenon.

3. FRITZSCHE proved qualitatively that a considerable expansion accompanies the transformation of the silver-white into the grey condition. SCHERTEL and RAMMELSBERG found later that the specific gravity of the grey modification at 19° is about 5,8 whilst the silver-white form at the same temperature has the specific gravity 7,3.

4. The facts enumerated remained up to the present isolated; many points in the different memoirs could not be brought into harmony with each other.

A more accurate, quantitive treatment of the subject, based on the newer physico-chemical conceptions, may perhaps throw some light upon it; at the request of Prof. BAKHUIS ROOZEBOOM we have undertaken this and give in what follows a very brief account of some of the results thus far obtained.

5. The material used was obtained from Prof. EDV. HJELT of Helsingfors, who was kind enough to send us 25 grams of grey tin.

This tin was part of a piece of Banca-tin which had fallen into powder in the warehouse of a Helsingfors firm.

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[1]) Journ. russ. phys. chem. Gesellschaft 1881, 358; Bulletin de la Société chimique de Paris (2) 37, 347 (1882).

[2]) Congress russischer Naturforscher und Aerzte Petersburg 1890.

[3]) Chemiker Zeitung 16, 1197 (1892); „Ofversigt af Finska Vetensk. Soc. förhandlin". 32.

[4]) Chem. Zeitung 1892. 1339.

[5]) Verh. d. Ges. Deut. Naturf. u. Aerzte. Nürnberg 1893.

[6]) Die Arten der Isomerie. Habilitationsschrift, Marburg 1897.

If the tube containing the grey tin is immersed in warm water the tin immediately takes on the colour of ordinary tin. The reconversion into grey tin occurs when the tube is cooled. At — 83°, in a paste of solid carbonic anhydride and alcohol the change from white to grey tin took place in about 24 hours. Prolonged cooling to a temperature not lower than —20° was fruitless. On the other hand the change of grey into white tin was only observed at temperatures above + 30°. From this point, however, the velocity of the change increased very rapidly with rising temperature. It appeared therefore to be difficult to find a transition point. It is, however, known that transition phenomena are accelerated when the materials undergoing the change are present in a finely divided state, and also that solvents accelerate the change [1]).

After a number of preliminary experiments we found that a solution of ammonium stannic chloride afforded an excellent means of causing the change to take place readily in either direction.

For example, the change white tin → grey tin, which without the ammonium stannic chloride solution required 24 hours at —83°, took place in 6 hours when a few drops of a 10% solution of the salt in water were added to the tin. When the change has been carried out in both directions several times with the same quantity of tin, it takes place more and more readily. In general, it may be said that the phenomena are here quite analogous to those observed with salts containing water of crystallisation when they are heated above their transition points and again cooled.

6. In order to determine the transition point of the change

$$\text{grey tin} \rightleftarrows \text{white tin}$$

we used the dilatometric- and the electric methods.

a. *Determinations with the dilatometer.*

The dilatometer contained about 2 cc. and was filled with white tin; a 10% aqueous solution of ammonium stannic chloride served as measuring liquid. The position of the liquid in the very narrow capillary was read on a porcelain millimeter scale.

The following table contains the observations.

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[1]) See for example: L. Th. Reicher, De temperatuur der allotropische verandering van de zwavel. Dissertatie. Amsterdam, 1883

TABLE I.

Temperature.	Time in hours.	Rise of the level in the capillary in mm.	Rise per hour. in mm.
— 5°,0	23	104	4,5
0°	20	48	2,4
+ 5°,0	17	2	0,1
10°,0	13	0,9	0,0
15°,0	11	0,0	0,0
17°,0	23	0,0	0,0
20°,0	24½	— 2,0	— 0,1

From these observations follows that the transition point lies between + 10° and + 20°. More exact results would be obtained by prolonged observations at constant temperature.

b. *Electric determination.*

A transition element was set up as follows:

white tin — 10% ammonium stannic chloride solution — grey tin,

and its E. M. F. at different temperatures determined by POGGENDORFF's method. A WESTON-cell was used as standard and a small accumulator as the working cell.

Our transition cell stood in a thermostat. The change of pole occurred at 20°.

7. The two methods thus lead to the result that the change

$$\text{grey tin} \rightleftarrows \text{white tin}$$

has a transition point (at 1 atmosphere) at 20° C.

Since all tin articles in every day use, consist of the white modification, the above research leads to the striking result, *that our whole tin-world exists, except on a few hot days, in the metastabile condition.*

Amsterdam, Chem. Laboratory of the University,
June 1899.

Chemistry. — "*On the Enantiotropy of Tin* (II)." By Dr. ERNST COHEN and Dr. C. VAN EYK. (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

(Will be published in the Proceedings of the next meeting.)

Chemistry. — "*The mixture crystals of* Hg J_2 *with* Hg Br_2." By Prof. H. W. BAKHUIS ROOZEBOOM.

(Will be published in the Proceedings of the next meeting.)

Chemistry. — "*On a new kind of Transition Elements (sixth kind).*" By Dr. ERNST COHEN. (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

(Will be published in the Proceedings of the next meeting.)

Chemistry. — "*On Isodialdane.*" By Prof. C. A. LOBRY DE BRUYN and Mr. H. C. BIJL.

(Will be published in the Proceedings of the next meeting).

Zoology. — Mr. HUBRECHT presents on behalf of Dr. J. F. VAN BEMMELEN: "*The results of a comparative investigation concerning the palatine-, orbital- and temporal regions of the Monotreme-skull*".

I. *Palate.*

In both Ornithorhynchus and Echidna the palate has been secondarily prolonged backwards, in consequence of their mode of life, and therefore independently of each other, and in two different ways.

The palatine bones of O. are as broad behind as in front, the pterygoïds being situated entirely along their lateral borders, quite unconnected with the bones forming the wall of the cerebral cavity.

In the E. skull on the contrary, the palatines are prolonged backwards into slender points, which causes the pterygoïds to find a place at the roof of the mouth much nearer to the middle line, between the oblique postero-exterior border of the palatines and the petrosa, thereby allowing them to enter into the formation of the cerebral skull-wall.

The horizontal mouth-plates of the Echidna-palatines are provided at their lateral border with two vertical wings: a larger one in front, forming the basal part of the wall of the orbital cavity, and a smaller one behind, stretching upwards in the temporal groove and separating the foramen ovale from a large bipartite opening at the border of the orbita, which represents the united foramina rotunda, optica and spheno-orbitalia. In O. the first mentioned of these apertures is separated from the two following by a short bone-column.

At the ventral side of this temporal palatine-wing in E. we notice the front end of a tiny canal, which may possibly represent the homologue of the well-developed canalis pterygoideus seu vidianus of O., this latter running longitudinally along the margin of the palatine-plate, between for. ovale and for. rotundum. The difference is explained by the occurrence of a large artery in O., branching off from the carotis interna, crossing the tympanic cavity externally to the stapes, and entering the vidian canal to reach the orbital cavity. This artery, called art. stapedia by TANDLER, is absent in E., where the orbits are provided with blood by the carotis externa, but perhaps the small artery occupying the above-mentioned tiny canal is the last remnant of the art. stapedia.

II. *Sphenoïd.*

The corpus sphenoïdei in E. appears long and slender, owing to the want of connection with ali-sphenoïdea (alae magnae). It shows a concave ventral side, caused by its curving down at both sides in slightly elevated but very elongated pterygoïdprocesses. At its hinder margin it is pierced by the foramina carotica, and laterally to these it is provided with backward prolongations of the processus pterygoïdales, viz. the spinae angulares. These latter are much more developed in O., where they extend over the ventral surface of the petrosa. In this animal they form a narrow partition dividing the foramina ovalia from the choanae, whereas in E these two are separated from each other by the whole diameter of the pterygoïds, which also hide the spinae angulares under their projecting median edge. The sella turcica of O. is much more elongated in a sagittal direction than that of E. This contrasts with the extraordinary development in the latter animal of the lamina cribrosa ethmoïdei, which totally anchyloses with the sphenoïd. In O. no trace of such a cribrous plate can be detected.

The space of the ali-sphenoïds is occupied in E. by thin bony plates, separated by suture from all the surrounding bones: the basi-sphenoïd as well as the others. These plates ossify at a very late period, so late indeed that even in the almost adult skull a large fontanella is found in this spot, leaving the for. ovale not encircled by bone at its lateral border. In the partly-ossified skull of a young E. removed from the pouch, this fontanella even extended to the foramina rotunda, optica and spheno-orbitalia, which all confluated into one large vacuity in the lateral skull-wall. The same fact occurred in the skull of an Ornithorhynchus-foetus: the bony plate that was going to close up this open space, was growing out from under the squamosal as a dermal bone. In this character it resembled the *postfrontale,* which is destined to anchylose with the orbito-sphenoïd.

In consequence of this latter occurrence the orbital wings of the sphenoïd reach an enormous size in Monotremes. The presence of *postfrontals* in these animals, resembling those of Sauropsids, already mentioned by SEELEY, is proved beyond all doubt by the investigation of the skulls of new-born individuals. The orbital wings of the sphenoïd anchylose with the median corpus, in E. as well as in O., thus contrasting with the alisphenoïdplates in the former animal.

III. *Petrosum.*

The petrous bone of O. is separated from the surrounding bones by three large perforations of the skull-wall; 1st. an anterior one, the foramen ovale, dividing it from the alisphenoïd, 2d. a posterior one, the for. pro nervo vago et glossopharyngeo, separating it from the exoccipital (occ. later.); 3d. a median one, through which no structures enter or leave the cerebral cavity and which separates the petrosum from the basi-occipital.

In E. these holes are apparently wanting, but in reality they are all present, only they are lying much farther apart, and moreover the anterior and median ones are separated from the petrosum by the large pterygoïd. The posterior opening is divided into two orifices, an anterior one which serves as an outlet to the nerves and is situated within the borders of the petrosum, and a posterior one, which is nothing but a fontanella, closing up in the full-grown animal and surrounded by the exoccipital. In O. the large size of the corresponding single opening is also due to incomplete ossification in the neighbourhood of the nerve-foramen.

This scattered position of the three apertures around the petrosum in Echidna brings this bone into an all-round contact with other bones viz. the alisphenoïd, pterygoïd, basioccipital, exoccipital and squamosal.

At the lateral wall of the skull the petrous bone of E. appears to be continued in a dorsal direction as a large patch of bone, but in reality it is separated from this patch longitudinally by a suture that runs through the lateral part of the tympanic cavity. By its form and position this patch resembles the mastoïdal part of the temporal of other Mammals, but as for its size and independence, it may be compared to the opisthoticum and epioticum, taken conjointly, of Sauropsida.

This mastoïdal part of the skull-wall is a chondrostosis, which fact is in itself sufficient to forbid its comparison with a squamosal, a comparison one might otherwise be much inclined to make, considering that the dermal bone which is situated on its outer surface might easily be mistaken for the jugal, with which it shows many points of resemblance, and which, but for this hypothesis, must be considered as absent in the Monotreme-skull.

IV. *Arcus zygomaticus.*

The malar arch of Monotremes is made up of two bony processes, running side by side for the greater part of their length. The anterior belongs to the maxillary, the posterior to the above-mentioned dermal bone, that I take to be the squamosal. A jugal bone is totally absent in E. In O. on the contrary a little prominence occurs on the dorsal side of the arch, marking the limit between orbital and temporal fossae. In some skulls this prominence was found separated by a suture from the underlying zygomatic process of the maxillary. Most probably we may look upon it as the last remnant of a disappearing jugal. The foetal O. skull did not show any trace of it.

V. *Canalis temporalis.*

Between the squamosal and the wall of the primordial-cranium (mastoïdal bone), a canal is left open from before backwards in both E. and O.

In no other Mammalian skull a trace of such a canal was found. In E. it is longer but narrower, in O, shorter but wider. Its lumen is filled up with fibres of the temporal muscle.

Moreover in E. an artery penetrates into the skull-wall by the posterior opening of this canal, but immediately leaves it to continue its way through the diploë of mastoïdal, parietal and frontal as far as the ethmoïdal region. Hyrtl calls it art. occipitalis.

Mathematics. — *On: "The Formation of the Resultant".* By Mr. K. Bes. (Communicated by Prof. J. Cardinaal.)

The method of elimination by means of the Bezout function as shown by me in my treatise "Théorie Générale de l'Élimination" (Verhand. der Kon. Akademie van Wetensch. te Amsterdam 1e Sectie, Dl. VI, N°. 7) offers a means to form the resultant that is to be obtained, if between $n - 1$ homogeneous equations of arbitrary degrees with n variables $n - 2$ of those variables are eliminated.

I intend shortly to treat this subject in extenso; but looking forward to the time necessary for this work I thought it my duty at present to acquaint your assembly with the obtained result. For this the special case is taken of two homogeneous equations of the degrees l and m with three variables, viz.:

$$\left.\begin{array}{l} \varphi(x, y, z) \equiv a_1 x^l + a_2 x^{l-1} y + a_3 x^{l-1} z + a_4 x^{l-2} y^2 + a_5 x^{l-2} y z + \\ \qquad + a_6 x^{l-2} z^2 + a_7 x^{l-3} y^3 + \ldots\ldots + a_{\frac{(l+1)(l+2)}{2}} z^l = 0, \\ \psi(x, y, z) \equiv b_1 x^m + b_2 x^{m-1} y + b_3 x^{m-1} z + b_4 x^{m-2} y^2 + b_5 x^{m-2} y z + \\ \qquad + b_6 x^{m-2} z^2 + b_7 x^{m-3} y^3 + \ldots\ldots + b_{\frac{(m+1)(m+2)}{2}} z^m = 0 \end{array}\right\} (1).$$

It is known that in this case the resultant is of the degree lm.

If we form an homogeneous function F of the degree lm as follows:

$$F \equiv \Phi \varphi + \Psi \psi \ldots\ldots\ldots (2),$$

where Φ and Ψ are respectively homogeneous functions of the degrees $lm - l$ and $lm - m$ with provisionally undetermined coefficients s the equation

$$F = 0 \ldots\ldots\ldots\ldots (3)$$

will represent the resultant, if we can determine the coefficients s in such a manner that all the terms containing one of the three variables disappear from the equation.

The function F can be developed in two ways, as was shown in the above-named treatise on the theory of elimination:

1st. according to the successive arguments of an homogeneous function;

2d. according to the undetermined coefficients s_1, s_2, s_3, etc.

Thus it gives rise to the formation of an "assemblant" consisting of

$$v = \frac{(lm+1)(lm+2)}{2} \text{ rows and } v_1 = \alpha_1 + \alpha_2 \text{ columns,}$$

where

$$\alpha_1 = \frac{(lm-l+1)(lm-l+2)}{2} \text{ and } \alpha_2 = \frac{(lm-m+1)(lm-m+2)}{2}.$$

The columns of this "assemblant" are in general not independent of each other but connected by

$$v_2 = \frac{(lm-l-m+1)(lm-l-m+2)}{2}$$

independent linear relations.

We now see that between the numbers v, v_1 and v_2 the relation

$$v - v_1 + v_2 = lm \, . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

exists, as is easily shown by substituting the values.

We determine the v_1 undetermined coefficients s in the following way: In the function F we make equal to zero the coefficients of all the terms containing the same variable. This produces $\frac{lm(lm+1)}{2}$ linear homogeneous equations between the coefficients s which are moreover, as was said above, connected by v_2 linear relations of dependence.

So the difference between the number of underdetermined coefficients and that of the mutually independent linear homogeneous equations existing between them is:

$$v_1 - v_2 - \frac{lm(lm+1)}{2} = v - lm - \frac{lm(lm+1)}{2} =$$

$$= \frac{(lm+1)(lm+2)}{2} - \frac{lm(lm+3)}{2} = 1,$$

which proves that the v_1 undetermined coefficients s can be determined quite unequivocally out of the indicated homogeneous linear equations.

By substitution of the obtained values in the equation $F = 0$ the demanded resultant is arrived at. The given method is rather simple to apply.

As an example we take the system of two homogeneous equations of the second degree with three variables:

$$\left.\begin{array}{l} a_1 x^2 + a_2 x y + a_3 x z + a_4 y^2 + a_5 y z + a_6 z^2 = 0, \\ b_1 x^2 + b_2 x y + b_3 x z + b_4 y^2 + b_5 y z + b_6 z^2 = 0, \end{array}\right\} \quad . \quad . \quad (5).$$

The function F is represented by

$$\begin{aligned} F \equiv (s_1 x^2 + s_2 x y + s_3 x z + s_4 y^2 + s_5 y z + s_6 z^2) \\ (a_1 x^2 + a_2 x y + a_3 x z + a_1 y^2 + a_5 yz + a_6 z^2) \\ + (s_7 x^2 + s_8 x y + s_9 x z + s_{10} y^2 + s_{11} y z + s_{12} z^2) \\ (b_1 x^2 + b_2 x y + b_3 x z + b_4 y^2 + b_5 yz + b_6 z^2). \end{aligned}$$

From this follows the "assemblant"

$$\begin{array}{c|cccccccccccc|} & s_1 & s_2 & s_3 & s_4 & s_5 & s_6 & s_7 & s_8 & s_9 & s_{10} & s_{11} & s_{12} \\ \hline x^4 & a_1 & & & & & & b_1 & & & & & \\ x^3y & a_2 & a_1 & & & & & b_2 & b_1 & & & & \\ x^3z & a_3 & & a_1 & & & & b_3 & & b_1 & & & \\ x^2y^2 & a_4 & a_2 & & a_1 & & & b_1 & b_2 & & b_1 & & \\ x^2yz & a_5 & a_3 & a_2 & & a_1 & & b_5 & b_3 & b_2 & & b_1 & \\ x^2z^2 & a_6 & & a_3 & & & a_1 & b_6 & & b_3 & & & b_1 \\ xy^3 & & a_4 & & a_2 & & & & b_4 & & b_2 & & \\ xy^2z & & a_5 & a_4 & a_3 & a_2 & & & b_5 & b_4 & b_3 & b_2 & \\ xyz^2 & & a_6 & a_5 & & a_3 & a_2 & & b_6 & b_5 & & b_3 & b_2 \\ xz^3 & & & a_6 & & & a_3 & & & b_6 & & & b_3 \\ y^4 & & & & a_4 & & & & & & b_4 & & \\ y^3z & & & & a_5 & a_4 & & & & & b_5 & b_4 & \\ y^2z^2 & & & & a_6 & a_5 & a_4 & & & & b_6 & b_5 & b_1 \\ yz^3 & & & & & a_6 & a_5 & & & & & b_6 & b_5 \\ z^4 & & & & & & a_6 & & & & & & b_6 \end{array} \quad . \quad (6),$$

to which

$$\begin{array}{c|cccccccccccc|}
 & s_1 & s_2 & s_3 & s_4 & s_5 & s_6 & s_7 & s_8 & s_9 & s_{10} & s_{11} & s_{12} \\
t_1 & b_1 & b_2 & b_3 & b_4 & b_5 & b_6 & -a_1 & -a_2 & -a_3 & -a_4 & -a_5 & -a_6
\end{array} \quad . \; . \; (7).$$

belongs as supplementary "assemblant".

If we omit one of the columns from the "assemblant" (6) the determinants in the remaining columns (see Chapter I of the above-named paper) are divisible by the supplementary determinant of the assemblant.

From this "assemblant" the coefficients of the resultant follow immediately.

Thus we find for the resultant between y and z:

$$p_{12,13,14,15}\, y^4 + p_{11,13,14,15}\, y^3 z + p_{11,12,14,15}\, y^2 z^2 + p_{11,12,13,15}\, y\, z^3 + \\ + p_{11,12,13,14}\, z^4 = 0 \quad . \quad . \quad . \quad (8),$$

for the resultant between x and z:

$$p_{3,6,10,15}\, x^4 + p_{1,6,10,15}\, x^3 z + p_{1,3,10,15}\, x^2 z^2 + p_{1,3,6,15}\, x z^3 + \\ + p_{1,3,6,10}\, z^4 = 0 \quad . \quad . \quad (9),$$

for the resultant between x and y:

$$p_{2,4,7,11}\, x^4 + p_{1,4,7,11}\, x^3 y + p_{1,2,7,11}\, x^2 y^2 + p_{1,2,4,11}\, x y^3 + p_{1,2,4,7}\, y^4 = 0 \,.\, (10),$$

where the coefficients represent determinants contained in "assemblant" (6) after one of the columns having been omitted and where the indices indicate which rows must be left out of the "assemblant" to obtain the determinant represented by the symbol. All the coefficients of the equations (8), (9) and (10) are now still divisible by the same linear factor, namely by b_6 if we leave the sixth column out of the "assemblant", in general by the supplementary determinant of the "assemblant" (7).

Chemistry. — Prof. V. A. JULIUS presents on behalf of Dr. A. SMITS of Amsterdam a paper on „*Investigations with the Micromanometer.*"

After I had published in 1896 the first results obtained with the micromanometer[1]), I continued my investigations to inquire whether the course observed for Na Cl, K O H and cane-sugar would also appear in other compounds.

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[1]) Dissertation „Untersuchungen mit dem Mikromanometer" 1896. Verslag Konínkl. Akad. v. Wetensch. te Amsterdam, Wis- en Natuurk. Afd. pag. 292, 1897. Archives Neerl. Série II, Tome I, p. 89, 1837.

Before, however, examining other compounds, I wished to make some further experiments with Na Cl, K O H and sugar solutions, because I had made a slight improvement in the apparatus; I had namely brought the legs of the manometer nearer together, so that they were only 2 m.m. distant, which diminished the error in the observation. Before communicating the results of those observations, I shall first shortly state my former results, to facilitate a comparison. The meaning of p_w, p_s, p_m N and n is as follows.

p_w = tension of the gas of pure water expressed at 0° in m.m. Hg.
p_s = " " " " " solution " " " " " "
p_m = mol. decrease of the tension of the gas " " " " " "
N and n indicate the number of mol. of water and solved substance found in the solution:

Na Cl.

Concentration in gr. mol. per 1000 gr. H_2O.	$p_w - p_s$ in m.m. Hg.	p_m in m.m. Hg.	$i = \frac{p_w - p_s}{p_w} \cdot \frac{N}{n}$
0.02842	0.00314	0.121	1.5
0.03546	0.00477	0.131	1.6
0.08813	0.01223	0.139	1.67
0.17680	0.02477	0.140	1.69
0.35587	0.05026	0.141	1.70
0.8854	0.12646	0.143	1.718
1.8228	0.26757	0.147	1.765

K O H

Concentration in gr. mol. per 1000 gr. H_2O.	$p_w - p_s$ in m.m. Hg.	p_m in m.m. Hg.	$i = \frac{p_w - p_s}{p_w} \cdot \frac{N}{n}$
0.03035	0.00409	0.135	1.6
0.05564	0.00763	0.137	1.65
0.09992	0.01382	0.138	1.66
0.16626	0.02321	0.140	1.68
0.33161	0,04786	0.143	1.72
0.51342	0.07504	0.146	1.76
0.75044	0.11170	0.149	1.790
1.0356	0.15867	0.153	1.812
2.6422	0.47601	0.180	2.166

CANE SUGAR.

Concentration in gr mol per 1000 gr. H_2O.	$p_w - p_s$ in m.m. Hg.	p_m in m.m. Hg.	$i = \frac{p_w - p_s}{p_w} \cdot \frac{N}{n}$
0.02138	0.00178	0.083	1.0
0,01630	0.00388	0.084	1.0
0.08488	0.00705	0.083	1.0
0.17287	0.01410	0.083	1.00
0.28310	0.02366	0.084	1.00
0.77912	0.06185	0.083	1.001
1.8821	0.17453	0.093	1.115

For NaCl and KOH-solutions I found that the molecular depression of the vapour tension, and so *i*, became greater, when the concentration increased. For cane sugar solutions the molecular depression of the vapour tension and so *i*, was found constant between the concentration 0,02138 and 0.77912 gr. mol. per 1000 gr. H_2O. Only for the last concentration 1.8821 gr. mol. per 1000 gr. H_2O a higher value was found for the mol. depression of the vapour tension and for *i* than for the other concentration.

The results of the observations with the improved manometer follow. As the determination of the course was my principal object, I chose some solutions with a great difference of concentration.

Na Cl

Concentration in gr. mol per 1000 gr. H_2O.	$p_w - p_s$ in m.m. Hg.	p_m in m.m. Hg.	$i = \frac{p_w - p_s}{p_w} \cdot \frac{N}{n}$
0.033028	0.00435	0.132	1.6
0.34057	0.04793	0.141	1.69
1.7533	0.25724	0.147	1.764
2.1927	0.33406	0.153	1.832
1.6362	0.78315	0.169	2.032

KOH

Concentration in gr. mol. per 1000 gr. H_2O.	$p_w - p_s$ in m.m. Hg.	p_m in m.m. Hg.	$i = \frac{p_w - p_s}{p_w} \cdot \frac{N}{n}$
0.03476	0.00470	0.135	1.6
0.42374	0.06454	0.152	1.83
1.1912	0.19505	0.164	1.969
2.5995	0.48440	0.186	2.241

CANE SUGAR.

Concentration in gr. mol. per 1000 gr. H_2O.	$p_w - p_s$ in m.m. Hg.	p_m in m m. Hg.	$i = \frac{p_w - p_s}{p_w} \cdot \frac{N}{n}$
0.02602	0.00219	0.084	1.0
0.17225	0.01479	0.086	1.03
0.45413	0.03972	0.087	1.05
1.0811	0.09074	0.090	1.08

These few determinations were sufficient to prove that for Na Cl, K O H and cane sugar the molecular depression of the vapour tension, and so i, increases with the concentration.

The second series of K O H solutions is more reliable than the first, because great care has been taken to keep the second series of solutions free from carbonic acid. Probably this is the reason, that the values for i in the second table of solutions of K O H are a little higher than in the first.

The second table of solutions of cane sugar is also more accurate than the former, because the temperature of the waterbath in which the manometer is placed, was about 10° lower in the second series than in the first. At a lower temperature the accuracy is greater, because the manometer then reaches its position of equilibrium sooner than at a higher temperature.

It is evident that it is not much use to calculate the value for i for concentrations above 1 gr. mol. per 1000 gr. water. Nevertheless this calculation has been made here to facilitate a comparison with my former observations.

After this repetition of my former observations, experiments were made with solutions of the following substances:

$$H_2SO_4, \quad C_uSO_4 . 5 H_2O \quad \text{and} \quad KNO_3$$

The results are given in the following tables.

H_2SO_4

Concentration in gr. mol. per 1000 gr. H_2O	$p_w - p_s$ in m.m. Hg.	p_m in m m. Hg.	$i = \frac{p_w - p_s}{p_w} \cdot \frac{N}{n}$
0.02090	0.00336	0.161	1.9
0.04968	0.00819	0.165	2.0
0.24960	0.04204	0.168	2.03
0.50418	0.08713	0.173	2.08
1.11431	0.21057	0.184	2.215
2.1795	0.44246	0.203	2.411

$CuSO_4$

Concentration in gr. mol per 1000 gr H_2O	$p_w - p_s$ in m.m. Hg.	p_m in m.m. Hg.	$i = \frac{p_w - p_s}{p_w} \cdot \frac{N}{n}$
0.02318	0.00086	0.037	0.6
0.09860	0.00525	0.053	0.7
0.21519	0.01585	0.065	0.78
0.19378	0.03276	0.066	0.80
0.99612	0.06790	0.068	0.820
1.2162	0.09656	0.079	0.955

By concentration the number of gr. mol. $CuSO_4$ per 1000 gr. H_2O is represented.

KNO_3

Concentration in gr mol. per 1000 gr. H_2O.	$p_w - p_s$ in m.m. Hg.	p_m in m.m. Hg.	$i = \frac{p_w - p_s}{p_w} \cdot \frac{N}{n}$
0.02051	0.00287	0.140	1.7
0.25312	0.03211	0.130	1.51
0.51074	0.05569	0.109	1.31
1.0465	0.08671	0.083	0.996

It appears from what precedes that of the examined compounds KNO_3 is the only exception with regard to its course.

If the concentration of H_2SO_4 and $CuSO_4$ increases, the molecular depression of the vapour tension, and also *i*, becomes greater, whereas for KNO_3 the reverse takes place.

It is remarkable, that the values for *i* of $CuSO_4$ always remain below unity, if we assume that there are in the solution $CuSO_4$ molecules, whereas the values for *i* calculated from the conductivity have been always found to be larger than unity.[1]

The most interesting result, however, is that of KNO_3, for it shows that the course of NaCl etc. is probably not general.

When I was occupied with these observations, Mr. DIETERICI[2])

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[1]) PICKERING, Berl. Ber. 25 pg. 1315, 1892.

[2]) Wied. Ann. 62, pg. 616, 1897.

published a treatise „Ueber die Dampfdrucke verdünnter wässeriger Lösungen bei 0° C.”

He describes there in what way he has succeeded in making his aneroid more sensible, so that he could also examine diluted solutions with it. The results obtained for solutions which I have also examined, follow. To facilitate comparison some of my results are also mentioned.

Na Cl

DIETERICI		SMITS	
Concentration in gr. mol. per 1000 gr. H_2O.	p_m in m.m. Hg.	Concentration in gr. mol. per 1000 gr. H_2O.	p_m in m.m. Hg
0.0732	0.121	0.02842	0.121
0.154	0.131	0.03546	0.131
0.294	0.146	0.08813	0.139
0.454	0.144	0.17680	0.140
0.961	0.147	0.35587	0.141
		0.8854	0.143
		1.8228	0.147

H_2SO_4

DIETERICI.		SMITS	
Concentration in gr. mol. per 1000 gr. H_2O.	p_m in m.m. Hg.	Concentration in gr. mol. per 1000 gr. H_2O.	p_m in m.m. Hg.
0.0512	0.141	0.02090	0.161
0.0871	0.127	0.04968	0.165
0.1088	0.145	0.24960	0.168
0.1771	0.143	0.50418	0.173
0.224	0.156	1.41131	0.184
0.263	0.159	2.1795	0.203
0.350	0.159		
0.436	0.167		
0.892	0.177		

CANE SUGAR.

DIETERICI.		SMITS	
Concentration in gr. mol. per 1000 gr. H_2O.	p_m in m.m. Hg.	Concentration in gr. mol. per 1000 gr. H_2O.	p_m in m.m. Hg.
0.116	0.067	0.02602	0.084
0.255	0.078	0.17225	0.086
0.506	0.080	0.45413	0.087
0.991	0.088	1.0811	0.090

It appears from these tables that Mr. DIETERICI's results for Na Cl and cane sugar agree very well with mine.

The same might be said of $H_2 SO_4$, but that Mr. DIETERICI found a lower value for p_m for the concentration 0,0871 than for the concentration 0,0542. He makes the following remark about this :

„Die Lösungen der Schwefelsäure zeigen eine deutliche Abnahme der molecularen Dampfspannungsverminderung mit der Verdünnung in dem Concentrationsintervall 1 bis 0.1 gr. mol.; unterhalb dieser Verdünnung scheint wieder eine Zunahme einzutreten; indessen lässt sie sich aus den Dampfspannungsbeobachtungen allein nicht sicher constatiren und ich würde die Zahlen überhaupt nicht mitgetheilt haben, wenn nicht die Gefrierpunktsbeobachtungen von LOOMIS [1]) und PONSOT [2]) auch eine Zunahme der molecularen Gefrierpunktsverminderungen bei grösserer Verdünnung als 0.1 gr. mol. ergeben."

By repetition of his experiments, which will be discussed presently, Mr. DIETERICI found no decided increase of p_m for concentrations below 0.1 gr. mol., but oscillating values, so that we may say, that also for H_2SO_4 qualitative agreement exists, as the oscillations just mentioned are due to the influence of errors of observation.

Mr. ABEGG [3]) has tested Mr. DIETERICI's observations by comparing the latter's results quantitatively with those obtained by the determination of the lowering of the melting point.

In doing this Mr. ABEGG came to the conclusion, that there must be a fault in Mr. DIETERICI's method of observation, which induced

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[1]) LOOMIS, Wied. Ann. 51, pag. 500—524, 1894; 57, pag. 465—529, 1896; 60, pag. 523—547, 1897.

[2]) PONSOT, Recherches sur les congélations, GAUTHIER et VILLARS, Paris, 1896.

[3]) R. ABEGG, Wied. Ann. 64, pag. 500—505, 1898.

Mr. **Dieterici** [1]) to repeat his experiments once more, now making use of an aneroid which could give a deviation not to one side only as before, but to both sides. As changes of temperature exercise a great influence on the zero position of the aneroid, it was placed in a waterbath. After having determined the constant of this aneroid, he repeated his observation and obtained the following results.

To facilitate comparison I shall again add some of my results.

Na Cl

DIETERICI.		SMITS.	
Concentration in gr. mol. per 1000 gr. H_2O.	p_m in m.m. Hg	Concentration in gr. mol. per 1000 gr. H_2O.	p_m in m.m. Hg.
0.0690	0.152	0.02812	0.121
0.0976	0.156	0.03546	0.134
0.1500	0.150	0.08813	0.139
0.2176	0.148	0.17680	0.140
0.2996	0.1505	0.35587	0.141
0.4900	0.1515	0.88510	0.143
0.9788	0.1515	1.8228	0.147

H_2SO_4

DIETERICI.		SMITS.	
Concentration in gr. mol. per 1000 gr. H_2O.	p_m in m.m. Hg.	Concentration in gr. mol. per 1000 gr. H_2O.	p_m in m.m. Hg.
0.0624	0.168	0.02090	0.161
0.1106	0.180	0.04968	0.165
0.1472	0.167	0.24960	0.168
0.2323	0.168	0.50118	0.173
0.4483	0.171	1.11131	0.184
0.9505	0.177		

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[1]) **Dieterici**, Ann. der Phys. und Chemie, 27, 4, 1898.

CANE SUGAR.

DIETERICI.		SMITS.	
Concentration in gr. mol. per 1000 gr. H_2O.	p_m in m.m. Hg.	Concentration in gr. mol. per 1000 gr. H_2O.	p_m in m.m. Hg.
0.1506	0.084	0.02602	0.086
0.2653	0.084	0.17225	0.086
0.4993	0.087	0.45413	0.087
1.0122	0.0905	1.0811	0.090

It is remarkable that the agreement of Mr. DIETERICI's results with mine for Na Cl-solutions, which was closest before, is now least perfect, while the agreement for cane sugar may be said to be absolute.

If we leave the oscillation for the two smallest concentrations out of account, the agreement of the H_2SO_4 solution is also very close. It is very difficult to find an explanation for this fact, as an error in the constants of our apparatus cannot cause this difference.

Mr. DIETERICI puts the solutions and the water in small platinum tubes, 3 cm. high and with a diameter of 1,2 c.m., which are connected with the apparatus in such a way (cemented), as to exclude shaking, whereas I put the solutions and the water in glass bulbs connected with the apparatus by means of mercury valves, in order to be able to shake them thoroughly. I consider this of the highest importance, both when freeing the solution and the water from air and during the experiment.

I consider shaking as necessary for preventing differences of temperature, Mr. DIETERICI, on the other hand, fears to bring them about by shaking. If, however, I read the manometer ten minutes after having shaken the bulbs carefully, I get always the same results by repetition of the experiment.

Moreover in Mr. DIETERICI's experiments the platinum tubes which lead to the bottle and are cemented to glass tubes, are not quite immersed in the icebath, which may cause slight differences of temperature, specially because these small platinum tubes have a small thermal capacity.

Mr. DIETERICI, who himself, makes the preceding remark, thinks it possible that a difference of temperature of 0,0025° may occur, in spite of this careful protection of the icebath against absorption of heat. As a difference of temperature of 0,0025° agrees with a difference of tension of 0.001 mm. Hg., Mr. Dieterici takes as limit of his accuracy 0,001 mm. Hg. Therefore he states clearly, that he draws only qualitative conclusions. I am, however, convinced, that the difference in temperature in my bulbs, which have a volume of 100 ccm., is less than 0,0025°, which also appears from the fact that when I read the manometer, when comparing water with water, the manometer indicated accurately to 0,1 mm. the same difference of position, as when there was communication between the two sides of the manometer, and the bulbs were closed.

As a deviation of the manometer of 0,1 mm. agrees with ÷ 0,00025 mm. Hg, the difference of temperature of the two bulbs must be exceedingly small.

Some time ago prof. Jahn at Berlin wrote to me to ask, whether I was sure, that my solution had been perfectly free from air and if I would repeat some of my experiments once more, after having first reduced the solutions in vacuum to half of its original volume by means of evaporation.

First I tried to comply with Prof. Jahn's wish in the following way.

The bulbs with water and solution were successively shut off from the apparatus by turning a tap and the air was exhausted by means of a velocity pump, while they were heated softly. During this the tube, connecting the bulb with the apparatus, was moistened with condensed vapour of water. Through the rise of the temperature the grease with which the tap (by means of which the communication of the bulb with the apparatus was broken off or restored), was greased, spread over the inside wall of the tube, and this is the reason why I could not make use of this way of boiling. It seems namely, that the vapour tension of a layer of water on the greased part of the tube is so small, that the water was not distilled into the bulb, though the bulb was cooled to 0° and the temperature of the room was ± 20°. I was therefore obliged to apply another method, by which rise of temperature was excluded. The most practical method appeared to be the following.

When at the ordinary temperature most of the air was exhausted from the bulbs with water and solution by means of the velocity-pump, all the remaining air was expelled by bringing about the communication of the bulbs with the apparatus, after first having closed the bulbs for drying. The communication between the bulbs and the apparatus was interrupted after some moments, and when the vapour of water had been absorbed by the drying bulbs, the air of the apparatus was exhausted by means of an automatical mercury airpomp. This was repeated till the bulbs were free from air.

In order to comply with Prof. JAHN's wish, I brought about a communication between the bulbs with water and solution and one of the drying bulbs (filled with H_2SO_4). When the air is greatly rarefied, H_2SO_4 absorbs the vapour of water quickly and the water and the solution, having the temperature of the room ± 20° (the bulbs being continually shaken), evaporated quickly, in consequence of which the temperature of the water and the solution fell considerably. To prevent congelation the bulb was now and then warmed with the hand. The temperature of the bulb with H_2SO_4 rose considerably during this absorption of water, and it was also frequently shaken. When the water and the solution had been reduced to the half of their former quantity by evaporation, the bulbs were shut off from the apparatus. Every solution was first treated in this way, after which the bulbs were placed in ice, and the experiment began.

The concentration of the solutions was determined by weighing ± 50 gr. solution in a flask with a long neck, and then the water was evaporated according to the method applied by Mr. ANDREAE [1]) While the flask was being heated in a waterbath, a weak current of air was drawn over the solution. After all the water had been evaporated, the flask was placed in an airbath of 170°, while all the time a stream of air was drawn over it. In this way it is also possible to expel the water from $NaCl$-solutions without any loss of weight of salt.

I may further add that I had altered the apparatus somewhat for these experiments. Instead of two bulbs, I used three; one filled with water and the two others with solution. One of these bulbs with solution remained untouched during the whole series and served as a test. These three bulbs were placed in a copper trough, which was surrounded by a larger wooden one in such a way that there remained a space of 6 cm. all round. This space was filled up with small pieces of ice, while the copper trough was filled with a paste of fine ice and water. Two pieces of paste board, which could move across each other and were provided with slits, served as a lid. In this way I was quite sure of a constant temperature and yet I could shake the bulbs thoroughly.

In order to make it possible to read the manometer more accurately,

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[1]) Journ. f. prakt. Chem. 22, p. 456, 1884.

a glass scale divided into m.m. was adjusted behind the legs of the manometer. The error of reading amounted to less than 0,1 mm, so to less than $\frac{1}{4000}$ m.m. Hg.

The results of the research with Na Cl solutions follow.

Na Cl

Concentration in gr. mol. per 1000 gr. H_2O.	$p_w - p_s$ in m.m. Hg.	p_w in m.m. Hg.	$i = \frac{p_w - p_s}{p_w} \cdot \frac{N}{n}$
0.05185	0.00675	0.130	1.6
0.10733	0.01476	0.138	1.65
0.25770	0.03650	0.141	1.70
1.0307	0.11626	0.142	1.706
1.6078	0.23082	0.144	1.726

From this table follows that the changed method of experimenting has had no influence on the course of the molecular depression of the vapour tension. The differences of the absolute values are due to the use of a new manometer, the sensibility of which was to be determined anew.

As to the results obtained by another method, we have to mention, that LOOMIS and PONSOT have found that in general the molecular lowering of the freezing point of greater concentration to the concentration of 0,1 gr. mol. decreases in case of rarefaction as well for electrolytes as for non-electrolytes, whereas below these concentrations both investigators observed an increase of the molecular lowering of the freezing point, when the rarefaction increased. Mr. LOOMIS expresses his astonishment, that other investigators have not discovered this minimum, as this is so evident for binary chlorides, that it may be easily shown with an ordinary thermometer divided into $^1/_{10}$° and with a beaker.

Mr. R. ABEGG, who points out some inaccuracies in his criticism on the researches of Mr. LOOMIS, doubts of the results of Mr. LOOMIS and also of those of PONSOT.

Mr. ABEGG finds for K Cl between the concentrations 0.009 gr. mol. and 0.4007 gr. mol. per 1000 gr. water a mol. lowering of the freezing point, increasing with the rarefaction. He has not observed a minimum.

Nor has Mr. RAOULT [1]) found a minimum, but he found nearly constant values down to 0,1 gr. mol. for the molecular lowering of the freezing point. They did not differ more than 0,1 pCt.

In my opinion, however, the question remains, whether at this moment the highest degree of accuracy has already been reached in the method of the lowering of the freezing point.

It is quite possible that the air which is solved in the water and the solutions, causes the results, obtained for the determination of the lowering of the freezing point, to be faulty.

If e.g. the quantity of air in a solution depends upon the quantity of salt solved in it, the error made is not constant, and it can even render the course of the mol. lowering of the freezing point, quite faulty.

Mr. RAOULT has tried to reduce the error caused by solution of air in water and solution to a minimum by saturating at the temperature af the room the water and the solution with air. Mr. RAOULT states further that diluted solutions absorb the same quantity of air as pure water. Prof. JAHN, however, communicated to me in a letter that the coefficient of absorption of air for diluted solutions depends on the concentration and increases by diluting.

It is therefore of the greatest importance for the determination of the freezing point to examine accurately the influence of the concentration on the coefficient of absorption for air. As long as this influence is not sufficiently known, Mr. RAOULT's determinations, however accurately made, are in my opinion not quite reliable.

In connection with what precedes, it seems to me, that Mr. ABEGG [2]), who, led by the differences between the results obtained by means of the lowering of the freezing point and the decrease of vapour tension, came to the conclusion that there must be a fault in the method of the determination of the decrease of the vapour tension of Mr. DIETERICI, has attached too much importance to his determinations.

In the first place the influence of concentration on the absorption of air has not yet been fully ascertained, as I said before, and secondly, even though this influence were perfectly known, a quantitative comparison between the results of the determination of the decrease of vapour tension and the lowering of the freezing point is not yet raised above doubt, when the solutions and the water are not in exactly the same circumstances in both methods. There would, however, be no objection to a comparison, when the lowering

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[1]) Zeitschr. f. Phys. Chemie: 27. pg. 617. 1898.

[2]) Wied. Ann. 64, pag. 487, 1898.

of the freezing point was determined of solutions quite free from air.

I regret that Mr. DIETERICI, who was acquainted with my investigations, has not mentioned, that in 1896 I published results which agreed perfectly with those he found with his aneroid and which he published in 1897.

I intended to investigate other substances than Na Cl in the way Prof. JAHN recommended, but my manometer got defect while I was engaged with experiments on K Cl, so that I had to put off this investigation.

At the end of this treatise I feel obliged to express my thanks to Prof. H. C. DIBBITS for the great kindness with which he placed at my disposal the apparatus required for my researches.

Physics. — Prof. VAN DER WAALS presents on behalf of Mr. E. H. J. CUNAEUS a paper on: *"The determination of the refractivity as a method for the investigation of the composition of co-existing phases in mixtures of acetone and ether"*.

Introduction.

The aim of this investigation was to examine the relation between the compositions of the co-existing vapour- and gas phasis and to find out the relation between the composition of the vapour and the pressure.

When I began my experiments only the investigation of LINEBARGER[1]) had been published; since then those of LEHFELDT[2]) and HARTMAN[3]) have also appeared.

The great difficulty of the investigation of this relation lies in the determination of the composition of the vapour; I have tried to do so without first condensing the vapour, and without chemical analysis, by means of the determination of the refractivity. I was induced to use this method by the experiments of RAMSAY and TRAVERS on the refractivity of gases and some gaseous mixtures[4]).

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[1]) Journ. of the American Chem. Soc. Vol. XVII N⁰. 8; Aug. 1895. Chem. News, Vol. 72, N⁰. 1871, v.v. Oct. 1895.

[2]) Phil. Mag. (5) Vol. 40, 46.

[3]) Dissertation for a doctor's degree, Leyden 1899.

[4]) Proc. Roy. Soc. Vol. LXII, p. 225, 1897.

The Method.

In their investigation RAMSAY and TRAVERS found that the refractivity of a mixture of gases may be found, not accurately indeed, but yet with a high degree of approximation, from the molecular proportion of mixing and the refractivity of the components. In order to determine whether this deviation occurs always, or must be attributed to accidental circumstances, but at the same time in order to try and find the cause, I have first examined a series of mixtures of gases; viz. carbonic acid and hydrogen in different proportions. These gases were chosen, because their refractivity differs considerably and because they may be prepared sufficiently pure in a simple way.

The carbonic acid was prepared according to the method described by Mr. KUENEN [1]), by dripping a solution of $Na\,H\,C\,O_3$ in $H_2\,SO_4$ and by drying the gas by means of H_2SO_4 and $P_2\,O_5$.

Hydrogen was obtained by electrolysis of diluted $H\,Cl$ with an apparatus similar to that used by Prof. KAMERLINGH ONNES for filling the hydrogen-thermometer. [2])

The determination of the refractivity was made according to the method of Lord RAYLEIGH [3]), which was also followed by RAMSAY and TRAVERS. A nearly parallel pencil of light is split into two parts, which pass through tubes of equal length closed by plate glass and which are made to converge by an achromatic lens. The interference phenomenon obtained in this way was observed with an eye-piece, consisting of two cylindric lenses. These tubes (A and B fig. 1) are respectively connected with the open manometer E and F and with the reservoirs C and G; the latter are partly filled with mercury and the pressure in them may be changed by moving the bulbs D and I up and down.

The right half of this apparatus is filled with dry air freed from CO_2. The left side was filled with the gases and gaseous mixtures which were to be examined. To this end G was connected with another reservoir H with a bulb K filled with mercury, by means of the three-way cock e, and it was also connected with the tube N, which may be connected by means of the taps g and h with two gas-reservoirs L and M; by means of i with the air pump; and by means of f with the apparatus for the preparing of gas. G and H serve for preparing the mixtures.

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[1]) Phil. Mag. (5) Vol. 44, p. 179.

[2]) Versl. Kon. Akad. 30 Mei 1896.

[3]) Proc. Roy. Inst. Vol. XV Jan. 1896.

If the substances used followed the laws of BOYLE and GAY-LUSSAC, the refractivity would be directly found from the proportion of the changes in pressure, which the gas and the air must undergo, when the interference phenomenon is twice brought into that position which it occupies when the two parts of the pencil of light pass through equal ways; so for instance when the two tubes are filled with air of one atm. So if p and p' are the pressures for air; p_1 and p'_1 those for the gas whose refractivity B is is to be determined, we get: $B = \frac{p - p'}{p_1 - p'_1}$.

The gases, however, do not follow these laws, and therefore the refractivity is not to be found from the proportion of the change of the real pressure (p, p', p_1 and p'_1), but from that of the pressures which would prevail, when the gases followed the laws of BOYLE and GAY-LUSSAC and had the same volumes and temperatures (P, P', P_1, P'_1). So that we may put:

$$P = p - \frac{b(1+a)(1-b)T}{V(V-b)273} + \frac{a}{V^2}$$

from which follows with some approximation:

$$\mathfrak{B} = \frac{P - P'}{P_1 - P'_1} = \frac{p - p'}{p_1 - p'_1} \cdot \frac{1 - (p+p')\left(\frac{273}{T}\right)^2 \left(a - b\frac{T}{273}\right)}{1 - (p_1 + p'_1)\left(\frac{273}{T}\right)^2 \left(a_1 - b_1\frac{T}{273}\right)}$$

$$\mathfrak{B} = B \left\{ 1 + \left(\frac{273}{T}\right)^2 \left[(p_1 + p'_1)\left(a_1 - b_1\frac{T}{273}\right) - (p+p')\left(a - b\frac{T}{273}\right) \right] \right\}.$$

This correction was also applied in calculating the composition of the mixtures.

In order to find the values a and b for the mixtures CO_2 and H_2, I made use of the formula, deduced by Prof. VAN DER WAALS from the experiments of Dr. VERSCHAFFELT [1]).

$$y = 0.999546 + 0.001618\ (1 - x) + 0.00497\ (1 - x)^2$$

this gives for 18° C. ($T = 291$) at once the value of $a_x - b_x \frac{T}{273}$.

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[1]) Proc. Roy. Acad. April 1899.

In this way I obtained from my experiments the results given in Table I (hydrogen considered as the solved substance).

TABLE I.

x	B	$\mathfrak{B}$	$\mathfrak{B}_1(1-x)+\mathfrak{B}_2 x$	x'
0.	1.53285	1.5398		
0.2082	1.3057	1.3095	1.3183	0.2165
0.3000 [1]	1.2052	1.2080	1.2206	0.3118
0.4192	1.0826	1.0843	1.0938	0.4281
0.5077	0.9884	0.9891	0.9997	0.5176
0.6498	0.8399	0.8400	0.8485	0.6577
0.7085	0.7799	0.7796	0.7850	0.7145
1.	0.4765	0.4759		

There is evidently a difference between the observed values (column 3) and the calculated ones (column 4), the difference amounts at the utmost to about 1 pCt.; when from the observed refractivity the composition (x', column 5) is calculated, the difference amounts at the utmust to a unity in the 2nd decimal. So I considered the method as suitable for the purpose.

I hope soon to publish some further details about the difference found and the probable cause.

Investigation of the vapour-mixtures.

For the investigation of the vapour-mixtures an apparatus may be used of nearly the same construction as has been described above. The apparatus was modified only in so far that a branch-tube Q (fig. 2) with bulb P was added to tube B (fig. 1). The bulb was provided with a neck R with a stopper S well ground in and closed by mercury. Two platinum wires, T and T', passed through the stopper; they were one m.m. in diameter and connected inside the bulb by a bent kruppin-wire U with an electric resistance of ± ½ Ohm. The liquid or the mixture of liquids which was to be examined, was fused in a thin-walled glass tube, which was suspended in U; then the air

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[1] The accuracy which might be expected of the 2nd mixture is smaller than that of the others on account of a deviation in the experiments.

was exhausted from the whole apparatus, and by passing an electric current through the wires $T U T'$, the tube was heated till it burst. While the bulb P was constantly kept at 0°, the refractivity of the gas could be determined, by changing the pressure of the gas in the other side of the apparatus, till the interference phenomenon reached again the normal position and by reading this pressure and that of the gas. On account of the great refractivity of the gases, air could not be used as the gas, serving for comparing them; I have therefore used carbonic acid.

The investigation was made with ethylether and acetone; both from MERCK in Darmstadt.

These substances were chosen because at 0° they have a vapour tension of less than one atm., and yet it is large enough to be measured pretty accurately; moreover the refractivity of the gases had to differ as much as possible.

The compositions of the liquids was obtained by weighing, while the weights of the quantities of each of the two substances in the vapour were afterwards subtracted from the original quantities.

The results are given in Table II (see also fig. 3) ether being considered as the solved substance.

TABLE II.

Refractivity.	x_v	x_d	p in mm.
3.7788	0.	0.	69.6
4.4956	0.156	0.446	110.5
4.7709	0.364	0.617	142.4
4.8552	0.510	0.670	159.
4.9497	0.617	0.728	166.8
5.1636	0.835	0.861	181.2
5.3869	1.	1.	185.6

They give rise to the following observations. There is no maximum or minimum pressure; so the mixture belongs to what HARTMAN calls the first type. There is greater difference in the composition of the liquid and the gas when a little ether is mixed with acetone, than when a little acetone is mixed with ether.

The curve representing the pressure as function of the composition of the vapour ($p = f$ (x_d) in fig. 3), shows a point of inflection at $x = 0.65$; which has never yet occurred in former experiments. I have not succeeded in finding a simple meaning of this; the condition for the occurrence of such a point of inflection leads to an intricate relation, in which also the unknown relation between x_d and x_v occurs.

That the point of inflection really exists and that it is not due to an inaccurate method follows, in my opinion from the following considerations:

1st the deviation from the observed curve, required to get a curve without a point of inflection is much greater than the investigation of the method would give us cause to expect.

2nd When we calculate the composition of the gas by means of the approximated formula

$$\frac{1}{p} \cdot \frac{dp}{dx_v} = \frac{x_d - x_v}{x_v(1 - x_v)}$$

given by Prof. VAN DER WAALS in his „Théorie moléculaire”[1] we find the points indicated by ⊙ in fig. 3, which points agree very well with the observed curve, at least at the ends; that the deviation is greater in the middle was to be expected, according to the approximations used in the deduction.

A curve drawn through these points, shows also a point of inflection.

If we draw a tangent at a point of the curve $p = f(x_v)$, we arrive by means of the former formula at the values which are given as calculated in Table III.

TABLE III.

x_v	p	$\frac{dp}{dx_v}$	$x_d - x_v$		x_d	
			calc.	observed.	calc.	observed.
0.05	85.5	301	0.167	0.165	0.217	0.215
0.1	99.5	264	0.227	0.253	0.327	0.353
0.2	120.6	179	0.237	0.305	0.437	0.505
0.3	134.4	137	0.215	0.280	0.515	0.580
0.4	147.1	115.5	0.180	0.232	0.580	0.632
0.5	158.0	94	0.150	0.170	0.650	0.670
0.6	166.7	74.5	0.107	0.15	0.707	0.75
0.7	173.7	63	0.077	0.08	0.777	0.78
0.8	179.2	50.5	0.045	0.042	0.845	0.842
0.9	183.4	31	0.016	0.02	0.916	0.92

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[1] Arch. Nêerl. 24. p. 44.

3d Some observations made at ± 15° make it very probable, that the $p = f(x_d)$ curve will show a point of inflection also at that temperature, and even at about the same x_d as that at 0°.

If it was not our intention to make the existence of a point of inflection probable, it would be better for testing the results at the theory, to use instead of the former formula, the formula

$$\frac{1}{p} \cdot \frac{dp}{dx_d} = \frac{x_d - x_v}{x_d (1 - x_d)}$$

as this formula may be expected to hold good with much greater approximation, also for the values of x_d which are not near 0 or 1.

It appears, however, from Table IV and the points ⊗ of fig. 4 which are derived from it, that the agreement is not much closer

TABLE IV.

x_d	p	$\frac{dp}{dx_d}$	$x_d - x_v$		x_v	
			calc.	observed.	calc.	observed.
0.1	76	73	0.086	0.082	0.014	0.018
0.2	84	84	0.160	0.155	0.040	0.045
0.3	93.5	102.5	0.230	0.224	0.070	0.076
0.4	105	128.5	0.294	0.273	0.106	0.127
0.5	129.5	168.5	0.325	0.295	0.175	0.205
0.6	139	204	0.352	0.270	0.248	0.330
0.7	163	171	0.220	0.155	0.480	0.545
0.8	176	103	0.094	0.075	0.706	0.725
0.9	183	50.5	0.025	0.020	0.875	0.880

This is the first time that the formula, derived from the theory of the mixtures, has been used for the attempt of deducing one of the two curves $p = f(x_v)$ and $p = f(x_d)$ from the other, when both have been determined experimentally. Only when x and $1-x$ are small, the result is satisfactory. Further investigation will have to prove, whether the great differences for x near $\frac{1}{2}$ are to be attributed to the observations or to the formula.

Physics. — *"On the Theory of* LIPPMANN'S *Capillary Electrometer".*

By Prof. W. EINTHOVEN (Communicated by Prof. T. ZAAIJER.)

In a paper on the capillary electrometer and on the action currents of the muscle HERMANN[1]) has put forward the statement, that the results obtained by BURCH[2]) and myself[3]) in the investigation of the motion of the mercury in the capillary electrometer are immediate consequences of his theory, and that since BURCH and I should have obtained empirically our results, they ought to be regarded as a „schöne Bestätigung" of his theory. An answer of BURCH[4]) hereupon has already appeared.

In answering HERMANN I will try by means of some new experiments to advance somewhat our knowledge of the laws governing the motion of the mercury in the capillary electrometer.

On a former occasion I have given the equation:

$$\frac{dy}{dT} = C\,(y^{*}-y) \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

where C is a constant, y the distance the meniscus has moved from its zero position at the time T and y^{*} the distance the meniscus would have moved if the P. D. of the poles of the capillary electrometer at the time T had been constantly applied.

In order to obtain for all capillary electrometers comparable values of the constant, we shall in this paper always measure the time T in seconds[5]), whereas y and y^{*} will be given in arbitrary but equal units. The value of C is apparently unaffected by a change of the unit in which y and y^{*} are measured. The constant C is, as I remarked on a former occasion, determined by the properties of the instrument, especially by the mechanical friction in the capillary and the ohmic resistance w in the circuit; the precise relation between C and w I did not mention till now, but it will be given in the following.

HERMANN thinks that the mentioned relation is very simple, and assumes that C varies as the inverse of w. The equation his theory

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[1]) PFLÜGER'S Arch. f. d. ges. Physiol. 1896, Bd. 63, S. 440.

[2]) Philosoph. Transact. of the Royal Soc. London, 1892, Vol. 183, p. 81.

[3]) PFLÜGER'S Arch. f. d. ges. Physiol. 1894, Bd. 56, S. 528 und 1895, Bd. 60, S. 91.

[4]) Proceedings of the Royal Soc. London, 1896, Vol. 60, p. 329.

[5]) In formerly given calculations of the constant, the time was given in twentieth to fiftieth parts of a second dependent on the velocity of the photographic plate, on which the normal curves were recorded, being 20 to 50 mm. per second.

arrives at, differs from formula (1), in having $\frac{h}{w}$ instead of C, h being an instrumental constant.

According to HERMANN formula (1) must be: [1])

$$\frac{dy}{dT} = \frac{h}{w} (y^* - y)$$

This formula represents the facts in so far as the *increment* of the resistance varies directly as the *increment* of $\frac{1}{C}$ in accordance with what I have said in a former paper and as will be discussed further on. This is occasioned by the fact, that the mechanical friction in the capillary has a similar influence on the motion of the mercury as the ohmic resistance in the circuit. HERMANN wrongly concludes that the constant must be proportional to $\frac{1}{w}$, whereas from the experiments is to be inferred only, that it is proportional to $\frac{1}{a + bw}$. Differently stated HERMANN wrongly assumes that $a = 0$.

The error of his formula is to be ascribed to a misconception of the action of the capillary electrometer.

He neglects entirely the influence of the mechanical friction in the capillary on the motion of the meniscus, whereas this mechanical friction is with most capillary electrometers of the foremost importance. This may be inferred from the following.

Using capillary G 103 and suddenly applying a P. D. remaining constant, a normal curve was described, no additional resistance being inserted in the circuit. This curve was measured and the constant, which we will call C_α [2]), determined according to formula (1). Then a normal curve was taken with the same instrument, a resistance of 0,1 Megohm now being inserted in the circuit, and the value of the constant, now indicated by C_1, was determined again.

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[1]) HERMANN's formula in his own symbols is:

$$\frac{\delta y}{\delta t} = \frac{h}{w} (kE - y);$$

kE being here identical with y^* of formula (1).

[2]) The manner in which the constant C is calculated from the normal curve was given formerly, vid. PFLÜGER's Arch. l. c.

$\frac{1}{C_\alpha}$ was equal to 0.0815

$\frac{1}{C_1}$ " 0.107

According to HERMANN's theory it must be possible to calculate from these data the internal resistance of the capillary electrometer.

Let the internal ohmic resistance of the capillary electrometer be denoted by w_i, the resistance intentionally inserted in the circuit w_u, then

$$w = w_i + w_u,$$

$$C_\alpha = \frac{h}{w_i}, \quad \text{and} \quad C_1 = \frac{h}{wi + w_u};$$

hence we must have

$$w_i\ (\text{HERMANN}) = \frac{w_u}{C_\alpha \left(\frac{1}{C_1} - \frac{1}{C_\alpha}\right)}.$$

Substituting the values of C_α, C_1 and w_u we obtain

$$w_i = 0{,}320 \text{ Megohm.}$$

Now w_i may be calculated also from the dimensions of the capillary, in which case a knowledge of the dimensions of the sulphuric acid thread is principally necessary. Calculating the resistance from the dimensions, w_i was found 0,029 megohm; hence more then 11 times smaller than the amount required by HERMANN's theory.

Here follows a table with the correspondent calculations for four capillary electrometers.

TABLE I.

Number of the capillary.	w_i as calculated according to HERMANN's theory.	w_i as calculated from the dimensions of the capillary.
G. 103	0,320 Megohm	0,029 Megohm
B. 101	1,545 "	0,124 "
B. 102	1,411 "	0,101 "
B. 103	0,665 "	0,026 "

We see that HERMANN's theory gives far too high values of w_{i}, with the above mentioned four capillary electrometers 11 to 25 times greater than is to be calculated from the dimensions of the apparatus [1]).

The value adopted for the length of the sulphuric acid thread in the calculations was one never exceeded in recording the curves, hence the figures in the last column of our table are maximum values. It seems difficult to misinterpret the results described above and they are certainly sufficient to refute HERMANN's theory.

That really the mechanical friction neglected by HERMANN is of primary importance with most capillary electrometers, will be clear from a series of experiments of entirely different character, in which the mechanical friction in the capillary was measured in a direct manner.

A capillary tube, after having been used for the recording of normal curves, is placed above a small glass vessel filled with mercury in such a manner that the end of the capillary is below the surface of the mercury.

For a short time the air above the mercury in the tube is highly compressed so that it flows in the vessel, the free air being admitted however immediately again. The mercury continues flowing if there has been but once a direct mercury connection between the interior of the tube and the vessel. The total quantity of the flow in a given time varies according to POISEUILLE's law directly as the pressure, in our case the difference of level between the mercury in the tube and the mercury in the vessel.

The flow is continued during some hours and the vessel is weighed before and after the experiment. From the difference of weight, q grams, the duration of the flow, T seconds, the mean difference of level, D centimetres, can be calculated how many grams of mercury G are pressed through the capillary tube under a pressure of 1 cm. in one second,

$$G = \frac{q}{TD} .$$

Let the radius of the capillary tube at its point be $= r$ cm., then the mean velocity in a section near the end is

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[1]) In this communication a short account of our results must suffice, more particulars concerning the mentioned and yet to be given measurements and calculations will be published elsewhere.

$$v_0 = \frac{G}{r^2 \pi s}$$

centimetres per second under 1 cm. of mercury pressure; in this formula s is the density, whereas v_0 is dependent only on the mechanical friction.

Let us suppose that in a capillary electrometer the ohmic resistance in the circuit is reduced to zero, then in our formula (1) the constant C is determined only by the mechanical friction in the capillary 1). We will call the constant, when this is assumed, k. For a given value of $y^* - y = u$ the formula can then be put 2) in the form

$$\frac{du}{dT} = k\,u\,.$$

If u represents the displacement of the mercury meniscus for 1 cm. change of mercury pressure, then

$$\frac{du}{dT} = v_0\;,$$

hence also

$$v_0 = ku. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2).$$

The constant k is, as appears from formula (2), determined only by the magnitude of the displacement of the meniscus with a given change of pressure and the mechanical friction in the capillary; k can be calculated from u and v 3)).

Moreover k can be calculated in an entirely different manner viz: from 1st. the constants of the normal curves, recorded without and with resistance purposely inserted in the circuit, 2nd. the internal resistance of the capillary electrometer. For k is the con-

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1) Vid. on this point a former paper l.c.

We remind the reader that y and y^* denote the displacements from the zero position of the meniscus. In formula (1) we indicated as the cause of these displacements the change of P. D. between the poles of the capillary electrometer, the pressure in the capillary remaining constant. The formula remains unchanged if with a constant P. D. the displacements of the meniscus are caused by a change of pressure in the capillary.

3) In calculating k the difference between the friction of the sulphuric acid and of the mercury in the inferior part of the capillary has been neglected. It was supposed that the friction in the capillary electrometer equalled that in the capillary when totally filled with mercury. The error hereby introduced is but small and amounts only to a small percentage of the final result, see the more detailed publication.

stant of a normal curve that would have been recorded by a capillary electrometer if the internal resistance could have been annulled.

The double calculation of k has been made for two electrometers, and the results are united in Table II.

TABLE II.

Number of capillary-electrometer.	$k = \frac{1}{a} = \frac{1}{\frac{1}{C_\alpha} - p \cdot \frac{w_i}{0,1}}$ calculated from the normal curves and internal resistance of capillary electrometer.	$k = \frac{v}{u}$ calculated from friction in capillary and magnitude of displacement of meniscus by change of pressure.
B. 102	4,59	4,95
B. 103	2,92	2,78

The agreement between the values of k in the two columns, obtained in so different a manner and which have required independent series of measurements is certainly quite sufficient.

According to HERMANN's theory we must have $C = \frac{h}{w}$, hence $k = \infty$.

Let us now consider more closely formula (1)

$$\frac{dy}{dT} = C\,(y^* - y)$$

and let us see in what manner the resistance in the circuit influences the value of C. Already on a former occasion [1]) the normal curves of capillary *G* 103 were examined, recorded with several resistances, purposely inserted in the circuit.

An increase of the resistance with 0,01 megohm gave an increase of $\frac{1}{C}$ 0,0025

An increase of 0,1 megohm increased $\frac{1}{C}$ . . . 0,0255

An increase of 1 megohm increased $\frac{1}{C}$ 0,2545

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[1]) l. c. Bd. 60.

We see, that the increase of the value of $\frac{1}{C}$ varies directly as the increase of the resistance. Hence it follows immediately that,

$$\frac{1}{C} = a + bw \ ,$$

a and b being constants, determined by the properties of the instrument independent upon the internal ohmic resistance.

w represents the resistance in the circuit in megohms.

Hence our formula (1)

$$\frac{dy}{dT} = C\,(y^* - y)$$

now becomes

$$\frac{dy}{dT} = \frac{1}{a + bw}\,(y^* - y) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

For $w = 0$, is $\frac{1}{a + bw} = \frac{1}{a}$, hence the constant k is equal to $\frac{1}{a}$.

The constant b is the increase of $\frac{1}{C}$, when the resistance in the circuit is increased with 1 megohm.

In the subjoined table the values of a and b are given for four capillary electrometers.

TABLE III.

Number of the capillary.	a	b
G. 103	0,0741	0,225
B. 101	0,1599	0,1124
B 102	0,2181	0,166
B. 103	0,3429	0,5365

We may obtain a better insight into the action of the capillary electrometer in considering in which manner and to what amount the different forms of energy are transformed with a given displacement of the meniscus. For this purpose the following representation may prove of use in this connection.

Suppose that the drawn-out tube of the capillary electrometer, see fig. 1, is connected with two vertical tubes, a and b, filled with mercury and widened at the upper end. By means of the stop-cocks α and β the communication of a and b with the capillary tube can be stopped.

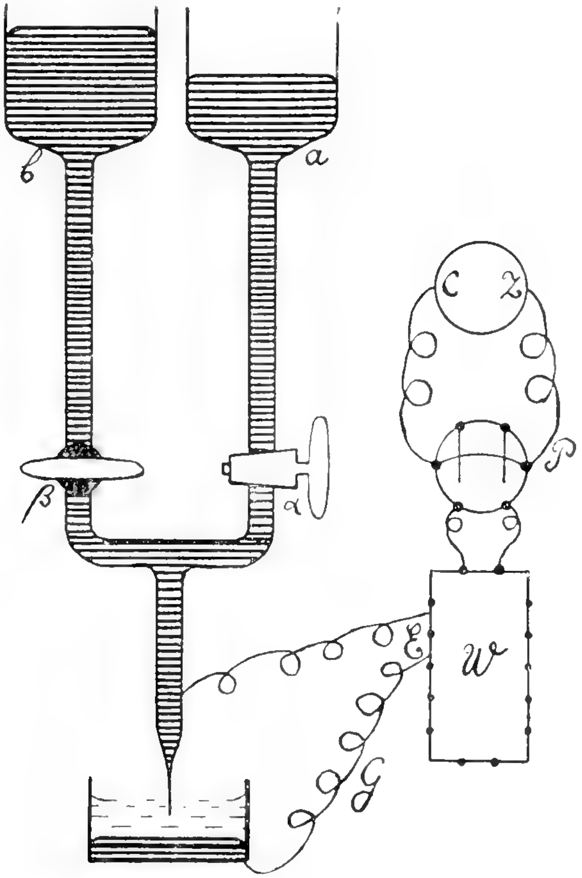

Fig. 1.

The poles of the capillary electrometer are connected by the conductor G. W is a resistance box, CZ a cell and P a POHL's mercury key insulating at the beginning the cell from the capillary electrometer, so that at E there is no P. D.

We think at the beginning stop-cock α opened, β closed: 1st position of stop-cocks. Let the meniscus have its equilibrium position at the height m_1. Suddenly the position of the stop-cocks is interchanged; 2d position of the stop-cocks. The meniscus will move, at first fast, then slower and will at last attain the equilibrium position m_2. If now the stop-cocks are placed again in their first position, then the meniscus will return also to its initial level m_1.

The work done in displacing the meniscus up and down is easily calculated. For the only final change in the apparatus is the passage of mercury from b to a. The quantity of mercury passed can be calculated from the section of the capillary tube d, the distance $m_1 - m_2$ and the specific gravity of the mercury s. This quantity is $M = ds(m_1 - m_2)$,

M being given in grams

d in square centimetres

and m_1 and m_2 in centimetres. Let the difference of level between a and b be n centimetres, then the work done is $A = nM$ gram-centimetres.

The potential energy of the displaced mercury is transformed into heat, partially by means of electric currents, partially by mechanical friction.

It merits attention that the amount A is not changed by changes in the resistance of the circuit G. An increase of the resistance causes retardation in the movement of the meniscus; the energy of mechanical friction is diminished, whereas that of electric currents is increased with the same amount.

If the stop-cocks have only changed the first for the second position and the meniscus has moved from m_1 to m_2, the energy of the heat produced is $= \frac{1}{2} A$; for the motion of the mercury in the capillary — viz. the cause of the mechanical friction and of the electric currents — is, while the meniscus returns from m_2 to m_1 in all phases perfectly equal — but of contrary direction — to the motion of the original displacement from m_1 to m_2.

Hence in first changing the position of the stop-cocks a quantity of energy must not have been transformed into heat, but must have accumulated as elastic tension in the meniscus. It is only in returning from m_2 to m_1, that the meniscus delivers its energy.

An analogous reasoning can be used if the meniscus is displaced by the sudden application of a constant P. D. between the poles of the capillary electrometer, the pressure in the capillary remaining unchanged.

If the P. D. E is applied by closing the key, see fig. 1, then there will be a temporary current in the circuit G. The work done by the current will be $Q = E \sum idT$ Joules, if E, i and T are, as usually, expressed in Volts, Ampères and seconds.

$\frac{1}{2} Q$ is transformed into heat, whereas $\frac{1}{2} Q$ is accumulated in the meniscus as in a condensor in the form of an electric charge. If with circumstances as for the rest unchanged the applied P. D. — by opening of the key — is removed, the meniscus returns to its original position and delivers its energy, which once more is partially transformed into electric currents. The amount of $\Sigma\, idT$ in returning must be equal to $\Sigma\, idT$ in the original displacement. This was easily controlled experimentally.

The experiments which we have made with a sensitive high-resistance THOMSON-galvanometer, used as ballistic galvanometer, and kindly lent by Prof. KAMERLINGH ONNES, perfectly confirmed the statements given above.

The theoretical conclusions, that the value of the integral current increases directly as the P. D. used and that it remains unchanged with variation of the resistance of the circuit we could not rigorously prove by experiment because the time of oscillation of the galvanometerneedle was too small. The duration of a displacement of the meniscus was with some of the capillary electrometers a considerable part of the oscillation time of the galvanometer [1]).

Yet the results of the galvanometer experiments are far from unsatisfactory as may be proved from the data concerning capillary *B* 102 in the subjoined tables IV and V.

TABLE IV.

Difference of potential.	Mean deflection with suddenly applied P. D.	Mean deflection with suddenly removed P. D.	Mean deflection calculated per 1 millivolt. e_1.
40 millivolt.	10,5 mm.	10,6 mm.	0,264 mm.
100 "	28,5 "	28,5 "	0,284 "

TABLE V.

Resistances introduced in the circuit.	Mean deflection of the galvanometer with applied constant P. D.
6000 Ohm	35,5 mm.
0.4 Megohm	34 "
1 "	31,5 "

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[1]) It proved unpracticable to arrange the galvanometer for large period. The damping soon became excessive.

The columns 2, 3 and 4 of Table IV give the mean values, obtained from experiments with the mercury as positive pole and the sulphuric acid as negative pole and reciprocally. Usually the deflections, calculated for 1 millivolt at first slightly increased with increasing P. D. then reached a maximum and further decreased.

On account of the above mentioned relatively too short oscillation time of the galvanometer, the maximum value of e_1 probably will be the most accurate for calculating the work done, we therefore will make use only of the maximum.

The values in column 2 of Table V are obtained only with mercury as the positive pole, sulphuric acid as negative pole. They represent the means of observations with suddenly applied and suddenly annulled P. D.

For three capillary electrometers I have calculated the work necessary for the motion up and down of the meniscus, the difference of potential being $E = 1$ millivolt.

The calculation always was made in two different manners, in the first place from mechanical principles using the difference of pressure, necessary for the displacement and the dimensions of the capillary; in the second place from electrical principles using the deflections of the galvanometer, see Table VI.

TABLE VI.

Number of the capillary.	Work done as calculated from dimensions of the capillary-electrometer and the manometer readings.		Work done calculated from galvanometer readings in Joules.
	in gram-centim.	in Joules.	
B. 101	$1{,}282 \times 10^{-9}$	$1{,}258 \times 10^{-13}$	$1{,}405 \times 10^{-13}$
B. 102	2,209 „ „	2,162 „ „	2,137 „ „
B. 103	8,05 „ „	7,9 „ „	6,16 „ „

The agreement between the values of columns 3 and 4 of the given Table VI, though not very beautiful may yet be called satisfactory considering the different measurements necessary in calculating the result.

Concluding, we will see what part of the work done is spent in surmounting the mechanical friction, what part for the production of electric currents.

Let the total quantity of heat developed in a complete up and down motion of the meniscus by the sudden application and annulling of a given P. D. be A, the heat produced by mechanical friction A_1, by electric currents A_2, then

$$A = A_1 + A_2 \quad \ldots\ldots\ldots \quad (4)$$

Let the initial velocity of the meniscus after the application of the given P. D. be v_0, then is

$$v_0 = \frac{dy_0}{dT}.$$

Formula (3) reading

$$\frac{dy}{dT} = \frac{1}{a + bw}(y^* - y),$$

becomes for $y = 0$

$$v_0 = \frac{dy_0}{dT} = \frac{1}{a + bw} \cdot y^* .$$

A_1 varies directly as v_0 hence with a given value y^*, also as $\frac{1}{a + bw}$. Therefore we write

$$A_1 = \zeta \cdot \frac{1}{a + bw} \quad \ldots\ldots \quad (5)$$

ζ being a constant.

For $w = 0$ the heat produced by mechanical friction becomes equal to the total work. The last remains the same for every value of w, hence we may put

$$A = \zeta \cdot \frac{1}{a} \quad \ldots\ldots\ldots \quad (6)$$

From the formulae (5) and (6) follows

$$\frac{A_1}{A} = \frac{a}{a + bw} \quad \ldots\ldots\ldots \quad (7)$$

and from (6) and (7)

$$\frac{A_2}{A} = \frac{bw}{a + bw} \quad \ldots\ldots\ldots\ldots \quad (8)$$

In the subjoined table are given for a few capillary electrometers, examined without purposely inserted resistance the values of A_1 and A_2 in percentages of A.

TABLE VII.

Number of the capillary.	$100 \times \frac{A_1}{A}$	$100 \times \frac{A_2}{A}$
G. 103	91	9
B. 101	92	8
B. 102	93	7
B. 103	96	4

In the course of these experiments valuable assistance has been given by Mr. H. W. Blöte and Mr. H. K. de Haas.

Botanics. — Prof. Beijerinck speaks: "*On the Formation of Indigo from the Woad (Isatis tinctoria)*" [1]).

Some years ago I wished to become acquainted with the so-called "indigo-fermentation", about which nearer particulars had been communicated by Mr. Alvarez. He examined *Indigofera* and says:[2]).

"If a decoction of the plant is prepared and sterilised atfer passing it into test-tubes or Pasteur's-flasks, the reddish colour of

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[1]) It was first my intention to treat „On the function of enzymes and bacteria in the formation of indigo." I have declined this plan for the moment, and give now only part of my experiments, because I see that also Mr. Hazewinkel, of the Experimentstation for Indigo at Klaten, Java, has obtained important results about that very subject, which results, for particular reasons, have however been imparted till now to a few experts only. Yet I cannot avoid mentioning some facts, found by me, the priority of which perhaps pertains to Mr. Hazewinkel, without my being able to acknowledge his claim. One indiscretion, however, I am obliged te commit: Mr. Hazewinkel has, already before me, established the fact, that by the action of the indigo-enzyme and of acids on indican, indoxyl is produced.

[2]) Comptes rendus T. 105, pag. 287, 1887.

the liquid remains many months unchanged without the appearance of indigo. But if some microbes of the surface-membrane of an ordinary indigo-fermentation are added, as also the special active bactery of it in an isolated condition, after some hours an abundant indigo-formation is observed."

I then tried to make from woad *(Isatis tinctoria)*, in which, according to the literature, indican, i. e the same indigo-producing substance as in the other indigo-plants should be present, a decoction with which I might repeat the experiment of ALVAREZ. But I could, neither by boiling, nor by extraction at low temperature, obtain from this plant a sap which remained unchanged at the air. Constantly, after a short time, indigo will separate out of it, without there being any question of the influence of bacteria or enzymes, so that the word "indigo-fermentation" would here be quite misplaced. Neither do purposely added bacteria or enzymes favour the indigo-formation from woad-decoction.

Later, however, I was enabled to convince myself that the statement of ALVAREZ is correct, as well with regard to the decoction of *Indigofera leptostachya* as to that of *Polygonum tinctorium* [1]), for which latter plant the same fact as described by ALVAREZ, has also been established by MOLISCH [2]).

So it was evident that the indigo-plants must belong to two physiologically different groups, and I subjected the concerned chromogenes to a further examination with the following results.

1. *The Chromogene of the Indigo-plants is Indoxyl or Indican.*

The chromogene of woad is not as is usually accepted indican, but the very instable indoxyl C^8H^7NO. *Indigofera leptostachya* and *Polygonum tinctorium*, on the contrary, contain the constant glucoside indican, the constituents of which are, in accordance with the supposition of MARCHLEWSKI and RADCLIFFE [3]), indoxyl and sugar,

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[1]) Much material of this *Indigofera*, as well full grown plants as seeds, I owe to the kindness of Mr. VAN LOOKEREN CAMPAGNE of Wageningen. This interesting plant, a native of Natal, has been cultivated, very rich in indican, in the open ground in the Laboratory-garden at Delft; at Wageningen several specimens had grown this summer to more than 1.5 M. height.

Polygonum tinctorium comes from China and is, as the woad, in the seed-commerce of VILMORIN in Paris.

[2]) Sitz.ber. d. Akad. d. Wiss. zu Wien. Math. Naturw. Klasse Bd 107 pg. 758, 1898.

[3]) Journ. Soc. for chem. Industry T. 87 pag. 136, 1898; Chem. Centralblatt Bd 65 pag. 204, 1898. With thankfulness I remember the aid lent me by my chemical colleagues HOOGEWERFF and BEHRENS in the determination of indoxyl.

which has first been brought to certainty by Mr. HAZEWINKEL, and, without my knowing of his experiments, by myself. Woad, as an „indoxyl-plant" containing no indigo-glucoside, wants also an enzyme to decompose it. The two mentioned „indican-plants", on the other hand, do contain such an enzyme, which had already in 1893 been rendered probable by Mr. VAN LOOKEREN CAMPAGNE with regard to *Indigofera* [1]). I have prepared this enzyme, albeit in a very impure state, in rather great quantity and I hope afterwards to describe the experiments made with it.

The important difference between „indoxyl-" and „indican-plants" becomes particularly clear when comparing the different extraction methods. Thereof what follows.

If „indican-plants" are extracted with water below the temperature at which the indigo-enzyme becomes inactive, for instance below 40° C. or 50° C. („cold extraction"), and under careful exclusion of air, an indoxyl-solution is obtained. If, however, the same „indican-plants" are extracted by boiling („decoction"), the indigo-enzyme will be destroyed, and independently of removal or access of air, an indican-solution results, which can be kept perfectly unchanged when microbes are excluded, but either by the separately prepared indigo-enzyme, or by certain bacteria or yeasts, or also by boiling with acids, it can be converted into the constituents indoxyl and sugar. I have prepared from it the crude indican in a dry state, by evaporating to dryness the decoctions of both *Indigofera leptostachya* and *Polygonum tinctorium*. The brown matter, thus produced, resembles sealing-wax, is very brittle and can quite well be powdered.

Woad on the contrary, as an „indoxyl-plant", both by „cold extraction" and by „decoction" always gives the same produce i. e. an indoxyl-solution. Here, in both cases, the greatest care must be taken to exclude the air in order to prevent that the indoxyl, which is so easily oxidised, is converted already in the leaf itself, for then the indigo-blue is lost. Besides, access of air in a dying wood-leaf gives still in another way cause to loss of indoxyl under formation of unknown colourless and brown substances.

A sufficient removal of air during the preparation of the extracts is easily effected in the following way [2]). A well closing, wide-mouthed stoppered bottle is quite filled up with woad-leaves, hot

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[1]) Verslag omtrent onderzoekingen over indigo, pag. 12, Samarang 1893.

[2]) The technical preparation of indigo from woad is described in GIOBERT, Traité sur le Pastel, Paris 1813, and in DE PUYMAURIN, Instruction sur l'art d'extraire l'Indigo du Pastel, Paris 1813.

water is poured in, the leaves are pressed together until all air is replaced, and the stopper is put on so as not to leave the smallest air-bubble. By the exclusion of the air, together with the high temperature, the leaves soon die and already after a few hours a clear, light yellow liquid can be decanted, which is rich in indoxyl. If some alkali is added and air blown through, the indigo-blue precipitates, the colour of which appears only pure after acidification. In a sufficient time of extraction there can be thus obtained from woad a liquid of which the proportion of indoxyl, according to REINWARDT [1]) who in 1812 applied the decoction-method on a rather large scale, answers to 0.3 pCt. "pure indigo" for the fresh leaves, which, as he remarks, might rise to the double amount in the South. If we consider that the indoxyl is especially concentrated in the youngest organs still in a state of cell-partition, that it diminishes considerably in full grown parts, and is almost or wholly absent in old leaves, we must conclude that the youngest organs may contain more than 0.3 pCt indigo. As the woad-leaves contain about 85 pCt water this would correspond to a little less than 2 pCt indoxyl in the dry matter [2]).

The indoxyl-containing sap, whether prepared by "cold extraction" from the indican-plants or by decoction from the indoxyl-containing woad, has the following characteristics. It is a light yellow, in cold greenish fluorescent fluid; at warming the fluorescence diminishes and comes back at cooling. The reaction is feebly but distinctly acid, of course not by the neutrally reacting indoxyl but by organic acids. At the air a copper-red film of indigo-blue is formed at the surface of the liquid.

$$2\,(C^8 H^7 N O) + O^2 = C^{16} H^{10} N^2 O^2 + 2\, H^2 O,$$

but this oxidation follows so slowly in the feebly acid solutions, that evaporating to dryness at the air is possible without too much loss of indoxyl. The indoxyl itself is soluble in water, ether, alcohol and chloroform, in the two last under slow decomposition when the air finds access.

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[1]) In a report of 6 December 1812 to the President of the Agricultural Comittee for the Department of the Zuiderzee, present as a manuscript in the library of the Academy of Sciences, Amsterdam.

[2]) But according to GEORGEVICS, Der Indigo, pag. 2 and 18, Wien 1892, the rate of indigo for woad would only amount to 0.03 pCt. In my laboratory Mr. VAN HASSELT found in three special cases 0.05 pCt., 0.07 pCt. and 0.09 pCt. indigo-blue in relation to the weight of the living leaves, which latter amount corresponds to c.a 0.6 pCt indoxyl with regard to the dry weight.

As soon as the liquid becomes alkaline, however feebly, the indoxyl oxidises at the air with much greater quickness to indigo-blue.

The statement of Bréaudat[1]), that in the sap of *Isatis* there would be present an oxidase, by which this oxidation is effected, is not proved; in none of the three indigo-plants I have been able to find an oxidase producing indigo-blue from indoxyl. For, by preparing from the woad-leaves "crude enzyme" by finely rubbing them under, and extracting them with strong alcohol, whereby, after pressing and drying, a completely colourless powder is obtained in which all the enzymes must be present, it is found that the oxidising effect of this "crude enzyme" on an indoxyl-solution is very slight, ceases soon, and does not change by boiling, from which must be concluded that the oxidation cannot be attributed to oxidase, but is of a purely physical nature[2]).

The leaves of the indican-plants give quite the same result.

Though there originates during the slowly dying of woad-leaves at the air, a substance which gives rise to a total destruction of the indoxyl, yet about the nature of it I cannot express a supposition. If it might prove to belong to the group of the oxidases, it is surely in no other relation to the formation of indigo from indoxyl, than that it is very pernicious to it. For the indican-plants the same has been observed. In *Indigofera* this destructive influence is so strong that the „alcohol-experiment", of which later, wholly fails with this plant.

Hydrogen-superoxyd, too, causes the indoxyl gradually to vanish from the solutions, without any coloured products originating.

Strong acids, just as alkalis, though in far less degree, favour the formation of indigo from indoxyl, but then part of this substance constantly changes into a brownish-black matter.

In feebly alkaline and in moderately acid solutions, indoxyl, warmed with isatine gives, in absence of air, a precipitate of indigo-red, which is isomeric with indigo-blue

$$C^8 H^7 NO + C^8 H^5 NO^2 = C^{16} H^{10} N^2 O^2 + H^2 O.$$

This precipitate separates quickly out of alkaline solutions as fine red, from acid ones as coarser dark crystal-needles and can easily be filtered. It is soluble in alcohol and so can be separated from

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[1]) Comptes rendus T. 127, pag. 769, 1898 en T. 128, pag. 1478, 1898.

[2]) In a small porcelain vessel the menisc of the fluid furthers the oxidation of indoxyl to indigo-blue just in the same way as "crude-enzyme", strewed as a powder on the surface of the liquid.

the indigo-blue. On warming an indican solution with isatine and dilute hydrochloric acid, all the indoxyl which is set free precipitates as indigo-red, and I presume that a good quantitative indican determination may be based upon this reaction.

All the here mentioned characteristics of the indoxyl-containing plant-saps are also announced in the literature of the chemically prepared indoxyl, except the conduct towards isatine and hydrochloric acid which has perhaps not been examined.

Natural indigo prepared from woad, contains a small quantity of indigo-red; but whether this originates from the same indoxyl as the blue, or from an isomeric indoxyl, I cannot decide. Indigo-red I could also find in the indigo made from indican, whether chemically by boiling with acids, or by bacteria, or by enzymes. Consequently, if two indoxyls should exist, there should also exist two indicans.

2. *Demonstration of Indigo in the Indigo-plants themselves.*

For the demonstration of indigo in the plants themselves, Mr. MOLISCH described in 1893 his „alcohol-experiment" to which he afterwards repeatedly recurred [1]). In this experiment the parts of the plants to be examined are exposed, in a confined atmosphere, to alcohol- or chloroform-vapour, for instance by putting them into a glass-box, in which a small vessel with these substances is placed. Thus slowly dying all the indigo-plants become more or less blue, which is perceptible after the chlorophyll has been removed by extraction with alcohol. I found, however, that never all the present indoxyl or indican changes into indigo. The „alcohol-experiment" succeeds the best with *Polygonum tinctorium*, where at least most of the indoxyl changes into indigo. For woad the result is greatly dependent on the length of time which the experiment requires, even on the season, but invariably only a part, though it may be a great part, of the indoxyl passes into indigo. With *Indigofera* only a little indigo precipitates in the youngest leaflets and buds, while the older leaves become quite colourless by the alcohol-extraction though they are extremely rich in indican, so that, for this plant, the „alcohol-experiment" is without any value [2]).

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[1]) Sitz.ber. der k. Akad. d. Wiss. zu Wien Bd. 102, Abt. 1, pag. 269, 1893; Bd. 107, pag. 758, 1898, and Berichte d. deutschen Botan. Gesellsch. Bd. 17, pag. 230, 1899.

[2]) Quite wrongly Mr. MOLISCH declares: „Die präcisesten Resultate erhält man bei *Indigofera* mit der „Alkoholprobe," and as wrong is his assurance „Durchwegs war zu bemerken, dass die in Europa gezogenen Pflanzen (von *Indigofera*) auffallend viel weniger Indigo lieferen wie die tropischen" (Berichte d. deutsch. Bot. Ges. Bd. 17, pag. 231, 1899).

For woad, as an indoxyl-plant, the alcohol-experiment can be improved by changing it into an „amoniac-experiment", by which the percentage of indigo is much heightened. If near the woad-leaves in the glass-box a vessel with ammoniac instead of alcohol is placed, death follows almost instantly. The leaves then first become of an intense yellow and afterwards, by the indoxyl-oxidation, of a deep blue colour. By subsequent extraction with alcohol the leaves become deeply blue as compared to the lightly coloured „alcohol-leaves". The „ammoniac-experiment" proves that all growing parts of the woad, even the roots, the rootbuds [1]), the cotyledons and the hypocotyl, contain indoxyl.

The explanation of the „alcohol-experiment" is, of course different for the different indigo-plants. This explanation must at the same time elucidate the following fact: Suddenly killed leaves, for instance leaves, which have been kept in vapour of 100° C., do not colour at the air, neither of woad, nor of *Polygonum*, nor of *Indigofera*, why then do they become blue when slowly dying off?

The answer for *Polygonum* and *Indigofera* lies partly at hand. By the temperature of the boiling-point, the indigo-enzyme has been killed, so the indican can no more be decomposed. If slowly dying, on the contrary, the indigo-enzyme can become active and indoxyl is formed [2]). But the explanation of the second part of the process, that is the transformation of indoxyl into indigo, — at the same time the only point which for woad, as an indoxyl-plant, requires our attention, — is less clear. I think that the course is as follows. In slowly dying leaves the indoxyl changes into indigo-blue, because, in this form of death of the cells, some alkali originates. In suddenly killed leaves, on the other hand, alkali-formation does not occur, they do not grow blue, and the indoxyl disappears in another way.

If in the leaves of indigo-plants the presence of an oxidase, acting on indoxyl, could be demonstrated, this would certainly explain quite well the action of higher and lower temperatures. But, as I said, I could not convince myself of its existence, so that I am necessarily led to the alkali-hypothesis.

The cause of the great lack of indigo-blue which, as above observed, diminishes the value of the „alcohol-experiment", lies in the

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[1]) The production of leafbuds on the roots of the woad seems nowhere else mentioned. Other biennal Cruciferae produce also rootbuds, for exemple *Brassica oleracea, Sisymbrium alliaria* and *Lunaria biennis.*

[2]) Also a slow death of the leaves by drying or by frost renders the protoplasm permeable and the indigo-enzyme active.

fact, that during the slowly dying of the leaves *at the air*, a considerable quantity of indoxyl is lost in an unknown way. And in this circumstance I see one of the reasons why, in woad-leaves, there is produced so much more indigo by the „ammoniac-experiment'' than by the „alcohol-experiment'', because in the former the leaves die almost instantly, whilst the latter requires much more time.

With *Indigofera*, as said above, the „alcohol-experiment'' produces hardly any indigo. I have therefore tried to substitute for it a better one, which is effected in the following way, and by which, also excellent results are to be obtained with *Polygonum*.

At the direct action of ammoniac, indican-plants form no indigo at all, for thereby not only the protoplasm is killed, but the indigo-enzyme, too, is so quickly destroyed that it cannot decompose the indican. But we can, before exposing to the alkaline vapour, decompose the indican and free the indoxyl, by making the plants die by complete exclusion of air, but which in this case should occur in such a way, that the indoxyl remains within the plant itself. Indican-plants turn then into „dead indoxyl-plants'' and can in this condition, quite like the living woad, be subjected to the „ammoniac-experiment'' with a very good result.

The simplest way by far to reach the double aim of killing the plants by exclusion of air and leaving the indoxyl in the cells, is by entirely plunging them into mercury, whereby asphixion follows with surprising quickness, the protoplasm becoming permeable and the indigo-enzyme and the indican mixing together. At a proper temperature [1]) the indican is then decomposed after a few hours and the freed indoxyl remains in the leaf, albeit not exclusively in the cells in which originally the indican was localised. The leaf is then taken out of the mercury, ammoniac-vapour is allowed to act upon it, and at last the chlorophyll is extracted by boiling with alcohol and some hydrochloric acid. Even old *Indigofera*-leaves, which by the "alcohol-experiment'' become quite colourless, take a brilliant blue colour by this "mercury-ammoniac experiment.''

Before I had worked out the mercury-method, I examined the results of killing the leaves by the asphixion in hydrogen, carbonic acid and the vacuum, in each case followed, in the same manner as in the mercury-method, by subsequent exposition to ammoniac-vapour and extraction of the chlorophyll with alcohol.

When the hydrogen was mixed with air a singular phenomenon

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[1]) The influence of temperature on the action of the indigo-enzyme is interesting, I hope on another occasion to return to it.

was observed: the indoxyl disappeared so completely from the leaves, that, after the said treatment, they became quite colourless, whilst pure hydrogen produced intensely blue leaves.

In the carbonic-acid atmosphere there appeared, with the indigo, a small quantity of brown pigment, probably because the carbonic acid was not wholly free from air. The action of pure carbonic acid I have not yet examined.

The vacuum in a barometer-tube, above mercury, gives the same result as the submersion in mercury itself, but this method is, of course, more complicated.

3. *On the „coloured strip" in partly killed leaves.*

The following phenomenon is in near relation to the preceding. In many leaves, when partly dying off, a coloured matter will appear, just on the border between the living and the dead tissue; with woad and with *Polygonum tinctorium*, the chromogene of this coloured strip is indigo [1]). The experiment succeeds best if the leaf is partly killed by keeping it for a moment in the vapour of boiling water. The killed part remains green, although it may be a little more brownish than the living one.

As for woad I think the phenomenon should be explained as follows.

On the border between the dead and the living tissue, a strip of cells must occur which are in a condition of slowly dying. According to the preceding description, alkali will be formed in these cells and the indoxyl quickly oxidises to indigo-blue, nothing of it finding time for disappearing in another way. If the partly killed woad-leaf, immediately after death sets in, is exposed to ammoniac-vapour, it becomes, as might be expected, over its whole extent deeply blue. If it is, before the action of the ammoniac, left for some time to the influence of the air, then some indoxyl gets lost from the killed part which colours with ammoniac, a little less strongly than what remained living.

For *Polygonum tinctorium* the explanation is somewhat different, because the indoxyl must first be originated by the action of the indigo-enzyme. But this enzyme is destroyed by the hot vapour in the quickly dying part, whilst on the border between the living and the dead part there must be a number of cells in which the

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[1]) With woad this experiment succeeds best with leaves from the rosettes of the first year in June; with *Polygonum* always equally well. In many other plants the „coloured strip" does not contain indigo but a black or a brown pigment.

protoplasm is killed or hurt, but in which the enzyme remains active. During the dying the protoplasm becomes permeable, indican and enzyme are mixed up, and indoxyl-formation is the result. But in the same cells there occurs, in consequence of the slowly succeeding death, an alkaline reaction, by which the indoxyl soon oxidises to indigo-blue, which therefore precipitates in these cells alone, and not in the quickly killed nor in the living cells. Put into ammoniac-vapour the living, as well as the dead part of the *Polygonum*-leaf remain uncoloured, in opposition to the woad-leaf, this, after the preceding, requires no further elucidation.

Of course, these phenomena would find a somewhat simpler explanation if they could be brought back to the action of an oxidase, present from the beginning. But an oxidase, producing indigo from indoxyl is, as said, not to be found.

To conclude I wish to observe, that some other phenomena, which are attributed to the effect of a „wound-irritation", for instance, the formation of starch and of red pigment, as also the development of warmth in hurt parts of plants, possibly repose also on alkali-formation in or near the damaged cells.

Physics. — Communication N^0. 51 from the Physical Laboratory at Leiden by Prof. H. Kamerlingh Onnes: "*Methods and apparatus used in the cryogenic laboratory*". I.

1. Last year the completion of the safety-arrangements, thought desirable for the cryogenic laboratory by the Privy Council, in accordance with the Report of the committee appointed by the Academy, enabled us again to take up the work. I intend now to publish, whenever the completion or the progress of researches allow, something about the methods and apparatus used in working at low temperatures and with liquefied gases.

In this way the short survey (Comm. N^0. 14) of the arrangement of the cascade formed by the methylchloride-, ethylene- and oxygen-cycles will be continued or elaborated.

2. *Cryostat (boiling-glass and boiling-case) for measurements with liquefied gases (especially with liquid oxygen).*

In the above mentioned communication a method was described (§ 8) for using liquid gases in measurements. A sketch, shown on plate I of Communication N^0. 27 [1]), may serve in some way to

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[1]) Verslag der Vergad. Kon. Akad. 96/97. pg. 37. Comm. Leyden, N^0. 27.

illustrate that §. For that purpose however the drawing, to be found in the description of the cryogenic laboratory by Prof. MATHIAS [1]) is better adapted. Whereas the apparatus described by him was made for measurements in a permanent bath of oxygen with a capacity of from $^1/_4$ to $^1/_2$ Litre, in the experiments of Dr. HASENOEHRL, treated of in Communication N°. 52, a cryostat (boiling-glass with boiling-case) was used, designed on the same principle, but which contained a bath with a capacity of from $^1/_2$ to $^3/_4$ Litre [2]).

This also offers the advantage of being more quickly and easily mounted, and being more certainly air-tight, thus being better able to keep the enclosed gas pure and dry. It was built by Mr. J. J. CURVERS, head mechanic of the cryogenic laboratory, to whom I owe my best thanks for the care and ingenuity displayed in these works. Plate I gives an elaborate drawing ($^1/_3$ nat. size) of the apparatus together with the electric condenser for measurements with liquefied gases [3]), which was fastened in it in the experiments of Dr. HASENOERHL. Hence this plate may serve at the same time to illustrate the description of his research.

The gas liquefied under pressure e.g. liquefied oxygen at —140° C. from the ethylene boiling-flask, (Comm. N°. 14 § 5) is introduced by means of the tube a, which is wound in numerous turns b round the piece of wood carrying the cock. When the apparatus has been working for a short time, part of the gas streaming out in drops and clouds passes along these turns and so even further cools the liquefied gas before it escapes. The cock-pin v having been opened by means of the handle h_6, the gas passes through a filter f filled with glasswool enclosed by gauze, and flows out through the tube c against the cylindrical glass C, which fits exactly round the turns of the spiral b. If we apply the eye to the observing tube K_1 [4]), and the light obtained by means of the illuminating tube V_1 is sufficient, as long as liquid flows out from the tube c we see the jet spread out in a fan over the glass C, the jet-catcher [5]). Part of the cooled liquid escapes along the spiral b, as remarked

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[1]) MATHIAS, le laboratoire cryogène de Leiden, Revue générale des Sciences, 1896, p. 387 fig. 3.

[2]) By placing other beakers in the boiling-glass the apparatus may be used for baths of almost twice that volume.

[3]) For this compare the section Pl. I of Comm. N°. 52.

[4]) The construction of V_1 is exactly like that of K_1; in the drawing the front-view of K_1 or V_1 is given near V_1.

[5]) The disappearance of this fan-shaped form indicates that no more liquid is supplied by a and that we must therefore shut the cock.

above, but by far the greater part flows down along the inner wall of this cylindrical glass; it is conducted further by an exceedingly thin brass continuation D_1 and flows out over the lip D_2 into the beaker B_1 destined for receiving the liquid. Applying the eye to the oval observing-tube K_2 and securing a sufficient illumination by means of the opposite oval illuminating-tube V_2 we may see the liquid descending in a little jet or in drops and gathering in the beaker.

The cylindrical glass C, suspended by means of thin copper strips [1]), as well as the continuation D_1 which is kept in its place by means of little pieces of cork γ, are almost unaccessible for heat by conduction, especially when the cold vapours of the liquid which ascend from the receiving vessel B_1 have exerted for some time their refrigerating action on the surroundings [2]). Again the beaker B_1 is screened from external heat by a double gas-layer between the beakers B_1, B_2 and B_3 round which the escaping vapours are conducted in a manner to be described presently. By means of a glass ring, R_1 and a border of ebonite R_2 the beaker is fastened to the inner of two thin copper pieces E_1 and E_2, constituting together a double cover. In this cover are placed, as in the model described in Dec. '94, two tubes F_1 and G_1, one of which receives the jetcatcher C, whilst the other one serves to admit the measuring-apparatus, to be immersed in the bath of liquefied gas. In the case depicted this latter is the covering of Dr. HASENOEHRL's condenser, the glass tube g of which is fastened by means of a tube of caoutchouc g_2 and brass tightening bands g_3 in the tube F_1 which is on the right hand of the boiling-glass. By this means the boiling-glass is closed on this side.

The vapours evolved from the liquid escape through the tube G_1 on the left hand, which is covered by a second, wider tube G_2. This latter tube, which by means of a caoutchouc tube G_5 and a brass band is fastened to the wooden cock-box S_2, prevents the gas from escaping and conducts it towards the outer piece E_2 of the double cover. The glass tube [3]) is fastened to this by means of a cork ring E_4, and the two pieces of the double cover are united by the caoutchouc ring E_3. The outer cover fits by means of R_4 on to a beaker B_4, a little wider than the receiving beaker B_1 together with its surrounding glasses. Besides these beakers, which moreover are sus-

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[1]) To the glass G_1; (the strips are omitted in the drawing).

[2]) Silvering the glass where it does not need to be transparent was not yet necessary and was therefore omitted for the sake of simplicity.

[3]) G_3 serves to screen G_2 from external heat.

pended to the cover by means of fiddle-strings strained round them, B_4 also rests, by means of a ring L_1 on a very thin supporting-board L_2, which is itself suspended by means of fiddle-strings L_6 and L_7. The gas escapes from the boiling-glass through the holes in the supporting ring L_1 and the supporting board L_2 into the boiling-case and leaves the apparatus through the exit tube T_1 which leads through the cover of the boiling-case and the caoutchouc cap stretched over it. In this way the cold vapours are forced to follow the route indicated by the arrows and so to prevent the passage of heat to the bath.

The whole boiling-glass with the supportingboard L_2 is suspended to the cover of the boiling-case as appears from the description given above.

This cover has the shape of a cap with three holes in the upper sheet of thin copper, strengthened by ribs [1]). Through one of these holes leads the above mentioned exit tube T_1. The two remaining holes serve to admit parts of the boiling-glass. The left hand one beneath Q_1 is for the wooden cock-box, consisting of two pieces screwed on to each other and to which the left hand part of the boiling-glass is suspended; while the right hand hole beneath P is for the tube admitting the measuring-apparatus. The latter is also connected to the cover by means of a wooden ring, consisting of two pieces I_1 and I_2, which are screwed on to the cover from both sides. The closure of the holes in the cover is obtained by means of a caoutchouc cap, having on its upper surface three tubes, which fit on the tubes emerging from the case and are pressed on to these by means of brass bands (C. f. Q_1, Q_2).

From the more detailed description of the mode of connecting it will appear, that the cock-box and the experimenting tube together with the cover are permanently united into a frame, to which the rest of the boiling-glass is suspended. In order to build up the apparatus, we first connect to this frame the double cover E_1 E_2 of the receiving beaker by means of the above described glass-tubes F_1 and G_1. Then we should generally adjust in its place the apparatus to be immersed in the liquefied gas. So in Dr. HASENOEHRL's case the glass-tube g, carrying the cover m of the condenser, was introduced into the experimenting tube and fastened by means of the caoutchouc-tube g_2 and the brass band g_3 [2]). The thin wire φ, which is to put the

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[1]) See section through upper surface of cap next to it.

[2]) g is pushed through the cover from beneath, the side-tube u_2 is then connected to g as follows: the brass T-piece u_1, u_2 (comp. Pl. I, Comm. N°. 52) is slid from above over g, and fastened by means of the caoutchouc-tubes w_1 and w_2 and brass bands so that u_2 comes opposite to a hole made in g.

brass cover of the condenser to earth was connected to the tube a, and then the beakers B_1 B_2 B_3 B_4 were mounted in their places and together with the supporting-board L_2 suspended to the cover by means of L_6.

Into the cock-box S_3 we place the cock-piece of wood S_1; this fits in it first by means of the caoutchouc-packing H_1, which serves only to prevent the gas from taking the way upwards and also by means of the caoutchouc-packing H_3, which is compressed by the screws S_4 till an air-tight fit has been obtained. In the cock-piece the supply-tube a and the glass cock-tube p [1]) are also introduced. The design of the cock is for the rest exactly like that of '94 (see also MATHIAS l.c.). At the lower end of the glass tube p a hexagonal brass cap has been cemented, in which is a nut, turning together with the glass tube p and screwed on to the brass cock-piece h_7 which contains the washer. When the washer has been screwed on sufficiently, the hexagonal portions of nut and cock-piece are fixed together by means of a hollow hexagonal piece. Then the tubes a and p are fixed hermetically into M with elastic cement. The pin v is moved by a wooden stem h_5, ending at the upper end also in a pin, which goes through the packing h_8. Sideways a tube j is placed, serving to test the cock for leakage of the packing h_7 and to lead away the gas possibly escaping at high pressure through that packing, as otherwise the glass tube p' might burst. It is very convenient that the cock-piece with the cock can be taken out of the apparatus, if the packing, the filter or one of the tubes has gone wrong.

By pressing the packing N_1 by means of the screws N_5 between the flanges of the cover N_3 and of the boiling-case N_6 we obtain an air-tight fit of the cover on the case. The conical ring L_4, supported by felt, guides the ring L_3 when the boiling-glass is lowered into the case, until through the fitting of the ring L_3 into another similar ring fastened into the bottom of the case a centric and elastic mounting is obtained.

The case itself consists of two thin copper cylinders strengthened by rings, the lower and somewhat narrower of which cylinders, U_2 has been soldered excentrically into the bottom U_3 of the upper and somewhat wider, U_1. A sufficient rigidity in the connection of both cylinders has been secured for by inner strengthening-bars U_4.

The case carries at the upper part two circular and at the lower part two oval opposite flanges λ_1 and λ_2, on to which the observing and illuminating-tubes are clamped air tight by means of flanges

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[1]) Constructed exactly like the cock, depicted Pl. I Comm. N°. 52, where the drawing is more distinct.

α_1 α_2 and caoutchouc packing. The line joining the upper couple has been turned about the axis of the case with respect to the line joining the lower couple, in order to obtain a sufficient illumination of the issuing jet [1]).

The loose bottom W_1, which may be pushed outward by inner pressure, rests on exhaustion with the border W_4 on the border of the case, and is sufficiently strengthened by ribs to be able then to resist the outer pressure. By means of the caoutchouc cap W_5, which is stretched over the bottom and fastened air-tight to the borders once for all with the utmost care, a fitting is obtained, whilst nevertheless in case of accident the whole bottom would act as a safety-valve.

The whole apparatus can be exhausted through the cock X_1. This is connected together with the vacuum-manometer X_8 to the case at the flange X_3 (dotted in the section, and depicted beside the case separately in section), to which the glass tube X_5 has been fastened in the same manner (by means of X_4) as the observing tubes. In this tube $P_2\,O_5$ is introduced for drying the apparatus.

The whole inner wall of the case is coated with a layer of felt and the bottom with several layers while the inner surface of this layer has been rendered reflecting by lining it with nickel-paper. The thin layer of nickel however has been removed over a length of a few centimeters at all places where heat might be supplied to it by conduction. Where the inside of the case or of the observing and illuminating-tubes has not been coated with felt, or a layer of felt would not be rigid enough, insulation has been secured by introducing wood or caoutchouc, as appears sufficiently from the drawing [2]).

The dust-box Y_1 provided with an extremely light valve Y_2 opening outward, and made of cotton wool enclosed between gauze with a border of wash-leather, allows the gas to escape without appreciable fall of pressure and prevents the gas, which might flow

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[1]) Further explanation of symbols: π_1, π_2 loose-fitting, thin plate-glasses, separating the back observingtube-chamber from the case, while nevertheless the pressure of the gas in the case and the observing tube remains equal; σ_1, σ_2 wooden packing tubes, in order to supply as little heat as possible to the gas in the observing tube-chamber; ρ_1, ρ_2 thick observing glasses, fitting air-tight in μ_2, and further fastened by means of bands ν_1, ν_2; θ_1, θ_2 caoutchouc-tubes, fitting round the brass-ring of foremost observing tube-chamber; ω_1, ω_2 observing-glasses cemented in border, with packing fitting on τ_1, τ_2; ζ_1, ζ_2 tubes serving for sucking dry, heated air through foremost chambers (commonly closed). In the various chambers stand drying-dishes with $P_2\,O_5$. The tube at τ_1 should have been drawn broken off.

[2]) The case has room to place still another athermanous layer between the wall and beaker B_4.

back from the conduit Y_3, from introducing dust into the apparatus. For the tube Z_3 through which in the experiments of Dr. HASENOEHRL the gas escaped which evaporated from the electric measuring-condenser, a simpler dust-box Z_1 (filled only with cotton wool between gauze) was sufficient, as this has not to transmit so much gas at once. It has already been pointed out above, that the arrangement of this cryostat offers a great advantage as concerns easy mounting and dismounting. This is especially due to the use of flanges with packing for all the air tight joints that have to be made and temporarily broken in working with the apparatus.

The copper wall with flanges soldered to it will of course occasion no leakage, and can be tested previously by means of a temporary bottom soldered into it and temporary closing plates on the flanges. When we are quite certain everything is tight, the caoutchouc cap, which is to close the bottom, is spread over with rubber-solution, and by means of bands W_6 once for all united with the case. In the same manner the cap N_3 is fitted onto the cover and the parts going through the holes. When all this has been done carefully, the joints are tested by immersing the case with bottom and cover, closed with temporary plates on the flanges, in a tub filled with water, and protecting the caoutchouc caps from without against inflation; then admitting air into the case under a little excess of pressure (0,2 atm.), and seeing whether any air bubbles escape. These fittings which demand much care are permanent, so that if they are found in this manner to be secure, they will not generally require any more attention. In the same way we may also carefully cement once for all the thick plate glasses ϱ_1, ϱ_2 and the flanges of the observing and illuminating-tubes in the caoutchouc-tubes μ_1 μ_2, and test the joints by means of temporary flanges before fastening them to the apparatus.

In commencing to use the cryostat we need only screw the case on to the cover N_2 and the observing-tubes onto the side-flanges, and secure an exact fit of the packing between the flanges, a thing which can always easily be attained. This is the case also if we wish to lift the boiling-glass with the cover for a moment out of the case, or if we must renew the P_2O_5 in the drying-dishes in the observing- and illuminating-tubes.

The cryostat rests with N_6 on a wooden ring supported by three legs and is packed up in wool.

It was described above how in the experiments of Dr. HASENOEHRL the measuring-apparatus was mounted in the boiling-glass. We may add here only that, as explained by him in Comm. N°. 52, the beaker B_1 was filled with liquid oxygen from the ethylene-boiling-

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flask (Comm. N⁰. 14 § 5), the liquid was sucked over partly into the condenser through the tube r by means of the cock h, and the beaker B_1 was then filled up with liquid oxygen and remained so [1]). All these operations were watched through the observing-glasses and proceeded without offering the least difficulty.

3. *The arrangement of a Brotherhood air compressor for the compression of gases, to be kept free from admixture with air.*

In Communication N⁰. 14 this was dismissed in a few words. Plate II gives a view of the compressor with its separator and the newly devised accessories ($^1/_9$ nat. size). As for the pump itself, in Plate III ($^1/_3$ nat. size) figs. 1 and 2 what has been newly added is indicated with thicker lines. By means of figs. 1 and 2 together, completed by fig. 3, the construction and working of the compressor may be understood [2]). As explanation we may remark, that the cock B_1 supplies the steam, which drives the miniature steam-engines B_2, B_3 placed at both sides of the body of the pump. When working at full speed the shaft B_5, which moves the plunger of the compressor up and down makes up to 500 revolutions per minute. Usually the air to be compressed is drawn directly from the atmosphere, through the suction-valve d, d — which is in the shape of a flat ring enclosed between two concentric circles — in which process it becomes mixed with water and a lubricant. To suck a gas which must be kept free from air this valve is covered with a head, consisting of a brass ring e_1, a thick observing-glass e_4 and a caoutchouc-tube e_2 which is firmly and hermetically fixed to both by means of bands e_3 and e_5 and cement [3]). The lubricant mixed with water, which in the case of the compression of N_2O (and also of O_2) was glycerine with $^2/_3$ of water, drops from the tube f_1 [4]) and the gas is supplied through the tube g_1 (Pl. III). It also sometimes happens as will appear later on, that liquid is let off through this supplying tube. In order to prevent in such case the observing glass, through which we wish to watch the regular working of the valves, from becoming dull the screen g_2 has been introduced. Received through the sucking-valve

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[1]) Through z_2 the measuring-condenser is exhausted, by means of Z_4 and X_8 we may judge of the difference of pressure required to suck over the liquid from B_1 into w.

[2]) E. g. by following the letters aq the circulation of cooling water may be traced.

[3]) The metal-cage fig. 4 serves to prevent the projection of the glass in the possible case of accident.

[4]) In compressing air we might use spermaceti oil with water, but in the case of oxygen and nitrous-oxide explosions might then be dreaded.

in the room a the gas is compressed in three steps, first in the room a itself, whence it escapes through valves, then in the annular space b, and lastly in the narrower and also annular space c, which it enters also through valves, and whence it goes over the cooling spiral k, through a feeding valve and passing a safety valve to the separator S. When the cock k_1 of this is shut, the gas may escape along a little screw [1]) as well as through the safety-valve. The safety-valve comes into use only when the former is screwed tight and with the Leiden arrangement the gas, mixed with liquid, escaping from it is conducted back to the sucking-tube h_2. When the gas has reached a sufficient pressure by opening k_1 it is admitted into the separator, where the liquid gathers below and from which the gas may be conducted through the cock k_2. Thence it reaches first the wide drying-tube D_1 and then the narrower one D_2. In both it passes through P_2O_5, shut up between glass-wool and asbestos by means of gauze and little sieves [2]). Through cock K_8 and tube S_{11} the compressed and dry gas may be led to the apparatus where we wish to bring it; generally a tube like D_2, filled only with glass-wool, is added in order to arrest the P_2O_5 possibly carried over as dust.

The lubricating liquid flows in at the sucking chamber through the tube f_1 from the reservoir f_4. Care should be taken that this reservoir remains filled, (the best way is to keep the level constant) and to watch by means of the glass tube f_2, partly enclosed in brass, the regulation of the little jet by the cock f_3. (Compare for the construction Pl. III fig. 5).

The liquid from the separator is forced through the cock K_0. and the tube S_8 into the reservoir V, whence the gas dissolved in or escaping after the liquid returns along A (Pl. IV) to the sucking tube g_1 [3]). This arrangement besides that at the safety valve described above is intended to prevent the loss of pure gas, which usually is costly. The glass tubes cemented in brass-pieces l_1, l_2 with taps (see Pl. III fig. 5). allow us to see whether chiefly liquid or gas is forced out. A gauge-glass indicates the level of the liquid and a

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[1]) This little screw is not to be seen in the section represented, it is useful when starting the compressor, especially as it allows liquid to escape from the cooling-spiral.

[2]) Fig. 6 gives a section of these frequently used drying tubes, mentioned in N°. 14, and to be found in the drawing of Mathias and in other of these communications. The construction is cheap and fit for pressures up to 80 atmospheres. The brass nuts have been screwed and soldered onto a gaspipe tested up to 200 atm. and provided with a screw thread. The drawing should require no further explanation.

[3]) The cock K_9 is always opened while working with the apparatus but is useful to test the tightness of the apparatus.

safety-valve *v* beneath the liquid regulates the out-flow without permitting air to be sucked in.

Into this reservoir may escape also through the tubes S_2 and S_6, the cock K_7 and the tube S_{10} the contents of the joining-tube S_1, and the mixture of gas and liquid contained in the pump itself. The contents of each of the reservoirs S, D_1, D_2, which enclose gas under pressure, may likewise escape into the reservoir V, or directly into the sucking-tube on opening the cocks K_3, K_5 introduced for that purpose. Moreover the various parts of the arrangement may be connected through the cocks K_4 and K_6 to an air-pump, to the open air or to a gas reservoir.

4. *Pouring out little quantities of liquid nitrous-oxide.* Nitrous-oxide is a very important means for operating with low temperatures. The boiling point lies lower than that of carbon dioxide. It has further an advantage over carbon dioxide in remaining liquid at the boiling-point. Hence it may be used for transparent (liquid) baths, which for most experiments will be preferred to a snow-like substance. In physical and chemical laboratories however the free liquid is relatively seldom used for this purpose. One of the causes of this may have been that, on trying to pour out the liquid directly from the commercial cylinders, the cock was frozen. Or that, by neglecting to sufficiently close the glass-vessel (a vacuum-glass for instance) in which the liquid was poured out, part of the N_2O, the melting point of which lies very near the boiling point was allowed to congeal by evaporation in the air [1]) and so to form a solid mass in front of the orifice. However the principal reason will probably have been, that in all cases the quantity poured out was very small in proportion to the quantity employed, and hence the price of the free liquid thus obtained was far in excess of the moderate price by weight of the N_2O in the cylinder.

The N_2O may however be cooled easily and with little cost by means of carbon dioxide so much, that almost all the nitrous-oxide flowing out is received as liquid if the glass into which it is poured has been also closed sufficiently. For many experiments then the advantages enumerated above will outweigh the smaller cost and danger of the solid carbon dioxide. In such cooling experiments the gaseous N_2O is conducted through a drying tube with P_2O_5 (as in plate III fig. 5) which is connected with the reservoir of liquid gas, to a thick copper condensing spiral (7,5 mm. outer 4 mm. inner diameter) consisting of 24 turns, 12 with diameter 8 and 12 with

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[1]) See **Natterer**, Pogg. Ann. 62 p. 134. (1844).

diameter 11 cm. contained in a felt-coated copper vessel (height 14, width 12, 5 cm.), which is packed with solid carbon dioxide. The condensing spiral is provided on both sides with a regulating-cock (for the model see SIERTSEMA, Comm. Suppl. No. 1, Pl. III, fig. 9) and To the latter of these a narrow discharging tube is fastened.

5. *Boiling nitrous-oxide in large quantities. Cycle of nitrous-oxide.* If we wish to cool apparatus with larger volumes or capacities for heat in a bath of nitrous-oxide, it will be necessary to receive the gas evolved by the liquid and to compress it by means of a compressor with or without cooling. As at Leiden a methylchloride-cycle is at hand, the proper way was not to compress the nitrous-oxide at the ordinary temperature, but in the methylchloride refrigerator (Comm. N⁰. 14 § 3, see also Pl. I, MATHIAS l. c.). As compressor a Brotherhood-pump could be used, arranged as described above § 3.

If we condense the N_2O at a very low temperature, the vapours escaping from the refrigerator are very rare and the vacuum-pump, which sucks them up, can only move a small quantity of methylchloride. If we condense the N_2O at a higher temperature, more methylchloride will certainly evaporate and more nitrous-oxide will be condensed, but the latter will evaporate to a much greater degree on flowing out than more cooled N_2O. Usually we operated at the temperature — 45° C of the methylchloride-refrigerator and the safety-valve of the Brotherhood (see § 3) was adjusted for 25 atm. The separator in order to work well, should have a rather large capacity in which therefore a large stock of N_2O would be stored up at high pressure. This alone would make it desirable not to proceed to too high pressures, and moreover at the discharge of the gas, which deviates strongly from BOYLE's law, from the separator water might be frozen and so cause accidents.

Plate IV [1]) represents a scheme (the parts nearly $^1/_{35}$ nat. size) of the arrangement of the apparatus in Dr. HASENOEHRL's experiments with liquid nitrous-oxide (Comm. N⁰. 52) as an example of operations with the nitrous-oxide cycle. *B* is the Brotherhood-pump, with accessories, of which the principle may be understood from plates II and III together with § 3. The compressed gas is conducted through the regulating-cock (k_8 Plate II) along *D* (Plate IV) to the methylchloride-refrigerator, where it is cooled first by the cold methylchloride vapours

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[1]) For simplicity a case was here selected for which the refrigerator had been formerly described; but a refrigerator, wholly independent of the triple-cascade might be used.

in the spiral E of the regenerator (Comm. N⁰. 14 § 3), whence it flows through the condensing tube and a cock to the cryostat which is indicated only diagrammatically, but may be understood from Plate I together with § 2; the evaporated gas escapes through the dust-box Y_1 to the sucking-side of the pump, which communicates with the gas-sacks G_1 and G_2, into which also the gas from the condensor escapes through Z_3. The cocks indicated in these conduits are required to cut off and to test the separate apparatus.

Besides the possibility of closing these we should be able to shut off the gas-sacks G_1 and G_2 and to stop the Brotherhood. Therefore a safety-tube has been connected to the tube conducting the gas. The observer, who regulates the influx of liquefied gas by means of the observing glasses of the cryostat, keeps in view at the same time the vacuum-manometer. The entire cycle could be operated in the experiments of Dr. HASENOEHRL, where only a beaker containing $^3/_4$ Litre had to be kept full, with about 2 kg. of N_2O, which was admitted into the apparatus through the cock k_6 (Plate III) from a reservoir of compressed nitrous-oxide.

With the first experiments little care was bestowed upon the exhausting etc., and therefore a mixture of N_2O and air circulated. A remarkable phenomenon then occurred. While the observer looked through the observing glass at the jet, the jetcatcher was suddenly obscured by solid substance, and thick flakes of snow and accumulated snow heaps rushed down into the beaker B_1 (Pl. I), where they took some time to melt.

This singular phenomenon, for a moment suggesting the doubt as to whether something had gone wrong with the P_2O_5 or the circulation of water, could be simply explained as follows. From a mixture of N_2O and air a liquid phase is separated, which contains chiefly N_2O, the gas available in the cycle becomes then very impure N_2O. In the methylchloride refrigerator this on a sufficient increase of the pressure is condensed into a solution containing much air, which on being poured out sets free the air in a gaseous phase in which the partial pressure of the nitrous-oxide is less than that of solid nitrous-oxide, so that the liquid phase, consisting almost solely of pure nitrous-oxide, congeals.

Physics. — "*The dielectric constants of liquid nitrous oxide and oxygen.*" By Dr. FRITZ HASENOEHRL. (Communicated by Prof. H. KAMERLINGH ONNES).

(Will be published in the Proceedings of the next meeting).

Magnetism. — "*On Spasms in the Earth's magnetic force.*" By Dr. W. VAN BEMMELEN. (Communicated by Prof. H. KAMERLINGH ONNES).

(Will be published in the Proceedings of the next meeting).

(Octobre 25th, 1899.)

ERRATUM.

Page 41 line 13 for Fe_2SO_4 read $FeSO_4$
„ 42 „ 31 „ N_2O „ HCl
„ 44 „ 24 „ 44,16 . . 1603 „ 1603 . . . 44,16
25 „ 44,25 . . $\underline{1566}$ „ $\underline{1566}$ . . . 44,25
26 „ 44,47 . . $\underline{\underline{0194}}$ „ $\underline{\underline{0194}}$ . . . 44,47

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday October 28th, 1899.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 28 October 1899 Dl. VIII).

CONTENTS: "On Isodialdane". By Prof. C. A. Lobry de Bruyn and Mr. H. C. Byl, p. 143. — "Mixed Crystals of Mercury Iodide and Bromide." By Prof. H. W. Bakhuis Roozeboom, p. 146. — "On the Enantiotropy of Tin (II)". By Dr. Ernst Cohen and Dr. C. van Eyk (Communicated by Prof. H. W. Bakhuis Roozeboom), p. 149. — "On a new kind of Transition Elements (sixth kind)". By Dr. Ernst Cohen (Communicated by Prof. H. W. Bakhuis Roozeboom), p. 153. — "On mixed Crystals of Sodium nitrate with Potassium nitrate and of Sodium nitrate with Silver nitrate". By Prof. H. W. Bakhuis Roozeboom, p. 158. — "The Nature of inactive Carvoxime". By Prof. H. W. Bakhuis Roozeboom, p. 160. — "On Isomorphous Compounds of Gold and Mercury". By Prof. Th. H. Behrens, p. 163. — "A Remark on the Molecular Potential Function of Prof. van der Waals". By Dr. G. Bakker (Communicated by Prof. J. D. van der Waals), p. 163. — "Tidal Constants in the Lampong- and Sabangbay". By Dr. J. P. van der Stok, p. 178. — "On the Relation of the mean Sea-level and the Height of Half-Tide." By Mr. H. E. de Bruijn, (with 2 plates) p. 189. — "New Theorems on the Root of the Functions $C_n^{\nu}(x)$". By Prof. L. Gegenbauer (Communicated by Prof. Jan de Vries), p. 196. — "Spasms in the Terrestrial Magnetic Force at Batavia". By Dr. W. van Bemmelen (Communicated by Prof. Kamerlingh Onnes), p. 202. — "The dielectric Coefficients of liquid Nitrous Oxide and Oxygen". By Dr. Fritz Hazenoehrl (Communicated by Prof. H. Kamerlingh Onnes) (with one plate), p. 211. — "The Hall-Effect and the increase of Magnetic resistance in Bismuth in very low Temperatures." By Dr. E. van Everdingen Jr. (Communicated by Prof. H. Kamerlingh Onnes), p. 228.

The following papers were read:

Chemistry. — "*On Isodialdane.*" By Prof. C. A. Lobry de Bruyn and Mr. H. C. Bijl.

(Read in the meeting of September 30th 1899).

In his interesting and prolonged researches on aldole, Wurtz has described two condensation products of this substance, formed by the separation of a molecule of water from two molecules of aldole. One of these, dialdane, which is formed along with aldole from aldehyde, was more fully studied. The results of this study led WURTZ to propose a formula for dialdane according to which it still contains one aldehyde group, exhibits the properties of an alcohol twice and contains two carbon atoms united by a double bond. From two molecules of aldole

$$CH_3\,CHOH\;CH_2\,COH$$

dialdane

$$CH_3\,CHOH\,CH_2\,CH:CH\;CHOH\;CH_2\;COH$$

is therefore formed by the separation of water from the methylgroup of the one molecule and the aldehyde group of the other.

The second condensation product, which WURTZ called isodialdane, was only obtained by him in very small quantities, and was not further examined. He obtained it, along with other substances, by heating aldole to 125°; it melted at 112°.

In an attempt which one of us made long ago [1]) to combine aldole with hydrocyanic acid, pure hydrocyanic acid was mixed with aldole and the mixture left to itself for some months. It was found that the hydrocyanic acid had not combined with the aldole, or only to a very small extent; it had, however, acted as a dehydrating agent so that two molecules of aldole had formed one molecule of isodialdane.

As a result of this observation isodialdane was readily obtainable and a proper study of it was taken in hand. The result of the investigation possesses a more general interest because it leads to the conclusion, that isodialdane is to be regarded as a substance in some measure analogous to ordinary cane sugar, in the sense that the relation between isodialdane and the two aldole molecules, from which it is formed, is the same as that between cane sugar and glucose and fructose (laevulose).

It is known that cane sugar does not possess reducing powers and therefore does not contain an aldehyde group, but that under the influence of dilute acids, it very readily takes up a molecule of water, being converted into the two above mentioned reducing hexoses; the aldehyde group of glucose and the carbonyl group of fructose are therefore absent in the saccharose molecule. At the same time two of the ten hydroxyl groups of the two hexoses disappear, for saccharose only gives an octo-acetate. Let us now turn to the results of the study of isodialdane. It has no reducing power, but with dilute acids it at once obtains this; it is thus very readily inverted.

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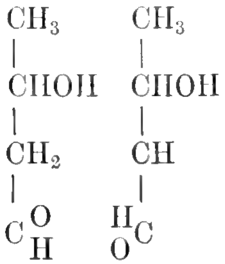
[1]) Bull. Soc. Ch. (1884) **42**. 161

Isodialdane contains no unsaturated bond, bromine is not taken up and alkaline permanganate is not decolorised. The two hydroxyl groups of the two aldole molecules have disappeared; the solutions in benzene and xylene giving no hydrogen when boiled with sodium and acetic anhydride and sodium acetate having no action on isodialdane even on boiling; acetic anhydride with a trace of sulphuric acid or of zinc chloride gave rise to resinous products from which an acetate could not be separated. The application of SCHOTTEN—BAUMANN's reaction with benzoylchloride also gives a negative result. Phenylhydrazine is quite without action even after boiling the alcoholic solution, so that a carbonyl group is not present in isodialdane. Sodium amalgam does not effect reduction or acts very slowly, since after four days reaction, partly at the temperature of the boiling water bath, almost the whole of the isodialdane was recovered unchanged.

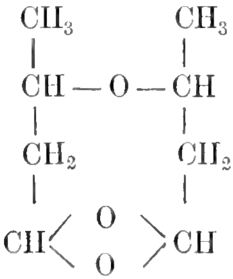
We consider that the structural formula, which satisfactorily represents the results obtained, must be that in which each of the three oxygen atoms still present in isodialdane are supposed to be connected to two carbon atoms.

This leads to the hypothesis that two aldole molecules



$$\begin{array}{cc} CH_3 & CH_3 \\ | & | \\ CHOH & CHOH \\ | & | \\ CH_2 & CH \\ | & | \\ C^{O}_{H} & {}^{H}_{O}C \end{array}$$

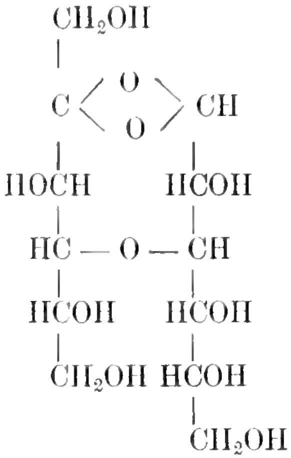
lose one molecule of water, yielding



This system is apparently very stable, except under the action of dilute acids.

We consider that there is some justification for the assumption of the existence of the group of carbon and oxygen atoms, found in isodialdane, in the saccharose molecule, the constitution of which is as yet unknown.

Making this assumption and using the stereochemical formulae of glucose and fructose the following formula is obtained. The left half represents the fructose molecule, the right the glucose molecule.



The investigation of isodialdane, which crystallises in two modifications and is inactive, is to be continued.

Chemistry. — Prof. H. W. Bakhuis Roozeboom presents Dr. W. Reinders' Dissertation on "*Mixed Crystals of Mercuric Iodide and Bromide*" respecting which be makes the following communication.

(Read in the meeting of September 30th 1899).

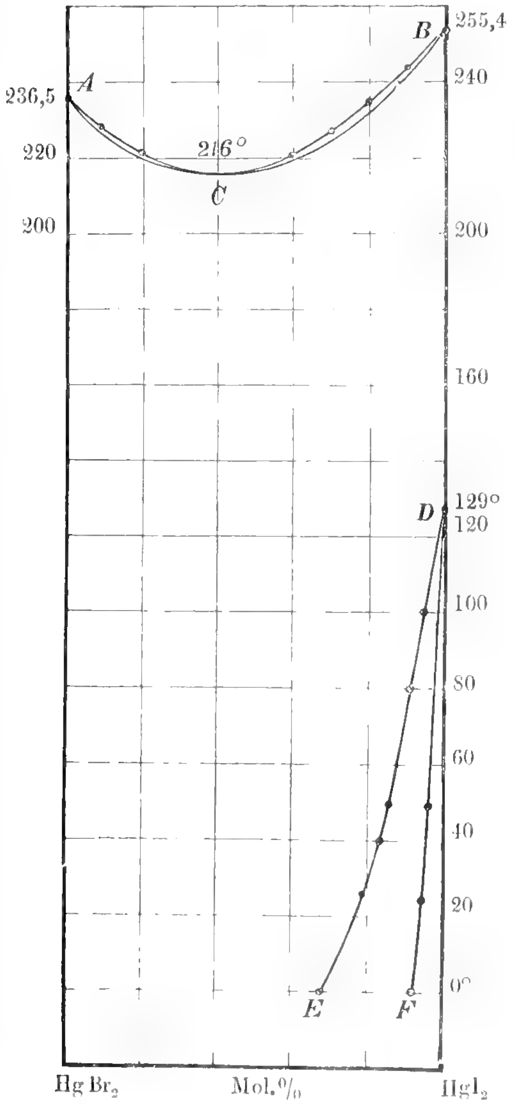
This research is a second contribution to our knowledge of the phenomena which may be observed during the solidification of fused mixtures of two substances to mixed crystals and the transformation of the mixed crystals into another modification.

Of the many types, which, according to the theoretical development of the subject given by the speaker, (See Report of the meeting of the Academy of Sept. 24th 1898, p. 134) are possible, one of the simplest is here realised.

The meltingpoint line is a continuous curve, showing that only one set of mixed crystals is deposited, the composition of which changes gradually with that of the fused mass.

The meltingpoint line, which extends from 236°.5, the melting point of $HgBr_2$, to 255°.4, the meltingpoint of HgI_2, possesses a minimum at 216°.1 and 59 pCt. (molecular) of $HgBr_2$. In this minimumpoint the mixed crystals have the same composition as the fused mass.

To the right of this point the crystals contain more HgI_2, to the left of it more $HgBr_2$ than the fused mass. The differences are, however, not large; the line of the crystals (lower curve *ACB*) lies close beside the meltingpoint line (upper curve *ACB*).



Below 216° therefore, mixed crystals of any composition are capable of existence. They belong to the rhombic system. At 127° pure HgI_2 is transformed into red, tetragonal crystals, (point *D*).

This transition point is depressed by admixture of $HgBr_2$. Further, it develops into a transition interval, bounded by a line *DE* for the yellow crystals, which runs from 127° and 0 pCt. $HgBr_2$ to 0° and 33 pCt. $HgBr_2$, and by a line *DF* for the red crystals which runs from 127° to 0° and 8.6 percent. $HgBr_2$. (in molecules).

The significance of these two lines is as follows. Below a temperature given by the line *DE*, mixed crystals of a certain concentration must separate red mixed crystals belonging to the line *DF*. The compositions of the two change as the temperature falls, until, at a sufficiently low temperature, homogeneous red crystals remain.

Since the two lines lie somewhat far apart, even when a small quantity of $HgBr_2$ is present, the interval of temperature through which the transformation takes place is very considerable. The change, further, is subject to great retardation. For this reason the determination of the transition interval was not possible either by the dilatometric or by the thermometric method.

By observing the change of colour it was possible to determine the composition at which the red crystals were completely converted into the yellow crystals at a given temperature. The circumstance that yellow mixed crystals containing up to 20 pCt. in molecules of $HgBr_2$ may be converted into the red modification by grinding at the ordinary temperature was here used.

The beginning of the change of the red into yellow crystals could not however be observed in this way. In order to do this the crystals which are deposited from mixed solutions at constant temperature were studied.

By allowing mixed crystals to deposit from a sufficient number of solutions, a solution is finally found from which both red and yellow mixed crystals are deposited and which therefore represents the two points of DE and DF which lie on the same temperature line.

Theoretically, the nature of the solvent should have no influence on the result. This conclusion was confirmed by the results of experiments with alcohol and acetone as solvents. In spite of the fact that the solubilities of the two mercury salts and their ratio were very different, the same values were found for the coexisting yellow and red crystals.

Even by this method, however, it was impossible to determine points on DE and DF below 0°. The direction of the two lines indicates that if $HgBr_2$ possesses a transition point, it is probably at a very low temperature. Experiments in this direction gave no indication of a transition down to —83°.

It is to be remembered that even at ordinary temperatures, and much more so at higher temperatures, solid $HgBr_2$ and HgI_2 diffuse into each other, so that the transition temperature of a finely ground mixture agrees closely with that which would be found for mixed crystals containing the same proportion of $HgBr_2$.

Finally it was possible to show, by means of the known heat of transformation of mercuric iodide, that for moderate admixtures of $HgBr_2$ the course of the lines DE and DF agreed with a formula which ROTHMUND has recently given for the case that the concentrations of the two coexisting phases are known. This is the first case in which it has been possible to verify the laws of dilute solutions in the case of the relationship between two solid solutions.

Chemistry. — "*On the Enantiotropy of Tin* (II)." By Dr. ERNST COHEN and Dr. C. VAN EYK. (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

(Read in the meeting of September 30th 1899.)

1. Continuing our researches on grey (stable) and white (metastable) tin [1]) we first attacked the question of the velocity of change of the white into the grey modification.

According to our first communication the velocity is zero at + 20° C, the transition point.

In the course of our experiments we had received the impression that the change white tin → grey tin, took place more slowly at — 83° than at somewhat higher temperatures.

Such a phenomenon recalls the solidification of super-cooled fused substances where the rate of crystallisation increases as the temperature falls below the melting point until a maximum is reached after which it decreases again [2]).

2. A dilatometer, of 2 cc. capacity, was filled with grey tin which had already repeatedly undergone transformation in both directions. By warming the dilatometer for a few moments to 50° a part of the contents was converted into white tin. The dilatometer was then filled with a solution of pink-salt in alcohol, in order to avoid complications which might arise from crystallisation of the salt at very low temperatures.

The dilatometer was then placed successively in different baths at constant temperatures.

Since the conversion of white tin into grey tin is accompanied by a considerable increase of volume the rise (per minute) of the liquid in the capillary of the dilatometer is a measure of the velocity of transformation. It is necessary, of course, to take care that the quantity of white tin undergoing change remains constant during the whole course of the experiments. For this reason the capillary tube of the dilatometer was made very narrow; the conversion of a very small quantity of white tin then gives a sufficient rise. One mm. of the capillary = 0,00028 cc. Taking the specific gravity of white as 7.3, and that of grey tin as 5.8 the transformation of 8 mgrm. of white tin into the grey modification gives a rise of 1 mm. In this way the following results were obtained.

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[1]) These Proceedings, June 24 1899.

[2]) Compare GERNEZ, Journal de Physique (2) 4. (1885) p. 349.
TAMMANN, Zeitschr. für phys. Chemie 23, 326 (1888).
COHEN, These Proceedings, February 25 1899.

Temperature —83° (Paste of solid carbonic anhydride and alcohol).

Time in minutes	Height of the level of the liquid in the dilatometer (in mm.)	$\frac{\triangle h}{\triangle t}$	
0	100.2		
		2.3	
1	102.5		
		2.5	
2	105.0		
		2.5	
3	107.5		Mean rise
		2.5	
4	110.0		
		2.5	per minute
5	112.5		
		2.5	
6	115.0		2.5 mm.
		2.6	
8	120.2		
		2.8	
9	123.0		
		2.7	
10	125.7		

Temperature —48°.

Time in minutes	Height of the level of the liquid in the dilatometer (in mm.)	$\frac{\triangle h}{\triangle t}$	
0	44.0		
		5.0	
1	219.0		
		4.5	
2	253.5		Mean rise
		4.5	
3	258.0		
		5.0	per minute
4	263.0		
		4.0	
5	267.0		4.5 mm.
		4.0	
6	271.0		
		4.0	
8	279.0		

Temperature —15° (Cryohydrate of NH_4Cl.)

Time in minutes	Height of the level of the liquid in the dilatometer (in mm.)	$\frac{\triangle h}{\triangle t}$	
0	232		
		0.40	
3	233.2		
		0.45	Mean rise
7	235.0		
		0.44	
12	237.2		per minute
		0.43	
15	238.5		
		0.50	0.4 m.m.
24	243.0		
		0.33	
30	245.0		

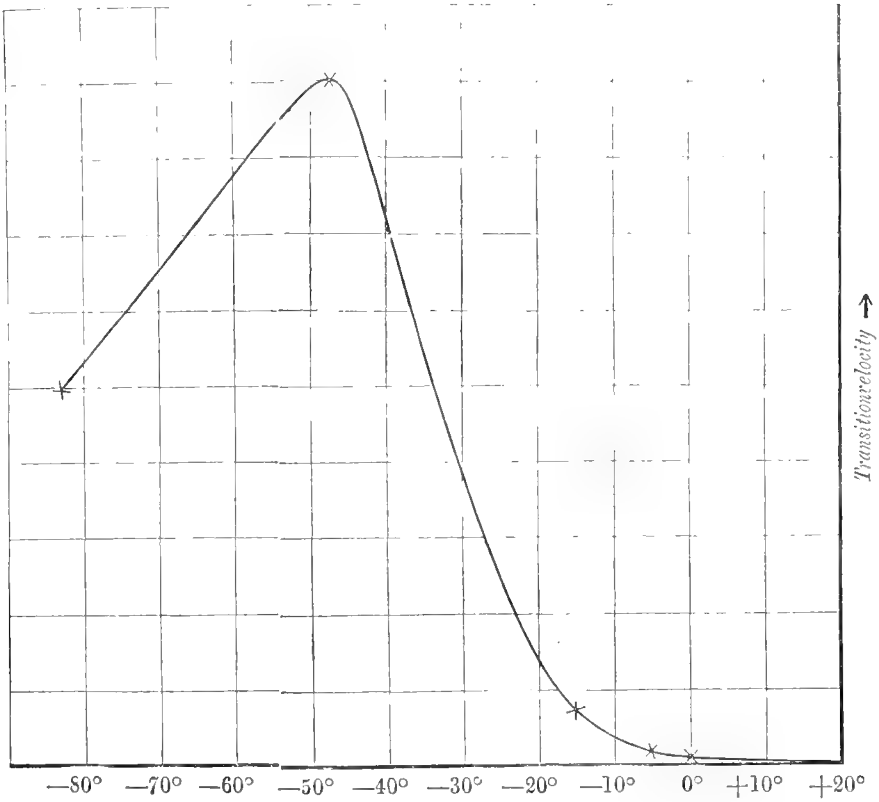
Temperature — 5° (Cryohydrate of $MgSO_4$).

Time in minutes	Height of the level of the liquid in the dilatometer (in mm.)	$\frac{\triangle h}{\triangle t}$	
0	82		Mean rise per minute 0.07 mm.
		0.07	
1200	167		

Temperature 0°.

Time in minutes	Height of the level of the liquid in the dilatometer (in mm.)	$\frac{\triangle h}{\triangle t}$	
0	186		Mean rise per minute 0.04 m.m.
		0.03	
1230	234		

The curve in the figure is obtained by means of these data, the velocities of transformation being taken as ordinates and the temperatures as abscissae.



This curve shows precisely the same course as that above mentioned. There is a maximum at about — 48°; this agrees well with the fact that we had received the impression that the change took place more slowly at — 83° than at a somewhat higher temperature.

If it is desired to convert common white tin into the grey modification a temperature should therefore be selected for the conversion, lying not far from — 48°.

3. So far our experiments had been made with grey tin received from Prof. HJELT of Helsingfors. This was Banca tin which had fallen to powder in a tin store in Helsingfors. The question arose whether the transformation was completely mastered, whether it would be possible to convert any piece of white tin completely into the grey modification.

Our researches in this direction have been crowned with success. We would here express our thanks to Mr. W. HOVY of Amsterdam, who permitted us to make use of one of the so called "evaporators" in his brewery; this is a reservoir through which a current of brine passes without interruption the temperature of which during our experiments varied between — 7° C. and — 4° C.

The result of the experiments is briefly as follows: (The tin employed was part of a block of Banca tin belonging to the collection of the laboratory).

a. Quite dry, white tin, in the form of a block, was converted into grey tin at the temperature mentioned. The process takes place slowly and begins at the edges.

b. Quite dry white tin, in the form of a block, in contact with traces of powdered grey tin, undergoes change more rapidly. The change begins at the places where the white tin is in contact with the grey tin.

c. White tin in the form of a block immersed in a solution of pink salt undergoes more rapid change than the combination *b.*

d. White block tin, immersed in a solution of pink salt and also in contact with traces of grey tin, is transformed more rapidly than *c.*

e. When the white tin is exposed to the low temperature in the form of filings the process takes place much more rapidly than when the tin is in coherent lumps. The velocities of change under the circumstances mentioned under *a*, *b*, *c* and *d* retain the same order as before.

4. Grey tin, therefore, behaves under all circumstances as if it was infectious. If the change is once started it goes on at higher temperatures (up to 20° C.). *It is thus necessary in these investigations to exercise caution and to take care that traces of grey tin are not imported into tin stores, where their presence might, as it were, give rise to a tin plague.* Grey tin and the finely divided white tin formed from it above 20° C. can hardly be fused together to a coherent mass, a part becoming useless owing to the violent oxidation which it undergoes in the finely divided state.

5. We have already converted large quantities of white tin into the grey modification. In order to attain this result quickly, 500 grams of tin filings were divided between several bottles and some grams of grey tin, which we possessed at the time, were added to the contents of each bottle. The solution of pink salt was also used in the transformation. At — 5° C. a hundred grams of grey tin were obtained in this way in eight days.

6. The destruction of the white tin due to the formation of the

grey modification is enormous. One of our tin blocks is entirely fissured and eaten away on the lower side whilst on the upper surface a number of grey protuberances are visible which gradually become greater finally developing into large cracks.

We shall shortly report on some physical constants of grey tin and on its crystalline form.

We shall be pleased to send a sample of grey tin to any one interested in the matter.

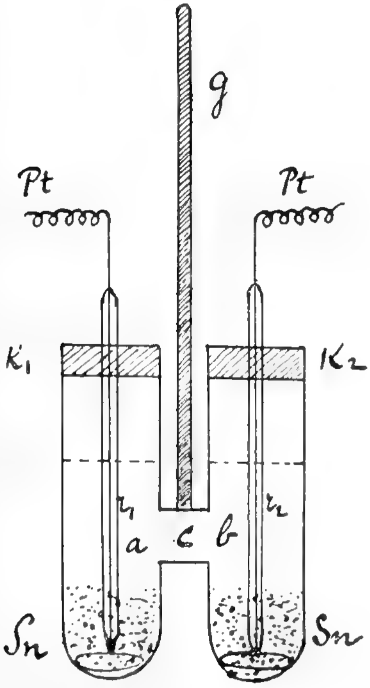
Amsterdam, Chemical Laboratory of the University,
September 1899.

Chemistry. — "*On a new kind of Transition Elements (sixth kind).*" By Dr. ERNST COHEN. (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

(Read in the next meeting of September 30th 1899.)

1. The name, sixth kind of transition element, will be applied to elements built up in accordance with the formula:

Electrode of a metal M in the modification α (stable modification).	Solution of a salt of the metal M.	Electrode of the metal M in the modification β (metastable modification).



Since, up to the present, no metal was known which, at suitable temperatures, occurs in two modifications, it was impossible to realise an element of this kind. As Dr. VAN EYK and I have shown [1]), the metal tin has a transition point at 20° C. Below this temperature the socalled grey tin is the stable form, above it the white.

Since the white modification may be considerably supercooled we may put together, below 20° C., an element (see Fig.) of the form

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[1]) Report of the session of June 24th, 1899, p. 36, and of this session, p. 149.

Electrode of grey tin.	Solution of a tin salt.	Electrode of white tin.

In the figure, a and b are glass tubes, 7 cm. long and $1\frac{1}{2}$ cm. wide united by the wide middle-piece c.

The grey modification of the tin is placed in a, the white in b. In contact with the powder in each tube is a platinum wire, r_1 and r_2, which is fused into a glass tube and bent into a ring at its lower end. An electrode made in this way has many advantages in practice [1]).

An aqueous solution of a tin salt is poured into a, b and c, and a and b are closed with corks, k_1 and k_2, which allow the wires r_1 and r_2 to pass. The whole element thus formed may be suspended in a thermostat by means of the glass rod g which is fused to it.

2. The theory of this element is easily given and offers, as will appear, many points of interest.

If an electrode of grey tin is placed in a dilute solution of a tin salt, in which the tin ions have an osmotic pressure p_1, the potential difference between the electrode and the solution at the temperature T is

$$E_1 = \frac{RT}{n\,\varepsilon_0}\,log.\,\frac{P_g}{p_1}\ ,$$

where n is the valency of the tin, ε_0 the number of coulombs attached to 1 gramion, P_g the electrolytic solution tension of the grey tin at the temperature T and R the gas constant.

If an electrode of white tin is now placed in the same solution we obtain

$$E_2 = \frac{RT}{n\,\varepsilon_0}\,log.\,\frac{P_w}{p_1}\ .$$

The E. M. F. of the transition element so obtained is then represented by the equation

$$E = E_1 - E_2 = \frac{RT}{n\,\varepsilon_0}\,log.\,\frac{P_g}{P_w}\ Volt = \frac{0.0001983}{n}\,log_{10}\frac{P_g}{P_w}\ Volts.\ \ .\qquad (I)$$

Since $\frac{0{,}0001983\ T}{n}$ is a constant at a given temperature we see

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[1]) See Richards and Lewis, Zeitschr. für phys. Chemie, Bd. 28, S. 1 (1899).

from this that the E. M. F. of the element is simply a function of the electrolytic solution tensions of the two modifications of tin.

The employment of the element described as a transition element depends on the fact that at the transition temperature the two modifications become identical, the grey modification being transformed into the white. In equation (I), P_g and P_w are then equal and $E = 0$.

In order to discover the transition point of the change

$$\text{grey tin} \rightleftarrows \text{white tin}$$

it is therefore only necessary to find the temperature at which $E = 0$. The application of this method is to be found in the communication which Dr. VAN EYK and I made some time ago on the Enantiotropy of tin [1]).

We can now go a step further and investigate the electrolytic solution tensions. We require the equations

$$E_1 = \frac{RT}{n\,\varepsilon_0} \, log. \frac{P_g}{p_1} \quad \text{and} \quad E_2 = \frac{RT}{n\,\varepsilon_0} \, log. \frac{P_w}{p_1} \; .$$

By placing an electrode of grey or of white tin in a dilute solution of a tin salt and combining it with a normal (Hg—HgCl—$^1/_{10}$N . KCl) electrode, E_1 and E_2 may be separately determined. If the dissociation of the tin solution is known, all the quantities required to calculate P_g and P_w are then known.

From the equations we obtain

$$P_g = p_1 \, . \, 10^{\frac{n\,E_1}{0.0001983T}} \quad \text{and} \quad P_w = p_1 \, . \, 10^{\frac{n\,E_2}{0.0001983T}}$$

4. In the first place an element was prepared with a sample of grey tin from Prof. HJELT of Helsingfors and the ratio $\frac{P_w}{P_g}$ determined at different temperatures.

Recently we have succeeded in converting ordinary Banca tin into the grey modification in any desired quantity [2]). The measurements here described are to be repeated with this material which is particularly pure and the results together with the details of manipulation will be described in a later communication.

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[1]) See note 1 on pag. 149.

[2]) See pag. 152.

Temperature.	Ratio $\frac{P_w}{P_g}$
5°	1,067
10°	1,043
15°	1,017
20°	1,000

The ratio is calculated by means of the equation

$$\frac{P_g}{P_w} = 10^{\frac{n\,E}{0.0001983T}} .$$

5. Below the transition temperature the modification which is metastable (the white) should have a greater solution tension than the grey ($P_w > P_g$). From this it follows that grey tin must be precipitated from tin solutions below 20° C. when white tin is brought in contact with them, just as copper is precipitated from a copper solution into which a zinc rod, for example, is dipped.

The metal with the greater solution tension goes into solution whilst that with the smaller is precipitated.

6. In our researches on the Enantiotropy of tin ¹) it was found that the conversion of white tin into the grey modification is highly favoured by the presence of traces of grey tin.

What has just been said about the solution tension of the two modifications explains the fact that the presence of a solution of a tin salt is also very favorable to the conversion of white tin into grey tin.

Below 20° C. grey tin is always precipitated from the solution of a tin salt by white tin; this process takes place, by analogy with what we know of other metals, very fast. In contrast to what so often happens with salt solutions, supersaturation does not occur.

If traces of grey tin are once present, they have a further accelerating action on the process. (According to experiment.)

7. We may now deduce another relationship which must exist between the displacement of the transition point of the reaction

$$\text{grey tin} \rightleftarrows \text{white tin}$$

with the external pressure exerted on the system and the temperature coefficients of our transition element.

For the grey tin electrode we have

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¹) See note on pag. 149.

$$E_1 = \frac{i_1}{n\,\varepsilon_0} + T\frac{d\,E_1}{dT} \quad \ldots\ldots\ldots\ldots \quad (1)$$

Here E_1 is the difference of potential, at the absolute temperature T, between the grey tin and the tin solution in which it is immersed, i_1 is the heat of ionisation of the grey tin, n the valency, and $\varepsilon_0 = 96540$ Coulombs.

For the white modification we have:

$$E_2 = \frac{i_1 + r}{n\,\varepsilon_0} + T\frac{d\,E_2}{dT} \quad \ldots\ldots\ldots\ldots \quad (2)$$

in which r represents the heat of transition.

From (1) and (2) we obtain, since $E_1 = E_2$ at the transition temperature,

$$\frac{i_1}{n\,\varepsilon_0} + T\frac{d\,E_1}{dT} = \frac{i_1 + r}{n\,\varepsilon_0} + T\frac{dE_2}{dT}$$

of

$$r = n\,\varepsilon_0\;T\left(\frac{dE_1}{dT} - \frac{dE_2}{dT}\right) \quad \ldots\ldots\ldots\ldots \quad (3)$$

Now we know that

$$T\,\frac{dD}{dT} = \frac{r_1}{V_w - V_g} \quad \ldots\ldots\ldots \quad (4)$$

where T is the absolute transition temperature, D the external pressure, r_1 the quantity of heat which is evolved when 1 kg. of white tin is converted into the grey modification, that is the heat of transition for 1 kg., and V_w and V_g are the volumes of 1 kg. of each modification in cubic metres. Since r in equation (3) relates to one gram atomic weight and r_1 in (4) to 1 kilogram, we have $r_1 = \frac{1000\,r}{A}$, where A is the atomic weight of the metal forming the electrode.

From (3) and (4)

$$\frac{dD}{dT} = \frac{1000}{A}\,\frac{n\,\varepsilon_0\left(\frac{dE_1}{dT} - \frac{dE_2}{dT}\right)}{V_w - V_g} \quad \ldots\ldots\ldots \quad (5)$$

The quantity to the right of the sign of equality is now expressed in Volt-Coulombs, or ergs × 10^7. If we wish to ascertain the change of the transition point produced by a change of pressure of 1 atmosphere, we may write (5) as follows:

$$\frac{dD}{dT}=\frac{n\,\varepsilon_0\left(\dfrac{dE_1}{dT}-\dfrac{dE_2}{dT}\right)}{101.4\,A\,(V_w-V_g)}$$

or :

$$\frac{dT}{dD}=\frac{101.4\,A\,(V_w-V_g)}{n\,\varepsilon_0\left(\dfrac{dE_1}{dT}-\dfrac{dE_2}{dT}\right)}=0{,}00105\,\frac{A\,(V_w-V_g)}{n\left(\dfrac{dE_1}{dT}-\dfrac{dE_2}{dT}\right)}\;.$$

The advantage of this equation, which so far as I am aware is deduced here for the first time, is, from the practical point of view, that it is possible to determine the displacement of the transition temperature by external pressure by means of electrical measurements, if the specific gravities of the two modifications forming the electrodes have been determined.

For the electrical determinations of the temperature coefficients of the two electrodes of the transition element in the neighbourhood of the transition point quite small quantities of the electrode material (1 or 2 grams) suffice, whilst for calorimetric determinations, which in the nature of things are less accurate, considerable quantities are required.

The result of the measurements will be communicated as soon as the specific gravity of the grey tin has been determined in a completely satisfactory way.

Amsterdam, Chem. Lab. of the University, September 1899.

Chemistry. — Prof. H. W. BAKHUIS ROOZEBOOM in presenting the dissertation of Dr. D. J. HISSINK: "*On mixed Crystals of Sodium nitrate with Potassium nitrate and of Sodium nitrate with Silver nitrate*", makes the following communication with respect to it.

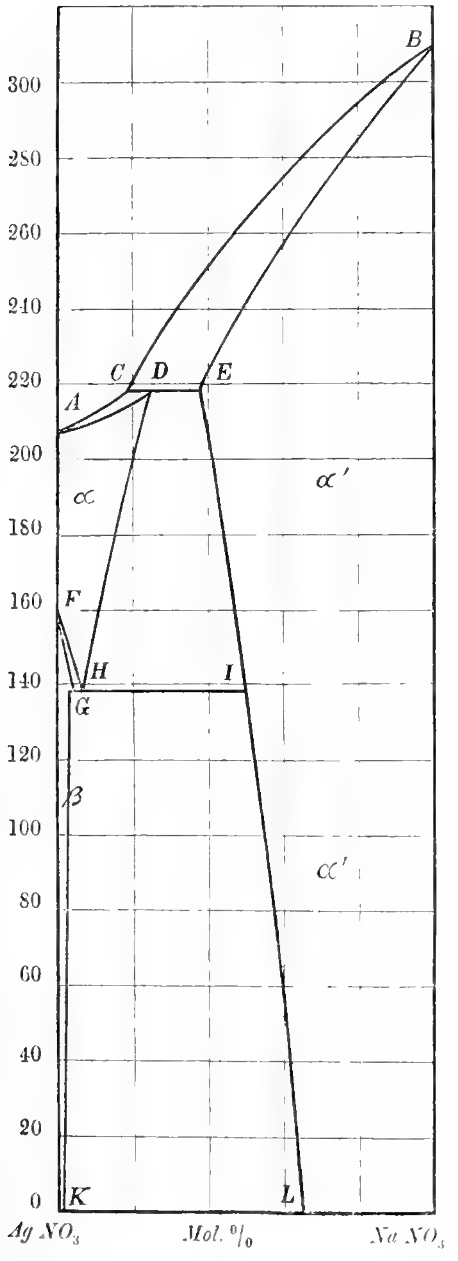
This research is a third contribution to our knowledge of the phenomena observed in the solidification of fused mixtures of two substances which form mixed crystals and in the transformation of the mixed crystals into another modification.

With respect to the system $KNO_3 + NaNO_3$ the fact is mentioned that mixed crystals are formed on solidification; the limits within which these can exist are, however, so narrow that it did not appear to be worth while to investigate the exact connection between the phenomena.

The solidification of the system $NaNO_3 + AgNO_3$ belongs to a type of which no example was known. The meltingpoint line rises continually from the meltingpoint of $AgNO_3$ (208,°6) to that of $NaNO_3$ (308°). It consists, however, of two branches, AC and CB, which join each other at an angle at 217,°2. Although all the mixed crystals are rhombohedral, the series of mixtures is discontinuous; at 217°2 there is a sudden transition from mixed crystals with 38 % (in molecules) $NaNO_3$ (*E*) to those with 26 % (*D*). The fused mass which is in equilibrium with both contains 19.5 % (in molecules) of $NaNO_3$ (*C*).

On cooling the following transformation takes place at 217°,

$$\text{Fused mass } C + \text{crystals } E \rightarrow \text{crystals } D.$$



This temperature possesses all the characteristics of a transition temperature.

The points on the lines *EB* and *AD* represent the compositions of the mixed crystals which are deposited from a liquid having the composition represented by points on the lines *CB* and *AC* corresponding to the same temperature.

Below *AD* a series of homogeneous mixed crystals containing from 0 to 26 % $NaNO_3$ exists, and below *EB* a similar series from 38—100 % $NaNO_3$.

The mixed crystals containing 26 and 38% which coexist at 217°, gradually change in composition as the temperature falls, in such a way that the limits between which no mixture exists become more widely separated, so that at 138° they are 4.2 and about 50 % $NaNO_3$ (*H* and *J*). The region within which homogeneous mixed crystals exist, becomes smaller and smaller.

Below 160° a change occurs in the series which is rich in silver, in consequence of which the rhombohedral crystals are converted into rhombic crystals. With pure silver nitrate this takes place at 160°, the addition of sodium nitrate depresses this temperature.

The limiting mixed crystal of the series which is rich in silver undergoes the change at 138°.

Below 138° only rhombic crystals, containing much silver, and rhombohedral crystals, containing much sodium, are capable of existence.

No transformation has been observed in the latter down to — 50°.

The limits of composition of the two kinds of crystals become more and more restricted as the temperature falls below 138°, so that at 15° they are 0—1,6 % (in molecules) $NaNO_3$ and 64.4—100 % $NaNO_3$.

The compositions of the coexisting limiting crystals were determined by allowing them to deposit beside each other from suitable solutions.

The transformation of the rhombohedral into rhombic crystals on the lines *FH* and *FG* was determined by means of an air dilatometer.

Chemistry. — By Prof. H. W. BAKHUIS ROOZEBOOM: "*The Nature of inactive Carvoxime.*"

In continuation of the investigations of Mr. ADRIANI on the phenomena of fusion and solidification of mixtures of optical antipodes, carvoxime has been examined. Samples of the *d*- and *l*-oximes were prepared for us through the kindness of Prof. GOLDSCHMIDT of Heidelberg.

Up to the present time the inactive carvoxime has been regarded as a racemic compound. This view rested on the facts that the melting point is higher than that of the active substances and that the density is greater (1.126 against 1.108).

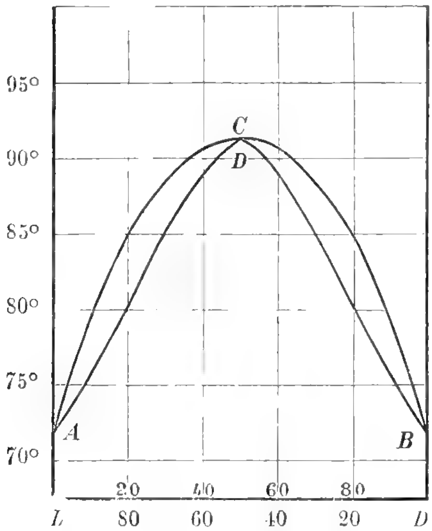
The investigation of the melting and solidifying points gave the following results.

Composition of the fused mass.	Commencement of solidification.	End of solidification.
100% *d* of *l*	72°	72°
99 " "	72°4	—
98 " "	73°0	—
95 " "	75°4	73°
90 " "	79°0	75°
80 " "	84°6	80°
75 " "	86°4	82°
70 " "	88°2	85°
60 " "	90°4	—
50 " "	91°4	91°.4

The results of these determinations are reproduced in the accompanying figure. The line *ACB* represents the beginning, *ADB* the end of the solidification. To begin with, it is to be remarked that, setting out from the end points, the first line *at once* rises on addition of the active compound of opposite sign.

There is therefore only one meltingpoint line and, consequently, the solid mass must consist of mixed crystals, and the inactive substance (50 pCt. *d* of *l*) is not a racemic compound but a pseudoracemic mixed crystal.

It were however conceivable that from *A* or *B* a small fall occurs, which escapes observation, because the rise begins at a very small concentration of the second oxime. If this were the case the inactive oxime would really be a racemic compound. The matter can, however, be readily decided. If it is a racemic compound the solidification of *all* mixtures, from 0 to 50 pCt. *d* or *l*, must terminate at the temperature of the eutectic point, which exists where the short falling lines from *A* and *B* meet the line of the racemic compound.



In our case therefore the solidification of all mixtures between 0 and 50 pCt. would have terminated just below 72°.

The final solidifying points, which were susceptible of very accurate observation, lie however on the line *ADB* and change continuously with the concentration.

For some concentrations the end point was determined by observing the course of the cooling as a function of the time in a bath at constant temperature. By this means the time, and therefore also the temperature, at which the solidification is complete may be observed with great accuracy.

The curve *ADB* confirms the view that mixed crystals are formed on solidification at all concentrations.

Thirdly it is supported by the analysis of crystals which were deposited from a fused mixture containing 20 pCt. of *l*-oxime. If the line *ACB* were the melting point line of a racemic compound, this compound would be deposited from the fused mass; if mixed crystals are formed they must have the composition given by the point on the line *DB*, which lies on the horizontal line drawn through the point on *CB* which corresponds to 20 pCt. of *l*-oxime.

The solid mass, weighing 0.69 gram, which was deposited from 7 grams of liquid, containing 21.7 pCt. of *l*-oxime, was found to contain 32 pCt. The composition of the solid was determined by polarisation and corrected for the adhering mother liquor. The quantity of the latter was determined by adding some $CH\,Br_3$ and determining the bromine in the liquid and in the drained crystals. The result agrees very well with the position of the line *DB* determined from the final solidification points.

Not only do we obtain thus a continuous series of mixed crystals on solidification, but we have here the first example of such a series with a maximum meltingpoint, which naturally lies at 50 pCt. In agreement with the theory the composition of the fused mass and of the mixed crystals is the same at this point and the interval of solidification therefore vanishes.

The opinion, which I expressed, that even in the case of mixed crystals of optical isomers the equality of melting points, looked for by KIPPING and POPE, does not necessarily exist, is confirmed by this example.

It is worthy of attention that the rule, that racemic compounds with a higher density than their active components also have a higher meltingpoint, appears to be applicable also to mixed crystals; always providing that the difference in density observed at the ordinary temperature still exists near the melting points. Probably this will remain, at least qualitatively, unchanged.

The possibility still exists that carvoxime forms mixed crystals on solidification, which change at lower temperatures wholly or partially into a racemic compound.

Between 10° and 90° however no indication of such a change could be found by means of the dilatometer with an inactive mixture.

That at lower temperatures the inactive oxime, obtained from solutions for example, is a mixed crystal and not a compound is supported by the great crystallographic similarity between the inactive and active crystals which BEYER has observed (Zeits. Krystall. 18, 296, 1890).

The density rule of RETGERS would, therefore, not hold good for this kind of mixed crystals.

Chemistry. — *"On Isomorphous Compounds of Gold and Mercury."* By Prof. TH. H. BEHRENS.

In his Manual of Microchemical Analysis the auther has pointed to analogies between thiocyanates of gold and mercury.

Renewed investigation of this subject has shown, that the isomorphism of these double thiocyanates cannot be fully established by means of compound crystals. Halogen compounds have then been tried, and from these complete series of compound crystals have been obtained. They were prepared by adding to mixed solutions of the chlorides and bromides of gold and mercury chlorides or bromides of thallium, caesium and rubidium. Thallous compounds act promptly; the compound crystals are interspersed with flakes of trichloride or tribromide of thallium. The action of caesium and rubidium compounds is slower and less energetic. It can be hastened and furthered by adding about one tenth part of alcohol. This takes up one third of the halogen, that was combined with gold (shown by a change of colour in the solution of bromides) while gold dichloride or — dibromide is fixed in the compound crystals along with dichloride or dibromide of mercury. If no alcohol is added the halogen, split off from the gold trihaloid must form trihaloid of caesium or rubidium, which is also readily attacked by hydrolysis.

Finally it may be mentioned, that the compound crystals of bromides will be found useful in testing for gold. With caesium the solubility is small, and the yellow colour of the crystals is seen without difficulty with a proportion of one part of gold to fifty parts of mercury.

Physics. — Prof. J. D. VAN DER WAALS presents on behalf of Dr. G. BAKKER of Schiedam a paper on: *"A remark on the Molecular Potential Function of* Prof. VAN DER WAALS."

In his „Thermodynamische Theorie der Capillariteit in de onderstelling van continue dichtheidsverandering" Prof. VAN DER WAALS finds for the potential of two material points at a distance r the expression

$$P = C - f\frac{e^{-\frac{r}{\lambda}}}{r}$$

in which C, f and λ represent the constants.

Some time later[1]) Prof. van der Waals pointed out a remarkable property of that function. He found that if a coefficient depending on the radius, is left out of account, in consequence of this function the potential of a homogeneous sphere for an exterior point is determined by the distance between the point and the centre of the sphere in the same way as if the whole mass were concentrated in the centre.

On account of the great importance, practical as well as theoretical, of such a function for a theory of gases and liquids, which assumes spherical molecules (by which the potential energy might be determined in a simple way by the configuration of the centres of the molecules), I examined the question whether there are more potential functions, which possess this property. As a solution I found the general function:

$$\varphi(r) = \frac{A\,e^{-qr}}{r} + \frac{B\,e^{qr}}{r} + C \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which A and B are arbitrary positive and negative constants. For a spherical shell the coefficient depends on the radius in the following manner:

$$F(R) = \frac{e^{qR} - e^{-qR}}{2\,q\,R} \ .$$

If however, we restrict ourselves to *attractive* forces, which decrease according to the distance, the *most general* function is that of van der Waals, viz:

$$\varphi(r) = C - \frac{f\,e^{-qr}}{r} \ .$$

If for this potential function a spherical (homogeneous) mass assumes this property, it will also be the case for a spherical shell and *vice versa*.

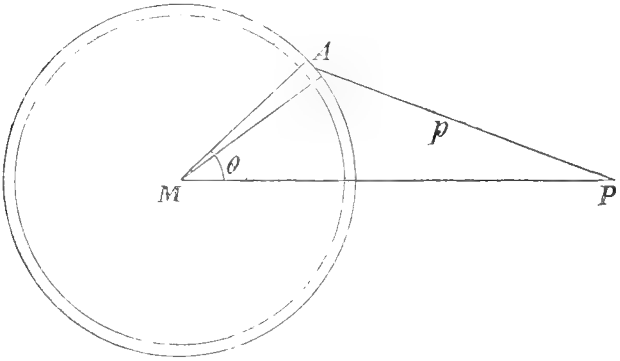


Fig. 1.

Let R be the radius of a spherical shell which is thought infinitely thin, P the point on which the shell acts, dR the thickness and M the centre of the shell.

Let us imagine a cone with an infinitely small aperture

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[1]) See "Zeitschrift für physikalische Chemie", XIII, 4, Seite 720, 1894.

$d\omega$, of which M is the vertex, then this cone will cut from the shell a volume $R^2\,dR\,d\omega$. If ϱ is the density, the mass of the element in A is: $R^2\,dR\,d\omega\,\varrho$. If $\varphi(r)$ represents the form of the potential function, the potential energy of a unity of mass in P in consequence of the element in A is: $R^2\,dR\,d\omega\,\varrho\,\varphi(p)$, p representing the distance between A and P.

If we turn the figure round MP as axis, the element in A describes an annular space, so that $\int d\omega = 2\pi \sin \theta\, d\theta$; θ representing $\angle AMP$. In consequence of the annular space the potential energy in P is:

$$2\pi R^2\,dR \sin\theta\, d\theta\,\varrho\,\varphi(p) = -2\pi R^2\,dR\,d\cos\theta\,\varrho\,\varphi(p)\ .$$

Now $p^2 = R^2 + r^2 - 2Rr\cos\theta$, in which $r = MP$, so

$$2p\,dp = -2Rr\,d\cos\theta\ .$$

The expression for the potential energy becomes therefore:

$$\varrho\,\frac{2\pi R^2\,dR}{Rr}\,p\,dp\,\varphi(p)$$

or because $4\pi R^2\,dR\,\varrho$ represents the mass of the shell:

$$\frac{1}{2}\,\frac{M}{Rr}\,p\,\varphi(p)\,dp\ .$$

The integration over the whole of the shell gives:

$$\frac{1}{2}\,\frac{M}{Rr}\int_{r-R}^{r+R} p\,\varphi(p)\,dp\ .$$

If F(R) represents the before mentioned coefficient and $F(R)$ a function of R which is also to be determined, we may write:

$$\frac{1}{2}\,\frac{M}{Rr}\int_{r-R}^{r+R} p\,\varphi(p)\,dp = \mathrm{F}(R)\,M\,\varphi(r) + F(R)\,M\ ,$$

If we leave an *absolute constant* out of account, this equation furnishes the potential function, belonging to a force acting in the required manner.

Let us put:

$$\int_{r-R}^{r+R} p\,\varphi(p)\,dp = 2\,Rr\,\mathrm{F}(R)\,\varphi(r) + 2\,Rr\,F(R) \quad . \quad . \quad . \quad (a)$$

If we differentiate this identity twice with respect to r and also twice with respect to R, and put $\int r\,\varphi(r)\,dr = \psi(r)$, we get:

$$\psi''(r+R) - \psi''(r-R) = 4\,R\,\mathrm{F}(R)\,\varphi'(r) + 2\,Rr\,F(R)\,\varphi''(r)$$

and

$$\begin{aligned}\psi''(r+R) - \psi''(r-R) = 4\,r\,\varphi(r)\,\mathrm{F}'(R) + 2\,Rr\,\varphi(r)\,\mathrm{F}''(R) + \\ + 4\,r\,F'(R) + 2\,Rr\,F''(R)\,.\end{aligned}$$

The left side members of these equations are the same, so also

$$\begin{aligned}2\,R\,\mathrm{F}(R)\,\varphi'(r) + Rr\,\mathrm{F}(R)\,\varphi''(r) = 2\,r\,\varphi(r)\,\mathrm{F}'(R) + \\ + Rr\,\varphi(r)\,\mathrm{F}''(R) + 2\,r\,F'(R) + Rr\,F''(R)\end{aligned}$$

or

$$\frac{2\,\varphi'(r) + r\,\varphi''(r)}{r\,\varphi(r)} = \frac{2\,\mathrm{F}'(R) + R\,\mathrm{F}''(R)}{R\,\mathrm{F}(R)} + \frac{1}{\varphi(r)}\;\frac{2\,F'(R) + R\,F''(R)}{R\,\mathrm{F}(R)}\,.$$

R and r not being dependent on each other, we get separately

1 . . . . $\dfrac{2\,\mathrm{F}'(R) + R\,\mathrm{F}''(R)}{R\,\mathrm{F}(R)} = C_1$, in which C_1 is an absolute constant

2 . . . . $\dfrac{2\,F'(R) + R\,F''(R)}{R\,\mathrm{F}(R)} = C_2$ also absolutely constant

and 3 . . . . $\dfrac{2\,\varphi'(r) + r\,\varphi''(r)}{r\,\varphi(r)} = C_1 + \dfrac{C_2}{\varphi(r)}$.

The solution of equation 3 will furnish the general form for the required potential function.

If we write $r = x$ and $\varphi(r) = y$, the last equation becomes

$$\frac{d^2y}{dx^2} + \frac{2}{x}\,\frac{dy}{dx} - C_1\,y = C_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

or

$$x\,\frac{d^2y}{dx^2} + 2\,\frac{dy}{dx} = C_1\,xy + C_2\,x$$

or

$$\frac{d^2\left(xy + \dfrac{C_2}{C_1}\,x\right)}{dx^2} - C_1\left(xy + \frac{C_2}{C_1}\,x\right) = 0\,.$$

This equation has, according to C_1 being positive or negative, the solutions:

$$xy + \frac{C_2}{C_1} x = Ae^{-x\sqrt{C_1}} + Be^{x\sqrt{C_1}}$$

or

$$xy + \frac{C_2}{C_1} x = A_1 \sin (x\sqrt{-C_1} + \alpha)$$

in which A, B, A_1 and α are arbitrary constants.

The potential function becomes therefore:

$$\varphi(r) = \frac{Ae^{-r\sqrt{C_1}} + Be^{r\sqrt{C_1}}}{r} - \frac{C_2}{C_1} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

or

$$\varphi(r) = \frac{A_1 \sin (r\sqrt{-C_1} + \alpha)}{r} - \frac{C_2}{C_1} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

If we put $C_1 = q^2$ in the first case and $C_1 = -q^2$ in the second case, the potential functions become:

$$\varphi(r) = \frac{Ae^{-qr} + Be^{qr}}{r} - \frac{C_2}{q^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5a)$$

or

$$\varphi(r) = \frac{A_1 \sin (qr + \alpha)}{r} - \frac{C_2}{q^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6a)$$

If we restrict ourselves to functions which relate to forces as they occur in nature, the second potential function must be excluded, and according to an above mentioned remark, the most general expression becomes:

$$\varphi(r) = \frac{Ae^{-qr} + Be^{qr}}{r} - \frac{C_2}{q^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5b)$$

The factor $F(R)$ is determined by equation 1. This equation becomes identical with equation 4, if we put $C_2=0$. The general solution becomes therefore:

$$F(R) = \frac{Me^{qR} + Ne^{-qR}}{R} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

According to equation (2) the following equation holds good for function $F(R)$:

$$2\,F'(R) + R\,F''(R) = C_2\left(Me^{qR} + Ne^{-qR}\right)$$

We find easily:

$$R\,F(R) = \frac{C_2}{q^2}\left(Me^{qR} + Ne^{-qR}\right) + E\,R + D \quad . \quad . \quad . \quad (8)$$

in which E and D represent constants.

If in equation a we substitute the expressions we have found, for $\varphi(r)$, $\mathrm{F}(R)$ and $F(R)$, we find the relations which must exist between the constants. We shall easily find:

$$M = \frac{1}{2q} \qquad N = -\frac{1}{2q}$$

Therefore

$$\varphi(r) = \frac{Ae^{-qr} + Be^{qr}}{r} - \frac{C_2}{q^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

and

$$\mathrm{F}(R) = \frac{e^{qR} - e^{-qR}}{2\,qR} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

The potential for a spherical shell in point P (see fig. 1), becomes therefore [1]:

$$M\,\mathrm{F}(R)\,\varphi(r) = M\,\frac{e^{qR} - e^{-qR}}{2\,qR} \times \frac{Ae^{-qr} + Be^{qr}}{r}$$

If ϱ is the density, then $4\,\pi\,R^2\,d\,R\,\varrho = M$. For the whole sphere we get therefore for the potential in an outside point:

$$4\,\pi\,\varrho\,\varphi(r)\int_0^R \mathrm{F}(R)\,R^2\,d\,R = 4\,\pi\,\varrho\,\frac{Ae^{-qr} + B\,e^{qr}}{2\,qr}\int_0^R R\left(e^{qR} - e^{-qR}\right)dR =$$

$$= 2\,\pi\,\varrho\,\frac{Ae^{-qr} + Be^{qr}}{qr}\left\{\frac{1}{q}\left(R - \frac{1}{q}\right)e^{qR} + \frac{1}{q}\left(R + \frac{1}{q}\right)e^{-qR}\right\}$$

---

[1] We put the constant of the potential function $= 0$.

or, if we substitute λ for $\frac{1}{q}$:

$$2\pi\varrho\lambda^2 \frac{Ae^{-\frac{r}{\lambda}} + Be^{\frac{r}{\lambda}}}{r} \left\{ (R-\lambda)\,e^{\frac{R}{\lambda}} + (R+\lambda)\,e^{-\frac{R}{\lambda}} \right\}.$$

Starting from the function $\varphi(r) = -f\frac{e^{-\frac{r}{\lambda}}}{r}$: (Thermodynamische Theorie der Kapillar. Zeitschrift für phys. Chem. XIII, 4, 1894 p. 721) Prof. VAN DER WAALS finds:

$$P = -2\pi f\varrho\lambda^2 \frac{e^{-\frac{r}{\lambda}}}{r} \left\{ (R-\lambda)\,e^{\frac{R}{\lambda}} + (R+\lambda)\,e^{-\frac{R}{\lambda}} \right\}.$$

The coefficient is the same as in the more general form of the potential function. If we take the more general expression $\varphi(r) = \frac{Ae^{-\frac{r}{\lambda}} + Be^{\frac{r}{\lambda}}}{r}$ for $B = 0$ and $A = -f$, we get the function of VAN DER WAALS.

The theory of capillarity requires forces, which decrease with the distance and are attractive. The latter condition furnishes:

$$-\varphi'(r) \text{ negative or } \varphi'(r) \text{ positive.}$$

We have:

$$\varphi'(r) = -\frac{Ae^{-\frac{r}{\lambda}} + Be^{\frac{r}{\lambda}}}{r^2} + \frac{-Ae^{-\frac{r}{\lambda}} + Be^{\frac{r}{\lambda}}}{\lambda r}$$

So:

$$Ae^{-\frac{r}{\lambda}}\left(1 + \frac{r}{\lambda}\right) < Be^{\frac{r}{\lambda}}\left(-1 + \frac{r}{\lambda}\right)$$

for all positive values of r.

If we take $r = \lambda$, we get:

$$\frac{2A}{e} < Be \times 0$$

from which follows that A must be negative. Put $A = -f$, in which f represents a positive value, the last inequality but one becomes:

$$-fe^{-\frac{r}{\lambda}}\left(1 + \frac{r}{\lambda}\right) < Be^{\frac{r}{\lambda}}\left(\frac{r}{\lambda} - 1\right)$$

or

$$-f\,\frac{\dfrac{1}{r}+\dfrac{1}{\lambda}}{\dfrac{1}{r}+\dfrac{1}{\lambda}+\dfrac{1}{1.2}\,\dfrac{r}{\lambda^2}+\dfrac{1}{1.2.3}\,\dfrac{r^2}{\lambda^3}+\ldots} < Be^{\frac{r}{\lambda}}\left(\frac{r}{\lambda}-1\right)$$

For always increasing values of r, the left hand member tends to zero and the coefficient of B becomes infinite. Therefore (symbolically):

$$-0 < B \times \infty$$

So B cannot be negative.

The former condition furnishes:

$$\frac{d\,\varphi'(r)}{dr} < 0$$

$$\frac{-2fe^{-\frac{r}{\lambda}}+2Be^{\frac{r}{\lambda}}}{r^3}-\frac{fe^{-\frac{r}{\lambda}}+Be^{\frac{r}{\lambda}}}{\lambda r^2}-\frac{fe^{-\frac{r}{\lambda}}+Be^{\frac{r}{\lambda}}}{\lambda r^2}+\frac{-fe^{-\frac{r}{\lambda}}+Be^{\frac{r}{\lambda}}}{\lambda^2 r} < 0$$

or

$$B\left\{\lambda^2+(\lambda-r)^2\right\}e^{\frac{r}{\lambda}} < f\left\{\lambda^2+(\lambda+r)^2\right\}e^{-\frac{r}{\lambda}}$$

(A is replaced by $-f$).

If r is always more increased, the left hand member becomes infinite, whereas the right hand member decreases infinitely.

Therefore symbolically

$$B \times +\infty < f \times +0.$$

So B cannot be positive.

As therefore B can be neither negative nor positive, B must be 0.

The function of VAN DER WAALS is the most general function which fulfils the conditions of the theory of capillarity and possesses the above mentioned property.

In answer to a letter on the subject discussed here, Prof. VAN DER WAALS and Prof. KORTEWEG were so kind to draw my attention to the work of Dr. C. NEUMANN: „Allgemeine Untersuchungen über das NEWTON'sche Princip der Fernwirkungen mit besonderer Rücksicht auf die elektrischen Wirkungen" Leipzig B. G. TEUBNER, 1896.

The principal problem, discussed by the author is as follows: What must be the form of the potential function of electric agens, spread over different conductors, in order to make an electrostatic equilibrium possible. (The possibility of such an equilibrium is considered as an axiom).

Dr. NEUMANN finds as the most general potential function:

$$\varphi(r) = \frac{Ae^{-\alpha r}}{r} + \frac{Be^{-\beta r}}{r} + \frac{Ce^{-\gamma r}}{r} + \ldots$$

α, β, γ . . . A, B and C are unknown positive and negative quantities.

After this the conditions are inquired into, which these quantities must fulfil, in order to make an equilibrium possible. The result may be expressed in this thesis:

„Es sei gegeben irgend ein System von Conductoren und Isolatoren. Jeder Isolator sei mit einer *festen* electrischen Vertheilung in seinem Innern, und zugleich mit einer *festen* electrischen Belegung an seiner Oberfläche versehen. Andererseits sei jeder Conductor entweder zur Erde abgeleitet, oder aber isolirt und mit einer gegebenen Elektricitätsmenge geladen.

Alsdann wird für dieses System, unter Zugrundelegung der Potentialfunction:

$$\varphi(r) = \frac{Ae^{-\alpha r}}{r} + \frac{Be^{-\beta r}}{r} + \frac{Ce^{-\gamma r}}{r} + \ldots .$$

stets ein elektrischer Gleichgewichtszustand existiren, falls nur die Constanten α, β, γ . . . alle *positiv*, und die Constanten A, B, C . . . alle von *einerlei* Vorzeichen sind.

Zu diesen Bedingungen wird offenbar für den besondern Fall, dass die Reihe ins Unendliche fortschreitet, noch die hinzuzufügen sein, dass die Reihe convergirt, sowie auch die, dass Integral

$$\int \varphi(r)\, \varepsilon\, d\tau$$

$\{\varepsilon =$ cubic density and $d\tau =$ element of volume$\}$

einen bestimmten Sinn habe.

In that particular case that we restrict ourselves to the first term, and so assume as potential the form $\varphi(r) = \frac{Ae^{-\alpha r}}{r}$ — the function is simply the potential function of VAN DER WAALS $\left(A = -f \text{ and } \alpha = \frac{1}{\lambda}\right)$.

For this case Dr. NEUMANN points out the property which Prof. VAN DER WAALS has also found for his potential function. (Zeitschrift für phys. Chemie XIII, 4, 1894, p. 721). He states his thesis as follows:

Die Einwirkung einer homogenen materiellen Kugelfläche auf *äussere* Punkte wird, bei Zugrundelegung des Gesetzes:

$$\varphi(r) = \frac{Ae^{-\alpha r}}{r}$$

genau dieselbe sein, als rührte sie her von einem einzigen im Centrum der Fläche befindlichen materiellen Punkt.

Und zwar hat die Masse M dieses der gegebenen Fläche äquivalenten materiellen Punktes den Werth:

$$\mathrm{M} = M \frac{e^{\alpha R} - e^{-\alpha R}}{2 \alpha R} = M \left(1 - \frac{(\alpha R)^2}{\pi 3} + \frac{(\alpha R)^4}{\pi 5} + \ldots\right)^{1)}$$

wo M die Gesammtmasse der gegebenen Fläche, und R den Radius derselben bezeichnet. Es ist mithin:

$$\mathrm{M} \geqq M$$

und zwar wird der Fall $\mathrm{M} = M$ nur dann eintreten, wenn die Constante α des Gesetzes $\varphi(r) = \frac{Ae^{-\alpha r}}{r}$ verschwindet, jenes Gesetz also in das NEWTON'sche Gesetz sich verwandelt.

Moreover the remark is made, that if as potential the general function

$$\varphi(r) = \frac{A\, e^{-\alpha r}}{r} + \frac{B\, e^{-\beta r}}{r} + \frac{C\, e^{-\gamma r}}{r} +$$

is taken, also in this case a homogeneous spherical shell acts on an exterior point, as if the mass:

$$\mathrm{M} = M \left\{ \frac{e^{\alpha R} - e^{-\alpha R}}{2 \alpha R} + \frac{e^{\beta R} - e^{-\beta R}}{2 \beta R} + \ldots \ldots \right\}$$

were concentrated in the centre.

---

1) $\pi(n) = 1.2.3 \ldots n$ = Function of GAUSS.

I must, however, point out that this thesis is not of the same nature as that proved by Prof. VAN DER WAALS for the function $\varphi(r) = \frac{Ae^{-\alpha r}}{r}$. In this case namely we must be able to find the potential in the point in question by a simple multiplication of the potential function with a coëfficient, depending on the radius of the shell. This is not the case with the general function.

Every *term* of the function $\varphi(r)$ must be multiplied with the corresponding coefficient, to get the total potential. So it remains a superposition of different potentials.

The problem which I have treated: what must be the form of the potential function, by which a spherical shell acts on exterior points, as if (leaving a coefficient out of account), the mass was concentrated in the centre, was not discussed.

The second problem which I have tried to solve, is this. Is there a potential function which possesses the property just mentioned, while it is constant for a point inside the shell.

For the potential of a sperical shell at an exterior point we have found:

$$\frac{1}{2}\,\frac{M}{Rr}\int_{r-R}^{r+R} p\,\varphi(p)\,dp \qquad \varphi = \text{potential function.}$$

For an interior point we should have got:

$$\frac{1}{2}\,\frac{M}{Rr}\int_{R-r}^{R+r} p\,\varphi(p)\,dp\ .$$

If we put $\int r\,\varphi(r)\,dr = \psi(r)$, we get

$$\mathrm{V} = \frac{M}{2\,Rr}\left\{\psi(R+r) - \psi(R-r)\right\}.$$

The general form for the potential function, fulfilling the first condition was:

$$\varphi(r) = \frac{A\,e^{\;\;qr}}{r} + \frac{B\,e^{qr}}{r} + C\ .$$

A, B, C and q are arbitrary constants. The mass-coefficient depends only on q. Now the question is: is it possible to choose those constants in such a way that the potential of a spherical shell with a radius R becomes constant for points inside the shell?

$$\psi(r) = \int r\,\varphi(r)\,dr = \int (A\,e^{-qr} + B\,e^{qr} + Cr)\,dr =$$

$$= -\frac{A}{q}e^{-qr} + \frac{B}{q}e^{qr} + \frac{1}{2}Cr^2 .$$

So

$$V = \frac{M}{2\,Rr}\Big\{ -\frac{A}{q}e^{-q(R+r)} + \frac{B}{q}e^{q(R+r)} + \frac{1}{2}C(R+r)^2 +$$

$$+ \frac{A}{q}e^{-q(R-r)} - \frac{B}{q}e^{-q(R-r)} - \frac{1}{2}C(R-r)^2 \Big\} .$$

The expression must now depend on r. It is easy to see that we have only to take $A = f\,e^{qR}$ and $B = -f\,e^{-qR}$, to get (f = constant):

$$V = \frac{M}{2\,Rr}\Big\{ -\frac{f}{q}e^{-qr} - \frac{f}{q}e^{qr} + \frac{f}{q}e^{qr} + \frac{f}{q}e^{-qr} + 2\,C\,Rr \Big\} = M \,.\, C$$

in which we have also fulfilled the second condition.

The potential function becomes therefore:

$$\varphi(r) = f\,e^{qR}\frac{e^{-qr}}{r} - f\,e^{-qR}\frac{e^{qr}}{r} + C .$$

Considered superficially we now get in contradiction with the theorem of LAPLACE, which states that the law of NEWTON is the only law which fulfils the condition, that the spherical shell exercises no force on a point inside it. In reality this theorem includes more. The function of forces must namely keep this property without change of the constant, whatever the radius of a spherical shell may be. However in the case discussed by us the radius of the shell is given and in the potential we have therefore introduced constants depending on the radius of the shell.

As solution of equation (4) we found two integrals. If we had substituted function (6a) in equation a and if, in the same way as before, we had sought the conditions which the different coefficients must fulfil, we should have found that $C = 0$ and further

$$F(R) = \frac{\sin q\,R}{q\,R} .$$

The potential of a spherical shell in point P becomes therefore:

$$M\,\frac{\sin q\,R}{q\,R}\;\frac{A_1\sin(qr+\alpha)}{r}$$ 1) .

Though the function $\frac{A_1\sin(qr+\alpha)}{r}$ is of no importance for the theory of the molecular forces, it has nevertheless another remarkable physical signification.

By twice differentiating with respect to x, we shall easily find:

$$\frac{d^2\varphi}{dx^2}=-\frac{A_1\sin(qr+\alpha)}{r^3}+\frac{3\,A_1\sin(qr+\alpha)\,x^2}{r^5}-\frac{3A_1\,q\cos(qr+\alpha)x^2}{r^4}+$$

$$+\frac{A_1\,q\cos(qr+\alpha)}{r^2}-\frac{A_1\,q^2\sin(qr+\alpha)\,x^2}{r^3}\,.$$

In the same way we find for $\frac{d^2\varphi}{dy^2}$ and $\frac{d^2\varphi}{dz^2}$ corresponding expressions. By adding these equations, we get:

$$\nabla^2\varphi=-\frac{A_1\,q^2\sin(qr+\alpha)}{r}=-q^2\varphi\,.\quad .\quad .\quad .\quad (11)$$

As is well known this differential equation is of great importance in the theory of the conduction of heat. The function found is an extension of the caloric potential of MATHIEU.

If we had deduced for the first found function $\varphi(r)=\frac{A\,e^{-qr}+B\,e^{qr}}{r}$ the second differential coefficient according to x, we should have found:

$$\frac{d^2\varphi}{dx^2}=-\frac{A\,e^{-qr}+B\,e^{qr}}{r^3}+\frac{3\,q(Ae^{-qr}-Be^{qr})x^2}{r^4}+\frac{3\,(A\,e^{-qr}+B\,e^{qr})\,x^2}{r^5}-$$

$$-\frac{q\,(A\,e^{-qr}-B\,e^{qr})}{r^2}+\frac{q^2\,(A\,e^{-qr}+B\,e^{qr})\,x^2}{r^3}\,.$$

If we calculate in the same way the corresponding expressions for $\frac{d^2\varphi}{dy^2}$ and $\frac{d^2\varphi}{dz^2}$, we find by putting the three quantities together:

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1) In putting $q=0$ we refind the potential which we should have found according to the law of attraction of NEWTON.

$$\nabla^2 \varphi = q^2 \frac{A\,e^{-qr} + B\,e^{qr}}{r} = q^2 \varphi \quad . \quad . \quad . \quad . \quad . \qquad (12)$$

In the particular case that $A = -\frac{1}{2q}$ and $B = \frac{1}{2q}$, the relation between the two equations (11) and (12) is evident. The function $\varphi(r) = \frac{A\,e^{-qr} + B\,e^{qr}}{r}$ becomes: $\frac{e^{qr} - e^{-qr}}{2\,qr}$. If we substitute $q\sqrt{-1}$ for q, the latter expression becomes:

$$\frac{e^{qr\sqrt{-1}} - e^{-qr\sqrt{-1}}}{2\,qr\sqrt{-1}} = \frac{\sin qr}{qr} \,.$$

This function is a special case of the more general

$$\varphi(r) = \frac{A_1 \sin(qr + \alpha)}{r} \,. \quad A_1 = \frac{1}{q} \quad \text{and} \quad \alpha = 0 \,.$$

By substituting in equation (12) $q\sqrt{-1}$ for q, we get equation (11). If $q = 0$ the two equations yield the well known equation:

$$\nabla^2 = 0 \,.$$

The functions

$$\varphi(r) = \frac{A\,e^{-qr} + B\,e^{qr}}{r} \quad \text{and} \quad \varphi(r) = \frac{A_1 \sin(qr + \alpha)}{r}$$

are solutions of two *different* partial differential equations of the 2nd order, but we have seen that they are also common solutions of the *same* problem.

We might also have deduced the partial differential equation (12) in the following way:

$$\frac{A\,e^{-ar}}{r} = \frac{A}{r}\left(1 - qr + \frac{q^2\,r^2}{\pi\,2} - \frac{q^3\,r^3}{\pi\,3} + \,.\,.\right) =$$

$$= \frac{A}{r} - Aq + \frac{A\,q^2 r}{\pi 2} - \frac{A\,q^3 r^2}{\pi 3} + \,.\,.$$

and

$$\frac{B\,e^{qr}}{r} = \frac{B}{r}\left(1 + qr - \frac{q^2\,r^3}{\pi\,2} + \frac{q^3\,r^3}{\pi\,3} + \,.\,.\right) =$$

$$= \frac{B}{r} + Bq + \frac{B\,q^2 r}{\pi 2} + \frac{B\,q^3 r^2}{\pi 3} + \,.\,.$$

So:

$$\frac{Ae^{-qr}+Be^{qr}}{r}-\frac{A+B}{r}=q(B-A)+\frac{(A+B)q^2r}{\pi\, 2}+\frac{(B-A)\,q^3r^2}{\pi\, 3}+\ldots$$

If we apply to the two members of this equation the operation ∇^2, we find

$$\nabla^2\left\{\frac{Ae^{-qr}+Be^{qr}}{r}\right\}=q^2\left\{\frac{A+B}{r}+(B-A)\,q+\frac{(A+B)\,q^2\,r}{\pi\, 2}+\right\}=$$

$$=q^2\,\frac{Ae^{-qr}+Be^{qr}}{r}$$

In the same way equation (11) may also be deduced.

On the other hand, if $x^2+y^2+z^2=r^2$, it is possible to show that the solutions of the differential equations $\nabla^2\,\varphi=\pm\,q^2\,\varphi$, give exactly those functions that possess the property found by Prof. VAN DER WAALS for the potential function $-f\,\frac{e^{-qr}}{r}$. We have, viz:

$$\frac{d\varphi}{dx}=\frac{d\varphi}{dr}\,\frac{dr}{dx}\qquad\frac{d^2\varphi}{dx^2}=\frac{d^2\varphi}{dr^2}\left(\frac{dr}{dx}\right)^2+\frac{d\varphi}{dr}\,\frac{d^2r}{dx^2}$$

and because $r^2=x^2+y^2+z^2$:

$$\frac{dr}{dx}=\frac{r}{r}\qquad\frac{d^2x}{dx^2}=\frac{1}{r}-\frac{x^2}{r^3}$$

therefore

$$\frac{d^2\varphi}{dx^2}=\frac{d^2\varphi}{dr^2}\,\frac{x^2}{r^2}+\frac{d\varphi}{dr}\left(\frac{1}{r}-\frac{x^2}{r^3}\right)$$

If we deduce the expressions for $\frac{d^2\varphi}{dy^2}$ and $\frac{d^2\varphi}{dz^2}$ in the same way, we find by addition:

$$\frac{d^2\varphi}{dr^2}+\frac{2}{r}\,\frac{d\varphi}{dr}=0\ .$$

The differential equations $\nabla^2\,\varphi=\pm\,q^2\,\varphi$ may therefore be written in the following way:

$$\frac{d^2\varphi}{dr^2}+\frac{2}{r}\,\frac{d\varphi}{dr}=\pm\,q^2\,\varphi\quad\ldots\ldots\ldots\quad(13)$$

We get these equations, when for C_1 we substitute $+q^2$ and $-q^2$ respectively in equation (4) and when we put $C_2 = 0$, and this proves that the solutions of (13) fulfil the condition in question.

In a further paper I hope to prove the two following theorems:

I. If in a region of space ϱ and v are functions of x, y and z, and v satisfies the three following conditions:

1st v and its differential coefficients with respect to x, y and z are everywhere continuous;

2nd with the exception of some points or surfaces in this space

$$\frac{d^2v}{dx^2} + \frac{d^2v}{dy^2} + \frac{d^2v}{dz^2} = q^2\, v - 4\,\pi\,(A + B)\,\varrho \;;$$

3rd the products xv, yv, zv, $x^2\,\frac{dv}{dx}$, $y^2\,\frac{dv}{dx}$ en $z^2\,\frac{dv}{dz}$ are nowhere infinite;

then v is the potential with respect to the point x, y and z of an agens, the density of which is ϱ, while the potential function is expressed by:

$$\varphi\,(r) = \frac{A\,e^{-qr} + B\,e^{qr}}{r}\;.$$

II. If the same conditions as in I hold for ϱ and v with this modification that $-q^2$ is substituted for q^2 and $A \sin \alpha$ for $A + B$;

then v is the potential with respect to point x, y and z of an agens, the density of which is ϱ, while the potential function is expressed by

$$\varphi\,(r) = \frac{A \sin\,(qr + \alpha)}{r}\;.$$

Hydrography. — *Tidal Constants in the Lampong- and Sabang-bay, Sumatra.* By Dr. J. P. VAN DER STOK.

I. *Telok Betong.*

a. From April 23,1897 to April 22,1898 tidal observations have been made in the Lampong-bay on the road of *Telok Betong*, situated in 5° 27′ Lat. S. and 105° 16′ Long. E. at the 6 hours of 8 and 10 a. m., noon 2, 4 and 6 p. m.

As in the eastern parts of Sunda-strait the normal (i. e. oceanic) tides of the Indian Ocean must show a more or less gradual transition to the peculiar tidal régime of the Java-sea, the cotidal lines run here very near to each other, by which reason two places, situated at no great distance may show very different tidal constants. For such stations a simple interpolation with respect to intensity or time of occurrence is not allowed, and the determination of the characterising constants is of great importance because it is the only way of obtaining exact data concerning the manner in which tidal waves progress and mutually interfere.

The observations have been made at the request of Major J. J. A. MULLER of the Topographical Service, who wanted an exact determination of the general water-level in the bay in behalf of the Topographical Survey of South-Sumatra.

b. The constants of the partial tides M_2, O and N have been computed in the ordinary way by arrangement of the records according to the different periods; the constants of the other tides S_1, S_2, K_1, K_2, Sa, Ssa and the value of the general mean W have been calculated by means of the monthly means. The problem, therefore, consisted in computing 15 quantities from 73 equations in the simplest and most advantageous manner; it would have been a tedious work to apply directly to this problem the method of the l. sq. and the results would not have been more accurate than by using the following abbreviated method.

c. The constants of the tides S_1 and S_2, as also the general mean value W, are deduced from the 6 equations given by the hourly means taken over the whole year.

These equations are for the given hours:

$$\left.\begin{array}{lll}
(1) & 8\text{ a.m.} = & W + S_1 \cos(300^\circ - C_1) + S_2 \cos(240^\circ - C_2) \\
(2) & 10\ ,, \ = & W + S_1 \cos(330^\circ - C_1) + S_2 \cos(300^\circ - C_2) \\
(3) & \text{noon} = & W + S_1 \cos C_1 \qquad\qquad\quad + S_2 \cos C_2 \\
(4) & 2\text{ p.m.} = & W + S_1 \cos(30^\circ - C_1) + S_2 \cos(60^\circ - C_2) \\
(5) & 4\ ,, \ = & W + S_1 \cos(60^\circ - C_1) + S_2 \cos(120^\circ - C_2) \\
(6) & 6\ ,, \ = & W + S_1 \cos(90^\circ - C_1) + S_2 \cos(180^\circ - C_2) \\
\text{Mean:} & & W + 0.644\, S_1 \cos(15^\circ - C_1).
\end{array}\right\} \quad (1)$$

By combination of (1) with (4), (2) with (5) and (3) with (6) S_2 is eliminated, the result is:

$$\begin{array}{l}
(1) + (4) = 220.2 \text{ c.M.} = 2S_1 \sin(75^\circ - C_1) \sin 45^\circ + 2W \\
(2) + (5) = 219.1 \quad ,, \quad = 2S_1 \sin(105^\circ - C_1) \sin 45^\circ + 2W \\
(3) + (6) = 218.7 \quad ,, \quad = 2S_1 \sin(135^\circ - C_1) \sin 45^\circ + 2W
\end{array}$$

These three equations are satisfied by the values:

$$W = 111.17 \text{ cM.}, \quad S_1 = 2.70 \text{ cM.}, \quad C_1 = 207°8'$$

Substituting these values in equations (1), we find, on putting:

$$Y = S_2 \sin C_2, \qquad X = S_2 \cos C_2$$

$$\begin{array}{lrcl}
(1) & 0.5\,X + 0.866\,Y & = & 12.731 \text{ cM.} \\
(2) & -0.5\,X + 0.866\,Y & = & 10.801 \;,, \\
(3) & X & = & 1.634 \;,, \\
(4) & 0.5\,X + 0.866\,Y & = & 12.731 \;,, \\
(5) & 0.5\,X + 0.866\,Y & = & 10.802 \;,, \\
(6) & X & = & 1.636 \;,,
\end{array}$$

and from these

$$(1) + (2) + (4) + (5) = 3.464\,Y = 47.065\,; \; Y = 13.587 \text{ c.M.}$$

Substituting this value of Y in (1) (2), (4) and (5) we find:

$$X = 1.930 \text{ cM.}$$

and in (3) and (6)

$$X = 1.634 \text{ cM.}$$

The difference is small, but it points to a systematic error, e. g. in the assumption that the diurnal variation may be represented by only two periodic terms instead of by three or more, owing to the somewhat aperiodic description of the influence of land- and seabreezes.

As a final value we take:

$$X = \frac{1.930 \times 4 + 1.634 \times 2}{6} = 1.832 \text{ cM.}$$

$$S_2 = 13.71 \text{ cM.} \qquad C_2 = 82°20'.$$

d. With a view of calculating the constants of the tides K_1 and P the following sums and differences of the monthly means are used.

	a (8)+(10)	*b* (12)+(2)	*c* (4)+(6)	*a—b*	*a—c*
April	210.1	212.6	215.6	— 2.5	— 5.5
May	155.8	218.2	237.5	—62.4	—81.7
June	184.5	247.9	269.4	—63.4	—84.9
July	198.8	263.6	283.9	—64.8	—85.1
August	220.2	290.9	294.8	—70.7	—74.6

	a (8)+(10)	*b* (12+(2)	*c* (4)+(6)	*a*—*b*	*a*—*c*
September	218.4	278.5	252.3	—60.1	—33.9
October	203.4	234.7	196.6	—31.3	6.8
November	206.4	212.0	170.4	— 5.6	36.0
December	197.9	182.6	161.6	15.3	36.3
January	210.1	199.2	201.8	10.9	8.3
February	189.2	207.5	217.0	—18.3	—27.8
March	179.9	217.8	231.8	—37.9	—51.9
April	188.8	245.3	231.2	—56.5	—42.4
				(—42.1)	(—32.6)

The differences ($a-b$) and ($a-c$) are independent of W, the general mean, of the annual and semi-annual variations and of disturbing influences as far as they may be considered to be the same at the different hours of the day or i. o. w. last for some days.

The influence of S_1 and S_2 is the same for every month, so that the *periodic* variation, which is evident in the differences, is caused exclusively by the tides K_1, P and K_2.

The figures in brackets —42.1 and —32.6 are obtained by combining the two values for the month of April in such a way that to each value is given a weight equal to the number of days of observation resp. 8 and 22.

The series is considered therefore to commence with May 1st, a fact which must be taken into consideration in applying the astronomical argument. Representing the single-periodic variation of the differences ($a-b$) and ($a-c$) by the expression:

$$\left.\begin{aligned} a-b &= A\cos 30^\circ x + B\sin 30^\circ x \\ a-c &= A_1\cos 30^\circ x + B_1\sin 30^\circ x \end{aligned}\right\} \quad \ldots\ldots \quad (2)$$

we find by the method of the l. sq.:

$$A = -26.58 \qquad B = -28.68$$
$$A_1 = -51.88 \qquad B_1 = -25.62$$

The influence of the tides K_1, P en K_2 in the monthly mean values may be represented by the expressions:

$$\left.\begin{array}{ll}
(1) & K_1 R_2 \cos(30^\circ x + 315^\circ - C_k) + PR_2 \cos(30^\circ x + 75^\circ + C_p) \\
(2) & K_1 R_2 \cos(30^\circ x + 345^\circ - C_k) + PR_2 \cos(30^\circ x + 45^\circ + C_p) \\
(3) & K_1 R_2 \cos(30^\circ x + 15^\circ - C_k) + PR_2 \cos(30^\circ x + 15^\circ + C_p) \\
(4) & K_1 R_2 \cos(30^\circ x + 45^\circ - C_k) + PR_2 \cos(30^\circ x - 15^\circ + C_p) \\
(5) & K_1 R_2 \cos(30^\circ x + 75^\circ - C_k) + PR_2 \cos(30^\circ x - 45^\circ + C_p) \\
(6) & K_1 R_2 \cos(30^\circ x + 105^\circ - C_k) + PR_2 \cos(30^\circ x - 75^\circ + C_p)
\end{array}\right\} (3)$$

$$\text{Mean.} \quad 0.644\, K_1 R_2 \cos(30^\circ x + 30^\circ - C_k) + 0.644\, PR_2 \cos(30^\circ x + C_p)$$

$$\left.\begin{array}{ll}(1) & K_2\,R_3\,cos\,(60°\,x - 90° - C_{2k})\\ (2) & K_2\,R_3\,cos\,(60°\,x - 30° - C_{2k})\\ (3) & K_2\,R_3\,cos\,(60°\,x + 30° - C_{2k})\\ (4) & K_2\,R_3\,cos\,(60°\,x + 90° - C_{2k})\\ (5) & K_2\,R_3\,cos\,(60°\,x + 150° - C_{2k})\\ (6) & K_2\,R_3\,cos\,(60°\,x + 210° - C_{2k})\end{array}\right\} \quad .\;.\;.\;.\;.\quad (4)$$

From the formulae (3) we deduce:

$$\begin{aligned} a - b = {} & p\,\{\,K_1\,cos\,C_k - P\,cos\,(C_p + 30°)\,\}\,sin\,30°\;t\\ & - p\,\{\,K_1\,sin\,C_k + P\,sin\,(C_p + 30°)\}\,cos\,30°\;t\end{aligned}$$

$$\begin{aligned} a - c = {} & q\,\{\,K_1\,cos\,(30° - C_k) - P\,cos\,C_p\,\}\,sin\,30°\;t\\ & + q\,\{\,K_1\,sin\,(30° - C_k) - P\,sin\,C_p\,\}\,cos\,30°\;t\end{aligned}$$

in which

$$p = 4 \times 0.966 \times 0.5 \times R_2$$
$$q = 4 \times 0.966 \times 0.866 \times R_2$$

and R_2 denotes the coëfficient of decrease, due to the fact that average values are used for a period of one month.

By equating the corresponding coëfficients of these equations and formulae (2) and putting:

$$Y = K_1\,sin\,C_k \qquad X = K_1\,cos\,C_k$$
$$Y' = P\,sin\,C_p \qquad X' = P\,cos\,C_p$$

We find:

$$\begin{aligned} A/p &= -\,Y - X'\,sin\,30° - Y'\,cos\,30°\\ B/p &= X - X'\,cos\,30° + Y'\,sin\,30°\\ A_1/q &= X\,sin\,30° - Y\,cos\,30° - Y'\\ B_1/q &= X\,cos\,30° + Y\,sin\,30° - X'\end{aligned}$$

which are satisfied by the values:

$Y = 12.23$ cM. $\qquad X = -\,11.14$ cM.
$Y' = -\,0.48$ » $\qquad X' = 4.21$ »

$K_1 = 16.54$ cM. $\qquad P = 4.24$ cM.
$C_k = 102°\,19'$ » $\qquad C_p = 353°\,30'$ »

In order to obtain a serviceable combination for the calculation of the constants of the tide K_2, the values

$$a + b - 2\,c$$

are formed.

In these values again the annual variations and the aperiodic disturbances are eliminated.

	$(a + b - 2c)$
May	—101.0 cM.
June	—106.4 »
July	—105.4 »
August	— 78.5 »
September	— 7.7 »
October	44.9 »
November	77.6 »
December	57.3 »
January	5.7 »
February	— 37.3 »
March	— 65.9 »
April	— 22.8 »

The double-periodic variation of these values, as computed by the method l. sq., may be represented by the expression:

$$27.575 \cos 60^\circ x - 14.015 \sin 60^\circ x \; . \; . \; . \; . \; . \qquad (5)$$

From (4) we find:

$$(1) + (2) = a = 2\,K_2\,R_3 \cos 30^\circ \cos(60^\circ x - 60^\circ - C_{2k})$$

$$(3) + (4) = b = 2\,K_2\,R_3 \cos 30^\circ \cos(60^\circ x + 60^\circ - C_{2k})$$

$$(5) + (6) = c = 2\,K_1\,R_3 \cos 30^\circ \cos(60^\circ x + 180^\circ - C_{2k})$$

$$a + b - 2c = 6\,K_2\,R_3 \cos 30^\circ \cos(60^\circ x - C_{2k}) \; . \; . \; . \qquad (6)$$

This equation shows that, by this method, the constants of K_2 can be determined from a periodic formula in which the amplitude is about 5 times larger than the value which has to be calculated. By equating the coefficients of (5) and (6) we find:

$$K_2 \cos C_{2k} = 5.558 \qquad K_2 \sin C_{2k} = -2.825$$
$$K_2 = 6.24 \text{ cm.} \qquad C_{2k} = 333^\circ 3'$$

e. The average monthly values of the water-level are found by correcting the mean values as obtained by direct computation for the influence of the tides S_1, K_1 and P. From formulae (1) and (4) it appears that (for the actual hours of observation) the correction due to the influence of S_2 and K_2 is nil; that for the single periodical tides is given by the average values of formula (1) and (3) and is to be applied with inversed signs.

Correction for	cm.	S_1	K_1	P	Correct. values cm.
May	101.9	1,70	2,27	—2.72	103.2
June	117.0	1.70	— 3.24	—2.50	113.0
July	124.4	1.70	— 7.88	— 1.62	116.6
August	134.4	1.70	—10.41	—0.31	125.4
September	124.9	1.70	—10.15	1.09	117.5
October	105.8	1,70	— 7.17	2.20	102.5
November	98.1	1.70	— 2.27	2.72	100.3
December	90.3	1.70	3.24	2.50	97.7
January	101.8	1.70	7.88	1.62	113.0
February	102.3	1.70	10.41	0.31	114.7
March	104.9	1.70	10.15	—1.09	115.7
April	109.7	1.70	7.17	—2.20	116.4
Mean	109.6	1.70			111.33

The corrected monthly means exhibit a principal maximum (low water) in August and a principal minimum (high water) in December; owing to the abnormal low value in May the position of the secondary extremes is doubtful.

The constants for *Sa* and *Ssa*, computed from these data, therefore do not give more than a rather rough approximation of the actual state of affairs.

The following expression is found:

$$W = 111.33 + 5.54 \cos (30^\circ\, t - 28^\circ 55') + 9.48 \cos (60^\circ\, t - 190^\circ 50')$$

in which the origin of time coincides with May 16th.

As might have been expected the accordance between the observed and calculated monthly departures from the annual mean leaves much to be desired:

	Observed. cm.	Calculated. cm.
May	— 8.1	— 4.03
June	1.7	— 0.37
July	5.3	7.71
August	14.1	11.56
September	6.2	5.81
October	— 8,8	— 5.83
November	—11.0	—13.73
December	—13.6	—11.45
January	1.7	— 1.78
February	3.4	6.20
March	4.4	6.02
April	5.1	— 0.11

A systematical investigation of the normal and abnormal motions of the mean water-level, if extended over a large area and over some years, might prove of great importance with respect to two interesting problems.

In the first place it would appear from such an inquiry that it will be always impossible to predict with great accuracy the *absolute* water-level at a given place even when the periodic terms of the tidal components are fully known; therefore it can be of no use to carry on the calculations in behalf of tidal prediction to an astronomical degree of accuracy; in the second place an inquiry into the aperiodic departures from the average normal values might lead to a better knowledge of the important and varying meteorological influences which prevail on the ocean, than by means of the incomplete and scattered observations taken on board ship.

It is not improbable that the variations of the water-level e.g. in the Gulf of Bengal and the Arabian Sea, which must be dependent on the "vis a tergo" in the Indian Ocean in and south of the area of the trade-winds, might give a clue to the prediction of the periods of drought to which the climate of India is subject.

f. In recapitulating the results obtained, it must be kept in mind that the zero-point of the tide-gauge is on the upper end, so that low figures denote high water. If positive numbers are to correspond with high, negative numbers with low water, the argument of the formulae must be augmented or decreased by 180° and the corrected monthly values subtracted from an arbitrary number.

After reduction to the conventional origin of time, application of the augmenting factor $^1/R$ to the amplitudes of the annual variations, reduction to average values of the constants in so far as they are dependent on the moon's declination and, finally, inversion of the sign, the following tidal constants are found for *Telok-Betong*:

	Telok Betong.		Java's 4th Point	
	H	$\varkappa$	H	$\varkappa$
S_1	2.7 c.m.	27°	—	—
S_2	13.7	262°	12.8 c.m.	280°
M_2	32.1	222°	24.2	210°
K_1	15.5	269°	6.8	226°
O	7.8	265°	3.4	216°
P	4.2	231°	1.7	171°?
N	5.6	192°	4.1	190°
K_2	5.3	246°	2.5	299°
Sa	5.6	263°	1.4	220°
Ssa	9.5	120°	5.6	149°
W	111.3		53.9	

Besides the constants for *Telok-Betong* these quantities are given also for the tidal station *Java's* 4th *Point*, situated too in *Sunda-strait*; they have been computed from a five-year series of observations.

A comparison between the data for the two places exhibit some important differences, whilst a look at the chart would show that their situation with respect to the tidal wave, progressing from the Ocean in the strait, is about the same.

For the differences of time, *Telok-Betong* minus *Java's* 4th *Point*, we find:

$S_2 \quad -18^\circ \quad = \quad -0.6$ hours.
$M_2 \quad +12^\circ \quad = \quad 0.4$ »
$K_1 \quad +43^\circ \quad = \quad 2.9$ »
$O \quad +49^\circ \quad = \quad 3.5$ »

The single diurnal tides in the Lampong-bay therefore lag behind those near *Java's* 4th *Point* in quite another way than the moon's semi-diurnal tide M_2 and this again in another way than the semi-diurnal solar tide S_2, which is in advance.

An estimation of the tides for the one place based on those of the other by assuming a constant difference of time — as is usually done along a coast — is therefore quite inadmissable here, as the differences of time are by no means constant, but variable according to the moon's phase and declination.

If we look at the hindrance which Sumatra's most southerly neck of land offers to the free propagation of the mono-diurnal tide-wave from the *Java-sea* into the Lampong-bay, we should expect a stronger influence of the K_1 wave near *Java's* 4th *Point* than on the road of *Telok-Betong*, but, on the contrary, the tide near the latter place may be regarded as twice as "monodiurnal" as the tide in the strait, as in shown by the proportion:

$$\text{Ampl.}\ \frac{K_1 + O}{M_2 + S_2} = 0{,}51 \text{ near } \textit{Telok Betong},$$
$$= 0.28 \text{ near } \textit{Java's } 4^{th} \textit{ point},$$

This prevailing influence of the *Java-sea* on the tides in the bay does not, however, give an explanation of the peculiar fact, that the S_2 tide in the bay causes high water *earlier* than in the strait proper, whereas the other tides occur *later*.

If we assume that the S_2 wave finds its way into the bay in the same way as the other waves, it ought to have rather a retarding effect, because near *Duizend-eilanden* the kappanumber of S_2 is 11°.

It is, therefore, as yet impossible to offer an explanation of this peculiar behaviour of the S_2 tide and we can only state that spring and neap near *Telok Betong* occur 1,64, and at *Java's* 4th *Point* 2,87 days after New and Full Moon and First and Last Quarter.

It must be remarked however, that the constants S_2 near *Java's* 4th *Point* are not quite exact owing to the fact that they had to be calculated from observations taken thrice daily, whilst (as appears from formulae (1)), for the complete determination of W, S_1 and S_2 at least five independent — i. e. not 6 or 12 hour distant) data are required.

In calculating the S_2 constants, therefore, it is assumed either that S_1 is small with respect to S_2, or that the kappa-number of S_1 (land- and seabreeze) is about 65° or 245°, in which case, for the hours of 9 a. m., 2 and 6 p. m., the influence of S_1 disappears altogether.

In fact the seabreeze at most places causes high water about 4 or 5 p. m. and, with the exception of only a few places, e. g. *Semarang*, the amplitude of S_1 is insignificant everywhere in the Archipelago.

The neglect of S_1 therefore, cannot in most cases have any appreciable influence on the determination of the S_2-constants and it is principially for this reason that, for the greater part of the tidal stations, the above mentioned hours of observation have been selected.

In this special case, moreover, it is highly improbable that the kappanumbers of S_2 for *Java's* 4th *Point* would undergo a decrease if it were possible to correct for the neglect of S_1, because, if we assume for S_1 the same kappanumber as near *Telok Betong*, viz. 27°, the kappanumber of S_2 becomes 285° instead of 280° so that the difference would increase rather than decrease.

The tides of long duration *Sa* and *Ssa* may be considered to run pretty well parellel if allowance is made for the fact that the constants have been calculated from observations made during different periods.

II. *Sabang-bay.*

In this bay of the isle of *Weh* or *Waai* situated north of Sumatra's most northerly point in 5°54′ N. Lat. and 95°20′ E. Long., tidal observations have been made since June 1st 1897 at the hours of 7 a.m., 11 a.m. and 4 p.m.

The results calculated from the first year-series may be given here and, for the sake of comparison, also the constants for the road of *Oleh-leh.*

As the hours of observation are not the same as those at which the observations have been made at *Telok-Betong*, new formulae had to be applied; the method however being essentially the same, the results of the computation only may be given here.

	Sabang.		Oleh-leh.	
	H	$\varkappa$	H	$\varkappa$
S_2	24.1 cM.	310°	13.3 cM.	329°
M_2	46.6	266°	23.0	285°
K_1	9.1	291°	6.3	318°
O	3.5	274°	2.3	323°
P	2.1	10°	?	?
N	8.3	265°	3.0	286°
K_2	4.9	312°	4.2	333°
Sa	9.2	165°	8.8	65°
Ssa	8.5	114°	6.8	145°
W	202.8		118.5	

The tidal constants for *Oleh-leh* have been computed from three series of observations made during three years from 1895 to 1898; it appears that the tide P is so small that it cannot be calculated with any degree of accuracy from the given data, which is proved by the fact that the three determinations for the different series widely differ.

No more importance can be attached to the constants of P in *Sabang-bay*, because its argument cannot possibly be 10°, but must be somewhat smaller than 291°, the argument of K_1.

For the rest the conformity of the arguments of S_2 and K_2, M_2 and N, and the differences between those of S_2 and M_2, K_1 and O are to be considered as so many proves of the reliability of the results.

The influence of the wind cannot be determined, as for neither station a calculation of S_1 can be effectuated from the available data; it cannot be of great importance because otherwise the difference between the arguments of S_2 and M_2, which is $44° = 1.80$ days, i. e. quite normal, would be sensibly affected.

As, for all practical purposes, both tides may be considered as almost exclusively semi-diurnal, it is possible to assume a constant difference of time; this difference *Oleh-leh* minus *Sabang* is:

S_2 19° = 0.6 hours,
M_2 19° = 0.7 »
N 21° = 0.7 »
K_2 21° = 0,7 »

so that the difference amounts to 42 minutes of time, whilst the amplitude may be assumed to be twice as large at *Sabang* — at least in the back parts of the bay — as on the road of *Oleh-leh.*

The mono- and semi-annual variations are for both places somewhat different; from the three series of observations at *Oleh-leh* it appears however that in these regions the monthly mean values of the sea-level widely differ for different years, so that a better agreement might be expected only if the observations extend over a long series or at least over simultaneous periods.

It is of some importance to remark that, whereas the semidiurnal tides at *Sabang* are nearly twice as strong as near *Oleh-leh,* the mono-diurnal tides seem to be amplified in a far less degree.

This point, concerning the way in which both tides propagate and are enlarged or diminished, is of great importance for the understanding of the mechanism of tides and requires a thorough investigation.

With a view of elucidating this point tide-gauges ought to be established at the entrance and in the back parts of bays and estuaries: for these experiments however stations should be chosen where the mono-diurnal tides are better marked than at *Sabang* so that an accurate determination of the characteristic constants is possible.

An analysis of tides at different parts of a river in which a tidal wave of mixed description propagates would also afford useful data for this purpose.

Hydrography. — "*On the relation between the mean sea-level and the height of half-tide.*" By H. E. De Bruyn.

The mean sea-level is the mean of the height of the water observed at short intervals i. e. every hour.

Observations have proved, that the mean of 3-hourly observations does not practically deviate from this; in this way the mean sea-level in the years 1884—1888 has been determined by the Royal Geodetical Commission (Annual report of the Commission 1889).

Generally it is admitted that there is a constant difference, between the mean sea-level and half-tide (the mean of high and low water), during several years or months.

This has been done by the above-mentioned Commission, in their calculation of the mean sea-level for several years for Den Helder. Dr. H. G. VAN DE SANDE BAKHUYZEN also in his communication "On the variation of latitude," to the meeting of the Royal Academy (24th of Febr. 1896), assumed that the mean value of that difference during a month was a constant quantity at Den Helder. In both cases this was perfectly justified, as this value for the annual means is very nearly constant at Den Helder, and in the last case differences that may exist, are eliminated by the method of determination. However, the supposition that the difference is constant is not true for the annual means at all stations, and is certainly not so, for the monthly means at some stations.

I intend to trace those causes, which produce a difference in this value, and to find its range for one tide-gauge. I took Delfzyl for the observation-station, as at Delfzyl the difference between half-tide and the mean of the sea-level, is greater and more variable than at any other station in our country. From another point of view, Delfzyl would not be so advantageous, as there a comparison with tide-gauges in the neighbourhood is not possible.

Before proceeding further, a few words, to point out the importance of the law of the variation of that difference, are necessary. The knowledge of the mean sea-level is not only important for the annual means, but also for the monthly means, as we can deduce from them the annual variation, and also because an exact knowledge of the monthly means, assists in the detection of the unavoidable changes of the zero's in the automatic tide-gauges, and the determination of their values. As the high and low water marks are always determined in the first place, their mean is naturally known; therefore it saves much trouble, if it is possible to deduce from that mean value, the true mean sea-level, as the hourly observations can be then neglected. Besides, in the event of interruptions, which happen frequently in using the automatic tide-gauges, it is much easier to guess, the positions of high and low water, than the hourly heights, as high and low water are independent of the exact time. Moreover meteorological circumstances have, by the retardation or the acceleration of the tide, a greater influence on the hourly heights than on high and low water.

The mean sea-level can therefore be deduced more exactly from the height of half-tide, the difference of both being known, than from the hourly observations when some of these must be guessed.

Further let the difference between the mean sea-level and the height of half-tide be A, the mean sea-level Z, high water V, low water E. Half-tide is $\frac{1}{2}(V+E)$ and the range of the tide $(V-E)$.

The causes, which have an influence on the value of A, are four in number:

1st. the range of the tide $(V-E)$;

2nd. the mean sea-level (Z);

3rd. the time of the year;

4th. the presence of ice.

In the last mentioned case, I am not alluding to the fact of the ice preventing the working of the tide-gauge, for I consider this to be an interruption, but to the fact, that the presence of ice at a certain distance from the tide-gauges, deforms the tide-curve. This deformation is, in my opinion, one of the most interesting researches on tides.

I propose to solve the following question. What corrections are wanted for Delfzyl in the value A, deduced from a certain number of years, in order to find that quantity for separate months?

The data, which I had at my disposal were the values of V and E for 18 years (July 1881—July 1899) the values of Z for 7 years (1884—1890) viz. the height at 2, 5, 8 and 11 o'clock, and in addition the height at 2 and 8 o'clock for 8 years (1891—1898).

The mean range of the tide at Delfzyl is, according to these data 2750 m.m., the mean sea-level Z is according to the calculations of the above-mentioned commission 128 m.m., reckoned from the zero of the tide-gauge during the years 1884—1890. The mean value A during these 7 years is 193 m.m., so we find that the mean of half-tide is 128—193 m.m. = — 65 m m. Tide-curves of spring and neap-tides accompany this paper.

It is difficult to determine, how much each of the four causes, influences A at Delfzyl, as they often modify A in the same direction. So, during the year, the correction for each of the three first-named causes, is generally a sinusoide of about the same amplitude and the same phase.

It is therefore necessary, to adopt a certain definite value for one of these causes. I assume that the correction, due to the first cause, is proportional to the difference of the mean range of the tide and the observed value of that range $V-E$ and that their proportion is equal to the ratio of the mean values A and $V-E$, or ceteris paribus, A is always proportional to $V-E$. In substance this will be he case. I adopted as this proportion $^1/_{15}$, the correction is therefore $^1/_{15}$ $(V - E - 2750)$ mm.

As concerns the second correction we see that when the sea-level is higher, A is smaller than the mean value, and vice-versa.

We do not know exactly the law governing these small changes, because various unforeseen circumstances e. g. storms influence them. The only thing that can be done, in my opinion, is to take for this correction a quantity proportional to the deviation of the mean sea-level. As it was my intention to deduce the value of Z from that of half-tide, which is known, I adopted for the value of that correction a quantity proportional to the deviation from the mean height at half-tide (— 65 mm.).

After comparing the same months of different years, I found that this correction amounts to about $^2/_{20}$ or $^2/_{30}$ of the value of that deviation i. e. $^1/_{20}$ or $^1/_{30}$ of $(V + E + 130)$. I have adopted $^1/_{25}$ $(V + E + 130)$.

That the height of Z has an influence on the form of the tide-curve, is probably due to the mud-banks in the Dollard. The surface that must be covered, constantly changes with the level of the sea, and so for equal tide-ranges, the quantity of water flowing in and out of the Eems at Delfzyl, is much greater for high sea-levels than for low.

Both corrections being applied another annual correction is still wanted. For this correction I adopted an annual sinusoide, the amplitude and the phase of which can be easily determined. The amplitude is in round numbers 10 mm. and the greatest positive value occurs about the 1st of July. From the observations in the seven-yearly period, there is no evidence of the existence of a half-yearly sinusoide. Considering also the heights at 2 and 8 o'clock for the period 1891—1898, there appears to be a semi-annual sinusoide, but the amplitude is very small, and it is questionable whether the sinusoide derived from those observations is not different from the mean sinusoide. It is better to entirely neglect this correction.

After applying these corrections, the values of the sea-level for some months, still show great negative divergencies. It is obvious that these are exactly the months in which we have a very low temperature, and in which there must have been ice. But as the mean temperature of a month is not an exact proof of the presence of ice, I adopted as a datum the thickness of the ice according to the observations at Den Helder (see the Proc. Kon. Inst. van Ingenieurs) as quoted in the following table.

Thickness of the ice in mm.

	1884	1885	1886	1887	1888	1889	1890
January	22	$\underline{387}$	201	298	310	204	43
February	53	34	$\underline{323}$	266	$\underline{360}$	156	171
March	6	24	$\underline{211}$	110	$\underline{223}$	124	93
November	46	74	6	43	145	27	267
December	95	58	96	121	51	199	$\underline{811}$

I took for the months in question the four ones in which the ice has the greatest thickness, and two other months in which the thickness too was great, following immediately on two of the former, as we may suppose the ice still existed during that time. The selected months are underlined in the table.

I found that in these months A is too small. It is difficult to find a cause for this, as, excepted at Delfzyl and Statenzyl, there are no tide-gauges in the Eems and the Dollard, and the gauge at Statenzyl does not work when the tide is low. Probably it is due to the ice on the mud-banks of the Dollard. Generally the effect of the ice is to raise high-watermark at the mouth of the river, but this is not the case at Delfzyl. On the contrary, the range of the tide is less in the months with ice. Probably both V and E are increased, but E more than V, and therefore the range is smaller and half-tide considerably higher, the mean sea-level is less increased than half-tide and hence the difference A is smaller.

The heights at 2 and 8 o'clock in the months January 1891 and February 1895, when there was much ice, give also corresponding results.

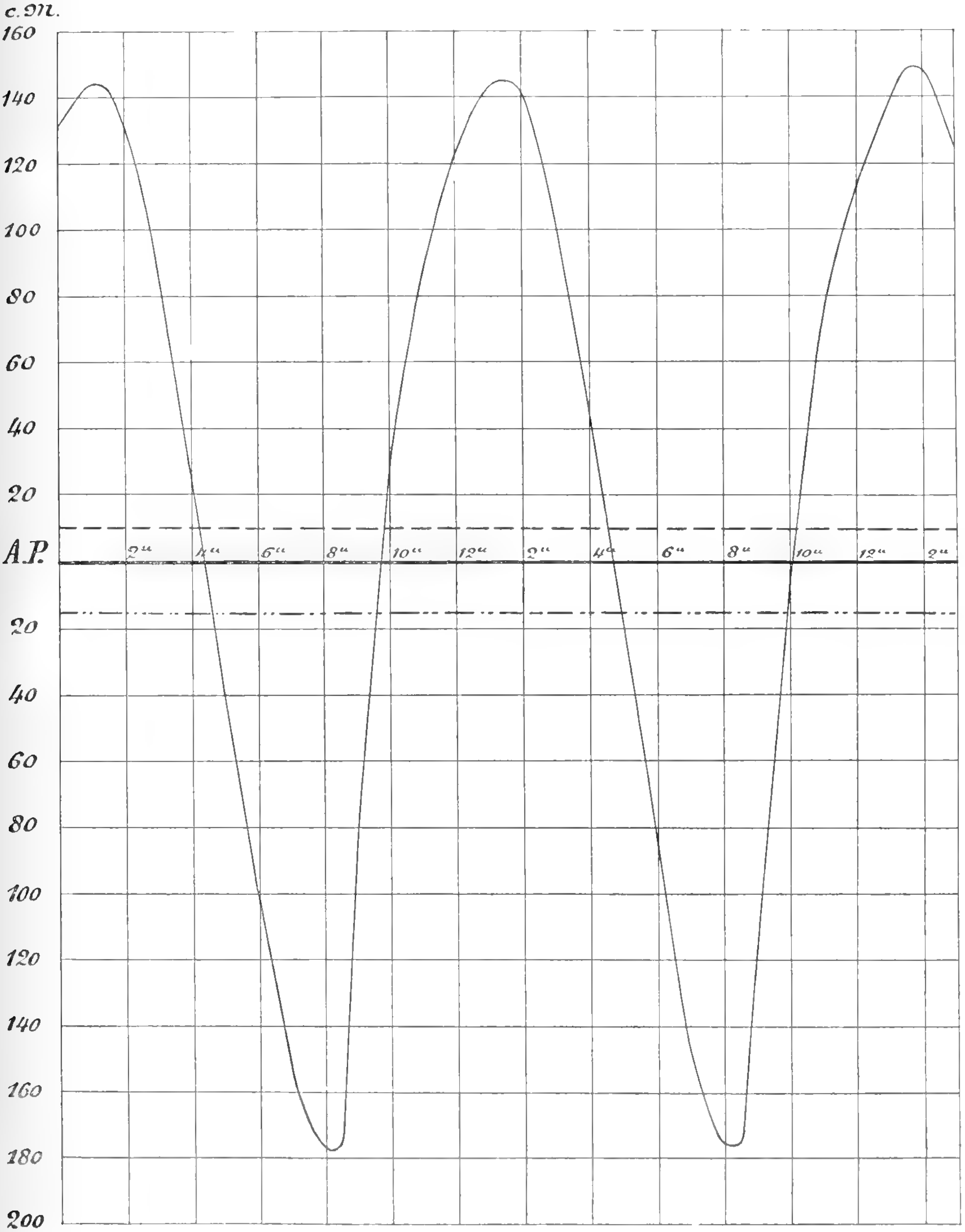
In the following table are given the values A, the corrections and the remaining differences, for the 5 months in which A is a maximum, the 5 months in which A is a minimum, the months with ice and two other months in which the error or the remaining difference is greater than 15 mm.

Month	Value A.	Correction for Tide-range.	 Z.	 Time of the year.	Remaining Difference.
		Maximum values of A.			
April 1884.	223^5	9	14^5	2^5	4^5
May 1886.	220^5	7^5	9^5	7	3^5
April 1888.	220	12^5	10	2^5	2
April 1889.	229	9	10	2^5	14^5
May 1889.	225^5	10	10^5	7	5
		Minimum value of A.			
October 1884.	148	—5	—23	—2^5	—14^5
December 1884.	158	—1^5	—15	—9^5	—6
February 1889.	158	— 3^5	—20^5	—7	—4
January 1890.	160	—5	—15^5	—9^5	—3
October 1890.	149	—1^5	—25	—2^5	—15
		Months with ice.			
January 1885.	178	—1	12	—9^5	—16^5
February 1886.	188^5	4	17^5	—7	—19
March 1886.	186	0^5	14	—2^5	—19
February 1888.	164	—1^5	15^5	—7	—36
March 1888.	183	—1	10	—2^5	—16^5
December 1890.	167	—7	21	—9^5	—30^5
		Months with differences greater than 15 mm.			
February 1890.	189	0^5	23^5	—7	—21
December 1888.	199^5	—2^5	—5^5	—9^5	24

From this it appears that the corrections and the errors are positive in the months with maximum values of A, negative in those with minimum values. We find concerning February 1890 that there also has been ice during a portion of this month, that the mean height was lowest of all months and that as low water occurred on the 28th a few minutes before midnight, it had to be considered as occurring in March. The great negative difference can probably be explained by these circumstances.

Tidecurve at Delfzijl (Spring-tide).

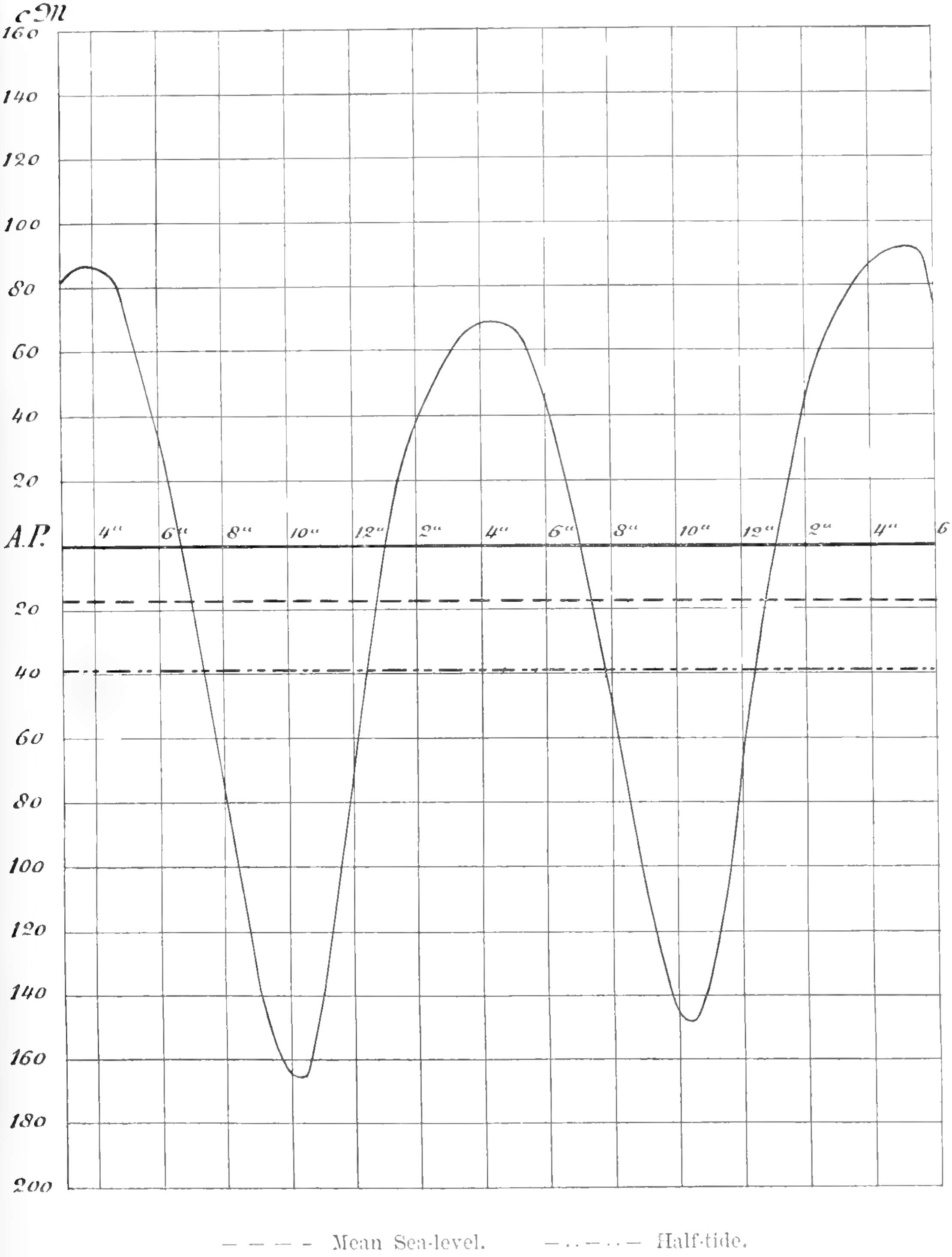
I.



- - - - Mean Sea-level. -..-..- Half-tide.

Tidecurve at Delfzijl (Neap-tide).

II.



The remaining differences for all months are given in the following table, in which half mm. have been neglected; the months with ice are underlined.

Month	1884	1885	1886	1887	1888	1889	1890
January	11	$\underline{-17}$	11	5	−2	−13	−3
February	9	12	$\underline{-19}$	−7	$\underline{-36}$	−4	−21
March	6	−13	$\underline{-19}$	2	$\underline{-16}$	−3	−1
April	4	−0	0	−8	2	14	−7
May	−3	1	3	−3	2	5	0
June	−1	−11	−1	−5	−1	−8	−3
July	4	−4	−3	1	7	3	−6
August	5	3	−5	−1	4	11	6
September	0	3	−4	12	−2	−12	−1
October	−14	5	0	−2	2	6	−15
November	−6	−2	7	14	−9	3	3
December	−6	3	12	14	24	0	$\underline{-30}$

The mean error of the sea-level for all months, those with ice excepted, is 6,0 mm. I computed this mean error also on the supposition that the second correction is $^1/_{20}$ or $^1/_{30}$ of $V + E + 130$. The mean error was found to be respectively 6,3 and 6,1 mm. When the value of Z is deduced from the heights at 2 and 8 o'clock and a mean correction $^1/_4$ (height at 5 + height at 11 — height at 8 — height at 2) is applied, the mean error of Z has been found to be 8,8 mm. It seems therefore that the deduction of Z from the height at half-tide gives more exact values, than the deduction from the heights at 2 and 8 o'clock.

Hence the value A for Delfzyl, after applying the above-mentioned corrections, the sun's longitude being φ and the correction for the presence of ice Y, is:

$$A = Z - {}^1/_2 (V + E) = 193 + {}^1/_{15} (V - E - 2750) - {}^1/_{25} (V + E + 130) + a_1 \cos(\varphi - \gamma) + Y,$$

γ being a constant angle.

Or: $$A = 5 + {}^2/_{75}\, V - {}^8/_{75}\, E + a_1 \cos(\varphi - \gamma) + Y.$$

Partly neglecting the variations of the monthly tide-ranges in different years, which are at a maximum 120 mm. and give only a maximum error of 3 mm. in the value of A, we can put $^2/_{75} \times 2750 + a_2 \cos(\varphi - \gamma_2)$ instead of $^2/_{75}\ V - {}^2/_{75}\ E$ mm.

The formula then becomes:

$$A = 78 - 0{,}08\ E + a_3 \cos(\varphi - \gamma_3) + Y.$$

The errors calculated from this formula do not differ much from the above-mentioned, for now the mean error is 6,4 mm. and the formula is therefore as exact, while the computation is much more easily carried out.

In conclusion I will add the following remarks.

First I should mention that I found some errors in the tables containing the observed height of the sea-level at Delfzyl during the months in which the greatest differences occurred and in those of two other tide-gauges during five months. For instance at Delfzyl I found a month in which one height had been read from the half hour-mark instead of the hour-mark, and also one reading with a wrong sign. After making the correction the great divergence was very much reduced. Although this is no proof, we may suppose that the greatest differences very nearly give the limit of precision.

Further I notice that the second correction mentioned above does not agree with the principle on which the method of harmonic analysis is founded, so that this method cannot give exact results in the reduction of the observations at Delfzyl. Still, I do not affirm that any other is better.

This want of agreement is demonstrated by the term 0,08 E in the preceding formula. For the same month in two different years (February 1889 and 1890) the difference of the two values of E is 583 mm., so that 0,08 E = 47 mm., and although this difference would not be of much importance for a single observation, it is far too great for an error of the monthly mean.

Mathematics. — Prof. JAN DE VRIES reads for Prof. L. GEGENBAUER at Vienna a paper entitled: "*New theorems on the roots of the functions* $C_n^{\nu}(x)$".

Up to this moment we know of the roots of the coefficients $C_n^{\nu}(x)$ of the development of $(1 - 2\,\alpha + \alpha^2)^{-\nu}$ according to ascending powers of α only this, that they are all real and unequal, are situated between $+1$ and -1 and — apart from the root 0 appearing in the case of an uneven n — have in pairs the same absolute value; finally that the roots of $C_n^\nu(x)$ and $C_{n-1}^\nu(x)$ as well as those of $C_n^\nu(x)$ $C_{n-1}^{\nu+1}(x)$ mutually separate each other.

In the following lines some new theorems on the roots of these functions will be found in a highly simple manner, one of which including as a special case a well known theorem of the theory of spherical functions.

1. From the addition-theorem of the functions $C_n^\nu(x)$ arrived at by me

$$C_n^\nu[xx_1+\surd(1-x^2)\surd(1-x_1^2)\cos\varphi] = \Pi(2\nu-2)\left[\frac{2^n\,\Pi(n+\nu-1)}{\Pi(\nu-1)}\right]^2$$

$$\sum_{\rho=0}^{\rho=n}(-1)\frac{2\nu+2\varrho-1}{\Pi(n-\varrho)\,\Pi(n+2\nu+\varrho-1)}\,C_n^{\nu,\rho}(x)\;C_n^{\nu,\rho}(x_1)\;C_\rho^{\frac{2\nu-1}{2}}(\cos\varphi)\ ,$$

$$(1 \geqq x,\ x_1 \geqq -1)$$

where the square roots are taken positively and

$$C_n^{\nu,\rho}(x) = \frac{\Pi(n-\varrho)\,\Pi(\nu+\varrho-1)}{2^{n-\rho}\,\Pi(n+\nu-1)}\,(x^2-1)^{\frac{\rho}{2}}\,C_{n-\rho}^{\nu+\rho}(x)\ ,$$

we find the relation

$$\int_0^\pi C_n^\nu[xx_1+\surd(1-x^2)\surd(1-x_1^2)\cos\varphi]\,\sin^{2\nu-1}\varphi\,d\varphi =$$

$$= \frac{2^{2\nu-1}[\Pi(\nu-1)]^2\,\Pi(n)}{\Pi(n+2\nu-1)}\,C_n^\nu(x)\;C_n^\nu(x_1)\ .$$

By putting x_1 equal to a positive root z_n of the function $C_n^\nu(x)$ the equation is transformed into

$$\int_0^\pi C_n^\nu[x\,z_n+\surd(1-x^2)\surd(1-z_n^2)\cos\varphi]\,\sin^{2\nu-1}\varphi\,d\varphi = 0\ ,$$

showing that the function $C_n^\nu(x)$ vanishes at least for one value of its argument lying between $x\,z_n+\surd(1-x^2)\surd(1-z_n^2)$ and $x\,z_n-\surd(1-x^2)\surd(1-z_n^2)$, as otherwise the function to be integrated would not change its sign in the entire region of integration, and hence the integral could not be equal to 0. This value certainly differs from z_n when

$$z_n > x\, z_n + \sqrt{(1-x^2)}\, \sqrt{(1-z_n^2)}\,,$$

which can only be the case, if

$$x < 2\, z_n^2 - 1\,,$$

and this leads, in case x might also be positive, to the supposition

$$z_n > \frac{1}{\sqrt{2}}\,.$$

The entire interval under discussion being a positive one when x is taken greater than $\sqrt{(1-z_n^2)}$, we find the theorem:

If z_n *be a positive root of the function* $\overset{\nu}{\underset{n}{C}}(x)$ *surpassing* $1:\sqrt{2}$ *and* α *a positive root lying between* $\left|\sqrt{(1-z_n)}\right|$ *and* $2\, z_n^2-1$, *then there must be in the interval* $\alpha\, z_n - \sqrt{(1-\alpha^2)}\, \sqrt{(1-z_n^2)}$ *to* $\alpha\, z_n + \sqrt{(1-\alpha^2)}\sqrt{(1-z_n^2)}$ *at least one other positive root of this function (smaller than* z_n*).*

A corollary of this theorem is the following:

The smallest positive root of the function $\overset{\nu}{\underset{n}{C}}(x)$ *is smaller than* $1:\sqrt{2}$.

2. In my paper "Some theorems on the functions $\overset{\nu}{\underset{n}{C}}(x)$" ("Einige Sätze über die Functionen $\overset{\nu}{\underset{n}{C}}(x)$") contained in the 47th vol. of "Denkschriften der mathematisch-naturwissenschaftlichen Classe der Kais. Akademie der Wissenschaften in Wien" I have given the four following equations:

$$\overset{\nu}{\underset{n}{C}}(\cos x) = \frac{(-1)^n\, \Pi\left(\frac{2\,\nu-1}{2}\right)}{2^{\nu-1}\sqrt{\pi}\, \Pi\,(\nu-1)\sin^{2\nu-1}\frac{x}{2}} \int_0^x (\cos\varphi - \cos x)^{\nu-1}$$

$$\overset{2\nu}{\underset{2n}{C}}\left(\sin\frac{\varphi}{2}\right)\cos\frac{\varphi}{2}\, d\varphi \quad (\nu > 0)\,,$$

$$C_n^{\nu}(\cos x) = \frac{\Pi\left(\frac{2\nu-1}{2}\right)}{2^{\nu-1}\sqrt{\pi}\,\Pi(\nu-1)\cos^{2\nu-1}\frac{x}{2}} \int_x^{\pi} (\cos x - \cos\varphi)^{\nu-1}$$

$$C_{2n}^{2\nu}\left(\cos\frac{\varphi}{2}\right)\sin\frac{\varphi}{2}\,d\varphi \qquad (\nu > 0),$$

$$C_n^{\nu}(\cos x) = \frac{(-1)^n\,\Pi\left(\frac{2\nu-3}{2}\right)}{2^{\nu-1}\sqrt{\pi}\,\Pi(\nu-2)\sin^{2\nu-1}\frac{x}{2}} \int_0^{x} (\cos\varphi - \cos x)^{\nu-1}$$

$$C_{2n+1}^{2\nu-1}\left(\sin\frac{\varphi}{2}\right)\sin\varphi\,d\varphi \qquad (\nu \geqq \tfrac{1}{2}),$$

$$C_n^{\nu}(\cos x) = \frac{\Pi\left(\frac{2\nu-3}{2}\right)}{2^{\nu-1}\sqrt{\pi}\,\Pi(\nu-2)\cos^{2\nu-1}\frac{x}{2}} \int_x^{\pi} (\cos x - \cos\varphi)^{\nu-1}$$

$$C_{2n+1}^{2\nu-1}\left(\cos\frac{\varphi}{2}\right)\sin\varphi\,d\varphi \qquad (\nu \geqq \tfrac{1}{2}),$$

which are a generalization of the integrals:

$$P_n(\cos x) = \frac{2}{\pi}\int_0^x \frac{\cos(n+\frac{1}{2})\varphi\,d\varphi}{\sqrt{2(\cos\varphi - \cos x)}},$$

$$P_n(\cos x) = \frac{2}{\pi}\int_x^{\pi} \frac{\sin(n+\frac{1}{2})\varphi\,d\varphi}{\sqrt{2(\cos x - \cos\varphi)}}.$$

given by MEHLER in his communication "Notice on integralforms of Dirichlet for the spherical functions $P_n(\cos\vartheta)$ and an analogous integralform for the cylindrical functions $I(x)$", "(Notiz über die Dirichlet'schen Integralausdrücke für die Kugelfunctionen $P_n(\cos\vartheta)$ und eine analoge Integralform für die Cylinderfunctionen $I(x)$)".

By putting x equal to the root of the function $C_n^{\nu}(\cos x)$ lying between 0 and $\frac{\pi}{2}$ we transform them into the following relations:

$$\int^{y_n} (\cos\varphi - \cos y_n)^{\nu-1}\, C_{2n}^{2\nu}\left(\sin\frac{\varphi}{2}\right)\cos\frac{\varphi}{2}\, d\varphi = 0\ ,$$

$$\int_{y_n}^{\pi} (\cos y_n - \cos\varphi)^{\nu-1}\, C_{2n}^{2\nu}\left(\cos\frac{\varphi}{2}\right)\sin\frac{\varphi}{2}\, d\varphi = 0\ ,$$

$$\int_{0}^{y_n} (\cos\varphi - \cos y_n)^{\nu-1}\, C_{2n+1}^{2\nu-1}\left(\sin\frac{\varphi}{2}\right)\sin\varphi\, d\varphi = 0\ ,$$

$$\int_{y_n}^{\pi} (\cos y_n - \cos\varphi)^{\nu-1}\, C_{2n+1}^{2\nu-1}\left(\cos\frac{\varphi}{2}\right)\sin\varphi\, d\varphi = 0\ ,$$

which relations show that the functions $C_{\varkappa}^{\mu}\left(\sin\frac{\varphi}{2}\right)$ and $C_{\varkappa}^{\mu}\left(\cos\frac{\varphi}{2}\right)$ vanish at least for one value of φ within the respective interval of integration. This gives rise to the following theorems:

The smallest among the roots of $C_{n}^{\nu}(\cos x)$ *lying between* 0 *and* $\frac{\pi}{2}$ *is larger than the smallest of the roots of* $C_{2n}^{2\nu}\left(\cos\frac{x}{2}\right)$ *fulfilling the same conditions and the greatest among the above named roots of* $C_{n}^{\nu}(\cos x)$ *is smaller than the greatest among the roots of* $C_{2n}^{2\nu}\left(\cos\frac{x}{2}\right)$ *belonging to this region.*

The smallest among the roots of $C_{n}^{\nu}(\cos x)$ *lying between* 0 *and* $\frac{\pi}{2}$ *is larger than the smallest of the roots of* $C_{2n+1}^{2\nu-1}\left(\sin\frac{x}{2}\right)$ *fulfilling the same conditions, and the greatest among the above named roots of* $C_{n}^{\nu}(\cos x)$ *is smaller than the greatest among the roots of* $C_{2n+1}^{2\nu-1}\left(\cos\frac{x}{2}\right)$ *belonging to this region:*

By putting in the first proposition ν equal to $\frac{1}{2}$ and by marking that

$$\overset{\frac{1}{2}}{C}_{n}(\cos x) = P_n(\cos x) \;,$$

$$\overset{1}{C}_{2n}(\cos \chi) = \frac{\sin(2\,n+1)\,\chi}{\sin \chi} \;,$$

$$\overset{1}{C}_{2n}(\sin \chi) = (-1)^n \frac{\cos(2\,n+1)\,\chi}{\cos \chi}$$

and that sin α increases, $\cos \alpha$ however diminishes with α, we arrive at the theorem:

The positive roots of the n^{th} spherical function $P_n(x)$ lie between $\cos\dfrac{n_1\,\pi}{2\,n+1}$ *and* $\cos\dfrac{\pi}{2\,n+1}$ *where n_1 is the greatest even number contained in n.*

This theorem is a corollary of the one deduced by **Bruns** in his treatise "On the theory of the spherical functions" (Zur Theorie der Kugelfunctionen) published in the 90th vol. of Crelle's Journal and recently proved by **Markoff** [1]) and **Stieltjes** [2]):

The roots of the spherical functions lie one by one in the intervals $\cos\dfrac{2\,i\,\pi}{2\,n+1} \;\ldots\; \cos\dfrac{(2\,i-1)\,\pi}{2\,n+1}$.

From the preceding theorems we can easily deduce the following:

The difference between the greatest positive root of the function $\overset{\nu}{C}_{n}(x)$ and unity is less than two times the square of the smallest positive root of $\overset{2\,\nu}{C}_{2n}(x)$.

The difference between the greatest positive root of the function $\overset{\nu}{C}_{n}(x)$ and unity is less than two times the square of the smallest positive root of $\overset{2\nu-1}{C}_{2n+1}(x)$.

The difference between the greatest positive root of the n^{th} spherical function and unity is less than $2\,\cos^2\dfrac{n_1\,\pi}{2n+1}$.

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[1]) „On the roots of certain equations", („Sur les racines de certaines équations") Mathem. Annalen, 27th Vol.

[2]) „On the roots of the equation $X_n = 0$," („Sur les racines de l'équation $X_n = 0$") Acta Mathematica, IX Vol. „On the polynomia of Legendre", („Sur les polynomes de Legendre"), Annales de la Faculté des Sciences de Toulouse. Vol. IV. **Markoff** and **Stieltjes** deduce in the cited treatise also the narrower limits $\cos\dfrac{i\,\pi}{n+1} \;\ldots\; \cos\dfrac{(2\,i-1)\,\pi}{2\,n}$.

Two times the square of the smallest positive root of $C_{2n}^{2\nu}(x)$ *is smaller than the smallest positive root of* $C_n^{\nu}(x)$ *increased by* 1.

Two times the square of the smallest positive root of $C_{2n+1}^{2\nu-1}(x)$ *is smaller than the smallest positive root of* $C_n^{\nu}(x)$ *increased by* 1.

The two latter theorems furnish us with a less narrow limitation for the smallest positive root of the function $C_n^{\nu}(x)$ than the theorem at the conclusion of § 1.

Terrestrial magnetism. — Dr. W. van Bemmelen. "*"Spasms" in the terrestrial magnetic force at Batavia.*" (Communicated by Prof. H. Kamerlingh Onnes).

(Read September 30th 1899).

Since the great development of Seismology, the instruments, which record photographically the quantities determining the earth's magnetism have also rendered good service as Seismographs in the researches on the propagation of earth-waves in the surface of the earth.

During half a year I had the opportunity of tracing the seismic disturbances in the Magnetograms at Batavia, and this under very favourable circumstances; for, not only was the fear of local disturbance very small, the temperature constant and the damping large, but since June 1st 1898 a new Milne Seismograph had been working and furnishing accurate information about seismic disturbances. When an earthquake is near, these appear in the curves of the Magnetograms as discontinuities, viz. the needle suddenly starts vibrating and continues doing so for some minutes; when at a greater distance, on the contrary, only a more or less considerable regular broadening of the curves appears. Comparison with the Milne-Seismograms quickly taught me that the seismic disturbances at Batavia seldom are large enough to appear in the Magnetograms, but also conversely, that no trace of a large number of analogous disturbances in the Magnetograms could be detected in the Seismograms.

Hence there is danger of considerable confusion: if for instance an earth-wave has passed at Batavia at 11.10 which has not appeared in the Magnetograms, then very likely a non-seismic disturbance, occurring at 11.5 for instance, will be mistaken for an earth-wave and an error of minutes will be made. Moreover it is necessary to inquire whether a new phenomenon does not mingle with those just mentioned.

I have given the name "*Spasms*" to these little motions. These appear as broadenings of the curves of the Bifilar-Magnetometer, which may be caused by vibrations of the magnetic force with an amplitude of from 3 to 15 g. (g = 0.00001 C. G. S.) during about 1 to 8 minutes. On the scale of the bifilar-magnetogram 1 m.m. represents 4 minutes and 5 g.

On trying to find an answer to the question, whether there is really evidence of a new kind of small disturbances, I employed two methods, that of statistics and that of direct observation. After the example of ESCHENHAGEN I constructed a Microvariometer for the Horizontal Intensity, in which a light magnet is held perpendicular to the magnetic meridian by the torsion of a German-silver wire. The period of a complete vibration was 9 seconds, the damping ratio 2—7, the value of the tenths of divisions, which could be estimated very easily, 0,06 g.

With this instrument I observed continuously during one or two hours for many nights, and often took readings every fifth second, but unfortunately I have not yet been lucky enough to observe an undoubted Spasm. It occurred on only one occasion and was even then not a striking one.

Notwithstanding this adversity I have been able to learn much from these observations.

For instance I happened to be behind the telescope when a series of faint earth-waves, distinctly registered by the Seismograph, passed Batavia, and though wholly unconscious of this, I nevertheless noted three times horizontal and vertical motions of the magnetic needle. Their period was 2,5 seconds, half that of the free vibration of the magnet.

This observation during the occurrence of a Spasm in the Magnetogram indicated that really a kind of miniature disturbance had passed, and not a prolonged motion, caused by an earthquake. On one occasion I noted, while everything else was quiet, a strong impulse three times in one minute, which caused deviations of 20 to 40 g. The Magnetograms did not show the least signs of these, as the damping of the magnet is too rapid and the paper is not sensitive enough to light. Although my direct observations have not until now met with much success, they nevertheless make the existence of very small *magnetic* disturbances appear probable in this case. Here at Batavia only the curves of the Horizontal Intensity show the Spasms, never those of the Declination which rarely exhibit perturbations at our tropical station.

In compiling the statistics we met with three difficulties:

1st. The number of Spasms detected depends upon the breadth and distinctness of the curves, which are very variable during the registering-period 1883—'99.

2nd. During a very unsettled state of the Magnet it was often impossible to distinguish between the various kinds of disturbances.

3rd. The possibility exists, that many earthquakes have not been noticed, though I had made extracts formerly from the statistics of earthquakes published in the "Natuurkundig Tijdschrift voor Nederlandsch Indië".

Only the difficulty mentioned under 1 is unevitable, and indeed its baneful influence has been keenly felt.

I searched the Magnetograms of the continuous series from March 27 1883 till March 27 1899; for the undulations only the years with narrower curves.

ANNUAL NUMBERS.

	Year	No. of Spasms.	Period.	No. of Spasms.
Sun-spot maximum	(27 III–31 XII) 1883	(37)	27 III 1883-27 III 1884	55
	» 84	43	» 84- » 85	50
	» 85	64	» 85- » 86	58
	» 86	74	» 86– » 87	81
	» 87	63	» 87- » 88	54
	» 88	43	» 88- » 89	36
(1889.6) Sun-spot minimum	» 89	31	» 89- » 90	51
	» 90	57	» 90– » 91	46
	» 91	45	» 91– » 92	44
	» 92	57	» 92- » 93	53
	» 93	83	» 93– » 94	88
(1894.0) Sun-spot maximum	» 94	75	» 94– » 95	74
	» 95	103	» 95– » 96	122
	» 96	114	» 96– » 97	106
	» 97	105	» 97- » 98	96
	» 98	89	» 98– » 99	99
	» 99	(30)		1113
		Total 1130		

If we take into account, that especially in the years 1888—91 the curves are very broad and during the years 92—97 almost invariable in breadth, then a concordance with the number of sunspots appears rather dubious.

ANNUAL VARIATION.

It soon appeared that an annual fluctuation existed in the frequency of the disturbances. Hence I have calculated for a closer inquiry the twelve day and not the monthly means. (Five 13 days periods were made, distributed equally throughout the year.)

Period.		No. of Spasms	△	Period.		No. of Spasms	△
1 I	—12 I	29	— 8	2 VII	—13 VII	21	—16
13 »	—24 »	36	— 1	14 »	—25 »	25	—12
25 »	— 5 II	39	2	26 »	— 7 VIII	19	—18
6 II	—17 »	57	20	8 VIII	—19 »	27	—10
18 »	— 1 III	73	36	20 »	—31 »	32	— 5
2 III	—14 »	64	27	1 IX	—12 IX	38	— 1
15 »	—26 »	51	14	13 »	—24 »	35	— 2
27 »	— 7 IV	48	11	25 »	— 6 X	49	12
8 IV	—19 »	41	4	7 X	—19 »	63	26
20 »	— 1 V	35	— 2	20 »	—31 »	47	10
2 V	—13 »	29	— 8	1 XI	—12 XI	30	— 7
14 »	—26 »	30	— 7	13 »	—24 »	41	4
27 »	— 7 VI	16	—21	25 »	— 6 XII	41	4
8 VI	—19 »	26	—11	7 XII	—18 »	23	—14
20 »	— 1 VII	20	—17	19 »	—31 »	28	— 9
						Mean 37	

Hence the annual variation of the Spasms is very clear, and with two maxima. In order to determine even more accurately the dates of the maxima etc., I have calculated the daily numbers for the adjacent months and compared them by means of the formula $a + 2b + c$. A principal maximum certainly appears from these on February 22, a second smaller maximum on October 17; a minimum on December 22 (close to Dec. 20, the mean of Oct. 17 and Febr. 22) and a second very uncertain minimum. Here the comparison of the daily numbers for the period May 23—August 7 by means of the formula

$$\frac{a + 2b + 4c + 6d + 4e + 2f + g}{20}$$

left the choice between June 22 and July 12; and as June 21 is midway between Febr. 22 and Oct. 17, we have good reason for choosing June 22.

The harmonic analysis of the numbers for the 12 days periods yields:

$$D = 37.1 + 10.2 \cos (n \times 12° - 24°15') + 8.3 \cos (n \times 24° - 67°53')$$

but this formula does not account for the steeply rising maxima, which demand the terms with $3\,\varphi$ and $4\,\varphi$ and so reduce the cosine-formula to a mere result of calculation. I think it therefore more suitable to defer the deduction of formulae until an explanatory and acceptable hypothesis has been found.

DIURNAL VARIATION.

Hour.	No. of Spasms	△	Hour.	No. of Spasms	△
0— 1 A M	91	45	0— 1 P M	48	2
1— 2	72	26	1— 2	45	— 1
2— 3	59	13	2— 3	46	0
3— 4	35	—11	3— 4	48	2
4— 5	19	—27	4— 5	39	— 7
5— 6	11	—35	5— 6	47	1
6— 7	8	—38	6— 7	25	—21
7— 8	7	—39	7— 8	43	— 3
8— 9	23	—23	8— 9	66	20
9—10	27	—19	9—10	58	12
10—11	46	0	10—11	103	57
11—12	37	— 9	11—12	110	64

Hence mean 46

Principal maximum (110) 11 —12 PM.
" minimum (7) 7 — 8 AM.
Secundary maximum (48) ± 2 PM.
" minimum (25) 6 — 7 PM.

The harmonic analysis of the hourly numbers yields:

$$S = 46.5 + 24.6 \cos (n.\,15° - 324°52') + 7.8 \cos (n.\,30° - 312°33') + 13.6 \cos (n.\,45° - 8°48') + 21.3 \cos (n.\,60° - 331°9')$$

Again the term with $4\,\varphi$ is very large. One receives the impression that in the daytime the height of the sun exerts a certain influence for, the minima appear about sunrise and sunset and the maxima, as frequently happens, about midday.

The mean diurnal variation calculated from four maximum and from four minimum months does not show any sensible difference.

DIURNAL VARIATION FOR MAXIMUM AND MINIMUM PERIODS.

H.	Febr.-March Sept.-Oct.	May-June July-Dec.	The Nos. for minimum periods multiplied by 2.
0— 1 AM	44	17	34
1— 2	37	18	36
2— 3	35	10	20
3— 4	12	13	26
4— 5	8	5	10
5— 6	6	2	4
6— 7	3 min.	4 min.	8
7— 8	3	2	4
8— 9	11	1	8
9—10	10	7	14
10—11	18	11	22
11—12	14	10	20
0— 1 PM	24	12	24
1— 2	21	11 max.	22
2— 3	12 max.	12	24
3— 4	21	6	12
4— 5	17	9	18
5— 6	20	12	24
6— 7	12 min.	8	16
7— 8	22	6	12
8— 9	34	18	36
9—10	31	9	18
10—11	42	21 max.	42
11—12	46	21	42
	503	248	496

I further investigated whether any connection existed between the frequency of the Spasms and the tropical and the synodical revolution of the moon, respectively 29,5306 and 27,3216 days; and moreover with the sun's rotation, for the periods: 25,787; 25,800; 25,815; 25,857; 25,929 and 26,071 days.

In none of these cases however was a marked periodicity found, at all events nothing pointing to a direct influence of these revolutions. Such an influence would have been useful for the explanation of the phenomena we are now considering.

It is not possible now to give an explanation; for that purpose we require, that

1st. The Microvariometer should furnish new material for research;

2nd. The phenomenon is also investigated at other magnetic observatories;

3rd. A theory of the variation of the earth's magnetic force, of the Aurora borealis and of the electric currents in the earth and the high atmosphere has been established.

I will only point out some analogies, which may perhaps contribute afterwards to an explanation.

The deviations, calculated according to VAN DER STOK's method of reduction, can serve as an indication of the amount of disturbance of the Horizontal Intensity at Batavia, especially for the shifting of the lines. The table [1]) for the period 1892—93 shows for these deviations

1st. A semi-annual period, with its maxima in March and September, its minima in June and January.

2nd. A diurnal period, with its maximum at 3 P. M. and its minimum at 1 A. M.

3rd. A concordance with the number of sun-spots.

Hence there is agreement between the annual variation of these deviations with that of the Spasms, but not between the diurnal variations.

The photograms giving the Potential of atmospheric electricity show nothing in particular during Spasms, the diurnal variation of the Potential is even reverse and is not semi-diurnal. The annual variation again only contains *one* maximum and *one* minimum. Coincidences in the variations of the meteorological elements are not to be detected. Important coincidences are found with the periodical fluctuations of the Aurora borealis here, in the nightly maximum and the semi-annual periodicity characteristic of this.

The observed numbers have shown, that the epochs of the maxi-

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[1]) Observations, Batavia, Vol. XVI.

mum and the minimum are altered together with the geographical position, and that the daily variation has no secundary maximum at noon. We should not forget however, how large the influence of moon- and daylight is, and how difficult it is to choose an adequate scale for the Intensity. At lower latitudes the maximum is reached a little before midnight, the minimum about six o'clock in the morning.

The annual variation of the Aurora australis according to BOLLER [1]) is given by:

Jan.	Febr.	March	April	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
63	104	119	77	44	25	39	52	58	67	63	65

which shows considerable analogy with that of the Spasms; but unlike the Spasms the Aurorae are more numerous during a disturbed magnetic state.

It seems however that a connection exists with a series of wholly different motions in the curves of the Horizontal Intensity, in which for a time varying from a few minutes to several hours the Magnet regularly executes little oscillations with an almost constant period of about 1—4 minutes, and an amplitude of from 1 to 7 g.

I had made these motions already the subject of a careful inquiry, when a remark in the second paper [2]) of Prof. ESCHENHAGEN made it appear probable to me, that Dr. ARENDT had made already a similar investigation for the curves at Potsdam.

Prof. ESCHENHAGEN writes (p. 679): "So far as has been observed until now, these vibrations appear principally in the daytime; at night they are very rare. But frequently at night larger oscillations occur, which are observed even macroscopically in the usual records and which usually occupy whole minutes, though the phenomenon itself seldom lasts for an hour, but usually only for a short time. Already at the beginning of the registering in 1890, attention was paid to this, as the greater distinctness and larger time-scale at Potsdam allowed the phenomenon to be observed there better and more easily than at other observatories. Since then Dr. ARENDT has studied this kind of waves, and he is inclined to the opinion, that they are connected with the phenomena of atmospheric electricity."

This paper of Dr. ARENDT's "Beziehungen der Elektrischen Erscheinungen unserer Atmosphäre zum Erdmagnetismus (das Wetter

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[1]) W. BOLLER. Das Südlicht. Beiträge zur Geophysik. Bd. III. Heft 4. S. 554. 1898.
[2]) Sitzungs Ber. d. Pr. Akademie d. Wiss. zu Berlin 1897. June 24.

1896, Heft 11 und 12)", is, I regret to say, not at my disposal here, therefore I will only touch slightly on this matter now.

I have given the name *Pulsations* to these wave motions in the curves, contrasting them thus with the Spasms, because of their resemblance to similar motions in the Seismograms, which were first detected by v. REBEUR-PASCHWITZ and afterwards by MILNE and EHLERT, and to which this name was given by VON REBEUR.

I have compiled statistics of the occurrance of these Pulsations in the years with narrow registering curves, which led to the following result:

1 Jan.—12 July 1885	278 series
1892	267 »
93	169 »
94	97 »
95	241 »
96	230 »
97	249 »
98	197 »

Annual variation for the Period 1892—98.

Jan.	127	July	99
Febr.	116	Aug,	115
March	142	Sept.	101
April	134	Oct.	96
May	144	Nov.	132
June	157	Dec.	87
	820 Series		630 Series

Monthly mean 121.

DIURNAL VARIATION.

Hour.	No. of series of pulsations.	Hour.	No. of series of pulsations.
0— 1 AM	223	0— 1 PM	42
1— 2 »	140	1— 2 »	45
2— 3 »	121	2— 3 »	42
3— 4 »	83	3— 4 »	37
4— 5 »	53	4— 5 »	33
5— 6 »	24	5— 6 »	31
6— 7 »	15	6— 7 »	45
7— 8 »	6	7— 8 »	70
8— 9 »	11	8— 9 »	111
9—10 »	26	9—10 »	127
10—11 »	36	10—11 »	162
11—12 »	46	11—12 »	199

Mean 72

The frequency of the Pulsations was tested in vain like that of the Spasms for a concordance with the tropical or synodical revolution of the Moon.

In the yearly values of the frequency of these Pulsations no parallelism with the numbers for the sun-spots can be found, and in the monthly values a not very distinct yearly undulation appears, which however is quite different from that of the Spasms. But, curiously enough, the daily variations in the frequency agree, without being however quite equal, as appears from the following table of the epochs of the maxima etc.

	Spasms	Pulsations
Principal maximum	11—12 P.M.	0—1 A.M
» minimum	7— 8 A.M.	7—8 A.M.
Secundary maximum	± 2 P.M.	± 1 P.M.
» minimum	6— 7 P.M.	5—6 P.M.

The Electrograms at Batavia show nothing remarkable during the occurrence of Pulsations, which means that no simultaneous changes in the Potential can be observed. As regards the slope of Electric Potential in the lower strata of the atmosphere, I think this will not have any influence on the magnet.

In concluding this preliminary communication I will point out, that a magnetic calm favours the development of the Pulsations, which is connected directly with the quiet of night, as shown by the magnetograms at Batavia. This nightly calm is clearly indicated by the diurnal variation of the above mentioned „deviations", and the epoch of the minimum (1 A.M.) practically coincides with the maximum epoch of the Pulsations. But also the minimum epoch of the deviations (3 P.M.) coincides with the epoch of the secondary maximum, and this makes the connection less clear.

Physics. — Dr. FRITZ HASENOEHRL. "*The dielectric-coefficients of liquid nitrous oxide and oxygen.*" (Communication N⁰. 52, from the Physical Laboratory at Leyden by Prof. H. KAMERLINGH ONNES).

(Read September 30th 1899).

Measurements of the dielectric-coefficients of liquid gases have been made up to the present only by LINDE [1]) and by DEWAR and

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[1]) LINDE, Wied. Ann. 56 p. 546.

Fleming [1]). The measurements of **Linde** are concerned with those gases which become liquid under high pressure at relatively high temperatures and are not in direct relationship with the following work. On the contrary **Dewar** and **Fleming** have sought the dielectric-coefficient of liquid oxygen under the same condition as I, namely at the temperature of the normal boiling point under atmospheric pressure.

The gases were liquefied in the cryogenic laboratory of the University of Leyden, the arrangement of which is described in another place [2]). I shall hence confine myself to mentioning here the special arrangements used in the determination of the dielectric-coefficients. During the experiments the cryogenic apparatus was under the personal care of Prof. **Kamerlingh Onnes**, through whom alone my research was brought to a satisfactory conclusion. I wish to express here, for this and much other valuable assistance, my warmest and most sincere thanks.

1. *The Method.*

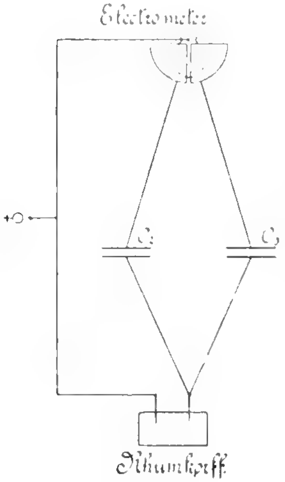

Fig. 1.

The method I used was a modification of **Gordon**'s, the principle of which is clearly and diagramatically shown in Fig. I. The inner surfaces of two condensors C_1 and C_2 are connected to the quadrant pairs of a **Thomson** electrometer, and the outer surfaces to one pole of an induction coil the other pole which is earthed together with the needle of the electrometer. Then, if the capacities C_1 and C_2 are equal, the needle will not be deflected on starting the coil. If C_1 is an adjustable condenser, then the capacity of C_2 with different media can be obtained and hence immediately the dielectric coefficients of these media. But this assumes that the electrometer is constructed symmetrically and that the capacity of the leads and also of the non-inductive parts of the condenser (i. e. other than the plates) are the same on the two sides. The simultaneous elimination of these two sources of error offers considerable difficulties.

If we call γ_1 and γ_2 the capacities of the quadrant pairs together

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[1]) **Dewar** and **Fleming**, Proc. R. S. Lond.

[2]) **Kamerlingh Onnes**, Comm. Phys. Lab. Leiden N⁰. **14.** **Mathias**, Le Laboratoire cryogène de Leyde, Rev. Gén. d. Sciences, 1896 p. 381. And especially **Kamerlingh Onnes**. Methods and apparatus used in the cryogenic laboratory I. loc. cit. No. 51.

with their leads; p_1 and p_2 the characteristic constants of their action on the needle (the differential quotients of the mutual induction coefficients by the rotations); C_1 and C_2 the capacities of the two condensers to be compared; c_1 and c_2 the capacities of the non-inductive parts of the condensors connected to the electrometer; then the equation for the equilibrium of the needle is [1])

$$\left(\frac{C_1}{c_1+\gamma_1}\right)^2 p_1 = \left(\frac{C_2}{c_2+\gamma_2}\right)^2 p_2 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

If however this equation is fulfilled the equality of C_1 and C_2 does not immediately follow. We can first make $p_1 = p_2$ by some known method. In this case equation (1) takes the form

$$\left(\frac{C_1}{c_1+\gamma_1}\right)^2 = \left(\frac{C_2}{c_2+\gamma_2}\right)^2 . \quad . \quad . \quad . \quad . \quad . \quad (1')$$

We can now reverse C_1 and C_2 thus changing their influence and, keeping p constant, alter γ through a capacity such that the equilibrium of the needle is not further altered by this reversal. Hence besides (1') we have

$$\left(\frac{C_2}{c_2+\gamma_1}\right)^2 = \left(\frac{C_1}{c_1+\gamma_2}\right)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

And from (1') and (2) it follows that we must have $\gamma_1 = \gamma_2$ and $c_1 = c_2$ if we wish to arrive at

$$C_1 = C_2 \; .$$

It would however be difficult to make these quantities p and γ equal with the necessary accuracy. Further they alter with every change in the nullpoint of the electrometer needle, and hence these equalizations would have to be often repeated and would be certainly very tedious and lengthy. On account of these difficulties I have modified the method as follows.

C_2 remains permanently unaltered, C_1 is an adjustable condenser, and is so arranged that the needle will not move when the coil is started. The condenser, of which the capacity is required, is now put in parallel with C_1. To bring the needle back to zero, the capacity C_1 must be decreased by a measurable amount which is equal to the required capacity. In this way the symmetry of the electrometer etc. requires no attention. The sole condition is that the wires, which put the unknown capacity in parallel with C_1, have not themselves

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[1]) See MAXWELL Electricity and Magnetism. Vol. I. p. 219.

a measurable capacity. Naturally this is not easily attained, but the respective corrections may be determined fairly simply as explained below.

2. *Description of the separate apparatus.*

The electrometer was a THOMSON's in its original form. When this is set up in the neighbourhood of the working pumps of the cryogenic laboratory it must be little sensitive to vibration. For this purpose I obtained the damping by air (after TÖPLER), instead of by sulphuric acid, and replaced the bifilar suspension of two cocoon fibres by a platinum wire about 70 cm. long and 30 μ in diameter which can carry a much greater weight.

After these changes had been made the vibrations were less than 0.1 mm. on a scale at 3.5 m. distance, even when the pumps of the cryogenic laboratory were working at a distance of 10 m., while with the original arrangement it was quite impossible to make observations under the same conditions.

The induction coil was worked by an alternating current making 200 vibrations per second, the spark distance at the ends of the secondary being about 0.05 mm.[1]

For the condenser an apparatus was used which was constructed according to NERNST[2] viz. two metal plates between which a glass plate can be displaced. Theoretically the alteration in the capacity is proportional to the position of the glass plate. In practice however the condenser must first be calibrated. This can be done with the help of a specially constructed condenser such as NERNST's Trough condenser[3]. The one used and shown in Fig. 2 only differs from this in that the ebonite cover has been replaced by a metal one; and the metal tube, to which the other plate is fastened, by a stiff wire *D* of 2 mm. diam. The latter is insulated from the metal cover by a small thickness of ebonite. In a condenser constructed thus the non-inductive capacity is exceedingly small.

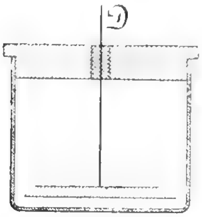

Fig. 2

In the construction of the experimental condenser there are two points to be primarily considered; as large a capacity as possible must be introduced into a somewhat limited space, and the non-inductive capacity which is connected to the electrometer must be as small as possible. These

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[1] Preliminary experiments showed that the passage of sparks of several millemeters long did not explode liquid nitrous oxide though this is endothermic.

[2] NERNST, Zeitschrift für physik. Chemie XIV. 4.

[3] NERNST, loc. cit.

conditions were fulfilled in the manner clearly shown in Plate I, which represents three different sections of the condenser together with the beaker of the cryostat, made to receive the liquefied gas, in which it is placed.

The two outer plates p_1 and p_2 are connected by the nut *s* to one another and by the pin *t* with the earth. The three screws *s* are placed in suitable glass tubes on which the five plate condenser is itself mounted. The plates themselves have a radius of 3 cm. and are separated from one another by small glass rods 1 mm. long. To reduce the errors so introduced to a minimum these glass rods must be made as small as possible, and it appeared to be best to cut them from a 1 mm. glass tube with a wall of $^1/_5$ mm. and then to grind them exactly equal. The above mentioned error cannot finally be more than 0.1 $^0/_0$ since it enters equally into the numerator and denominator of the expression for the dielectric coefficient. The 1st, 3rd and 5th plates are connected with a pole of the induction coil, the 2nd and 4th with the electrometer. The necessary wires for this, d_1 and d_2, are fastened to the 1st and 2nd plates respectively; they are drawn through small openings in the superimposed plates, and continue above through the glass tube *g*.

By means of a pin *t* the whole condenser is fastened to the cover of a hollow cylinder of brass *m* in which the liquid to be investigated is placed. The hollow cylinder is earthed together with the two outer plates [2]).

The method of filling the condenser with liquid gases must now be discussed, but some points should be first considered. The condenser and hollow cylinder must be protected as much as possible from external heat to prevent the formation of bubbles of vapour, whence they are immersed in the beaker B_1 under the liquid gas. The liquid gas must be employed in sufficient quantity to cool the condenser and to keep it cold, it must be kept from the deteriorating action of atmospheric air, and finally care must be taken that the vapours drawn off are not lost. All these conditions can be best obtained by the aid of a cryostat i. e. a boiling glass with its cases, such as is used in the cryogenic laboratory for measurements with liquid gases. The description of the latter can be found in another place [3]).

The following must also be considered. The principle of the method

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[1]) The section is taken partly through the tube *g* and partly through the tube *N*.

[2]) By the wire φ. See Plate I, Comm. N⁰. 51.

[3]) KAMERLINGH ONNES, Comm. N⁰. 51 § 3.

is to compare the capacity of the same condenser in air and in a given medium when all dimensions are kept strictly constant. When the capacity of the air condenser is obtained at the room temperature, and that of the liquid condenser at the temperature of boiling gases the geometrical proportions are probably altered by thermic expansion and deformation, and in consideration of the large difference of temperature it is possible that an appreciable error may thus enter.

For these reasons the condenser was arranged in the hollow cylinder so that this enclosed space could be evacuated and cooled in liquid gas. Then, in the manner described below, this evacuated space containing the condenser could be filled with liquid gas from the beaker.

It must be noticed that, however thin the leads may be they always will represent a measurable capacity and hence that the smallest displacement of the apparatus will produce considerable errors. Especially to avoid this it is desirable to mount the apparatus as in ONNES' method for the use of liquid gases in measurements. According to this method, the apparatus to be dipped in and filled with liquid gas is mounted in the closed boiling case, in which the liquid can be immediately poured out, so that the operations of exhausting cooling and filling with the liquid gas allow the position of the condenser and the leads to remain unaltered.

The manner in which the above mentioned hollow brass cylinder is mounted with the experimental condenser in the boiling glass is given in Comm. N°. 51 § 2 [1]). The further arrangement of the covering of the condenser is shown in Plate I. The inside of the cylinder communicates with the exterior in two ways. One is the fine copper tube *r* which communicates with the part of the beaker unoccupied by the cylinder. This can be opened or closed at pleasure from without by means of a cock in which the pin *h* is moved by the rod h_2 and handle h_3. The other outlet is the glass tube *g*, through which the expanding vapours can be drawn towards *u* to be collected in the caoutchouc bags [2]).

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[1]) Plate I is a detailed drawing of the cryostat containing the condenser. Plate IV is a diagramatic representation of the nitrous oxide circulation and the cryostat, for the oxygen circulation see MATHIAS l. c.

[2]) Further explanations: a_2 are small screws to fasten packing a_1, *b* wooden block to support glass tubes z_1 which the wires d_1 and d_2 pass through, *c* wooden block in two parts to support outflow tube without conducting of heat, *f* soldered in screw used in boring the canal for the liquid gas, k_1 packing under the level, k_3 brass mount for screwing on the same, k_2 leather cushion, *e* caoutchouc tube to connect the glass tube *g* with the brass covering of the condenser and protected by fishglue against the liquid gas. e_2 brass bands to make all tight with the help of the screws

Measurements are obtained with the above as follows. First the cock h is shut and the liquid gas allowed to stream into the boiling glass. When a sufficient quantity has collected there, and we may consider that the whole of the condenser has assumed the temperature of the gas, the inside of the hollow cylinder is evacuated through the glass tube g and the capacity of the condenser determined. The cock h is then opened so that the liquid gas streams into the inside of the cylinder in consequence of the pressure. When this operation is finished the cock h is again shut and the capacity of the condenser redetermined, this time with the liquefied gas as a medium[1]).

In order to be certain that the cylinder was full of liquid gas the gauge N was found to be necessary, in which the level of the meniscus indicates outside the level of the liquid in the cylinder or the glass tube g adjacent to it. The glass tube l which connects g to N allows an equalization of pressure[2]).

It was unfortunately impossible for the electrometer and above mentioned auxiliary apparatus to stand in the room where the refrigerating machinery is installed, partly from want of space and partly because of the inevitable vibration caused by the working of and attendance on the pumps. Hence I had simply the choice between, placing the boiling flask containing the condenser in the neighbouring room where the electrometer already stood; or keeping the boiling flask in the cryogenic laboratory and connecting the condenser to the electrometer by adequately long leads. In the former case the liquefied gas would have to be conveyed to the boiling flask through about 5 m. of tubing into which it would be very difficult to prevent the entrance of heat, and a successful termination of the research would be doubtful. This consideration caused me to primarily favour the latter arrangement, although the sensibility of the method is undoubtedly diminished owing to the non-neglectable capacity represented by the long leads. Finally I considered that the advantages of the latter arrangement outweighed its disadvantages.

It appeared to be necessary to eliminate the influence of the long

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indicated; j, p, q, u_1, u_2, w_1, w_2 see Comm. N°. 51 § 2; t_2 t_1 copper mountings to fasten steel pins v_1, v_2. The lateral opening of the glass tube g can be clearly seen in front of the side tube u_2 of the brass T tube.

[1]) In the first of the three sections given the beaker and condenser are empty, in the second the beaker is full and in the third both are full of liquid gas.

[2]) The gauge has been turned in the second section in order to show l. As remarked above the gauge has not been drawn in Plate I. Comm. N°. 51 § 2, it is observed through K_2 (Pl. I, loc. cit.).

leads, for which auxiliary capacities were required. These were made on the same principle as the experimental condenser; metal plates which are connected by glass tubes and separated by small glass rings. The so formed condenser is then insulated by a layer of paraffin and placed in a card-board box coated with tin foil. The foil is put to earth so that the capacity is quite invariable and independent of the presence of neighbouring bodies.

Such an auxiliary condenser is also useful when experimenting on a substance with a large dielectric-coefficient, for then the glass plate of **Nernst**'s adjustable condenser may not be sufficiently long to give the required change of capacity. In such a case the auxiliary capacity should be put in parallel with the adjustable condenser.

3. *Arrangement of the apparatus.*

In order to avoid the errors arising from the change of capacity of the leads, the whole apparatus must be immovably and permanently fixed. For the same reason the condensers should be very carefully switched on and off. This requires the use of a switch board to which the taunt wires are fixed and the capacity of which is as small as possible. Indeed for this purpose I employed small ebonite plates provided with mercury cups which could he connected by small metal bars. A diagramatic representation of the arrangement is shown in Fig. 3.

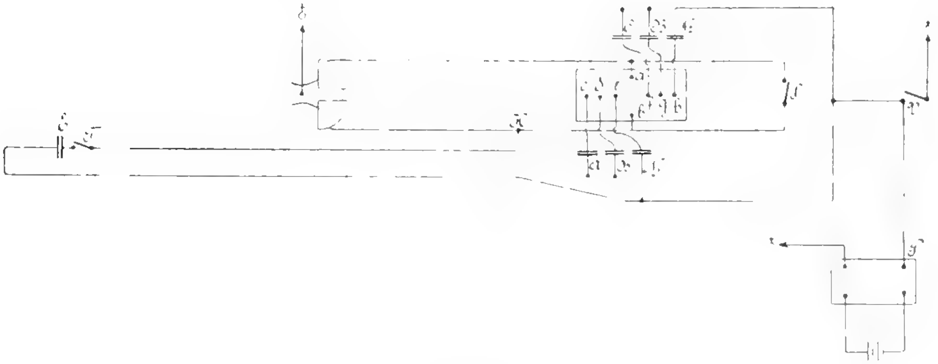

Fig. 3.

From the two quadrant pairs of the electrometer two wires proceed to the mercury cups *a* and *b*, and then to the small key *S*, by which a metallic connection between the quadrants can be made and the zero reproduced. From the six other mercury cups *c*, *d*, *e*, *f*, *g*, *h*, leads go to the inner plates of six condensers N_1, N_2, *A*, *B*, *C*, *D*, of which N_1, N_2 are adjustable **Nernst** condensers and *A*, *B*, *C*. *D* are auxiliary condensers as described above. The outer plates of these last four condensers can be connected as required to the earth or to the pole P of the Rumkorff coil to which the outer plates of N_1 and N_2 are always connected. When the key V is shut the condensers are earthed together. From H a wire proceeds into the neighbouring room, and can be connected by the key T to the experimental condenser E; the outer plate of which is always connected to the coil.

Although only one adjustable condenser is required by the theory of the method, the second N_2 is used partly for convenience, partly for the calibration of the former [1]) as described below.

4. *Calibration of the adjustable condensers.*

The adjustable condenser was, as mentioned above, an instrument constructed after NERNST's design. The alteration in the capacity would be proportional to the movement of the glass plate if the apparatus were theoretically exact. This is naturally not the case, so the condenser must first be calibrated. The method employed is also due to NERNST. The calibration condenser is put in parallel with the adjustable condenser as described above, and the displacement determined which is required to re-establish equilibrium.

When this is done the calibration condenser is again cut off, and equilibrium re-obtained with the help of the other adjustable condenser. The former condenser is again put in parallel with the calibration instrument, the necessary displacement measured and the process repeated until the glass plate is exhausted. In this way one finds the different positions of the glass plate which correspond to equal differences of capacity. The application of this method of calibration depends upon the supposition that the capacity of the non-inductive parts of the calibration condenser is negligible, as well as that of the wire which puts it in parallel with the adjustable condenser. The first condition is almost absolutely fulfilled by the condenser described above (see fig. 2). The use of the wire can moreover be avoided as shown by NERNST [2]). The condenser is insulated by an ebonite plate and is so arranged that the 2 mm. wire D, which projects above the cover of the condenser, stands at the same height as the wires of the adjustable condenser (Fig. 3). The calibration condenser can now be switched on and off by shifting it for about 2 mm. in a horizontal direction, so that the wire D is brought into contact with the lead. The respective positions of the

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[1]) See NERNST l. c.

[2]) l. c.

leads, condenser plates etc. will be so little altered by this, that an error from this change is scarcely to be feared.

The whole of the connecting wire is hence reduced to the above mentioned wire *D* which has already a small capacity. The error is still further reduced, as *D* is inductively affected by the metal cover of the calibrating condenser and hence may be considered as part of the inner plate of this.

The results of a calibration performed in the manner described above are given in the second column of Table I.

TABLE I.

Capacity.	Position of the glass plate	Diff.
0	8.40	
		6.65
1	15.05	
		6.40
2	21.45	
		6.20
3	27.65	
		5.95
4	33.60	
		6.10
5	39.70	
		6.20
6	45.90	
		6.35
7	52.25	
		6.58
8	58.83	
		6.70
9	65.53	
		6.78
10	72.31	
		6.41
11	78.72	
		6.16
12	84.88	
		5.59
13	90.47	
		5.25
14	95.72	
		4.96
15	100.68	
		4.54
16	105.22	
		4.17
17	109.39	
		4.13
18	113.52	
		3.62
19	117.14	

These numbers are the means of four series of observations in which the maximum difference was 0.2 mm. They form the basis of the following measurements. As only the differences of capacity are required we put the capacity in the position 8.40 as 0, in the position 15.05 as 1 etc., i. e. we take that of the calibrating condenser as unity. The corresponding numbers are given in the first column of the above table, from which intermediate values can be obtained by graphic interpolation.

As a control of the accuracy of the calibration values given in Table I the following work was undertaken. Measurements were made with another condenser in the same manner as before with the calibration condenser, but the connecting wire was about 12 cm. long and had hence a relatively large capacity. Let c be the capacity of this condenser, d that of the wire and γ that of the electrometer together with its leads, which were unaltered throughout the experiment. Further let $x_0, x_1, x_2 \ldots$ be the capacities of the adjustable condenser which correspond to the different positions of the glass plate obtained in the calibration. Hence, when the condition that the needle is in equilibrium is fulfilled, we have

$$\frac{x_0}{\gamma} = \frac{x_1 + c}{\gamma + d}\,; \qquad \frac{x_1}{\gamma} = \frac{x_2 + c}{\gamma + d}\,; \ldots . \quad \text{etc.} \qquad (3)$$

from which we have immediately

$$\frac{\gamma + d}{\gamma} = \frac{x_2 - x_1}{x_1 - x_0} = \frac{x_3 - x_2}{x_2 - x_1} = \quad \ldots \quad \text{etc.}$$

hence the consecutive displacements of the glass plate are proportional to one another. The numbers given in Table II were obtained in this manner and each is the mean of three values as satisfactory

TABLE II.

Position of the glass plate.	Capacity observed.	Diff.	Capacity calculated.	△
52 25	7.000		—	—
		1.439		
61.80	8.439		8.440	0.001
		1.475		
71.80	9.914		9.933	0.019
		1.573		
81.77	11.487		11.485	0.002
		1.612		
91.02	13.099		13.099	0.000
		1.684		
99.61	14.783		14.775	0.007
		1.743		
107.46	16.526		16.516	0.010
		1.809		
114.81	18.330		18.325	0.005

as in the former observations. The second column contains the capacities corresponding to the respective positions and obtained by the above graphic interpolation.

Column (3) contains the differences of the capacities in column (2) which should be proportional to one another. From the various consecutive quotients the geometric mean is obtained and the numbers calculated which are actually proportional to one another and which also agree as much as possible with the numbers in column (3). From these "calculated differences" column (4) is obtained by addition. The differences again between columns (4) and (2) are found in column (5) which we may safely call errors of observation. The greatest is 0.019 of the capacity of the calibrating condenser and is equivalent to a displacement of 0.13 mm. of the glass plate in the adjustable condenser. We can take this as the highest limit of attainable accuracy, being that with which a single capacity is itself determined.

Tables III and IV were obtained in the same manner. The former relates to the part of the glass plate which was not used in Table II, while the latter represents the results of an experiment in which the former method was carried out with a considerably greater capacity.

In will be seen that these tables show "observation errors" of the same magnitude as Table II, and the remarks made above concerning the accuracy of the determinations hold also with these values. On the magnitude of the errors we may notice the following. The accuracy of a single adjustment was at a maximum 0.1 mm. as shown by a number of observations, in which the readings

TABLE III.

Position of the glass plate.	Capacity observed.	Diff.	Capacity calculated.	Δ
52.25	7.000		—	—
		1.445		
43.15	5.555		5.545	0.010
		1.395		
34.55	4.160		4.164	0.004
		1.310		
26.70	2.850		2.854	0.004
		1.255		
18.90	1.595		1.611	0.016
		1.170		
11.25	0.425		0.431	0.006

TABLE IV.

Position of the glass plate.	Capacity observed.	Diff.	Capacity calculated.	Δ
27.15	2.920		—	—
		4.080		
52.25	7.000		6.988	0.012
		4.220		
80.10	11.220		11.233	0.013
		4.445		
103.70	15.661		15.663	0.002

with one adjustable condenser were repeated ceteris paribus. Each of the numbers given in the above four tables is deduced from three readings, two with the condenser N_1 and one with N_2. The values which are given in the second column of Tables II, III and IV have a larger inaccuracy, since the errors of direct reading are added to the eventually similar errors of the calibration curve. But all the values are the mean of four series of three observations, so the required error is reduced to 0.12 mm. This is in accordance with the maximum error seen in the Tables II to IV which is 0.13 mm., while most are much smaller.

These considerations are not however very precise, for the calculation of a capacity from the calibration curve implies the use of more than one observation, and the values „Capacity calculated" are derived from all the observations. Hence the calculated error must be greater than 0.12 mm., and therefore the maximum error of 0.019 in the capacity — or of 0.13 mm. in the position of the glass plate — is entirely explicable from the reading errors. This result leaves no doubt as to the accuracy of the principle of the experiments.

5. *Measurements.*

The final determinations were made in the following manner. The adjustable condenser N_1 was set at 21.45 and the key T (Fig. 3) opened, equilibrium was then attained by connecting up the auxiliary capacity and adjusting N_2. The key T was then closed and N_1 readjusted until equilibrium was again established. If now we call x_0 and x_1 the capacities of N_1 in the first and second positions respectively, γ the capacity of the electrometer and its leads including the wire from H to the key T, d that of the wire from T to the experimental condenser, c that of the experimental condenser with vacuum as a medium. Then we have as above in equation (3)

$$\frac{x_0}{\gamma} = \frac{x_1 + c}{\gamma + d}$$

or

$$x_0 - x_1 = c = x_0 \frac{d}{\gamma} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

When the experimental condenser is now filled with a dielectric fluid its capacity will be altered to c' and a considerable movement of the glass plate will certainly be required to compensate it.

If we call the capacity of the condenser in this third position x_2, then we have in analogy with the foregoing

$$x_0 - x_2 = c' - x_0 \frac{d}{\gamma} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The differences $x_0 - x_1$; $x_0 - x_2$ can be immediately read off. In the same way we may express the difference $c' - c$ as a measurable quantity from (4) and (5). From this we can determine the value of c'/c if we know the value of c, which can be obtained by measurements in which the value of γ is purposely varied. But we find that the differences of the readings occurring in the observations are so small that the value of c cannot be determined to a greater accuracy than 10 %, and is hence useless. A determination of the value of $x_0\, d/\gamma$ is required, and this can be made once for all by cutting off the lead close to the condenser and fixing it in almost exactly the same position as before by means of wax, but insulated from the condenser. One can now convince oneself that the error produced in fixing the wire does not reach 0.2 mm., by loosening and refixing it, moreover the error occurs equally in the numerator and denominator of the expression for the dielectric-coefficient. In the same way the capacity of the wire can be determined, by proceeding with the lead in exactly the same way as with the whole condenser, and thus arriving at the equation

$$x'_0 - x_0 = x_0 \frac{d}{\gamma} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

and hence

$$\frac{x_0}{\gamma} = \frac{x'_0}{\gamma + d}$$

in which x'_0 is the capacity of the adjustable condenser after the last alteration.

From (4), (5) and (6) one obtains immediately for the dielectric coefficient

$$\frac{c'}{c} = \frac{(x_0 - x_2) + (x'_0 - x_0)}{(x_0 - x_1) + (x'_0 - x_0)} = K \quad . \quad . \quad . \quad . \quad . \quad . \qquad (7)$$

In the following account of the results of my measurements let y_1 be the position of the glass plate of the adjustable condenser after switching on the experimental condenser with a vacuum as medium and at the temperature of the liquid gas; y_2 be the position when the medium is the liquid gas. The capacities corresponding to these positions are, as before, indicated by x_1 and x_2. Before the determinations the glass plate always stood at 21.45 (so $x_0 = 2.000$).

1. *Nitrous oxide.*

19 June:

$y_1 =$ . . . . (This reading was omitted)
$y_2 =$ 106.2; 106.5; 106.2.

20 June:

$y_1 =$ 58.85; 58.85; 58.90.
$y_2 =$ 107.90; 108.10; 107.95.

These determinations are not however really trustworthy, as it appeared that the nitrous oxide became quite impure.

The following results are final.

9 July:

$y_1 =$ 56.30, 56.40; 56.35 Means 56.32
$y_2 =$ 106.00; 105.90; 106.00; 106.20 106.03 (± 0.17).

The corresponding capacities are:

$(x_0 = 2.000)$.
$x_1 = 7.640$.
$x_2 = 16.191$.

2. *Oxygen.*

10 July:

$y_1 = 57.70$; 57.70; 57.75 Means 57.72

$y_2 = 86.15$; 86.10; 86.05; 85.85; 85.95 86.02 (± 0.17)

The corresponding capacities are.

$(x_0 = 2.000)$

$x_1 = 7.843$

$x_2 = 12.200$

This gives the above defined difference.

$x_0{}^1 - x_0 = 3.731.$

As the glass plate can only be moved from 21.45 to 8.40, an auxiliary condenser must be employed; it is however scarcely worth while to communicate the resulting data in extenso.

From the above results and formula (7) we obtain the following values for the dielectric-coefficients:

$$\left.\begin{aligned} K_{N_2O} &= \frac{14.191 + 3.731}{5.640 + 3.731} = 1.912 \\ K_{O_2} &= \frac{10.200 + 3.731}{5.843 + 3.731} = 1.455 \end{aligned}\right\} \quad \ldots\ldots\ldots (8)$$

To these values we can make a correction; we must consider that not only the experimental condenser but also the leads were immersed to a definite height in the liquid gas, while the entire length of the leads was 88 cm. The value

$$x'_0 - x_0 = x_0 \frac{d}{\gamma} = 3.731$$

only applies rigidly when the whole lead is in air. When the capacity of the condensers filled with liquid gas is required the quantities d and $(x_0' - x_0)$ must be multiplied by

$$\left(\frac{83}{88} + K \cdot \frac{5}{88}\right)$$

where K is the dielectric-coefficient of the medium. For this correction the approximate values given by (8) are quite sufficient, and the influence of the surrounding tubes is negligible in view of the accuracy obtained.

We arrive finally at the following values for nitrous oxide:

$$K_{N_2O} = \frac{14.197 + 3.731\left(\frac{83}{88} + 1.912\,\frac{5}{88}\right)}{5.640 + 3.731} = 1.933$$

for oxygen:

$$K_{O_2} = \frac{10.200 + 3.731\left(\frac{83}{88} + 1.455\,\frac{5}{88}\right)}{5.843 + 3.731} = 1.465\ .$$

As one sees the values of y_2 are a little more variable than those which refer to our condensers when filled with air (see § 4). This may be due to variations of temperature or small impurities. When we take this into account and assume for the other numbers the accuracy arrived at above, we find that the maximum error (if we assume that the errors are additive) in the dielectric-coefficient of nitrous oxide is 0.5 % and in that of oxygen 0.7 % while the error probably can be smaller.

The value 1.491 given by DEWAR and FLEMING for the D-C. of oxygen at the normal boiling point, differs from my value by 1.8 %, an agreement which may be considered as satisfactory, if we take into account the deviations in the various values arrived at by different workers, even where the experimental substance can be more easily produced than liquid gases.

6. *Application of the* CLAUSIUS-MOSOTTI *formula to the results.*

An obvious application of the above results is employing them to test the CLAUSIUS-MOSOTTI formula.

This is usually expressed

$$\frac{K+2}{K-1}\,.\,d = Const. = D$$

where K is the dielectric-coefficient, d the density.

This equation enables us to calculate the D.-C. of a substance in the liquid state when we know the D.-C. in the gaseous state and the densities of both aggregates.

This is unfortunately not possible for nitrous oxide as the density at the normal boiling point is not accurately known. However as it is very interesting to see how my value agrees with the observations of LINDE [1]), we will take 1.15 for the density of nitrous oxide after NATTERER [2]). Hence we obtain 4.85 as the value of D for liquid nitrous oxide at its boiling point, while LINDE found 5.42 for the same at 0° C. For gaseous nitrous oxide we obtain $D = 5.103$ assuming $d = 1.969 \times 10^3$, $K = 1.001158$ after KLEMENCIC.

With oxygen also only an approximate test of the formula is possible as the required data are inaccurate. More especially the value of the D.-C. of gaseous oxygen is unknown, and there exists only a well grounded supposition by DEWAR and FLEMING [3]) that it will not differ sensibly from that of air, which was found by both BOLTZMANN and KLEMENCIC to be 1.00059 at 0° C. and 760 mm.

The density of gaseous oxygen is 1.4292×10^{-3} at 0° C. and 760 mm. [4]), that of liquid oxygen is 1.124 after OLSZEWSKI [5]), 1.1375 after DEWAR [6]) and 1.134 after LADENBURG and KRÜGEL [7]).

If we then assume 1.00059 for the D. C. of gaseous oxygen, and 1.1375 for the density of the liquid we arrive at 1.556 as the D.-C. for the latter, which value agrees as far as the order of magnitude with the values found by DEWAR and FLEMING. Conversely assuming the D.-C. of the liquid oxygen we obtain the value of 1.00051 for the gas instead of 1.00059.

From the uncertainty of the data employed a better agreement cannot be expected. The experiments are at least not contrary to the CLAUSIUS-MOSOTTI formula, while the further consideration of its application to oxygen must be deferred for the present.

Physics. — "*The* HALL-*effect and the increase of Magnetic Resistance in Bismuth at very low Temperatures*". By Dr. E. VAN EVERDINGEN Jr. (Communicated by Prof. H. KAMERLINGH ONNES).

(Will be published in the Proceedings of the next meeting.)

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[1]) l. c.

[2]) Pogg. Ann. 62 p. 134.

[3]) l. c.

[4]) LANDOLT and BÖRNSTEIN, p. 116.

[5]) Ztschr. f. phys. Chem. XVI, 383.

[6]) Proc. Royal Instit. 96.

[7]) Ztschr. f. Compr. Gase 99 p. 77.

(November 22, 1899.)

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday November 25th, 1899.

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The following papers were read:

Physics. — Dr. E. VAN EVERDINGEN Jr. "*The* HALL-*effect and the increase of resistance of bismuth in the magnetic field at very low temperatures*". I. (Communication N⁰. 53 from the Physical Laboratory at Leiden, by Prof. H. KAMERLINGH ONNES).

(Read October 28, 1899).

1. In the Proceedings April 21 '97, p. 500 and June 26 '97, p. 74 measurements on the above subjects were just mentioned. These are

described at greater length elsewhere (Thesis for the doctorate, Chapt. VII). At that period however these measurements could not be very accurate, in consequence of the work in the cryogenic laboratory being legally prohibited on account of its alleged dangers, so that we could not adequately use liquid gases for reaching low temperatures. Hence I resorted to a mixture of solid carbon-dioxide and alcohol; but then the temperature remained constant only for a short time, and the value given is not quite accurate.

The difficulty mentioned being removed, I have taken this work up again, and am now able to communicate some figures, obtained by means of a bath of boiling nitrous oxide, i. e. at a temperature of about — 90° C.

2. *The liquid-bath.* Two forms of vessel for the liquid gas have been used.

The first consisted only of a very narrow vacuum-glass, outer diameter 33 m.m., inner diameter 21 m.m., height about 35 c.m. This was filled to two thirds of its height with liquid nitrous oxide by means of the spiral packed in solid carbon-dioxide, described in Comm. N⁰. 51, § 4 [1]). It was then mounted between the poles of an electromagnet. The experimental apparatus could be placed in the vacuum-glass before filling this, so that after filling only the necessary leads had to be connected; usually however it was lowered into the vacuum-glass after this had been placed between the poles, and was then quite ready for the experiment.

A single filling, in which about 0.4 kgm. of nitrous oxide in all was taken from the cylinder, was sufficient to cover the apparatus for more than two hours. A draw-back of the use of vacuum-glasses is however the large space between the poles, which is required even with this narrow glass, and prohibits the use of comparatively intense fields.

In order to meet this difficulty a second form without a vacuum wall [2]) was constructed, drawn in fig. 1. The vessel for the liquid in the strict sense of the word consists of a cylindrical wooden receptacle *a*, in the bottom of which a vessel made of compressed paper with oval section and wooden bottom is glued. Externally

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[1]) Verslag der Verg. Kon. Akad. v. Wet. Amsterdam, 30 September '99, p. 135. Comm. Phys. Lab. Leiden N⁰. 51.

[2]) In the same way in the ethylene boiling flask (Comm. N⁰. 14, Versl. Dec. '94) the condensed gas is only sufficiently protected against heat by air-spaces and wool wrapping.

these vessels are covered with shellac, internally with fish-glue. Round the paper wall about $^3/_4$ m.m. thick a cotton thread has been wound forming a layer also $^3/_4$ m.m. thick; while the inner minor axis is 12 m.m., the maximum thickness is thus restricted to 15 m.m. By means of the conical caoutchouc ring *c* the vessel *a* is connected to the glass tube *d*, which becomes narrower at the top. Onto this the brass **T**-tube *e* fits, which is connected to it by means of a caoutchouc tube. Through the caoutchouc stopper *g* lead four glass tubes $h_1 \ldots h_4$, containing the leads for the experimental apparatus. For pouring out the condensed gas a steel capillary tube *k*, covered by a rubber tube leads through the side-tube of *e* and is screwed on to the above mentioned condensing spiral.

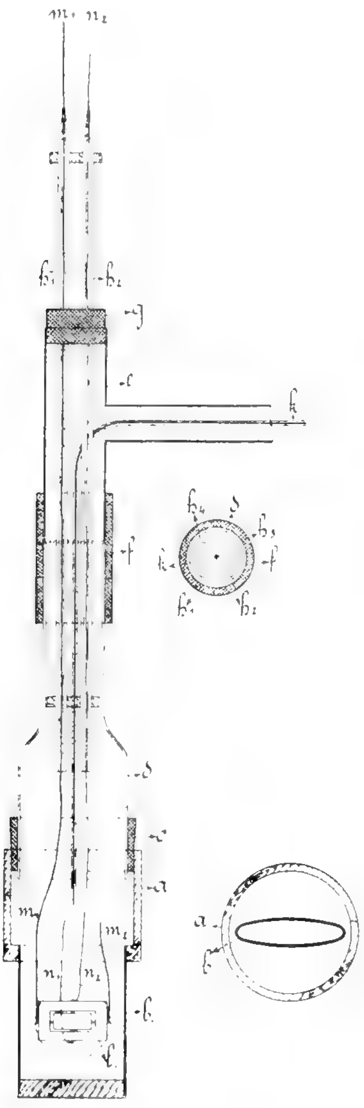

Fig. 1.

If it is desired to collect the evaporated gas, all connections may easily be made air-tight; for this purpose the glass tubes are drawn out at the top and the leads may be cemented there. Conduits leading to a pump or gas-sack can be then connected to the side tube of *e*.

The **T**-piece *e* fits also on the above described vacuum-glass and may serve to close it, as will be necessary in further researches. Untill now there was no objection to leaving both baths open and allowing the gas to escape.

In the observation of the HALL-effect in an electrolytic plate of bismuth, to be mentioned directly, the vessel *a* was about half filled after a small quantity of liquid had evaporated. It took more than an hour, before the level of liquid was lowered to the opening of *b*. In these operations about 0.7 kgm. of nitrous oxide was used. The space between the vessels *a* and *b*, the polepieces and the coils of the magnet was filled throughout with wool.

3. *The* Hall-*effect in electrolytic bismuth.* The plate is obtained n the way described in Comm. N°. 42 [1]).

The method of observation is the same as in all the previous experiments, and was described in Comm. N°. 26 [2]). The plate carrier l is made of ebonite.

The leads for the Hall-current $n_1\, n_2$ are only 0.1 mm. thick, in order that they may conduct as little heat as possible, the larger resistance being immaterial. The wires $m_1\, m_2$ supplying the primary current of about 0.5 amp. were chosen somewhat thicker, 0.25 mm., in order to decrease the heat produced in the liquid without increasing too much the heat conducted to it.

The following results were obtained for the coefficient of **Hall** R and the product RM (M = Magnetic force).

Temp.	MAGNETIC FORCE.											
	1300		2600		3900		5000		5800		8100	
	R	RM	R	RM	R	RM	R	RM	R	RM	R	RM
+ 15°	*11,2*	14,5	*10,9*	28,2	*10,0*	39,0	*9,4*	47,0	*9,1*	52,7	—	—
— 90°	*21,1*	27,1	—	—	*17,7*	69,0	—	—	*15,8*	91,4	*11,6*	118,0

(RM was expressed in the unit 1000 C. G. S.)

Hence in all fields the Hall-effect has been increased, especially in the weakest field. The latter particular was also observed before [3]) with other bismuth for temperatures ranging from 20° C. to 100° C.

The coefficient of Hall at — 90° C. in a field of 1300 C. G. S. units is 21,1 and exceeds by far the highest value formerly obtained. The question delt with in several earlier communications, as to whether or no a maximum Hall-effect exists at low temperatures, is not definitely answered by these measurements at only two temperatures, but the rapid increase points to the contrary. A more decisive answer will be obtained I hope before long by repeating the experiment in a bath of liquid oxygen.

The figures communicated for the temperature — 90° C. are not yet quite final, as the contact-resistance at the secondary electrodes

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[1]) Versl. 25 Juni '98, p. 98. Comm. N°. 42, p. 7.
[2]) Versl. 30 Mei '96, p. 47. Comm. N°. 26, p. 3.
[3]) Versl. 30 Mei '96, p. 5. Comm. N°. 26, p. 20.

increased considerably during the experiments. Though the resistance in the circuit of the HALL-current was measured several times during the experiments, some of the interpolated values may still contain a small percentage error. In future I intend to avoid this by altering the construction of the plate carrier.

4. *Magnetic increase of resistance and crystallographic direction.* The experiments made before on this subject with one of the bars (N⁰. 1) cut out of a crystalline piece from MERCK [1]) have now been repeated at — 90° C. The method of observation was the same as described in Comm. N⁰. 48. [2]) The use of the above described vacuum-glass offered especial advantage in this case, for the bar could be rotated, together with the whole frame in which it was placed, about its greatest axis, which was vertical. In this manner the lines of magnetic force could be made to coincide with different crystallographic directions, without altering anything in the adjustment of the electrodes etc. This easy turning had only one disadvantage, that it sometimes occasioned movements during the experiments. For accurate measurements therefore it will be necessary to fix to the frame a rigid stem provided with an index.

The following results are therefore only mentioned because they evidently prove that the differences in increase of resistance formerly observed in different positions of the bar were only caused by the change of the angle between the lines of force and the crystallographic directions.

In the following table column I contains the positions in which the direction of maximum resistance [3]) coincided with the lines of force, II the positions in which this direction was perpendicular to the lines of force.

Percentage increase of resistance.

Temp.	MAGNETIC FORCE			
	2650		3800	
	I	II	I	II
27°	1,3	3,2	2,2	5,8
— 90°	2,8	8,7	4,3	13,7

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[1]) Versl. 21 April '97, p. 498. Comm. N⁰. 37, p. 13.

[2]) Versl. 25 Maart '99, p. 486. Comm. N⁰. 48, p. 6.

[3]) Versl. 21 April '97, p. 498. Comm. N⁰. 37. p. 13.

For the sake of comparison we may note, that formerly at the temperature 15° C. and in a field of 7700 C. G. S. units the increase was found to be:

in the position I 6,5 II 14,9

Physiology. — "*The resorption of fat and soap in the large and the small intestine*". By Dr. H. J. Hamburger.

(Will be published in the Proceedings of the next meeting).

Mathematics. — "*On an application of the involutions of higher order*". By Prof. J. Cardinaal.

1. One of the best known problems of the theory of the pencil of conics is the determination of the number of particular conics in such a pencil, where one rectangular hyperbola, two parabolae and three pairs of straight lines are obtained. The corresponding problem of geometry in space, namely the determination of the number of particular quadric surfaces in a pencil of those quadrics (pencil of S^2), offers more difficulties.

It is true, it is easy to prove that there are three paraboloids in a pencil of S^2; but more difficult is it to trace the number of other particular groups of surfaces. The surfaces of revolution cannot be reckoned amongst these, having to satisfy two conditions. However, the orthogonal (rectangular) hyperboloids can be, as it will be proved that these are bound by one condition only.

My purpose in this communication is to investigate first how many rectangular hyperboloids appear in a general pencil of S^2 and consecutively to prove that the construction may be brought back to a problem of synthetic geometry in the plane, a problem where the theory of involutions of higher order must be applied.

2. According to definition an hyperboloid is rectangular when the cyclic planes are normal to two generatrices. With Clebsch [1]) we however think it preferable to choose a definition, in which we make use of the section of the hyperboloid with the plane at infinity. To investigate the rectangularity we set to work as follows:

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[1]) Clebsch-Lindemann: Vorlesungen über Geometrie, ("Lessons on Geometry"), Vol. II, Part 1, p. 195, where we also find the literature of this subject mentioned.

first we determine the section (H^2) of the hyperboloid with the plane at infinity, then we construct the chords of intersection of H^2 with the imaginary circle (C^2) in that plane. If the pole of one of those chords of intersection in reference to C^2 falls in H^2, the hyperboloid is rectangular.

3. By this method the problem of space is transformed into a problem of the plane; in the further treatment, however, we come across the difficulty of an imaginary conic C^2. For a better insight into the problem, we substitute for the present an arbitrary plane for the plane at infinity, a real conic for the imaginary circle and then the problem is formulated as follows:

Given a conic K^2 and a pencil of conics with the also real base points 1, 2, 3, 4; to determine a conic L^2 of the pencil, for which the pole of a chord of intersection with K^2 lies on L^2.

4. If L^2 is found, we can still make the following remark about the solution: Let L^2 intersect the conic K^2 in the points L_1, L_2, L_3, L_4; let L_{12} be the pole of $L_1 L_2$ in reference to K^2 and let L^2 be brought through L_{12}, then according to a known theorem L^2 will also pass through the pole L_{34} of the opposite chord $L_3 L_4$ 1). So the points 1, 2, 3, 4, L_{12}, L_{34} lie on the same conic. After this remark we can pass to the construction of the locus of the poles, supposing that L^2 describes the whole pencil.

5. Let A^2 be a conic of the pencil (1234): it intersects K^2 in the four points A_1, A_2, A_3, A_4. These four points will give rise to six common chords $A_1 A_2$, $A_1 A_3$, $A_1 A_4$, $A_2 A_3$, $A_2 A_4$, $A_3 A_4$ which correspond to six poles $A_{12} \ldots A_{34}$. If A^2 is replaced successively by all the conics of the pencil, every new conic gives rise to four new points of intersection: on K^2 these quadruples form an involution of the fourth order. It is clear, that if A_1 is chosen arbitrarily and conic A^2 is constructed, A_2, A_3, A_4 on K^2 are also determined, and that reciprocally when one of the last points, take A_2, is chosen, A_1, A_3 and A_4 are also determined. The six lines joining the quadruples of points by two envelop a curve C_3 of the third class 2).

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1) STEINER-SCHRÖTER: Theorie der Kegelschnitte, ("Theory of Conics"), II, 3rd edition, p. 526, problem 90.

2) R. STURM, Die Gebilde ersten und zweiten Grades der Liniengeometrie, ("The figures of the first and the second order in the geometry of the straight line)", I, p. 29.

MILINOWSKI, Zur Theorie der kubischen und biquadratischen Involutionen, ("Theory of cubic and biquadratic involutions") Zeitschrift f. Math. und Physik, 19, p. 212 etc.

We can determine the order of this curve C_3 in the following way: Construct one of the common tangents t_1 of K^2 and C_3; let T_1 be the point of contact of t_1 with K^2, then T_1 is a double point of the involution. Through T_1 still two tangents can be drawn to C_3; they intersect K^2 in the branchpoints of the involution; these branchpoints are common points of K^2 and C_3. We can conclude from the number 6 of the common tangents that there are 12 of these branchpoints; therefore C_3 intersects the conic K^2 in 12 points. Hence C^3 is of the sixth order and may be called C^6.

6. The locus of the poles of the tangents of C^6 in reference to K^2 is the reciprocal polar curve C^3 of C^6; it is of the third order and of the sixth class. We imagine once more a point A_{12} on C^3 as the pole of chord $A_1 A_2$ of K^2; A_1 and A_2 determine two points of the corresponding conic A^2 of the pencil which intersects K^2 moreover in A_3 and A_4; A^2 also intersects C^3 in the six points $A'_{12}, A'_{13} \ldots A'_{34}$. Moreover five other poles will appear on C^3 besides A_{12}, the poles of the chords A_1A_3, A_1A_4, A_2A_3, A_2A_4, A_3A_4. By assuming one point on C^3, two groups, each of 6, are determined on C^3, the group A and the group A'. If one of the points A is taken arbitrarily no point of group A will coincide with a point of group A'.

7. The following conclusions may be arrived at from the preceding:

a. If we assume successively the points A_{12}, B_{12}, $C_{12} \ldots$ on C^3, as many groups of 6 points are formed; each of the points of the group can determine the whole group unequivocally, so the points A, B, $C \ldots$ form an involution of the sixth order on C^3.

b. The points of intersection A', B', $C' \ldots$ of the conics with C^3 also form an involution of the sixth order.

c. Each point of group A' corresponds to any point of group A; reciprocally each point of group A corresponds to any point of group A'; so both involutions are projective.

d. The points of coincidence of both involutions determine the conics which give the solution of the problem (3).

8. The projective involutions on the same bearer are both of the sixth order, so they have 12 points of coincidence ¹). These points may be indicated more closely in the following manner:

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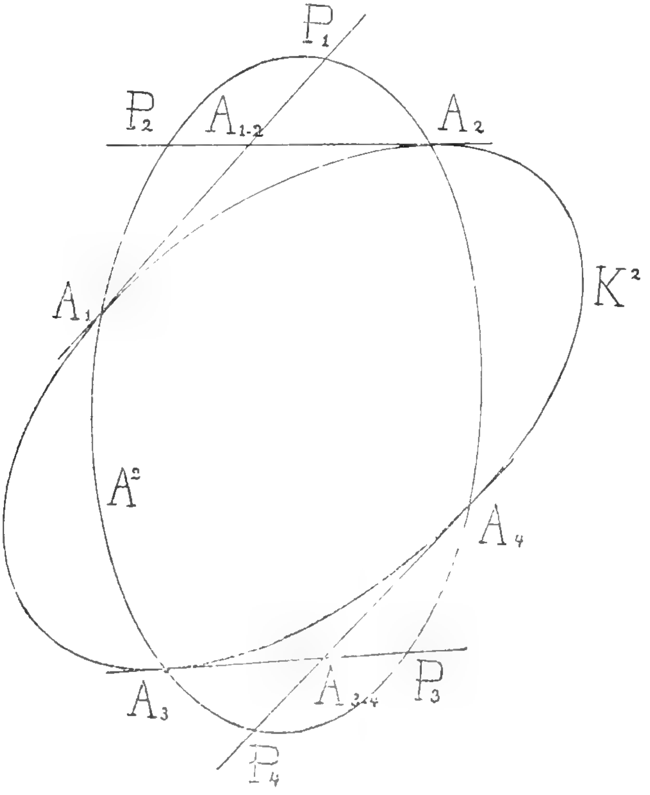
¹) E. Kötter, Grundzüge einer rein geometrischen Theorie der algebraischen ebenen Curven, ("Elements of a purely geometrical theory of the algebraic plane curves".) p. 88 etc.

C^3 intersects K^2 in 6 points; these 6 points are at the same time the points of contact on K^2 of the common tangents of K^2 and C^6. From this we can conclude that for these points the end-points of the chords of intersection coincide; so in these points conics of pencil (1 2 3 4) will touch K^2. If we imagine one of these points T_1 to be given, a conic of the pencil passes through this point, and as it touches K^2, the corresponding pole falls in T_1; from this we conclude that:

The 6 points of intersection $T_1 \ldots T_6$ of C^3 and K^2 are 6 of the points of coincidence of both involutions; so we have still to account for 6 other points of coincidence. Let us call one of these points A_{12}, then the conic through A_{12} will meet K^2 in A_1, A_2, A_3, A_4 and will pass through A_{34}, the pole of $A_3\ A_4$. Hence these six points can be divided into three pairs of points $(A_{12}\ A_{34})$ $(B_{12}\ B_{34})$ $(C_{12}\ C_{34})$.

By the way we remark that the obtained result is in accordance with the fact, that six conics of a pencil touch an arbitrary conic.

9. The found three pairs of points determine the three conics which will solve the problem. We however add a second deduction,



which is connected, as will be proved, with the theory of double points of curves of higher order.

Let A^2 again be a conic of the pencil (1 2 3 4); we imagine two of the points of intersection of A^2 with K^2 to be constructed, take A_1 and A_2, and moreover the pole A_{12} of $A_1\ A_2$ in reference to K^2 (see diagram).

The tangents $A_1\ A_{12}$ and $A_2\ A_{12}$ intersect the conic A^2 for the second time in the points P_1 and P_2; in the same way we can also determine the tangents in the points A_3 and A_4 with their second points of intersection P_3 and P_4. If A^2 describes the whole pencil, P_1, P_2, P_3, P_4 generate a locus; at the same time the poles $A_{12} \ldots A_{34}$ generate the locus C^3 found formerly. The conics forming the solution of the problem proposed sub (3) must now be brought through the points of intersection of the curve C^3 with the locus of the points P_1, P_2, P_3, P_4.

10. To determine the order of the locus lastly named, let us take a straight line l and determine how many points it has in common with it. We take a point A_1 on l, draw from that point two tangents to K^2 and construct the conic (1 2 3 4) through each of the points of contact; as we can construct two conics, four points of intersection A'_1, A'_2, A'_3, A'_4 on l will be found. So to one point A_1 belong 4 points A' in the just found correspondence.

Reversely if we construct the conic passing through A'_1, then it also passes through one of the other points A' say A'_2; it determines 4 points of intersection with K^2; the tangents to K^2 through those points determine still three points A_2, A_3, A_4 besides A_1. Consequently 4 points A' correspond to one point A and 4 points A to one point A'.

So there exists a projective correspondence (4,4) between these points A and A' which possesses 8 points of coincidence. So the required locus intersects l in 8 points, hence it is a curve of the 8th order.

11. However, this curve breaks up into two parts. It is clear that K^2 itself belongs to the locus of the points of intersection of the tangents to K^2 with the variable conic A^2. The remaining curve will be of the 6th order; we have now to investigate its particular points. These are the following:

a. The points 1, 2, 3, 4 are double points of K^6. To prove this we consider point 1, from which we draw the tangents t_1 and t_2 to K^2. There is a conic of the pencil (1 2 3 4) passing through the point of contact t_1 and a second through the point of contact t_2; if the variable conic describes the pencil, then the locus will pass two times through the point 1; so 1 is a double point and so are 2, 3 and 4.

b. The points of intersection of K^6 and C^3 are double points. C^3 is the locus of the poles $A_{12} \ldots A_{34}$; in these poles two tangents concur; so the locus also passes two times through these poles. It is evident that we are dealing with points of intersection of C^3 and K^6, not lying at the same time on K^2, so these are the six points (A_{12}, A_{34}), (B_{12}, B_{34}), (C_{12}, C_{34}) formerly found.

12. It is now evident, that the curve K^6 has ten double points; so it is unicursal. Of these points six lie on C^3, the remaining 4 are 1, 2, 3, 4. The six double points representing 12 points of intersection of K^6 with C^3, there are still 6 points; these are evidently the points where C^3 also intersects K^2, so that now all the points of intersection of C^3 and K^6 are found.

Moreover it is clear that the curve K^6 touches the curve K^2 in the six common points, so that it has no more points in common with it.

An additional remark is, that the 10 double points have a particular position in reference to each other. They are situated so, that the points A lie in pairs with the 4 points 1, 2, 3, 4 on a conic. This corresponds with the geometrical truth that the ten double points of a curve of the 6th order cannot have an arbitrary position in reference to each other.

13. The algebraic reckoning comes to a similar result. Let the hyperboloid be:

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} - \frac{z^2}{c^2} = 1 .$$

This is rectangular, if

$$\frac{1}{a^2} + \frac{1}{c^2} = \frac{1}{b^2} \quad \text{or} \quad \frac{1}{b^2} - \frac{1}{c^2} = \frac{1}{a^2} .$$

If we start from a general equation of a quadratic surface

$$a_{11}\, x^2 + a_{22}\, y^2 + a_{33}\, z^2 + \ldots . = 0 ,$$

then as is known $\frac{1}{a^2}$, $\frac{1}{b^2}$, $\frac{1}{c^2}$ are given as roots of the equation

$$\begin{vmatrix} a_{11}-\lambda & a_{12} & a_{13} \\ a_{21} & a_{22}-\lambda & a_{23} \\ a_{31} & a_{32} & a_{33}-\lambda \end{vmatrix} = 0 ,$$

or

$$\lambda^3 + 3A\lambda^2 + 3B\lambda + C = 0 ,$$

so that the condition, which must be satisfied by the 3 roots $\lambda_1, \lambda_2, \lambda_3$, is

$$\lambda_1 + \lambda_2 = \lambda_3 .$$

Now we have $\lambda_1 + \lambda_2 + \lambda_3 = -3A$, $\lambda_1\lambda_2 + \lambda_1\lambda_3 + \lambda_2\lambda_3 = 3B$, $\lambda_1\lambda_2\lambda_3 = -C$, from which results after some deduction as a relation between the coefficients

$$27A^3 - 36AB + 8C = 0 .$$

Expressed in the coefficients of the general equation this becomes

$$27(a_{11}+a_{22}+a_{33})^3 -$$
$$-36(a_{11}+a_{22}+a_{33})\left(a_{11}a_{22}+a_{22}a_{33}+a_{33}a_{11}-a_{12}^2-a_{23}^2-a_{31}^2\right)+$$
$$+8(a_{11}a_{22}a_{33}) = 0 ;$$

so we see, that this is a relation where the coefficients appear in the third order.

If there is a pencil of quadratic surfaces of the second order, we substitute $a_{11} + k\,b_{11}$ for a_{11}; for k we obtain a cubic equation, which proves that there are three rectangular hyperboloids in the pencil, a result corresponding with that of the geometrical considerations.

Up till now the treatment of the problem has borne a general character. For a complete insight the imaginary circle at infinity must be exchanged for the arbitrary conic K^2; there are moreover many particular cases. This would however lead to too extensive discussions; so this communication must be concluded here.

Mathematics. — *"On some special cases of* MONGE's *differential equation".* By Prof. W. KAPTEYN.

If as in general p, q, r, s, t represent the first and second differential coefficients of a function z of two independent variables x and y, the differential equation appearing in the title is

$$Hr + 2Ks + Lt + M = 0,$$

where H, K, L, M are functions of x, y, z, p and q. For the solution of this differential equation MONGE has given a method based on the determination of two intermediate integrals of the form

$$u = f(v) ,$$

where u and v are dependent on x, y, z, p and q and f represents an arbitrary function. This method is however deficient, the existence of intermediate integrals depending on certain relations between the functions H, K, L and M, thus far unknown.

For the purpose of making this method more practical, I have tried to trace these unknown relations. However, these relations are very intricate; for this reason I have confined myself for the present to the simple cases where MONGE's equation consists of two terms only. For these cases I have succeeded in finding the necessary and sufficient conditions which the only remaining function must satisfy, if we suppose that the equation has two intermediate integrals. From these conditions I have then deduced the most general forms for the only remaining function and determined the two intermediate integrals belonging to it.

The result of this investigation is the following, as for as concerns the most general forms of the function and the two corresponding integrals, f, φ, ψ representing everywhere arbitrary functions of the arguments indicated when necessary between brackets.

I. $r - \lambda s = 0.$

In this case the form is

$$\lambda = \frac{\psi(p)}{q - \varphi(y.p)}$$

and the intermediate integrals are

$$q e^{-\int \frac{dq}{\psi}} + \int e^{-\int \frac{dp}{\psi}} \frac{q}{\psi} dp = f(y)$$

$$z - (p - \psi) - \int \varphi \, dij = f\,(p)$$

II. $r - \lambda^2 t = 0$.

For convenience sake we have represented the unknown function by the square of a function λ; we then find for the most general form of λ

$$\lambda = \frac{A(AEN - Z^2) + 2AXZp - A(X^2 - {}^1/_4\beta^2)p^2}{Z^2 - AE(X^2 - {}^1/_4\beta^2) - AYZq + A^2 Nq^2},$$

where

$$X = Ax + C, \quad Z = Az + B, \quad Y = 2y - 2\gamma + \beta,$$
$$N = (y - \gamma)\;(y - \gamma + \beta)$$

and A, B, C, E, β and γ denote arbitrary constants.

To be able to express the intermediate integrals in a simple manner, we write

$$A(V) = \frac{\partial V}{\partial q} - \lambda \frac{\partial V}{\partial p},$$

$$B(V) = \frac{\partial V}{\partial x} - \lambda \frac{\partial V}{\partial y} + (p - \lambda q) \frac{\partial V}{\partial z},$$

$$A_1(V) = \frac{\partial V}{\partial q} + \lambda \frac{\partial V}{\partial p},$$

$$B_1(V) = \frac{\partial V}{\partial x} + \lambda \frac{\partial V}{\partial y} + (p + \lambda q) \frac{\partial V}{\partial z}.$$

Then the two intermediate integrals are

$$\frac{A^2(\lambda)}{\lambda^3} = f\left\{\frac{B(\lambda)}{A(\lambda)}\right\};$$

$$\frac{A_1{}^2(\lambda)}{\lambda^3} = f\left\{\frac{B_1(\lambda)}{A_1(\lambda)}\right\},$$

when by $A^2(\lambda)$ we understand $\left(\frac{\partial\lambda}{\partial q} - \lambda\frac{\partial\lambda}{\partial p}\right)^2$ and likewise by $A_1{}^2(\lambda)$ $\left(\frac{\partial\lambda}{\partial q} + \lambda\frac{\partial\lambda}{\partial p}\right)^2$.

III. $r - \lambda = 0$.

In this case it is only necessary that λ is independent of q. The two intermediate integrals are found by determining the three independent integrals u, v and w of the system of simultaneous differential equations

$$\frac{dx}{1} = \frac{dz}{p} = \frac{dp}{\lambda(x,y,z,p)} = \frac{dy}{0}$$

and by uniting these to

$$u = f(v)\,,$$

$$u = f(w)\,.$$

IV. $s - \lambda t = 0$.

Here λ must be equal to $p\,\varphi\,(q) + \psi\,(x,\,q)$ and the two intermediate integrals are

$$pe^{-\int\varphi dq} - \int e^{-\int\varphi dq}\psi dq = f(x)\,,$$

$$(1 - q\varphi)y + z\varphi + \int\psi dx = f(q).$$

V. $s - \lambda = 0$.

Let U represent an arbitrary function of x, y and z, then λ must be equal to

$$\frac{\partial U}{\partial x}pq - \frac{\partial U}{\partial y}p - \frac{\partial U}{\partial z} + D\,,$$

if

$$D = e^{-U}\int e^{U}\left(\frac{\partial U}{\partial x}\cdot\frac{\partial U}{\partial y} + \frac{\partial^2 U}{\partial x dy}\right)dz - e^{-U}\,W(xy)\,,$$

where W denotes an arbitrary function of x and y. This result was already given by GOURSAT, "Equations aux dérivées partielles du second ordre", II, p. 88.

The two intermediate integrals become

$$qe^U - \int e^U \frac{\partial U}{\partial y}\, dz + \int W(xy)dx = f(y)$$

$$pe^U - \int e^U \frac{\partial U}{\partial x}\, dz + \int W(xy)dy = f(x).$$

VI. $t - \lambda = 0$.

In this case the only condition is that λ is independent of p. The intermediate integrals are found by uniting the three integrals u, v, w of

$$\frac{dx}{0} = \frac{dy}{1} = \frac{dz}{q} = \frac{dq}{\lambda(x,y,z,q)}$$

to

$$u = f(v),$$
$$u = f(w).$$

Remark. It seems that the form sub I may still be chosen more generally.

Physical Geography. — "*Two earth-quakes, registered in Europe and at Batavia*". By Dr. J. P. VAN DER STOK.

A. 1. In the night of 29 to 30 September 1899, a heavy earth-quake caused serious damage at the south coast of the isle of Ceram and in the Mollucco's.

The first official report, sent by the Resident of Amboina to the Governor-General immediately after the disaster, runs as follows:

„In the night of 29 to 30 September at 1^h^ 45^m^ a. m. a heavy earth-quake, followed by a series of sea-waves, caused considerable damage at the south coast of Ceram and, in a less degree, also at the isles of Ambon, Banda and the Ulias-isles. Several villages at Ceram's south coast have been devastated; in the Elpaputih-Bay all except two. The prison at Amahei has been completely destroyed, the fortifications partially, whereas the presbytery and the churches remained unhurt, as also the garrison and the civil officers at Amahei and Kairatoe.

As the Government-steamer Arend proved incapable of doing all the work, the steamers Gouverneur-Generaal 's Jacob and Japara of the Royal Pakketvaart-Company were chartered in order to convey victuals and medical assistance and for the transport of the wounded, whilst also the Resident of Ternate was requested to give assistance.

Provisions and material for building are to be had at Ambon in sufficient quantities and have been provided immediately; but in other respects there is still much sufferance.

The steamer 's Jacob brought over to Amboina 27 wounded, whilst the Japara, by which boat the Resident and first medical officer went to the place of the disaster, conveyed 49 wounded from Amahei and Saparua.

From Banda, where the pier before fort Nassau has been destroyed, satisfactory information has been received.

According to preliminary reports the number of natives, killed by the disaster, amounts to 4000 and that of the wounded to 500.

The natives who survived have fled to the inland country and do not venture to come back to their hamlets: there is much agitation everywhere, where the effect of the earth- and seawaves has been felt. The petroleum-establishment at Bulobay has not suffered any damage."

2. The seismograms, received from Dr. FIGEE, show that this earth-quake has been registered very neatly at the Royal Observatory at Batavia.

As far as I know this is the first case that an earth-quake, originating in the Molucco's has been observed at Batavia by means of Milne's seismograph. The motion commences abruptly at $0^{h}\ 14^{m},6$ Batavia time, which corresponds to $1^{h}\ 43^{m},3$ local time, the difference in longitude between Amahei and Batavia being $1^{h}\ 28^{m},7$.

3. On the 29th of September an earth-quake has been also registered in the new Imperial Central-station for seismology at Strassburg by the Rebeur-Ehlert pendulums and also at Dr. SCHÜTT's seismic Institute at Hamburg.

Professor GERLAND at Strassburg has kindly forwarded the following dates, reduced to Greenwich time.

	Strassburg.	Batavia.
Beginning (about)	$17^{h}\ 23\overset{m}{,}5$	$17^{h}\ \ 7\overset{m}{,}6$
Maximum	$17^{h}\ 58\overset{m}{,}8$	$17^{h}\ 29\overset{m}{,}6$
End (about)	$18^{h}\ 49\overset{m}{,}4$	$18^{h}\ 23\overset{m}{,}0$
Duration	$1^{h}\ 25\overset{m}{,}9$	$1^{h}\ 15\overset{m}{,}4$

As the seismograms bear an entirely different character as the waves proceed from the centrum of disturbance, an exact comparison of the epochs of commencement, maximum effect and end offer, up to the present time, considerable difficulties.

Moreover in most cases the epochs of beginning and termination cannot be sharply indicated, as the seismograms generally exhibit a gradual increase and decrease of motion. An exact measurement of the velocities of propagation will be possible only when a reliable method has been found of analysing the compound movement in its elementary constituents.

With the hypothesis, that the vibrations have travelled along paths approximating the chords through the earth, we find that the velocity of propagation has been about 10 K.M. per second; the distance between Strassburg and Amahei being 10402 K.M.

As the distance between Batavia and Amahei is 656 K.M., the exact local time of the earth-quake can be fixed at 1^h $42^m,2$.

B. Concerning the other earth-quake, observed also at Batavia as well as at Strassburg, the following data are provided by the seismograms:

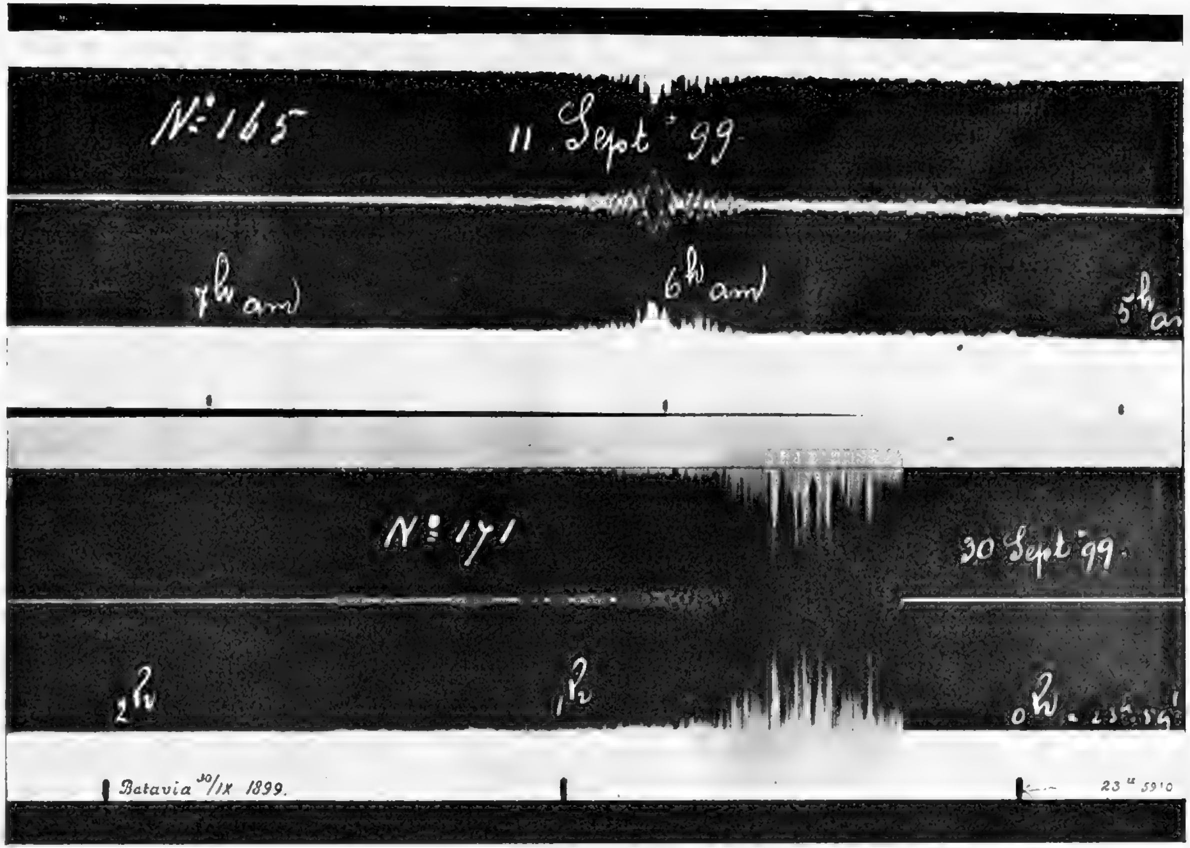
		Strassburg.		*Batavia.*
September 10 1899. Greenwich time	preliminary tremors	20^h $58^m,9$	beginning.	
		21^h $8^m,2$	maximum.	
		21^h $54^m,3$	beginning.	22^h $7^m,0$
		21^h $58^m,9$	maximum	22^h $54^m,5$
		24^h $28^m,9$	end	23^h $19^m,5$
	Duration	2^h $34^m,6$		1^h $12^m,5$

From these records we may conclude that the centre of the disturbance is situated at a greater distance from Batavia than from Strassburg; firstly because preliminary tremors have been registered at the latter place about 21^h; secondly because the epoch of maximum disturbance at Batavia is about one hour later than at Strassburg, and thirdly because the duration is considerable less at the former than at the latter station.

The last argument is, however, questionable, owing to the difficulty of fixing the characterizing epochs. In „Nature“ it is noted down, (presumably by Prof. Milne from the isle of Wight) that seismic disturbances occurred on the 3rd, 10th and 17th of September.

No indications of the exact time of occurrence are given, but it is stated that the centre of disturbance is in Alaska.

J. P. VAN DER STOK, „Two earth-quakes, registered in Europe and at Batavia."



Physics. — Prof. J. D. VAN DER WAALS offers on behalf of Dr. G. BAKKER of Schiedam a paper on: "*The potential function* $\varphi(r) = \dfrac{Ae^{-qr} + Be^{qr}}{r}$ *and* $\varphi(r) = \dfrac{A \sin(qr + \alpha)}{r}$ *and the potential function of* VAN DER WAALS".

In a previous paper I have pointed out that these potential functions lend to a spherical homogeneous shell or to a massive sphere, the density of which is a function of the distance from the centre, the property to attract an external point as if the mass were concentrated in the centre, if we leave a factor, depending on the radius, out of account. The differential equations, which are satisfied by these functions, are resp.:

$$\frac{d^2\varphi}{dr^2} + \frac{2}{r}\frac{d\varphi}{dr} = q^2\varphi \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and

$$\frac{d^2\varphi}{dr^2} + \frac{2}{r}\frac{d\varphi}{dr} = -q^2\varphi \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If we substitute $x^2 + y^2 + z^2$ for r^2, these equations may also be written:

$$\nabla^2\varphi = q^2\varphi \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1a)$$

and

$$\nabla^2\varphi = -q^2\varphi \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2a)$$

The resemblance of these differential equations with the well-known equation $\nabla^2\varphi = 0$ for the potential of NEWTON, made it probable that these potential functions would have more in common. The analogy was even closer than I expected. I found e. g. that the action between two systems of agens, spread over arbitrary spaces and surfaces, may be substituted by a system of tensions in the medium in a similar way as MAXWELL did for electric agens.

In the first place we state the following theorems:

I. If ψ represents the potential in a point x, y, z of an agens which fills several spaces continuously, and is spread over several surfaces, the potential function being $\varphi(r) = \dfrac{Ae^{-qr} + Be^{qr}}{r}$, we find for the potential, with the exception of some points and surfaces the differential equation:

$$\nabla^2\psi = q^2\psi - 4\pi(A + B)\varrho \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

in which ϱ represents the density in that point.

II. If ψ_1 represents the potential in a point x, y, z of an agens which fills several spaces continuously and is spread over several surfaces, the potential function being $\varphi_1(r) = \frac{A \sin(qr+\alpha)}{r}$, we get for the potential the differential equation:

$$\nabla^2 \psi_1 = - q^2 \psi_1 - 4\pi \varrho A \sin \alpha \quad . \quad . \quad . \quad . \quad . \quad (4)$$

some points and surfaces being excepted; ϱ represents the density in that point.

It is easy to find equation:

$$\frac{Ae^{-qr} + Be^{qr}}{r} - \frac{A+B}{r} = q(B-A) + \frac{(A+B)q^2 r}{\pi 2} + \frac{(B-A)q^3 r^2}{\pi 3} + .$$

Let us put:

$$\frac{Ae^{-qr} + Be^{qr}}{r} - \frac{A+B}{r} = u \quad . \quad . \quad . \quad . \quad . \quad (5)$$

By applying the operation ∇^2 to the two members of the last equation but one, taking into account that $\nabla^2 \frac{A+B}{r} = 0$, we find:

$$\nabla^2 \frac{Ae^{-qr} + Be^{qr}}{r} = \nabla^2 u = q^2 \left\{ \frac{A+B}{r} + (B-A) q + \frac{(A+B)q^2 r}{r} + \right\} =$$

$$= q^2 \frac{Ae^{-qr} + Be^{qr}}{r} \text{ or}$$

$$\nabla^2 \varphi = \nabla^2 u = q^2 \varphi \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The proof of the first theorem is based on this consideration. The potential ψ in a point x, y, z of an agens with a cubic density ϱ and a surface density σ, becomes if the potential function is $\varphi(r)$:

$$\psi = \Sigma \int \varrho \, \varphi(r) \, d\tau + \Sigma \int \sigma \, \varphi(r) \, ds$$

if r represents the distance from point x, y, z to the elements of space or of surface for which the density is represented by ϱ or σ.

We have:

$$\varphi(r) = \frac{A+B}{r} + u \quad \text{(equation 5)}$$

The potential may be written:

$$\psi = \Sigma \int \frac{(A+B)\,\varrho}{r}\,d\tau + \Sigma \int \frac{(A+B)\,\sigma}{r}\,ds + \Sigma \int \varrho u\,d\tau + \Sigma \int \sigma u\,ds$$

or

$$\psi = (A+B) \left\{ \Sigma \int \frac{\varrho\,d\tau}{r} + \Sigma \int \frac{\sigma\,ds}{r} \right\} + \Sigma \int \varrho u\,d\tau + \Sigma \int \sigma u\,ds$$

If we apply to both members the operation ∇^2, we get:

1st
$$\nabla^2 \left\{ \Sigma \int \frac{\varrho\,d\tau}{r} + \Sigma \int \frac{\sigma\,ds}{r} \right\} = -\,4\,\pi\,\varrho$$

and because $\nabla^2\,u = q^2\,\varphi$ (see equation 6):

2nd
$$\nabla^2 \Sigma \int \varrho u\,d\tau + \nabla^2 \Sigma \int \sigma u\,ds = \Sigma \int \varrho \nabla^2 u\,d\tau + \Sigma \int \sigma \nabla^2 u\,ds =$$

$$= q^2\,\Sigma \int \varrho\,\varphi\,d\tau + q^2\,\Sigma \int \sigma\,\varphi\,ds = q^2\,\psi$$

Hence:

$$\nabla^2\,\psi = q^2\,\psi - 4\,\pi\,(A+B)\,\varrho \quad . \quad . \quad . \quad . \quad . \quad . \qquad (7)$$

To prove the second theorem, we point out that:

$$A \sin\,(qr + \alpha) = A \cos\alpha \sin qr + A \sin\alpha \cos qr$$

If we substitute a new constant A_1 for $A \cos\alpha$ and B for $A \sin\alpha$ we may write the potential function $\varphi_1\,(r)$ as follows:

$$\varphi_1\,(r) = \frac{A_1 \sin qr + B \cos qr}{r}$$

We find easily:

$$\frac{A_1 \sin qr + B \cos qr}{r} - \frac{B}{r} = A_1\,q - \frac{Bq^2\,r}{\pi\,2} -$$

$$- \frac{A_1\,q^3\,r^2}{\pi\,3} + \frac{B\,q^4\,r^3}{\pi\,4} + \frac{A_1\,q^5\,r^4}{\pi\,5} -$$

If we put $\varphi_1\,(r) - \dfrac{B}{r} = v$ and apply the operation ∇^2, we get:

$$\nabla^2 v = - q^2 \left(\frac{B}{r} + A_1 q - \frac{B q^2 r}{\pi 2} - \frac{A_1 q^3 r^2}{\pi 3} - \qquad \right) =$$

$$= - q^2 \left(\frac{B}{r} + v\right) = - q^2 \varphi_1 \quad . \quad . \quad (8)$$

and on this the proof of the second theorem is based.

Now we have for the potential in a point:

$$\psi = \Sigma \int \varrho \, \varphi_1 (r) \, d\tau + \Sigma \int \sigma \, \varphi_1 (r) \, ds$$

Now $\varphi_1 (r) = \frac{B}{r} + v$. So also:

$$\psi = \Sigma \int \frac{B \varrho \, d\tau}{r} + \Sigma \int \frac{B \sigma \, ds}{r} + \Sigma \int \varrho v \, d\tau + \Sigma \int \sigma v \, ds \, .$$

If we apply to both members the operation ∇^2 we find in a similar way as we did when proving the preceding theorem:

$$\nabla^2 \psi = - 4 \pi B \varrho + \Sigma \int \varrho \, \nabla^2 v \, d\tau + \Sigma \int \sigma \, \nabla^2 v \, ds \quad . \quad . \quad (9)$$

Now we get in consequence of (7):

$$\Sigma \int \varrho \, \nabla^2 v \, d\tau = - q^2 \, \Sigma \int \varrho \, \varphi_1 \, d\tau$$

and in the same way:

$$\Sigma \int \sigma \, \nabla^2 v \, ds = - q^2 \, \Sigma \int \sigma \, \varphi_1 \, ds$$

or

$$\Sigma \int \varrho \, \nabla^2 v \, d\tau + \Sigma \int \sigma \, \nabla^2 v \, ds = - q^2 \left(\Sigma \int \varrho \, \varphi_1 \, d\tau + \Sigma \int \sigma \, \varphi_1 \, ds \right) = - q^2 \psi$$

Equation (8) becomes:

$$\nabla^2 \psi = - 4 \pi B \varrho - q^2 \psi$$

or because $B = A \sin \alpha$:

$$\nabla^2 \psi = - q^2 \psi - 4 \pi A \sin \alpha \, \varrho \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Let us now prove the reversed theorem of Theorem I [1]).

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[1]) With that modification that B is put 0.

III. If ψ and ϱ are functions of x, y and z, ψ satisfying the three following conditions:

1st ψ and its first derivatives with respect to x, y and z are continuous everywhere.

2nd some isolated points, lines and surfaces excepted, ψ fulfils in an acyclic region, the equation:

$$\nabla^2 \psi = q^2 \psi - 4 \pi A \varrho.$$

3rd the products $x\psi$, $y\psi$, $z\psi$, $x^2 \frac{d\psi}{dx}$, $y^2 \frac{d\psi}{dy}$ and $z^2 \frac{d\psi}{dz}$ become nowhere infinite; then the potential of an agens, the density of which is ϱ, is for that region ψ, the potential function being:

$$\varphi(r) = \frac{Ae^{-qr}}{r}$$

In order to prove this theorem, we take into account that the potential of an agens, for which the potential function is $\frac{Ae^{-qr}}{r}$, fulfils the differential equation:

$$\nabla^2 \psi = q^2 \psi - 4 \pi A \varrho \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

which is a special case of equation (3). If we can prove that on the given conditions only one solution of (11) is possible, the theorem is proved. We shall do so by proving that if there are two solutions, the difference of these functions will be zero everywhere.

If ψ and v are two solutions of equation (11) and if we put $\psi - v = u$, the new function u will satisfy the equation:

$$\nabla^2 u = q^2 u.$$

As ψ and v and their first derivatives with respect to x, y and z are supposed to be continuous everywhere, this is also the case with the function u and we may make use for this quantity of the well-known theorem of GREEN. This furnishes the equation:

$$\int (\nabla^2 u)\, u\, d\tau = \int u \left(\frac{du}{dx} \cos\alpha + \frac{du}{dy} \cos\beta + \frac{du}{dz} \cos\gamma \right) ds -$$

$$- \int \left\{ \left(\frac{du}{dx} \right)^2 + \left(\frac{du}{dy} \right)^2 + \left(\frac{du}{dz} \right)^2 \right\} d\tau \quad . \quad . \quad (12)$$

If we subtract $\int q^2 u^2 \, d\tau$ from the two members of this equation, we get:

$$\int (\nabla^2 u - q^2 u) u \, d\tau = \int u \left(\frac{du}{dx} \cos \alpha + \frac{du}{dy} \cos \beta + \frac{du}{dz} \cos \gamma \right) ds -$$

$$- \int \left\{ \left(\frac{du}{dx} \right)^2 + \left(\frac{du}{dy} \right)^2 + \left(\frac{du}{dz} \right)^2 + q^2 u^2 \right\} d\tau$$

DIRICHLET [1] in his proof of a corresponding theorem concerning the potential function $\frac{1}{r}$, has surrounded the spaces that present a singularity by closely surrounding surfaces, and he construed a cube, the centre of which coincides with the origin of the coordinate system, while it compasses all the spaces that present a singularity. By doing so we may make use of the above equation for the space contained between the sides of the cube and the surfaces construed round the places which offer a singularity. The first term of the right-hand member consists of the sum of a number of surface integrals, which are reduced to zero for the surfaces of the cube, when the edges of the cube increase infinitely, while the surface integrals taken over the surfaces which enclose the places offering a singularity, furnish two values of opposite sign, so that the result for every surface is zero. Then $\nabla^2 u = q^2 u$. The volume integral of the left-hand member is therefore also zero.

So:

$$\int \left\{ \left(\frac{du}{dx} \right)^2 + \left(\frac{du}{du} \right)^2 + \left(\frac{du}{dz} \right)^2 + q^2 u^2 \right\} d\tau = 0$$

from which follows:

$$u = 0 \quad \text{or} \quad \psi = v \quad q. d. e.$$

In these considerations the more general function:

$$\varphi(r) = \frac{Ae^{-qr} + Be^{qr}}{r}$$

must be excluded as potential function.

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[1] Vorlesungen über die im umgekehrten Verhältniss des Quadrats der Entfernung wirkenden Kräfte von P. G. LEJEUNE-DIRICHLET. blz. 32.

In this case the following equation would hold for points which are at an infinite distance from the agens:

$$\psi = M \frac{Ae^{-qr} + Be^{qr}}{r}$$

M representing the whole mass.

According to the third condition $r\psi$ will nowhere become infinite. Now $r\psi = M(Ae^{-qr} + Be^{qr})$ and e^{qr} become infinite, if $r = \infty$. Only for $B = 0$ this objection has no weight. We shall therefore confine ourselves to the function of VAN DER WAALS and a general reversion of theorem I cannot be proved in this way. Such a theorem, however, would not be of much importance here, as for $B \gtrless 0$ the potential function has properties, which are never found when examining molecular forces.

Potential energy in the unity of volume.

Let us seek the potential energy of an agens spread continuously over several spaces for the potential function of VAN DER WAALS, which we write:

$$\varphi(r) = -f\frac{e^{-qr}}{r}$$

If ψ is the potential and ϱ the density, we get for this quantity:

$$W = \frac{1}{2}\int \psi\,\varrho\,d\tau \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

We consider this as being taken over the infinite space. Now we get according to equation (11)

$$\nabla^2\psi = q^2\psi + 4\pi f\varrho$$

and so

$$\varrho = \frac{\nabla^2\psi - q^2\psi}{4\pi f}$$

By substitution in (13):

$$W = \frac{1}{8\pi f}\int \psi\,\nabla^2\psi\,d\tau - \frac{q^2}{8\pi f}\int \psi^2\,d\tau \quad . \quad . \quad . \quad (14)$$

Now we have:

$$\int \psi\, \nabla^2 \psi\, d\tau = \int \psi \frac{d^2\psi}{dx^2}\, d\tau + \int \psi \frac{d^2\psi}{dy^2}\, d\tau + \int \psi \frac{d^2\psi}{dz^2}\, d\tau \quad . \quad (15)$$

By partial integration:

$$\int \psi \frac{d^2\psi}{dx^2}\, d\tau = \iint \frac{d\psi}{dx}\, \psi\, dy\, dz - \int \left(\frac{d\psi}{dx}\right)^2 d\tau$$

Because ψ and $\frac{d\psi}{dx}$ become 1) zero at infinite distance from the agens, the surface integral becomes zero and so:

$$\int \psi \frac{d^2\psi}{dx^2}\, d\tau = - \int \left(\frac{d\psi}{dx}\right)^2 d\tau\ .$$

By substituting in equation (14) this expression for $\int \psi \frac{d^2\psi}{dx^2}\, d\tau$ and the corresponding expressions for the other surface integrals of (15), we find:

$$W = - \frac{1}{8\pi f} \int \Sigma \left(\frac{d\psi}{dx}\right)^2 d\tau - \frac{q^2}{8\pi f} \int \psi^2\, d\tau$$

$$\left\{ \Sigma \left(\frac{d\psi}{dx}\right)^2 = \left(\frac{d\psi}{dx}\right)^2 + \left(\frac{d\psi}{dy}\right)^2 + \left(\frac{d\psi}{dz}\right)^2 \right\}.$$

The energy in the unity of volume becomes therefore:

$$- \frac{1}{8\pi f} \left\{ \Sigma \left(\frac{d\psi}{dx}\right)^2 + q^2 \psi^2 \right\}.$$

Let us put:

$$R^2 = \left(\frac{d\psi}{dx}\right)^2 + \left(\frac{d\psi}{dy}\right)^2 + \left(\frac{d\psi}{dz}\right)^2$$

then we may also write:

$$- \frac{R^2 + q^2 \psi^2 \; {}^{2)}}{8\pi f} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

---

1) If the members of the last equation are added to those of the corresponding equation for the other axes, we may consider the surface integrals together as being one surface integral over a sphere. If $r = \infty$, this integral becomes 0.

2) $q\,\psi$ has the dimension of a force, for q is the reverse of a length.

or substituting $\frac{1}{\lambda}$ for q:

$$-\frac{1}{8\pi f}\left(R^2+\frac{\psi^2}{\lambda^2}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (16a)$$

If $f=1$ and $q=0$, we find once more the well-known expression:

$$-\frac{R^2}{8\pi}\ .$$

This expression is negative, because the constant of the potential function is equated to zero. So it represents without the — sign the work required to separate different parts of the agens at an infinite distance from one another, when the forces are attractive.

Tension in the medium.

MAXWELL has proved that the force which two electric systems exercise on each other, may be considered as a simple system of tensions in the medium. The same applies to the general potential function $\varphi(r)=\frac{A\,e^{-qr}+B\,e^{qr}}{r}$ and so also to the potential function of VAN DER WAALS.

Imagine an agens spread over different spaces, for which the potential function $\varphi(r)$ holds good, and enclose a certain region by a closed surface. Call this region system I and all other space system II. The resultant of the X-components of the forces exercised by system II on system I is:

$$X_1=-\int\frac{d\psi}{dx}\,\varrho\,d\tau \ ^{1})$$

According to equation (3):

$$\varrho=\frac{q\,\psi-\nabla^2\,\psi}{4\,\pi\,(A+B)}$$

so

$$4\,\pi\,(A+B)\,X_1=\int\nabla^2\,\psi\,\frac{d\psi}{dx}\,d\tau-q^2\int\psi\frac{d\psi}{dx}\,d\tau\ .$$

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1) Here the same remark holds good as I have made repeatedly in such like calculations. See e. g. Journal de Physique 1899, p. 546. Generally this expression for X_1 is proved in a lengthy way.

Now we get (see MAXWELL 1873, blz. 129, I):

$$\nabla^2 \psi \frac{d\psi}{dx} = \frac{d\psi}{dx}\left(\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d\psi^2}{dz^2}\right) =$$

$$= \frac{1}{2}\,\frac{d}{dx}\left\{\left(\frac{d\psi}{dx}\right)^2 - \left(\frac{d\psi}{dx}\right)^2 - \left(\frac{d\psi}{dz}\right)^2\right\} + \frac{d}{dy}\left(\frac{d\psi}{dx}\,\frac{d\psi}{dz}\right).$$

Let us put:

$$\left(\frac{d\psi}{dx}\right)^2 - \left(\frac{d\psi}{dy}\right)^2 - \left(\frac{d\psi}{dz}\right)^2 - q^2\,\psi^2 = 8\,\pi\,(A + B)\,p_{xx}$$

$$\left(\frac{d\psi}{dy}\right)^2 - \left(\frac{d\psi}{dz}\right)^2 - \left(\frac{d\psi}{dx}\right)^2 - q^2\,\psi^2 = 8\,\pi\,(A + B)\,p_{yy}$$

$$\left(\frac{d\psi}{dz}\right)^2 - \left(\frac{d\psi}{dx}\right)^2 - \left(\frac{d\psi}{dy}\right)^2 - q^2\,\psi^2 = 8\,\pi\,(A + B)\,p_{zz}$$

$$\frac{d\psi}{dy}\,\frac{d\psi}{dz} = 4\,\pi\,(A + B)\,p_{yz} = 4\,\pi\,(A + B)\,p_{zy}$$

$$\frac{d\psi}{dz}\,\frac{d\psi}{dx} = 4\,\pi\,(A + B)\,p_{zx} = 4\,\pi\,(A + B)\,p_{xz}$$

$$\frac{d\psi}{dx}\,\frac{d\psi}{dy} = 4\,\pi\,(A + B)\,p_{xy} = 4\,\pi\,(A + B)\,p_{xu}$$

then we get:

$$\frac{1}{4\,\pi}\,\frac{d\psi}{dx}\,\nabla^2\,\psi = (A + B)\left\{\frac{dp_{xx}}{dx} + \frac{dp_{yx}}{dy} + \frac{dp_{zx}}{dz}\right\}$$

and so:

$$X_1 = \left(\int \frac{dp_{xx}}{dx} + \frac{dp_{yx}}{dy} + \frac{dp_{zx}}{dz}\right) d\tau$$

or as a surface integral on the surface, which encloses system I:

$$X_1 = \int (l\,p_{xx} + m\,p_{yx} + n\,p_{zx})\,ds$$

and in the same way:

$$Y_1 = \int (l\,p_{xy} + m\,p_{yy} + n\,p_{zy})\,ds$$

$$Z_1 = \int (l\,p_{xz} + m\,p_{yz} + n\,p_{zz})\,ds$$

In exactly the same way as MAXWELL we may conclude from this that, when a part of the whole system is enclosed by a potential surface, we may consider the action of the other part on the enclosed part of the system as a tension (or pressure), normal to that potential surface, so in the direction of the lines of force, and a pressure (or tension) round the lines of force normal to them. The value of the tension is here:

$$\frac{R^2 - q^2\,\psi^2}{8\,\pi\,(A + B)} \quad \text{or if } B = 0 \text{ and } A = -f: \quad \frac{R^2 - q^2\,\psi^2}{8\,\pi\,f}$$

The quantity q is the reciprocal value of λ in the potential function of VAN DER WAALS. Hence:

$$-\frac{1}{8\,\pi\,f}\left(R^2 - \frac{\psi^2}{\lambda^2}\right).$$

If $R^2 > \frac{\psi^2}{\lambda^2}$, the expression becomes negative and the tension becomes a pressure. The value of this expression becomes:

$$\frac{1}{8\,\pi\,f}\left(R^2 - \frac{\psi^2}{\lambda^2}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

If we take the surface element for which the tension or pressure is to be determined, normal to the lines of force and represent by l, m and n the direction cosines of the normal measured outwards, then the x-component of the force, acting on the element (considered as a part of a closed surface) is:

$$l\,p_{xx} + m\,p_{yz} + n\,p_{xz}\;.$$

Now:

$$8\,\pi\,(A + B)\left\{l\,p_{xx} + m\,p_{yz} + n\,p_{xz}\right\} =$$

$$= l\left\{\left(\frac{d\psi}{dx}\right)^2 - \left(\frac{d\psi}{dy}\right)^2 - \left(\frac{d\psi}{dz}\right)^2 - q^2\,\psi^2\right\} + 2\,m\,\frac{d\psi}{dx}\,\frac{d\psi}{dy} + 2\,n\,\frac{d\psi}{dx}\,\frac{d\psi}{dz}\,.$$

and we get the relation:

$$l\,\frac{d\psi}{dx} + m\,\frac{d\psi}{dy} + n\,\frac{d\psi}{dz} = 0\;.$$

By combining these two equations, we find easily:

$$8\pi(A+B)\{l\,p_{xx}+m\,p_{yz}+n\,p_{xz}\}=$$

$$=-l\left\{\left(\frac{d\psi}{dx}\right)^2+\left(\frac{d\psi}{dy}\right)^2+\left(\frac{d\psi}{dz}\right)^2+q^2\psi^2\right\}.$$

As we have taken the force as a vector in the direction of the normal measured outwards, the above equation indicates the force which acts on the element from the inside towards the outside. The expression between the braces in the right-hand member is always positive, and we get therefore a negative tension or a positive pressure:

$$\frac{R^2+q^2\psi^2}{8\pi(A+B)}$$

For the potential function of VAN DER WAALS $B=0$, $A=-f$ and $q=\frac{1}{\lambda}$, so we find here a (positive) *tension*:

$$\frac{1}{8\pi f}\left(R^2+\frac{\psi^2}{\lambda^2}\right)$$

For an electric system the system of forces may be described as a system of *tensions* in the direction of the lines of force and a system of *pressures* normal to the lines of force, here however we see that we must assume both tensions and pressures in the direction of the lines of force. Normal to the lines of force there are only tensions, whereas for electric agens the reverse is found. For electric agens the numeric value of the tension is equal to that of the pressure; in our case the tension is not equal to the pressure, except where ψ and R are zero. For the potential energy per unit of volume we found:

$$W=-\frac{1}{8\pi f}\left(R^2+\frac{\psi^2}{\lambda^2}\right).$$

from which follows that:

the absolute value of the potential energy per unit of volume is equal to the tension normal to the lines of force.

The Surface-tension and the Molecular Pressure.

Let us imagine a liquid in equilibrium with its saturated vapour. In the transition layer we may assume the lines of force to be normal to the surface separating the two phases. Let us imagine this surface to be horizontal, therefore the lines of force in the capillary layer as being vertical. If the above considerations are correct, and if we assume that the substance fills the space continuously with a mean density, we shall find for the surface tension exactly the same value as is deduced from the calculations of VAN DER WAALS in his "Theorie der capillariteit". Let us first calculate the molecular pressure; i. e. the force, with which a column of the surface layer with the unity of transverse section is attracted downwards in the direction of the liquid by the surrounding substance.

Per unit of surface we found a pressure, indicated by the formula:

$$D = \frac{1}{8\pi f}\left(R^2 - \frac{\psi^2}{\lambda^2}\right).$$

The force we are speaking of, which we shall call K, is nothing but the difference between the absolute values of the pressure D on the upper and the lower surfaces of the column of the surface layer. Let us call the potential in the vapour ψ_2 and in the liquid ψ_1, and let us bear in mind that both in the vapour and in the liquid R may be put equal to zero, then we find:

$$K = \frac{1}{8\pi f \lambda^2}\left(-\psi_2^2 + \psi_1^2\right) = \frac{\psi_1^2 - \psi_2^2}{8\pi f \lambda^2} \quad ^{1)}$$

---

1) The pressures in consideration are here negative and therefore properly speaking, tensions. For the rest the ideas tension and pressure are somewhat arbitrary. There is no objection to adding an everywhere equal amount to the pressure and the tension through the whole mass. The new system of pressures and tensions will give a representation of the system of forces as well as the original. This appears immediately from the form of the space-integral, which represents the force between two parts of the system:

$$X_1 = \int\left(\frac{dp_{xx}}{dx} + \frac{dp_{xy}}{dy} + \frac{dp_{xz}}{dz}\right)d\tau$$

The coefficient of $d\tau$ consists of the sum of three differential coefficients. Therefore constant amounts may be added to p_{xx}, p_{xy} and p_{xz}.

If the hydrostatic pressure through the whole mass is equal to the external pressure and if only the pressure of the air acts on the system, the pressure $\frac{1}{8\pi f}\left(R^2 - \frac{\psi^2}{\lambda^2}\right)$ is equal to the pressure with reversed sign, leaving a constant out of account.

As further

$$\psi_1 = -4\pi f \lambda^2 \varrho_1 \quad \text{and} \quad \psi_2 = -4\pi f \lambda^2 \varrho_2$$

or

$$\psi_1 = -2a\varrho_1 \qquad \text{and} \quad \psi_2 = -2a\varrho_2$$

we may also write:

$$K = \frac{4a^2\varrho_1^2 - 4a^2\varrho_2^2}{4a} = a(\varrho_1^2 - \varrho_2^2) \quad . \quad . \quad . \quad . \quad (20)$$

If we neglect ϱ_2 with respect to ϱ_1, we get the well-known expresssion of LAPLACE:

$$K = a\varrho_1^2$$

LAPLACE, however, proved this relation only in the supposition that the density in the liquid (also in the surface layer) is constant everywhere.

For the tension *normal* to the lines of force, so in our case in the direction parallel to the separating surface, we found:

$$\frac{1}{8\pi f}\left(R^2 + \frac{\psi^2}{\lambda^2}\right).$$

This expression holds for a unit of surface. For an elementary-rectangle of transverse section of the capillary layer, (i. e. normal to the potential surfaces), two sides of which are parallel to the potential surfaces and have the length of a unit, whereas the other two sides have the direction of the tangents of the surface and a differential length dh, we get:

$$\frac{1}{8\pi f}\left(R^2 + \frac{\psi^2}{\lambda^2}\right) dh \; .$$

The total tension in the capillary layer will be equal to the sum of these differential-expressions, i. e.:

$$S\,^{1)} = \frac{1}{8\pi f}\int_1^2 R^2\,dh + \frac{1}{8\pi f\lambda^2}\int_1^2 \psi^2\,dh \quad . \quad . \quad . \quad . \quad (23)$$

---

[1] This quantity S is *not* the quantity H of LAPLACE.

The limits 1 en 2 relate to liquid and vapour.

In the theory of VAN DER WAALS is:

$$\psi = -2\,a\,\varrho - \frac{2\,c_2}{2}\,\frac{d^2\varrho}{dh^2} - \frac{2\,c_4}{\pi\,4}\,\frac{d^4\varrho}{dh^5} -$$

for

$$-R = -2\,a\,\frac{d\varrho}{dh} - \frac{2\,c_2}{2}\,\frac{d^3\varrho}{dh^3} - \frac{2\,c_4}{\pi\,4}\,\frac{d^5\varrho}{dh^5} -$$

By substitution of the squares of these expressions in (23), making use of the expressions:

$$\lambda^2 = \frac{\dfrac{c_2}{2}}{a} = \frac{\dfrac{c_4}{\pi\,4}}{\dfrac{c_2}{2}} = \frac{\dfrac{c_6}{\pi\,6}}{\dfrac{c_4}{\pi\,4}} = \ldots\ldots$$

we find easily:

$$\mathrm{S} = a\int_1^2 \varrho^2\,dh - a\,\lambda^2\int^2 \left(\frac{d\varrho}{dh}\right)^2 dh + a\,\lambda^4\int_1^2 \left(\frac{d^2\varrho}{dh^2}\right)^2 dh$$

As the tension normal to the lines of force per unit of surface was equal to the potential energy per unit of volume with reversed sign, we have also found this energy.

We can also easily derive the value of the energy directly from the equation for the energy, with which the energy of the unit of mass in a point of the surface layer exceeds that in a point within the liquid. Prof. VAN DER WAALS finds for this:

$$-a\,(\varrho-\varrho_1) - \frac{c_2}{\pi\,2}\,\frac{d^2\varrho}{dh^2} - \frac{c_4}{\pi\,4}\,\frac{d_4\varrho}{dh^4} -$$

For the whole separating layer we get per unit of surface a potential energy:

$$-a\int_1^2 \varrho^2\,dh + a\,\varrho_1\int_1^2 \varrho\,dh - \frac{c_2}{\pi\,2}\int_1^2 \varrho\,\frac{d^2\varrho}{dh^2}\,dh - \frac{c_4}{\pi\,4.}\int_1^2 \varrho\,\frac{d^4\varrho}{dh^4}\,dh -$$

$\int \varrho\,dh =$ mass of the separating layer per unit of surface $= m$.

We get further:

$$\int_1^2 \varrho \frac{d^2\varrho}{dh^2}\, dh = \int_1^2 \varrho\, d\frac{d\varrho}{dh} = -\int_1^2 \left(\frac{d\varrho}{dh}\right)^2 dh \; ^{1)}$$

$$\int_1^2 \varrho \frac{d^4\varrho}{dh^4}\, dh = \int_1^2 \varrho\, d\frac{d^3\varrho}{dh^3} = -\int_1^2 \frac{d^3\varrho}{dh^3}\frac{d\varrho}{dh}\, dh = -\int_1^2 \frac{d\varrho}{dh}\, d\frac{d^2\varrho}{dh^2} = \int_1^2 \left(\frac{d^2\varrho}{dh^2}\right)^2 dh$$

The potential energy per unit of surface becomes:

$$W = -a\int_1^2 \varrho^2\, dh + a\varrho_1 m + \frac{c_2}{\pi 2.}\int_1^2 \left(\frac{d\varrho}{dh}\right)^2 dh - \frac{c_4}{\pi 4.}\int_1^2 \left(\frac{d^2\varrho}{dh^2}\right)^2 dh + \,.\,.$$

As zero position we have taken that of the liquid. If we take infinite rarefaction as zero position, we get $a\varrho_1 m = 0$ and so:

$$S = -W$$

Astronomy. — S. L. VEENSTRA: "*On the Systematic Corrections of the proper motions of the stars, contained in* AUWERS'-BRADLEY-*Catalogue, and the coordinates of the Apex of the solar motion in Space*". (Communicated by Prof. J. C. KAPTEYN.)

The materials for these investigations have been taken from an yet unpublished catalogue, prepared by Prof. KAPTEYN. This catalogue contains for all the Bradley-stars, observed in both coordinates (with the exception of the Pleiades, the Hyades and the fainter components of physical double-stars) the position, the total proper motion μ, its components v and τ, in the direction from the apex and perpendicular to that direction and the quantities λ and χ 2), respectively the distance from star to apex, and the angle between the great circle on which this distance is measured and the declination-circle.

The quantities v, τ, λ and χ have been calculated with different

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1) The differential-quotients $\frac{d\varrho}{dh}$, $\frac{d^2\varrho}{dh^2}$ etc. are zero outside the separating layer.

2) In the *printed* catalogue the quantities χ have not been included.

sets of values for the coordinates of the apex and the precession. The set used by me is as follows:

$$A = +276^\circ \qquad D = +34^\circ;$$

$$\text{precession} = \text{prec. of Auw.-Bradley} \times \left(1 - \frac{1}{2240}\right).$$

Besides to the proper motions in Declination of AUWERS, the following preliminary corrections had been applied:

Declination.	Correction.
Southern Decl.	— 0″ 008
Decl. 0 tot + 20°	— 8
» + 20 » + 40	— 8
» + 40 » + 60	— 5^5 (mean)
» + 60 » + 90	— 1

According to the arrangement of the catalogue, I have calculated the systematic corrections of the P. M. in declination for these five belts, separately for the stars of *a*) Spectral Type I and unknown spectrum, *b*) Spectral Type II.

They have been derived from the condition that $\Sigma\, \tau$ must be *zero* for each half belt, *viz.* for the halves, in wich $\sin\chi$ is *only* positive or *only* negative.

The expression of this condition is:

$$\Sigma\, \tau + \Delta\mu_\delta\, \Sigma \sin\chi = 0$$

or

$$\Delta\mu_\delta = -\frac{\Sigma\, \tau}{\Sigma \sin\chi};$$

where $\Delta\mu_\delta$, taken constant in each half belt, is the correction, to be applied to the P. M. in declination.

In order to get reliable results, the stars with small $\sin.\chi$, which evidently have small weight, were omitted. The calculations have further been performed separately for:

1st. $\sin\chi \geqq \pm 0.80$; 2nd. $\sin\chi \geqq \pm 0{\cdot}60$.

Besides, the stars with a total yearly proper motion > 0″.3 have been left out too.

Combining the values of $\Delta\mu_\delta$ for both parts of each belt, according to their weights, the result is:

A. $\sin\chi > \pm 0.80$	corr. $\Delta\mu_\delta$	prel. corr.	total corr. $\Delta\mu_\delta$
Southern Declination	— 0″.0093 (226 st.)	— 0″.0080	— 0″.0173
Decl. 0° tot + 20°	— 16 (215 »)	— 80	— 96
» + 20° » + 40°	— 34 (258 »)	— 80	— 114
» + 40° » + 60°	— 2 (160 »)	— 55	— 57
» + 60° » + 90°	+ 17 (95 »)	— 10	+ 7

numb. of stars 954

B. $\pm 0.80 > \sin\chi > \pm 0.60$	corr. $\Delta\mu_\delta$		total
South. Decl.	— 0″.0024 (278 st.)	— 0″.0080	— 0″.0104
Decl. 0° tot + 20°	— 90 (218 »)	— 80	— 170
» + 20° » + 40°	— 52 (131 »)	— 80	— 132
» + 40° » + 60°	— 5 (62 »)	— 55	— 60
» + 60° » + 90°	+ 42 (32 »)	— 10	+ 32

numb. of stars 721

The combination of the values sub *A* and *B*, with weights proportional to $n \sin^2 \chi$ ($n =$ number of stars), is given in the following table:

C. $\sin\chi > \pm 0.60$	$\Delta\mu_\delta$	prel. corr.	Total $\Delta\mu_\delta$	prob. err.
South. Decl.	— 0″.0062 (504)	— 0″.0080	— 0″.0142	0″.0015
Decl. 0° tot + 20°	— 45 (433)	— 80	— 125	23
» + 20° » + 40°	— 38 (389)	— 80	— 118	16
» + 40° » + 60°	— 1 (222)	— 55	— 56	13
» + 60° » + 90°	+ 29 (127)	— 10	+ 19	20

numb. of stars 1675

What part is due to each Spectr. Type in making up these final values, is shown in the next table:

	$\sin \chi +$		$\sin \chi -$		tot.	tot.	tot.	tot.
	Type I.	Type II.	Type I.	Type II.	$\sin \chi +$	$\sin \chi -$	Type I.	Type II.
Southern Decl.	—0″.0020 (146 st.)	—0″.0071 (121 st.)	—0″.0114 (144 st.)	—0″.0034 (93 st.)	—0″.0013 (267 st.)	—0″.0083 (237 st.)	—0″.0067 (290 st.)	—0″.0055 (214 st.)
Decl. 0° tot + 20°	+ 10 (137)	+ 22 (97)	— 144 (117)	— 74 (82)	+ 14 (234)	— 115 (199)	— 61 (254)	— 22 (179)
» + 20° » + 40°	— 29 (134)	— 86 (89)	— 67 (87)	+ 31 (79)	— 54 (223)	— 20 (166)	— 44 (221)	— 31 (168)
» + 40° » + 60°	— 29 (80)	+ 32 (60)	— 30 (47)	+ 12 (35)	— 3 (140)	+ 1 (82)	— 29 (127)	+ 36 (95)
» + 60 » + 90°	+ 43 (60)	— 7 (38)	— 67 (13)	+ 138 (16)	+ 24 (98)	+ 46 (29)	+ 23 (73)	+ 36 (54)
numb. of stars	557	405	408	305	962	713	965	710

The values, found for $\Delta\mu_\delta$ have been used in computing the corrections, to be applied to the P. M. in right ascension.

This correction, $\Delta\mu_\alpha$, supposed to be $= 0$, when $\Delta\mu_\delta$ was calculated, is derived from the formula

$$\Delta\mu_\alpha = \frac{\Sigma\, r + \Delta\mu_\delta\, \Sigma \sin\chi}{\Sigma \cos\chi},$$

first for each spectr. Type, and each belt separately and taking $\Delta\mu_\alpha$ constant from 0^h to 3^h, from 3^h to 6^h, a. s. o. Afterwards the different values for the same R. A., but different types and declinations, were combined, with weights proportional to the numbers of stars.

The final values are

	0^h—3^h	3^h—6^h	6^h—9^h	9^h—12^h	12^h—15^h	15^h—18^h	18^h—21^h	21^h—0^h
$\Delta\mu_\alpha =$	$+0^s0005$	$+0^s0001$	$+0^s0003$	$+0^s0004$	$+0^s0004$	-0^s0011	-0^s0001	-0^s0001

Putting the weight proportional to $n \cos\delta$ instead of proportional to n, we get

$\Delta\mu_\alpha =$

$+0^s0005.6$	$+0^s0000.8$	$+0^s0003.2$	$+0^s0006.3$	$-0^s0001\ 3$	$-0^s0009.7$	$-0^s0006.6$	$-0^s.0000.7$

mean probl. err. $0^s.00042$.

As appears from the prob. errors, they are hardly to be considered real.

With these corrections to the proper motions, the coordinates of the apex have been calculated. The formulae used for the purpose, the derivation of which is easily seen, are

$$\frac{\sin\delta - \cos\lambda \sin D}{\sin^2\lambda}\, x - \frac{\sin(\alpha - A)\cos\delta}{\sin^2\lambda}\, y + \Theta = 0 \quad . \quad . \quad \text{(I)}$$

where $x = \Delta A =$ corr. to be applied to the R. A. of the apex.

$y = \Delta D =$ „ „ „ „ „ „ Decl. „ „ „

$$tg\,\Theta = -\frac{\Sigma\,(\tau + \Delta\mu_\delta \sin\chi)}{\Sigma\,(v + \Delta\mu_\delta \cos\chi)}$$

when $\Delta\,\mu_\delta$ only was applied and

$$tg\,\Theta = -\,\frac{\Sigma\,(\tau + \Delta\,\mu_\delta \sin\chi - \Delta\,\mu_\alpha \cos\delta \cos\chi)}{\Sigma\,(\upsilon + \Delta\,\mu_\delta \cos\chi + \Delta\,\mu_\alpha \cos\delta \sin\chi)},$$

on applying both corrections.

Dividing each belt in eight parts, of 3^h in R. A., and including all the stars (2503 in number) of which the proper motion does not exceed 0″.30, six sets of equations of condition of the form (I), of 40 equations each, were obtained. From each set was derived a value for $\Delta\,A$ and $\Delta\,D$.

The weight of Θ proves to be proportional to the respective number of stars. The Θ's, having negative denominator, evidently should be taken in the 2nd or 3rd quadrant.

The coordinates of the apex, found in this way, are:

		A	*D*
Type I.	corr. $\Delta\,\mu_\delta$	268°.3 ± 2°.4	+ 36°.7 ± 1°.5
	$\Delta\,\mu_\alpha$ and $\Delta\,\mu_\delta$	272 .1 ± 2 .3	37 .6 ± 1 .4
Type II.	$\Delta\,\mu_\delta$	273 .5 ± 4 .3	33 .9 ± 2 .8
	$\Delta\,\mu_\alpha$ and $\Delta\,\mu_\delta$	270 .6 ± 4 .0	34 .3 ± 2 .5
Types I and II together	$\Delta\,\mu_\delta$	269 .5 ± 1 .7	34 .3 ± 1 .2
	$\Delta\,\mu_\alpha$ and $\Delta\,\mu_\delta$	274 .2 ± 1 .7	35 .1 ± 1 .2

Besides, values of *A* and *D* have been derived in perfectly the same manner from 151 stars with annual P. M. > 0″.3, after applying $\Delta\,\mu_\delta$ to these P. M's.

For each of these 151 stars an equation of cond. (I) was constructed. The result is:

$$A = 262°.4 \pm 3°.4\,; \qquad D = +\,42°.2 \pm 2°.7\ .$$

These results confirm what Mr. PANNEKOEK wrote in 1895 (Bullet. Astr. XII p. 196): "Si l'on a égard à ces corrections des apex calculés, on peut en tirer la conclusion qu'ils ne montrent pas d'indication évidente d'un mouvement relatif entre les étoiles à spectres de types différents."

NEWCOMB goes a little farther yet (Astron. Journal XVII, p. 390): "The centres of gravity of two great classes of stars scattered through the celestial sphere will be at rest relatively. — I believe this hypothesis safe still when the classes differ by spectral type, as the positions of the apex in both cases are fairly well the same."

The calculations, of which the results only are given here, will shortly be published in extenso.

Groningen, November 1899.

Chemistry. — "*d-Sorbinose and l-sorbinose (ψ-tagatose) and their configurations.*" By Prof. C. A. LOBRY DE BRUYN and Mr. W. ALBERDA VAN EKENSTEIN, communicated by Prof. LOBRY DE BRUYN.

The configuration of *d*-sorbinose, a substance which has been known for a long time, has not up to the present been made out with certainty. It is only known that this sugar is a ketose, that it yields *d*-sorbite on reduction and that it can be formed again from this latter alcohol by oxidation.

d-Sorbinose which was formerly difficult to prepare in a tolerably large quantity, is now more easily obtained by the method of BERTRAND [1]). According to the interesting method of this chemist, sorbite can be oxidised to sorbinose by means of Bacterium xylinum (and B. aceti). By this method we have obtained yields of 25 to 30 percent [2]); we are indebted to the courtesy of Mr. BEYERINCK of Delft for the pure cultures of Bact. xylinum.

The final experiments with *d*-sorbinose were brought to a conclusion in the beginning of 1898; they proved that, on reduction with sodium amalgam, *d*-idite is formed as well as *d*-sorbite. The former alcohol was recognised, in the form of its tribenzal-compound, as the optically opposite form of tribenzal-*l*-idite prepared from *l*-idonic acid. [3])

This result was obtained many months before the publication, at a meeting of the Société chimique, by G. BERTRAND from the fact that on reducing *d*-sorbinose a second hexite is produced, in addition to sorbite, which according to BERTRAND must be *d*-idite. [4]) The publication of our work was, however, postponed because in the course of an investigation of ψ-tagatose (a new ketose which is formed along with tagatose by the action of alkalis on galactose [5]) it was becoming more and more probable that this sugar was to be regarded as *l*-sorbinose. More than a year ago, the two ketoses were submitted to a comparative crystallographic examination; Mr. VAN LIER was good enough to make this examination in the laboratory of Prof. SCHROEDER VAN DER KOLK at Delft. The result

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[1]) Bull. Soc. chim. **15**, 1196, 627.

[2]) 200 gr. sorbite gave 50 to 60 grams of pure sorbinose.

[3]) Recueil **18**, 150

[4]) Report of the meeting of March 11. 1898; Bull. **19**. 259. In the publication relating to this communication (Bull. **19**, 347) no details are given about the reduction of *d*-sorbinose to idite or about its configuration; BERTRAND has also not returned to the subject.

[5]) Recueil **16**, 267.

was that the two substances behave crystallographically and optically in exactly the same way.

At that time we still hesitated, however, to assume that *ψ*-tagatose was *l*-sorbinose; on reduction some *l*-dulcite was always obtained along with *l*-sorbite and *l*-idite. The specific rotatory power of *ψ*-tagatose to the right remained, even after repeated crystallisations from water, methyl- and ethylalcohols, about 4° less than that of *d*-sorbinose to the left; the crystals were never quite clear but always slightly turbid.

After many attempts to convert *ψ*-tagatose into a crystalline compound from which the pure ketose could be regenerated, we attained our object by the employment of aniline. It was then found that *d*-tagatose crystallises together with *ψ*-tagatose in a very persistent way, but forms an anilide much more readily than its isomer so that the latter is deposited in well formed, clear crystals from an alcoholic solution containing aniline. The *ψ*-tagatose purified in this way was then proved with certainty to be the optical opposite of *d*-sorbinose and it is therefore henceforth to be regarded as *l*-sorbinose. A short summary of the comparative experiments which place this view beyond doubt follows.

The melting points are the same (about 154°); from a mixture of equal quantities of the two ketoses a well crystallised racemic compound is obtained with approximately the same melting point and a somewhat higher specific gravity.

The specific gravities and the solubilities in water and methyl- and ethylalcohols are the same.

For *d*-sorbinose, $\alpha_{[D]} = - 42°.7$, for *l*-sorbinose $\alpha_{[D]} = + 42°.3$ (4 percent solutions at 17°). Both solutions show the same slight birotation.

It has already been remarked that the two ketoses are crystallographically identical; hemihedral faces will be again sought for.

The osazones have the same melting point (150 to 151°), the same solubility and equal and opposite rotatory powers.

l-Sorbinosazone is, as a comparison shows, identical with *l*-gulosazone. [1])

On reduction with sodium amalgam, *d*-sorbite and *d*-idite are formed from *d*-sorbinose, *l*-sorbite and *l*-idite from *l*-sorbinose; these

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[1]) The statement in VON LIPPMANN's „Chemie der Zuckerarten", p. 534, that sorbinosazone is not identical with gulosazone is, according to a communication from the author, a mistake.

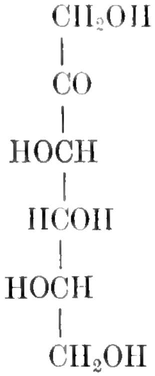
hexites were recognised in the from of the benzal-[1]) and formal-derivatives.

Both *d*- and *l*-sorbite have been prepared from the benzalcompounds and obtained in the crystalline form.

Crystalline methyl-*l*-sorbinoside was prepared by E. FISCHER's method from *l*-sorbinose; its specific rotation is equal and opposite to that of the known methyl-*d*-sorbinoside (88°.5). [2])

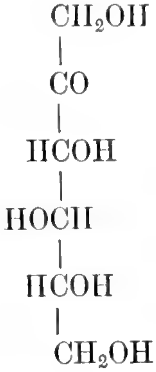
The results obtained, including the production of idite along with sorbite by reduction and the identity of *l*-sorbinosazone with *l*-gulosazone enable us to give the two sorbinoses the following configurations:

d-sorbinose:



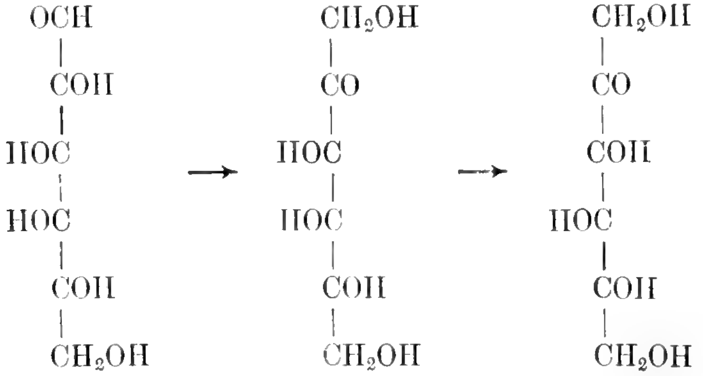
$$\begin{array}{c} CH_2OH \\ | \\ CO \\ | \\ HOCH \\ | \\ HCOH \\ | \\ HOCH \\ | \\ CH_2OH \end{array}$$

and *l*-sorbinose:



$$\begin{array}{c} CH_2OH \\ | \\ CO \\ | \\ HCOH \\ | \\ HOCH \\ | \\ HCOH \\ | \\ CH_2OH \end{array}$$

The formation of *l*-sorbinose from *d*-galactose under the influence of alkalis is an example of a direct transition from the dulcite series of the hexoses to the mannite series. This can be best represented by assuming the intermediate formation of *d*-tagatose; the OH and H attached to the third carbon atom must then change places in the transformation



$$\begin{array}{c} OCH \\ | \\ COH \\ | \\ HOC \\ | \\ HOC \\ | \\ COH \\ | \\ CH_2OH \end{array} \longrightarrow \begin{array}{c} CH_2OH \\ | \\ CO \\ | \\ HOC \\ | \\ HOC \\ | \\ COH \\ | \\ CH_2OH \end{array} \longrightarrow \begin{array}{c} CH_2OH \\ | \\ CO \\ | \\ COH \\ | \\ HOC \\ | \\ COH \\ | \\ CH_2OH \end{array}$$

d-galactose *d*-tagatose *l*-sorbinose

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[1]) Recueil **18**, 150. A tribenzalsorbite was obtained as well as the mono- and dibenzalsorbites.

[2]) E. FISCHER, Ber. **28**, 1159.

We shall try to determine whether pure tagatose readily yields *l*-sorbinose under the influence of alkalis.

We have also again taken up the investigation of the probable formation of a new ketose (called, for the present, ψ-fructose [1]) by the reciprocal transformation of glucose, fructose and mannose under the influence of alkalis.

The following triplets of hexoses (two aldoses and a ketose) are now known which give the same osazone:

d- and *l*-glucose, — fructose and — mannose

d- and *l*-gulose, — sorbinose and — idose

d-galactose, — tagatose and — talose. [2]

A complete account of this investigation will be published in the "Recueil".

Chemistry. — *"On the action of sodiummono- and -disulphides on aromatic nitro-compounds."* By Mr. J. J. Blanksma. (Preliminary communication). Communicated by Prof. C. A. Lobry de Bruyn.

It has been shown for orthodinitrobenzene by Laubenheimer [3]) and for paradinitrobenzene by Lobry de Bruyn [4]) that the nitrogroup can be readily replaced by other groups. The investigation of the behaviour of the alkalisulphides, although promised [5]), has not been taken up until the present. Some positive result may be expected from this study since Nietzki and Bothof [6]) have proved that the corresponding dinitrodiphenylsulphides are formed from *o*- and *p*-chlornitrobenzene and sodiummonosulphide.

It has now been found that orthodinitrobenzene reacts not only with sodium monosulphide but also with the disulphide in a similar

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[1]) Recueil, **16**, 278.

[2]) The *d*-tagatose has yielded *d*-talite along with dulcite.

[3]) Ber. **9**, 1828; **11**, 1155.

[4]) Recueil **13**, 121.

[5]) Recueil **13**, 105—106.

[6]) Ber. **27**, 3261; **29**, 2774.

way. In the first case *o*-dinitrodiphenylsulphide $NO_2C_6H_4SC_6H_4NO_2$, in the second *o*-dinitrodiphenyldisulphide $NO_2C_6H_4SSC_6H_4NO_2$, is formed, sodium nitrite being simultaneously produced.

The monosulphide is readily oxidised, first to a sulphoside and then to a sulphone; the molecule of the disulphide on the other hand is broken up and converted into two molecules of *o*-nitrobenzenesulphonic acid, of which some derivatives were prepared. By means of sodium disulphide it is therefore possible to substitute the sulphonic group for a nitrogroup in the orthoposition. From *p*-dinitrobenzene, neither the dinitrodiphenylsulphide nor the corresponding disulphide could be obtained; in this respect, therefore, it differs from its isomer. Both with Na_2S and with Na_2S_2 reduction to *p*-dinitroazoxybenzene first occurs; this substance has already been obtained by the action of potash on *p*-dinitrobenzene.[5] Small quantities of *p*-nitrothiophenol $NO_2C_6H_4SH$ are also formed. Parachlornitrobenzene, the behaviour of which with Na_2S has already been studied by NIETZKI and BOTHOF, reacts also with Na_2S_2 forming paradinitrodiphenyldisulphide $NO_2C_6H_4SSC_6H_4NO_2$. The crystals of this compound, which has already been prepared by LEUCKART[6]) by another method, have the interesting peculiarity of flying to pieces when warmed to 134°, subsequently melting at 170°. Inversely, the solid mass formed below 170° changes at the same temperature into another crystalline modification in a clearly visible manner. We are here obviously dealing with a transition point characterised by a great difference in the specific volumes of the two modifications; this is to be more carefully investigated.

Like the isomeric ortho-compound, *p*-dinitrodiphenyldisulphide is readily oxidised to nitrobenzene sulphonic acid. By this means, therefore, halogen united to the benzene nucleus has been replaced by the sulphonic group.

The results of some preliminary experiments make it probable that by direct substitution substances containing not only two, but also more sulphur atoms, connecting two benzene rings, may be prepared.

The investigation is being continued.

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[5]) Recueil **13**, 122.

[6]) J. Prakt. Chem. (2) **41**, 199; see also WILLGERODT, Ber. **18**, 331; KEHRMANN and BAUER, Ber. **29**, 2361.

Chemistry. — "*The alleged identity of red and yellow mercuric oxide*", *Part I.* By Dr. Ernst Cohen. (Communicated by Prof. H. W. Bakhuis Roozeboom.)

1. Some years ago, (1895), in a review [1] of Varets' thermochemical determinations [2] concerning red and yellow mercuric oxide, Ostwald said that in his opinion it was doubtful whether the two modifications were isomeric. He added the remark: "probably they only differ in the size of their particles, that is mechanically".

Shortly after this review, Ostwald published the results of some measurements [3], made at his request by Thor Mark with the object of seeing whether we are here confronted by a case of identity or isomerism.

Ostwald concluded that "the two kinds of mercuric oxide are no more different than crystallised and powdered potassium bichromate, which exhibit a similar difference of colour; they are not isomeric but identical".

This conclusion rests on the following experiment: a galvanic cell, arranged as follows:

Mercury	Red oxide in potash solution	Yellow oxide in potash solution	Mercury

showed, according to Mark's measurements, a difference of potential of less than 0,001 volt, since, as Ostwald said „no deflection could be observed with the electrometer used which was capable of measuring 1 to 2 millivolts".

Besides this electrometric determination of solubility, determinations of the solubility of the two oxides in solutions of potassium bromide, potassium iodide and sodiumthisosulphate were made. After saturation, the solutions, which had become alkaline [4], were titrated with hydrochloric acid. Equal volumes of the solutions required the following quantities of acid:

Potassium bromide solution saturated with		Potassium iodide solution saturated with		Sodiumthiosulphate solution saturated with	
Red oxide	Yellow oxide	Red oxide	Yellow oxide	Red oxide	Yellow oxide
6,16 ccm. HCl.	6,20 ccm. HCl.	49,82 ccm. HCl.	49,64 ccm. HCl.	51,84 ccm. HCl.	51,98 ccm. HCl.
				51,75 „	51,80 „
				51,81 „	51,82 „

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[1] Zeitschrift für physikalische Chemie 17. 183 (1895).

[2] C. R. 120. 622 (1895)., Ann. de chim. et de phys. (7) 8, 79 (1896).

[3] Zeitschrift für phys. Chemie 18, 159 (1895).

[4] Bersch, Zeitschrift für phys. Chemie 8, 383 (1891).

"It is proved by these experiments that the *free* energy of the two forms of the oxide is the same; since the same thing has been proved for the *total* energy by the experiments of VARET, the above conclusion, that the two forms are identical, follows of necessity."

2. In my researches on the difference in the free energy of the two isomeric forms of tin, the grey and the white [1]), of which I shall publish the details shortly, I had found that the difference between the forms is very small. Even at a considerable distance from the transition temperature (20° for example) the difference is only of the order of a few millivolts.

If now, in a case such as that of tin where the isomerism is so clearly marked, only such small differences in the free energy of the modifications are to be found, it is natural to assume that the scale with which OSTWALD measured in the case of the red and yellow mercuric oxides (1 to 2 Millivolts) was much too large to permit of the definite conclusion that there is no difference in the free energy of the two modifications.

I decided therefore to determine the difference of free energy between red and yellow mercuric oxides, choosing a scale a thousand times smaller than OSTWALD's ($^1/_{1000}$ millivolt).

3. In 1892 an investigation by GLAZEBROOK and SKINNER appeared [2]) in which a number of observations is described which indirectly have an important bearing on the question with which we are here occupied.

GLAZEBROOK and SKINNER investigated the E. M. F. of the GOUY normal cell [3]), which is constituted as follows:

$$\mathrm{Hg} \mid \mathrm{HgO} \mid 10\,^0/_0 \text{ solution of Zinc sulphate} \mid \mathrm{Zn},$$

and found a great difference between the E. M. F. of elements constructed with yellow and with red mercuric oxide.

For the E. M. F. of the GOUY cell containing red mercuric oxide they found 1,384 Volt, for that of the element with yellow oxide 1,391 volt at 12° C.

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[1]) See ERNST COHEN, A new kind of transition element (sixth kind). Proceed. Roy. Acad. Amsterdam. Vol. II. 1899 p. 153.

[2]) Phil. Trans. of the Royal Society 183. 367 (1892).

[3]) Journal de Physique Tome VII (1888), p. 532.

From this it might be deduced that the difference of free energy between red and yellow mercuric oxides was of the order of 7 millivolts, whilst OSTWALD gives it as smaller than 1 millivolt.

Here also a careful and exact investigation appears desirable.

4. In the first place it is rather surprising that neither OSTWALD nor GLAZEBROOK and SKINNER say anything about the purity of the materials, which is nevertheless of the greatest importance owing to the great sensitiveness of the electrometric method. In determinations made by this method, traces of impurity may have an enormous effect on the E. M. F. measured.

Further, the preparation of absolutely pure mercuric oxide, whether red or yellow, is to be counted among the more difficult tasks of preparative chemistry, as may be seen from what follows.

Four specimens (from different makers) of red mercuric oxide (hydrargyrum oxydatum rubrum praecipitatum pro analysi) and yellow oxide (hydrargyrum oxydatum via humida paratum pro analysi) could not be used on account of the many impurities which they contained.

In the red and yellow oxides from MERCK of Darmstadt, I could not discover any traces of impurity by analytical means; these preparations were therefore used as the starting point of the investigation.

The water which served for making the solutions employed, was very pure and possessed a conductivity of 1×10^{-6}. It was distilled from a heavily tinned copper vessel a trace of phosphoric acid being added; the middle fraction was used, carbonic acid being removed by means of an air current in the well known way.

The solution of potash used was made from potassium and this water, the carbonic anhydride of the air being excluded.

The mercury was, after a preliminary purification, twice distilled in vacuo. All glass vessels, flasks etc. with which the substances came in contact were steamed out.

5. A cell was now put together of the form shown in the figure; *aa* and *bb* are glass tubes $7\frac{1}{2}$ cm. long and 2 cm. wide, connected below with capillaries, which are bent round and carried upwards to 2 cm. above the caoutchouc stoppers *k k*. In this way it is possible to submerge the whole apparatus in water without the platinum wires P_1 and P_2, which must be heated to redness before each experiment, coming in contact with it. These wires terminate in the mercury which is placed on the bottom of *aa* and *bb*. Upon

this a layer of 1 cm. of yellow HgO is placed in *aa* and of red HgO in *bb*. The layer of oxide is made thick in order to prevent movement of the surface of the mercury electrodes.

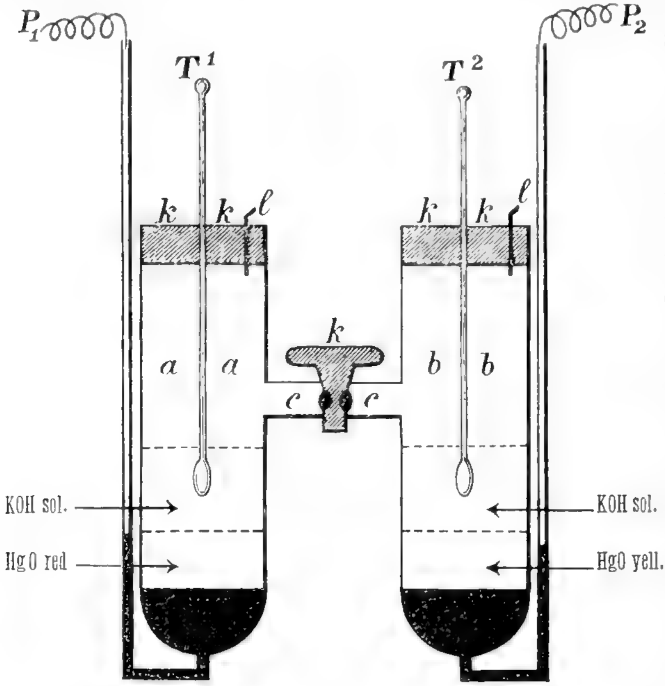

Fig. 1.

According to the measurements of HELMHOLTZ, irregular vibration of the surface of the electrodes may give rise to differences of potential between them, which must, of course, be avoided. The two limbs and the connecting piece *cc* with the tap *k* were filled with a solution of potassium hydroxide (about 15 percent), the tap remaining closed meanwhile. In this way the two oxides remain each in its own compartment whilst the cell is being prepared. After filling them, the two limbs are immediately closed by india-rubber stoppers *kk* and *kk*. A small ANSCHÜTZ thermometer, (graduated in $^1/_5$°) passes through each, the air being allowed to escape by means of capillary tubes *l* and *l*. These tubes are closed at once after filling in order to prevent entrance of water into the element when it is placed in the thermostat.

The use of the thermometers is necessary, because small differences of temperature between the liquids or the mercury in the two limbs of the element might give rise to thermocurrents which would interfere with the measurement of the very small differences ot potential which are being dealt with.

6. The arrangement and course of the measurements may be somewhat fully described, since the value of the results is very closely connected with them. The elements, also the standard cells, were kept in the dark during the whole course of the research. The influence of light on red and yellow mercuric oxide is not yet sufficiently studied to permit one to decide whether this agency would have any effect on the E. M. F. which is to be measured.

After the element has been set up in the way described, it is immersed in a thermostat, the temperature of which is maintained at 25° by means of a toluene regulator. By means of this regulator and a stirring arrangement (a small ships propeller kept in movement day and night by a HEINRICI's hot air motor) it was possible to keep the temperature at 25° during the whole period of the observations (about 6 weeks); the greatest variations, measured by means of a thermometer designed for thermochemical work, did not exceed 0°,004 C. The variations which occurred within 15 minutes could not, of course, appear in the element itself. It was, further, only of importance that the two limbs of the element should undergo the same changes of temperature.

The standard cells, which were used in the measurements by means of POGGENDORFF's compensation method, were placed in the same thermostat.

The standard cells were:

1. A WESTON-cell made in April 1899.
2. A CLARK-cell *A* „ in January 1899.
3. A CLARK-cell *B* „ in January 1899.

A small accumulator [1]) was used as the working cell.

Since all the measurements were reduced to the *Westoncell*, it appeared important to control it from time to time. This was done by means of the two CLARK-cells; as will be seen the E. M. F. of the WESTON-cell remained absolutely constant during the whole period of the measurements. (See Table I).

TABLE I.

Date	Ratio $\frac{\text{E. M. F. CLARK A } 25^\circ}{\text{E. M. F. WESTON } 25^\circ}$	Ratio $\frac{\text{E. M. F. CLARK B } 25^\circ}{\text{E. M. F. WESTON } 25^\circ}$
1 October	1.3946	1.3945
10 October	1.3946	1.3945
20 October	1.3946	1.3945
27 October	1.3946	1.3945
10 November	1.3946	1.3945
20 November [2])	1.3946	1.3945

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[1]) These accumulators, having the very small dimensions 55 × 42 × 150 m.m. capacity 5,5 ampère hours, (weight when filled 880 gr.) are obtainable from the Berlin accumulator factory Andreas Str. 32, Berlin (O) at a cost of 3 Marks. They are to be strongly recommended for measurements of this kind. My friend Dr. BREDIG of Leipzig drew my attention to these cells.

[2]) The great reliability of the standards is further evident from the fact that in another test made on June 17, 1899 the same ratios 1.3946 and 1.3945 were obtained.

If, in accordance with the completely harmonious determinations of KAHLE[1]) and CALLENDAR and BARNES[2]) we take the E. M. F. of the CLARK-cell at 25°,0 as 1,4202 volts, then the E. M. F. of the WESTON-cell at 25°,0 is, according to these determinations, 1,0184 volts. The comparisons made by JAEGER and WACHSMUTH[3]) also give the E. M. F. of the WESTON-cell at 25°,0 = 1.0184 volt.

Our standard was thus very trustworthy during the whole research.

An extremely sensitive THOMSON mirror galvanometer was used as zero instrument. The thermometers employed were compared with a thermometer standardised by the Physikalisch-Technische Reichsanstalt.

The thermometer which indicated the temperature of the thermostat was graduated in $^1/_{10}$°.

7. A series of measurements was first made with the red and yellow oxides from MERCK, which were used without further treatment, after it had been found that no impurities could be discovered in them by analytical means.

I first determined the potential difference red HgO — red HgO by setting up an element arranged thus:

Hg — red HgO — potash lye — potash lye — red HgO — Hg.

The potential difference was less than 0,000001 volt[4]).

In the same way the potential difference of yellow HgO — yellow HgO was measured. This also was less than 0,000001 volt.

8. The determination of the potential difference red HgO — yellow HgO then followed. An interesting phenomenon, which might have been foreseen, was here encountered.

It is known that the two oxides behave differently towards a number of reagents, the velocity with which they react being different. The yellow oxide, for example, dissolves in acids more rapidly than the red.

If now, as might be anticipated, the equilibria of the two oxides with the solution in the cell are attained with different velocities, it is to be expected that the E. M. F. of the mercuric oxide cell, regarded as a function of the time, will increase to a certain maxi-

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[1]) See Thätigkeitsbericht der Physikalisch Technischen Reichsanstalt 1896/97. Zeitschrift für Instrumentenkunde 17, 144 (1897); WIEDEMANN's Annalen 64, 94(1898). Zeitschrift für Instrumentenkunde 1898. 161.

[2]) Proc. of the Royal Society 62, 132 (1897).

[3]) WIED. Annalen 59. 575 (1896) en Zeitschrift für Instrumentenkunde 1898. 161.

[4]) The smallest quantity measurable.

mum, after which it will fall until a constant value is reached, which would indicate the attainment of equilibrium.

It was to be expected that the attainment of the final condition would be slow, considering that the contents of the cell were not stirred and that the saturation of the liquid with HgO was brought about by diffusion.

The correctness of these views was proved numerically by all the experiments. In the following table the time in hours, from the first filling of the cell, is given under *t*, the E. M. F. of the element (at 25°,0) at the time mentioned is given under *E* in millivolts.

TABLE II.

t. (hours)	*E.* (Millivolts)	*t* (hours)	*E* (Millivolts)
0	0,585	61	1.037
$^{3}/_{4}$	0,759	73	0,876
$1^{1}/_{2}$	0,843	97	0,756
$5^{1}/_{4}$	1,066	121	0,721
24	1,237	147	0,703
$29^{3}/_{4}$	1,237	171	0,686
49	1,169	194	0,685
		241	0,685

Representing the E. M. F. graphically as a function of the time, the curve in fig. 2 is obtained. A maximum is attained in 24 hours, the condition of equilibrium being reached only after the lapse of 171 hours; this was observed for a further 70 hours.

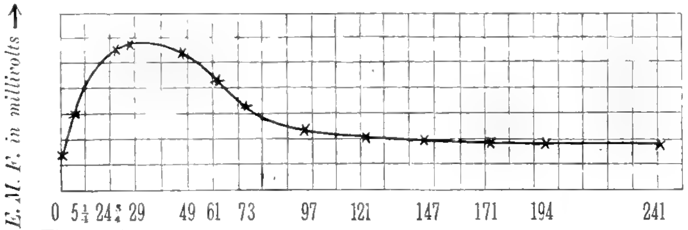

Fig. 2.

According to this experiment the difference of potential between red and yellow mercuric oxides at 25°,0 *is equal to* 0,685 *millivolts.*

2. Although, as above mentioned, impurities could not be discovered by analytical methods in the specimens of red and yellow mercuric oxide used yet, considering the great delicacy of the electric

measurements, it appeared to me to be of importance to obtain further confirmation of this result.

The red and yellow oxides from MERCK were shaken with water, of conductivity 1×10^{-6}, for some days in sealed tubes in order to remove all traces of soluble matters which might possibly still be present. The specimens, after filtration, were then dried for a week *in vacuo* over sulphuric acid.

A few grams of each material were placed in steamed glass tubes, a few cc. of potash lye added and the tubes, which had long necks in order to avoid warming the liquids in sealing them, sealed up before the blowpipe. They were then shaken in the thermostat at 25°,0 for 14 days and nights in order to saturate the lye with HgO and bring about equilibrium. The cell was then put together and placed in the thermostat at 25°.0.

In the following table the results obtained are given in the same way as in table II.

TABLE III.

t (hours)	E (Millivolts).
0	0,686
24	0,685
70	0,685
96	0,685
120	0,685
168	0,685

The potential difference found here is therefore the same as in the first series of experiments, which proves that the materials were quite pure before they were shaken with water and that in the first experiment equilibrium was obtained (by diffusion).

10. Between the free energies of red and yellow mercuric oxides, therefore, a sensible difference exist, viz. 0,685 millivolt at 25°.0, a difference at least 700 times greater than the difference which I was able to detect with the apparatus used between red and red or yellow and yellow oxide.

OSTWALD's statement, that the capillary electrometer employed, which was capable of detecting potential differences of 1 to 2 millivolts, showed no deflection, agrees completely with my result that the difference of potential in question is only 0.685 millivolt. (OSTWALD does not state at what temperature MARK's measurements were made.)

BLOCK OF BANCA TIN WITH TINPLAGUE.

Inoculated with grey tin; in solution of pink salt.
27 Sept.—13 Oct. 1899. Temp. —5° C.
Enlargement 1$^1/_2$ lin.

A second proof of the isomerism of the two oxides may be given by means of measurements of the temperature coefficient of the mercuric oxide cell. I shall shortly make a communication on this point.

Summary of the results of the investigation.

1. There is a difference in the free energy of red and yellow mercuric oxides (0.685 millivolts at 25°). Contrary to OSTWALD's opinion, therefore, the substances are isomeric and not identical.
2. The measurements of GLAZEBROOK and SKINNER, according to which a difference of 7 millivolts at 12° exists between the E. M. F.'s of GOUY standard cells made with the two oxides, are incorrect. The difference at 12° C. is less than 0.6 millivolt.

Amsterdam, University Chemical Laboratory.
November, 1899.

Chemistry. — "*The Enantiotropy of Tin*" (III). By Dr. ERNST COHEN. (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM.)

1. In continuation of the investigation of the two modifications of tin a large block of Banca tin, weighing about $^1/_2$ kilo, was inoculated with grey tin, and subsequently submitted to a temperature of — 5° C. for 3 weeks in contact with a solution of pink salt in order to observe the phenomenon on a larger scale.

The accompanying figure, from a photograph, shows that the whole surface is covered with grey warts, between which the original silver-white colour of the metal is to be seen only in a few places.

Once the change has begun the waste goes forward at the ordinary temperature.

2. It appears from the following communication, which I owe to Dr. VAN DER PLAATS of Utrecht, that the phenomenon of the spontaneous change of white tin into the grey modification has occurred in this country also. In 1883 it was found that the water in the water mains of Utrecht contained lead. Since that time tin lined lead tubes have been employed. At the beginning of 1884, Messrs. HAMBURGER of Utrecht, who made the tubes, stated that a number of blocks of Banca tin in their store had become grey and

brittle. On analysis Dr. v. d. Plaats found that the grey metal contained 99,9 pCt. of tin and therefore was to be regarded as pure tin. When remelted with borax and potassium cyanide a good regulus of ordinary tin was formed. The Messrs. Hamburger accordingly remelted the blocks of tin in this way, including, unfortunately, a quantity which Dr. v. d. Plaats had wished to investigate further.

Of interest is further that when Dr. v. d. Plaats mentioned the phenomenon to Mr. Cornelis de Groot, ex-chief of the mining department in the Dutch Indies, and one of the pioneers of the Biliton Company, he said that he was acquainted with the phenomenon and added: "And it is easy to get rid of: we put such tin in the sun, the spots disappear in the light".

That the heat-rays, and not the light, are the cause of the disappearance of the spots is at once evident from the facts now and previously communicated.

3. In the last paper [1]) (II) it was shown that the velocity of the reaction

white tin → grey tin

increases as the temperature rises from — 83° C., reaches a maximum at — 48° and finally becomes zero at + 20° C.

As may be seen from the curve in that paper, the velocity between + 10° and + 20° is extremely small. In order to study the change in this interval of temperature it would be necessary to make observations lasting many years.

On the other hand, if a piece of tin can be obtained which has been exposed to temperatures within that interval for a very long time, it is possible that it will have changed from the white into the grey modification.

4. Through the kindness of Dr. W. Reinders, at present resident in London, and of Dr. Gowland of London, a piece of an antique tin vessel, which had been dug up in England in the neighbourhood of Appleshaw in Hampshire, came into my possession.

Regarding the objects found in the excavation of an old Roman

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[1]) Proceedings Roy. Acad. Amsterdam. 1899. Vol. II. p. 149.

villa at that place, **Engleheart**[1]) says in a memoir dated Nov. 25, 1897:

About the set of metal vessels from Appleshaw now exhibited, I will say little, since they are submitted for the opinion of experts. It was my curious good fortune to hit upon them at once in a first experimental trench dug on the site already mentioned, one mile south of my house. They appeared to be designedly hidden in a pit sunk through a cement floor, 3 feet below the surface of the field. The smaller vessels were carefully covered by the larger dishes. One suggestion I may make with regard to their date. Lying at the floor below which they were buried was a fragment of wall plaster bearing a peculiar pattern of red flower buds on a white ground, absolutely identical with plaster found in the Clanville Villa. Now the inscribed stone found in the latter proves that the house was inhabited in the year 284 a. D., while the coins cease with Decentius, 351 a. D.

Therefore, on the not unreasonable suppositions (1) that the plaster as found represents the wall-decoration of the houses at the time of their destruction or abandonment, (2) that the identity of design shows a correspondence of dates, (3) that the vessels were concealed when the house was abandoned, we may assign the vessels to a period not by many years removed from 350 a. D.

Dr. **Gowland**[2]) adds the following notes regarding the vessel N°. 27, at present preserved in the British Museum at Londen.

"27. Portion of low vase, probably of oval section; foot rim. Height 2½ inches, diameter uncertain, about 8 inches.

Composition:

Tin	Lead	Iron	Copper	Oxygen, carbonic→ acid and loss
9. 35pCt	5.06	trace	trace	0.59.

The extraordinary molecular change which the metal of this vessel has undergone is of more interest to the physicist and metallurgist than to the antiquary; a brief note respecting it, however, cannot be omitted here. The metal is not much oxydised, yet it is so ex-

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[1]) On some Buildings of the Romano-British Period, discovered at Clanville, near Andover and on a Deposit of Pewter Vessels of the same Period, found at Appleshaw, Hants, communicated to the Society of Antiquaries by the Rev. G. H. Engleheart, M. A., with appendixes by Charles H. Read Esq. Secretary and William Gowland, Esq. F. S. A. F. C. S., Associate R. S. M.

[2]) Loc. cit. pag. 12 and 14.

ceedingly brittle that it can be easily broken with the fingers. The effect of time upon it has resulted in a complete alteration of its molecular structure, the mass of the alloy being converted into an agglomeration of crystals, and to this its brittleness is due. On melting and casting a small fragment I found that the cristalline structure disappeared and the metal regained its original toughness."

These observations agree so completely with the results so far obtained that it was decidedly worth while to investigate whether the plate described had been converted into the grey modification.

5. A dilatometer was filled with 4.8 grams of the material derived from the antique vessel. Petroleum was used as measuring liquid in the capillary. The dilatometer was placed in a bath, the temperature of which rose slowly. The change which occurred was shown by a considerable fall of the level of the petroleum in the capillary. The fall amounted to 537 mm.

The white tin had therefore been converted into the grey modification.

The following calculation shows that the change had taken place practically completely. Assuming the specific gravity of white tin to be 7.3 and that of grey tin 5.8 the volume of the 4.8 grams, containing according to **Gowland**'s analysis 94.35 percent of tin, should decrease, in consequence of the change from grey tin to white tin, by

$$\frac{4.8 \times 0.943}{5.8} - \frac{4.8 \times 0.943}{7.3} = 0.16 \text{ cc.}$$

The volume of 1 mm. of the dilatometer capillary tube was 0.00028 cc.; a fall of 537 × 0.00028 cc. = 0.15 cc.

If the white tin had been wholly converted into the grey modification, therefore, the change of volume in the dilatometer experiment would have been 0.16 cc., that found being 0.15 cc.

We may therefore conclude from this experiment that the white tin in the ancient vessel was practically completely converted into the grey modification.

I have to thank Dr. **van der Plaats** of Utrecht for further information respecting the mean temperature of the place where the vessel was discovered.

According to **Bartholomew**, Physical Atlas, Edinburgh, 1899, the mean temperature there is 10° C. The yearly variation of temperature at the surface is ± 12°.2. Under ground it is of course less. No secular variation is known. From these data it appears that the temperature to which the vessel was exposed for 22 centuries cannot, for any prolonged period, have been higher than 20° C.

6. In the last communication on the enantiotropy of tin, the velocity of the change

white tin → grey tin

was determined at different temperatures. It was found that the change

grey tin → white tin

(above + 20° C.) in absence of a solution of pink salt took place very slowly, so that it appeared possible to study the velocity also above the transition point.

In all systems investigated up to the present, which have a transition temperature, the change takes place so rapidly above this temperature that determinations of the velocity are impossible.

I filled a dilatometer with about 30 grams of grey tin and added water to serve as the measuring liquid. In this way the pure phenomenon may be studied.

The dilatometer was placed in a thermostat the temperature of which could be maintained constant within 0.03° by means of an electric regulator. The position of the liquid was read from time to time on the porcelain millimeter scale placed behind the capillary; the corresponding times were measured by a chronometer to $^1/_5$ sec.

In order to be able to regard the mass undergoing the change as the same at all temperatures, a very small quantity of tin was allowed to change at each temperature.

Temperature	Time (in minutes)	Fall of the level of the liquid in mm.	Fall per hour.	
30°,0	60	7,2	7,2	
30°,0	60	7,25	7,25	
31°,0	40	13,0	19,50	
32°,0	51	30,0	35,0	
33°,0	6	10,75	107,5	106,2
33°,0	6	10,5	105,	
34°,0	6	17	170	180
34°,0	6	19	190	
35°,0	3	25	500	
35°,0	$5^1/_2$	44	500	

Fig. 2.

At 40°,0 the velocity was so great that I could no longer measure it.

In Fig. 2 the measurements are represented. The abscissae are temperatures, the ordinates velocities.

I have also taken up the study of antimony which appears to undergo similar changes (explosive antimony, GORE). Other metals too, such as aluminium, invite investigation.

Amsterdam, University Chemical Laboratory.
November, 1899.

(December 20, 1899.)

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday December 30, 1899.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 30 December 1899 Dl. VIII).

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The following papers were read:

Physiology. — "*The resorption of fat and soap in the large and the small intestine*". By Dr. H. J. HAMBURGER.

(Read November 25, 1899.)

Introduction.

While investigating the distribution of fat in the bloodcorpuscles and plasma under the influence of respiratory gas exchanges, I tried some experiments which may be said to prove that the large intestine probably possesses the power of resorbing fatty matter by means of its blood vessels ¹). I have thought it necessary still further to pursue these preliminary experiments, as they touch on a question which, both from a theoretical and a practical point of view, seems to be of the greatest importance. From a theoretical point of view, because some light may, at the same time, be thrown on our present, in many respects, very inadequate knowledge of the resorption of fat in the more complicated small intestine; from a practical point of view, because the problem of rectal nutrition with fat has not yet been satisfactorily solved.

In this domain, indeed, there has hitherto been but little investigation. In 1874 CZERNY and LATSCHENBERGER ²) tried two experiments on a man to whom an anus praeternaturalis had been applied. They brought into the fistula a known quantity of some fat emulsion, then by rinsing out the contents after some time and ascertaining how much fat they contained, they determined how much emulsion had been absorbed.

In 1891 MUNK and ROSENSTEIN ³) administered some rectal injections of oil emulsion to a girl who had chyle fistula on her leg, and by quantitative determination of the fat in the issuing chyle ascertained how much fat had been absorbed. They found, as CZERNY and LATSCHENBERGER had also done, that the resorption was insignificant.

DEUCHER ⁴) and PLANTENGA ⁵) injected into persons with a normal intestine a clysma consisting of the yolk of an egg and milk; here too fat appeared to be resorbed, but the resorption was insignificant.

Though these experiments of MUNK and ROSENSTEIN have unquestionably shown that from a clysma fat may be resorbed, it has not yet been proved that this resorption takes place in the large intestine. What proof has there been afforded that, in the above mentioned experiments, a part of the clysma has not passed the valvula Bauhini?

And as for the experiments of CZERNY and LATSCHENBERGER,

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¹) Verhand. d. Koninkl. Akad. v. Wetensch. Dl. III N⁰ 10. 1894. p. 31.

²) CZERNY und LATSCHENBERGER, Physiologische Untersuchungen über die Verdauung und Resorption im Dickdarm. VIRCHOW's Archiv B. 59. 1874. S. 179.

³) MUNK und ROSENSTEIN, Zur Lehre von der Resorption im Darm, nach Untersuchungen an einer Chylusfistel beim Menschen. VIRCHOW's Archiv B. 129. 1891. S. 230 en 284.

⁴) DEUCHER, Ueber die Resorption des Fettes aus Klystieren. Deutsches Archiv f. Klin. Medizin. B. 58. 1896. S. 260.

⁵) PLANTENGA, Der Werth der Nährklystiere. Diss. Freiburg i/B. 1898.

they were only two in number, and, from more than one point of view, they are questionable.

If we consider that, as yet, no hypothesis even has been formed as to the way in which the fat is resorbed in the large intestine, an investigation of this subject will not be deemed superfluous.

In the first place we wish to know with certainty whether the large intestine is indeed able to resorb fat.

I. *Does the large intestine possess the power of resorbing fat?*

A loop is taken out of the large intestine of a dog in a state of narcosis, is cleaned out inside, and by means of strings tied round it is divided into three equal parts *a*, *b* and *c*. An emulsion of lipanine (olive oil with 6.4% of oleic acid) in a solution Na_2CO_3 of $^1/_2\%$ is then introduced into the middle part *b*; nothing is introduced into the exterior parts *a* and *c*. The intestine is then replaced, the central cavity closed, and four hours later the intestine is removed and by administering more chloroform the animal is killed.

The mucosa of the central part *b*, which contains no more fluid is prepared and cut into small pieces. As a means of control the mucosae of the two outer pieces are also cut into small pieces, placed in two small receptacles, and as much emulsion added as was injected into *b* at the beginning of the experiment. The fat in the three receptacles is then with the utmost precaution determined.

EXPERIMENT I.

Length of the pieces of intestine *a*, *b* and *c* 9 cM. Into *b* 12.5 cc of a 5 pCts. lipanine emulsion in Na_2CO_3 of $^1/_2\%$ is injected. Four hours later the intestine is eliminated. Isolation of the mucosae, cutting into pieces. To the mass *a* and *c* 12.5 cc of the emulsion is added. After it has been dried the extract of ether yields the following results:

Ether residu of intestine *a* (mucosa + emulsion) = 0.635 Gr.
" " " " *c* (" ") = 0.659 Gr.

Mean . . . = 0.649 Gr.

Ether residu of intestine *b* (mucosa + not resorbed fat = 0.499 Gr.

This proves that 0.649—0.499 = **0.150** Gr. of fat has been absorbed out of the intestine *b* during these four hours.

Another experiment on another animal resulted in a resorption of **0.182** gr. of fat in four hours.

These two experiments and many others of which we shall speak later (cf. page 293), *have decisively proved that the large intestine does really possess the power of resorbing fat.*

It was remarkable that the piece *b*, on being opened, proved to be nearly empty, and *that big drops of fat clung to the mucous membrane.* This gave rise to the suggestion that the Na_2CO_3 solution had probably been rapidly resorbed and the emulsion thus destroyed; the fat had got into a condition in which it could not be absorbed at all, or but very slightly.

This agrees with the views of MUNK and ROSENSTEIN, viz., that of an emulsion of 15 gr. lipanine in a NaCl solution of 0.4 pCt., in 7½—9 hours, 0.55 gr. of fat issues from the chyle fistula, but that the quantity amounted to 1.1, that is to say about double as much, when emulgent fluid Na_2CO_3 was used. Now it is known that with a Na_2CO_3 solution fat remains suspended much longer than with a NaCl solution. It appeared then that on using Na_2CO_3 the lipanine remained longer in an emulgent state in the intestine than on the application of NaCl.

Having obtained this result, which was confirmed by further experiments, we thought it of importance to employ, instead of the Na_2CO_3 solution, a fluid in which the emulsion would remain still longer existing in the intestine. It had therefore, to be a fluid of great emulgent power and moreover not rapidly absorbed in the wall of the intestine. For years clysmata of the yolks of eggs, of cream, and of milk have been used for these purposes. As these are compound mixtures these forms of emulsion seemed to me less fit; it is especially the albuminous investment of the fatglobules by which new factors are introduced into the problem of the resorption of fat. Besides DEUCHER and PLANTENGA had already shown that the quantity of fat which a man resorbs from such emulsions amounts but to about 10 gr. per 24 hours.

It now occurred to me to try a fluid which also in the small intestine exercises an important influence on the physiological emulgent, viz. a solution of soap.

After a preliminary experiment had shown that in a solution of sapo medicatus, the lipanine forms an emulsion which remains long in the intestine, and from which in the long run much fat is resorbed, we wished to determine the influence of soap on the large intestine. Such a research in itself seemed to us not destitute of importance, as under normal circumstances no inconsiderable quantities of soap occur in the contents of the large intestine and we are unacquainted with its functions in this part of the tractus intestinalis.

II. *Resorption of soap in the large intestine.*

In order to ascertain whether soap is resorbed in the large intestine we pursued three methods.

1st. Into a loop of the large intestine tied in two places we introduced a solution of soap. The loop having been replaced in the ventral cavity, it is left to itself for a few hours. From the quantity of soap still present we infer how much has been resorbed [1]).

2nd. From a dog in a state of narcosis a loop of the large intestine is ligatured at one end, and at the other furnished with a tube which is connected with a funnel that may be adjusted at different heights. A solution of sapo medicatus is introduced into the funnel and the intestine filled.

From time to time it is now necessary by replenishing, to raise to its original height the level of the fluid descending in consequence of resorption.

At the end of the experiment the contents of the funnel, connecting tube and intestine are rinsed out, and the quantity of soap contained in this and in the mucosa is determined. If we deduct this quantity from the whole of the soap solution used, what has been resorbed remains.

3rd. The large intestine is cut through close to the coecum. The free ends are attached to the ventral wall [2]). After a cure has been effected we dispose of a separate piece of the large intestine. Into this large quantities of a solution of soap are now introduced through the rectum. By ascertaining how much seap, after a limited time, still remains in this portion of the intestine, we can determine how much has been resorbed.

All the three methods agree in showing unanimously that the large intestine possesses in a large measure the power of resorbing soap.

III. *What happens to the soap resorbed?*

The researches of J. Munk [3]) and of J. Munk and A. Rosenstein [4]) have shown that the fatty acids taken into the body are

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[1]) We cannot enter into particulars here; they will be found in a paper which will appear in the Archiv f. Anat. u. Physiol. Physiol. Abth.

[2]) Dr. **Folmer**, surgeon, was so kind as to attach this intestine fistula for me.

[3]) J. Munk, Zur Kenntniss der Bedeutung des Fettes und seiner Componenten für den Stoffwechsel. Virchow's Arch. B. 80. 1880 S. 10.

[4]) l. c.

converted into fat, and as such appear for a great part in the chylevessels. The last is opportune; for as **Munk** first observed, the presence of relatively small quantities of soap in the blood circuit is dangerous to life; an intravenous injection of 0.12 gr. of soap per kilogr. of the weights of the rabbit already caused death.

These experiments made it highly probable that already in the *mucosa* of the small intestine the fatty acids combine [1]) with glycerine into fat. And the preliminary experiments of **Ewald** [2]) with finely minced mucosa of the small intestine have confirmed this hypothesis.

Now as there is no ground for assuming that the soap which is absorbed in the large intestine passes without injury into the blood it seemed to me not too hazardous to conjecture that the oleic acid in the large intestine is also converted into fat.

To test this hypothesis by observation, we made experiments in three directions.

1st We examined whether the mucosa of a loop of intestine which has been some time filled with a solution of soap shows an increase of fat. (As is known, some fat can always be extracted from the normal mucosa).

2nd We examined whether the formation of fat stated under 1st does indeed continue after the intestine has been taken out of the body and is left to itself at the temperature of the body.

3rd We inquired whether the fresh and still warm mucosa of the intestine, after having been minced fine and then saturated with a solution of soap in which was a little glycerine, was still able to convert soap into fat.

This proved to be really the case. The conversion, however, could no longer be observed when the mucosa had previously been heated to 80°. Hence this suggests fermentation.

There can be no doubt, then, that soap resorbed in the large intestine is, partially at least, converted into fat in the mucosa.

IV. *Resorption of fat from lipanine-soap emulsion.*

It having thus been established what happens to the soap resorbed in the large intestine, we went back to our point of departure and inquired whether, according to our theory, laid down at page 290,

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[1]) The origin of the glycerine is still uncertain.

[2]) C. A. **Ewald**. Über Fettbildung durch die überlebende Darmschleimhaut. Archiv. f. Anat. und Physiol. Abth. 1883. Supplem. S. 302.

more fat is resorbed from emulsions with solutions of soap then from emulsions with Na_2CO_3.

In order to answer this question, a loop was produced from the large intestine and by means of a string tied round it, divided into three parts, of equal length. Into the central part *b* a lipanine-Na_2CO_3-emulsion was introduced, into *a* lipanine-soap-emulsion. The two emulsions contain 20 cc lipanine to 80 cc emulgent fluid (soapsolution 5 $^0/_0$ and Na_2CO_3-solution $^1/_2$ $^0/_0$). The piece of intestine *c* serves as a control and does not contain anything.

Five hours afterwards the intestine is eliminated. On opening *b* there is no trace of emulsion to be observed; this section is empty, but a mass of fat is found lying against the mucosa. In *a* there is still a fine emulsion present; of a fatty mass or of drops of fat against the mucosa there is no trace.

The contents and mucosa of the two sections are taken in hand for the quantative examination of the fat still present.

The mucosa is also removed from the controlling section *c* and its fatcontents determined; but before proceeding to the last, we add, in order as much as possible to avoid mistakes the same quantity of lipanine-soap-emulsion as was injected into *a* in this case, thus, 20 cc.

The first experiment showed that from the lipanine-soap-emulsion **0.558** Gr. of fat had been resorbed, whereas, in the same time, only **0.156** Gr. of fat had been resorbed from the lipanine-Na_2CO_3-emulsion.

Further experiments yielded the same results.

Though it had hereby become certain that more fat is resorbed from lipanine-soap-emulsions than from lipanine-Na_2CO_3-emulsions and the power of the large intestine to resorb fat has hitherto been rated too low, yet, in order to form an idea of the resorbing power of the large intestine, it seemed desirable to compare it with that of the small intestine.

In making this comparison, the necessity of reducing the extent of the resorption to equal surfaces of mucous membrane, presents no little difficulty. If, however, in preparing the mucosa we make a circular incision which penetrates to the mucosa, and then strip off serosa with muscle from the mucous membrane, it is very easy to ascertain the surface of the mucosae of the two pieces of intestine to be compared.

The experiments have now shown that, for fat, the resorptive *power of the large intestine is, under the given circumstances, not inferior to that of the small intestine.*

I say: "the resorptive*power*," by which I do not mean, of course, that in normal life the large intestine resorbs as much, per unit, of the surface of the mucous membrane, as the small intestine. Nor is that the case. For the fat is supplied to the small intestine in a pulpy, sometimes almost liquid mass, whereas the large intestine must absorb the fat from a more solid condition, which is, of course, done with less facility. Moreover, on reaching the large intestine, the contents have already rejected the greater part of the fat, and consequently what, in normal life, the large intestine absorbs in fat will amount to less than what the small intestine resorbs.

What our experiments teach us is this: that when the lipanine-soap-emulsion is supplied to the unit of the surface of the mucous membrane, an almost equal quantity of fat is resorbed.

Besides in detached pieces of the intestine, we have now also studied the resorption of fat in a fistula of the large intestine. In somewhat over a day we saw from a lipanine-soap-emulsion about 10 gram of fat arrive at resorption in 12 hours.

If we consider that this quantity is about the same that PLANTENGA in the course of twenty-four hours could bring *in maximo* to resorption in a human being whose large intestine possesses a much larger surface of mucous membrane than that of the dog, it then becomes highly probable that also in man, if we also employ lipanine-soap-emulsions we shall be able to bring about a much more considerable resorption of fat than we have hitherto obtained with other emulsions.

The emulsion with soap solution yields another practical advantage, viz. that resorbed soap contributes as such to the absorption of fat, for, as we have seen, the soap is converted into fat.

From a practical point of view it would be of importance systematically to examine what will be the most favorable proportion of lipanine and soap-solution, and also what concentration must be given to the soap-solution in order to make the resorption as great as possible. We shall have further to discover how much the extent of the resorption depends on the volume of injected emulsion and, therefore also on the respective times of injection.

We have, however, not pursued the subject further in this direction.

We have occupied ourselves with another problem, viz. what path does the fat take in the mucosa.

V. *What way does the fat take in the mucosa?*

We may *a priori* assume that the particles of fat after leaving the epithelial layer of the Lieberkühns glands and entering the lymphducts, will, for a part at least, be carried off with the current of lymph. The remaining fat would then have to follow the path of the blood capillaries situated in the lymphducts, and seeing that in the mucosa of the large intestine the system of lymphatic vessels is relatively only slightly developed, it would not even be improbable that the blood capillaries form the principal channel of conveyance.

Meanwhile the question might be raised: has a transition from fat into blood capillaries ever been observed in other places? And this then suggests in the first place, the small intestine. That a great part of the fat there follows the way of the lymphatic vessels, few will question; but whether the blood capillaries are also responsible for a part of the transport has not hitherto been decided.

According to CLAUDE BERNARD the serum of the v. porta in mammalia during digestion looks as white as milk. On the other hand, comparative investigation of the blood of the v. porta and of the a. carotis, undertaken by BORNSTEIN [1] at the instance of HEIDENHAIN showed that the fat contents of the portal-blood are less than those of the a. carotis.

The experiments of ZAWILSKI [2] also seem to argue against a direct absorption of fat by the blood capillaries. Eighteen hours and a half after partaking of a rich meal, while the resorption of fat was still in active operation, the contents of the ductus thoracicus where drawn outside so that the blood no longer received any chyle. The fat contents of the blood amounted only to 0.05 %; to no more, then, than in a stato of hunger.

Over against the results obtained by ZAWILSKI and BORNSTEIN we must set those of VON WALTHER [3] and of FRANK [4]. VON

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[1] HEIDENHAIN, Beiträge zur Histologie und Physiologie der Dünndarmschleimhaut. PFLÜGER's Archiv Suppl. 1888. S. 95.

[2] ZAWILSKI, Die Abfuhrwege des Fettes. Arbeiten aus der physiologischen Anstalt zu Leipzig. Jahrg. XI. 1876.

[3] VON WALTHER, Zur Lehre von der Fettresorption, DU BOIS-REYMOND's Archiv. 1890. p. 328.

[4] FRANK, Die Resorption der Fettsäuren der Nahrungsfette, mit Umgehung des Brustganges. Ibid. 1892. p. 497.

Derselbe, Zur Lehre der Fettresorption. Ibid. 1894. p. 297.

Walther showed that only a very small portion of the whole quantity from 40 to 50 gr. of the resorbed fat is transported through the ductus thoracicus. And Frank observed that, after ligaturing the ductus thoracius, the resorption of fatty acids in the small intestine was considerable. „These observations", Hammarsten says rightly in his textbook on physiological Chemistry, hardly seem, however, under normal circumstances, capable of being transferred to the resorption of neutral fats in man". Munk and Rosenstein in their investigations on a girl who had a lymphfistula in the leg, could find again in the chyle scarcely more than 60°/₀ of the fat administered *per os.*

It will be seen that there is still little agreement with respect to the direct transition of fat into the blood capillaries. It appears to me that I have succeeded in showing with certainty that *in the small intestine of the dog the blood capillaries have a considerable share in the resorption of fat.*

The experiment was as follows.

In a large dog in a state of profound narcosis a loop of the small intestine was produced by means of an incision in the linea alba. In consequence of a rich meal (bread with a great deal of lard) which the dog had received the night before the chyle vessels were splendidly injected. At distances of 17 cM. strings are thrust through the *mesenterium,* close to the attachment of the intestine. By means of these strings pieces of the intestine will be shortly afterwards detached. The chyle vessels of the central piece of the intestine *b* are carefully bound together. Those of the adjoining parts *a* and *c* are not. The whole loop is then well rinsed with a tepid solution of Na Cl-solution of 0.9 °/₀. The strings are then tightened and the loop divided into three equal parts. Into each of the three parts is injected 25 c.c. of a lipanine-soap-emulsion, consisting of 200 cc. sapo medicatus of 5 °/₀ + 50 cc. lipanine. When from the side of *a* and *c* two pieces *a'* and *c'* had after rinsing been untied, everything was again restored to the ventral cavity, which was then closed.

Five hours later the intestine was removed from the animal, which was still in a state of narcosis and was now killed.

The determination of the percentage of the fat of the contents of the loop inclusive of the mucosae showed that in *b*, where the chylevessels were bound together, still 0.419 gr. was resorbed; whereas in *a* and *c*, that is to say in chyle-vessels not bound together, 0.714 gr. and 0.697 gr. respectively of fat were absorbed. Three more experiments yielded the same result.

There can be no doubt, then, that the blood capillaries possess in a large measure the power of resorbing fat.

This result agrees with that of MUNK's and ROSENSTEIN's experiments, which showed that only about 60 $^0/_0$ of the fat resorbed flows out through the chyle vessels.

With respect, now, to the experiments of other investigators who deny that the blood vessels have a direct share in the resorption, it seems to me, that considering the present state of our knowledge, those of ZAWILSKI are no longer conclusive. Of later years it has been shown that in the blood ferments occur (lipolytic ferment of COHNSTEIN and MICHAËLIS, lipase of HANRIOT) which possess the power of converting fat. When ZAWILSKI finds that on the effluence of chyle the blood does not contain more fat than about what is found in a state of hunger, this does not exclude the absorption of fat through the blood capillaries; owing to the slow resorption the fat always undergoes, what had passed into the blood-circulation could be regularly analyzed.

On the same grounds, comparative determinations in different sorts of blood, such as were made by BORNSTEIN cannot be decisive in this question. Moreover in these experiments no notice has been taken of the significance of the relative volume of blood corpuscles and plasma in the composition of the total of blood in the two cases.

It may now be further asked whether the fatglobules as such are absorbed in the blood capillaria, or not until they have first perhaps, been converted into a soluble combination.

CLAUDE BERNARD's experiments suggests, indeed, the first hypothesis, but it does not exclude the second.

On this question I hope soon to make some communications.

It has already been shown *that the blood capillaria take a direct part in the resorption of fat in the small intestine; and may also most probably do so in the large intestine.*

Summary.

1. It may now be considered as proved that the large intestine of the dog has the power of resorbing fat.

2. Contrary to the opinion hitherto held, this power is considerable, and is not inferior even to that of the small intestine.

3. In order to bring about a resorption so considerable, it is necessary to take an emulsion that can stay a long time in the intestine.

   The usual $Na_2 CO_3$ is not well adapted for the preparation of such an emulsion and the $Na Cl$ still less so, because both are rapidly resorbed and with them the emulsion neutralized. A solution of sapo medicatus, however, seems to answer the requirement.

4. As to the soap solution itself, it appears that this is resorbed, though much more slowly than the $Na_2 CO_3$, and during the resorption is, at least for a part, converted into fat already in the mucosa.

   This conversion continues in the intestine that has been cut out; nay it is effected even when the mucosa has been minced fine. Heating to 80°, however, neutralizes the said property.

5. As to the path taken by the fat in its resorption in the large intestine, it is highly probable that a part of it is transported through the blood capillaria. The experiments described above have at least shown with certainty that this is the case in the small intestine.

Physics. — "*Some Observations concerning an Asymmetrical Change of the Spectral Lines of Iron, radiating in a Magnetic Field*".

By Dr. P. ZEEMAN.

1. In observing spectral lines resolved into triplets by the action of the magnetic field, one is certainly struck by the symmetrical position and the equal intensity of the outer components of these triplets. There are especially in the case of iron not a few of the stronger lines, which seem to represent ideal cases of triplets, as originally predicted by LORENTZ's theory. It is only after more attentive inspection that several faint triplets are seen in which one of the outer components is apparently more intense than the other. On a former occasion [1]) I pointed out that there were reasons for expecting triplets with a more intense lateral component toward the

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[1]) Proceedings Royal Academy of Sciences Amsterdam, June 1898. Astrophysical Journal, Vol. 9. Jan. 1899.

red. In *strong* fields I noticed a few. I could show however that most of these asymmetrical triplets were due to superpositions and I concluded that we had no evidence of a directing influence of the magnetic field on the orbits of the light-ions. No more was done upon this subject.

2. Some time ago Prof. VOIGT of Göttingen kindly communicated to me that he had deduced from theory that normal triplets must show in *weak* magnetic fields a remarkable asymmetry viz. the outer component toward the *red* has the *greater intensity*, the outer component toward the *violet* has the *greater distance* from the original line. In low fields these asymmetries will preponderate, disappearing however in strong fields [1]).

It has given me much pleasure to undertake at Prof. VOIGT's request a testing of this result of his theory.

I made these observations the more willingly now I was in possession of a beautiful concave grating, which Prof. ROWLAND with kind courtesy has examined and selected for me. The grating is, like the one lent from the Leyden laboratory, ruled with 14438 lines to the inch and has a radius of about 3 M. The resolving power of the present grating is however superior to that of the one formerly used. Negatives now were taken generally in the second order.

3. I tried to study by eye observation, using the spectrum of the first order, the inequality of the outer components. Iron terminals (all following facts relate to this substance) were used. A NICOL's prism was placed before the slit with its plane of vibration vertical, in order that the outer components of the triplet only were visible.

But notwithstanding the lateral components were but slightly separated and therefore the circumstances, and as to intensity of the field and as to facility of comparison, very favourable, I could not conclude to an indubitable inequality of the outer components. It may be that the flickering of the spark interferes rather infavourable with these observations.

4. I had more success with the photographs taken. I studied the spectrum of the second and third orders; between 3400 and

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[1]) VOIGT's paper will be published shortly in Wiedemann Ann. under title; "Dissymmetrie der ZEEMAN'schen Triplets".

3900 tenth metres in the second and a somewhat smaller part in the third order.

I did not introduce a NICOL between the spark and the slit. The strength of the field may be roughly characterized by the statement that about two thirds of the more intense lines were resolved into triplets or quadruplets (showing with the field used for the greater part as doublets). It was now possible to look for inequality of intensities and at the same for asymmetry of the distances. Excluding the lines where the before mentioned perturbations interfered [1]), I have found several lines, which showed the asymmetries predicted by VOIGT; it is true, in a very small degree. Some lines showed the asymmetry of the intensities only or of the distances only, but other lines the two asymmetries at the same time. The phenomenon is however extremely small.

The difference of the distances between the components toward red and toward violet and the original line never exceeds a few percent.

For the moment I will not communicate the amount of the asymmetries of different lines. Either both or one of the asymmetries are shown by the following lines:

3498.00, 3687.60, 3709.40, 3735.01, 3763.91, 3878.71 [2]).

5. As the outer components of quadruplets behave in a normal manner I have looked for an inequality of intensity between these components. The field used was somewhat stronger than the one mentioned in § 4. There was a difference in the expected sense in the case of the lines:

3466.01, 3475.61, 3705.73, 3722.73, 3872.65.

Moreover 3466.01 and 3705.73 showed a displacement toward the violet of the mean of the outer components relatively to the mean of the inner ones. This result is confirmed, at least for 3466.01, by an observation of REESE: "but the most careful measurements that I could make indicated a possibility that in the case of 3466.0 the mean of the inner pair is a trifle further toward the red than that of the outer pair [3])." VOIGT's developments

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[1]) Proceedings Royal Academy Amsterdam, June 1898. Astrophys. Journal. Vol. 9. Jan. 1899.

[2]) The wave-lengths of the spare-spectrum according to EXNER and HASCHEK.

[3]) Notes on the ZEEMAN-Effect. Johns Hopkins Un. Circular. June 1899, N°. 140. Phil. Mag. Sept. 1899.

only refer to triplets, but, I think, we may consider also these observations concerning quadruplets as indications in favour of the theory.

6. The line 3733.46 is so modified as to be a triplet, the component toward the violet being at a *smaller* distance from the original line than the component toward the red. There seemed to be no inequality of intensity of the outer components. Of the triplet 3824.58 the component toward *the violet* is apparently more intense than the component toward the red. It does not seem to me very probable that in the last mentioned case there is some perturbation by the presence of the air-line 3824.4 (NEOVIUS), because the component is far from hazy and the air-line very faint. It is invisible upon a negative taken with a very low field but with a time of exposition equal to that used in taking the negative with the more intense component toward the violet.

It must remain for further inquiry to decide whether these observations must be explained by an extension of theory or by some perturbating cause not yet taken into account.

7. From the mentioned observations we may draw, I think, the conclusion that the observed asymmetries are very probably real. The extreme minuteness of the asymmetry makes it desirable however to establish further its reality. I hope to do this in a future paper.

Finally it is to be observed, as was remarked to the author by Prof. VOIGT, that my observation does not decide between his theory and that of LORENTZ, but confirms the common basis of both theories [1]).

[Addition of Jan. 15. I have lately found that in the case of the triplet and quadruplet of cadmium 4678 and 4800, and the triplet and quadruplet of zinc 4680 and 4722, the outer components toward red are decidedly more intense than the components toward violet. Measurements of the distances were not yet made.

The line 3733 mentioned in § 6 happens to be one of the lines showing "reversed polarisation." Probably this deviation from the normal polarisation will account also for the reversed asymmetry of the distances.

I doubt however at the possibility of the suggested explanation in the case of a few other lines, lately examined, and which apparently exhibit the behaviour mentioned in the beginning of § 6.]

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[1]) The relation between these theories is exposed by LORENTZ. Physik. Zeitschrift d. Riecke u. Simon. S. 39. 1899.

Mathematics. — "BOREL's *formulae for divergent series*". By Prof. J. C. KLUYVER.

In his memoir on divergent series (Ann. sc. de l'École norm., t. 16, p. 77, foot-note) BOREL suggested that in his "adjoint integer function"

$$E(a/z) = \sum_0^\infty \frac{u_n a^n}{n!}$$

perhaps the factor $a_n : n!$ might be advantageously replaced by $a^{\frac{n}{p}} : \Gamma\left(\frac{n}{p}+1\right)$, where p is a positive integer.

In the present communication the truth of this remark will be shown. It will appear that this slight alteration in $E(az)$ leads to a "region of summability", identical to those found by BOREL himself, and also by SERVANT (Ann. de Toulouse, 2^e^ série, t. 1, p. 152), when they considered other modifications of the adjoint integer function.

Starting with the function $f(z)$ and its expansion

$$f(z) = \sum_0^\infty c_n z^n = \sum_0^\infty u_n ,$$

which expansion we assume to have a finite radius of convergence, we consider the adjoint integer function

$$E_p(a/z) = \sum_0^\infty \frac{c_n z^n a^{\frac{n}{p}}}{\Gamma\left(\frac{n}{p}+1\right)} .$$

The integer p is arbitrary; if p be taken equal to unity, the function $E_1(a/z)$ becomes the function $E(az)$ of BOREL.

In the first place it will be necessary to express $E_p(a/z)$ by means of a definite integral. A suitable path of integration W is obtained in the following manner. In the complex x-plane we draw a curve nearly in the shape of a cardioid, the cusp at $x=0$ pointing in the direction of $x=-\infty$, and the curve itself enclosing the origin. We suppose that the path W begins at $x=0$ and that, along the cardioid, it goes in a positive direction round the origin, ending again at $x=0$.

With this assumption about W we have immediately

$$\frac{1}{\Gamma\left(\frac{n}{p}+1\right)} = \frac{1}{2\pi i}\int\limits_W \frac{e^{-\frac{1}{x}}}{x}\left(x^{\frac{1}{p}}\, e^{-\frac{\pi i}{p}}\right)^n dx \ ,$$

$$\frac{c_n\, z^n\, a^{\frac{n}{p}}}{\Gamma\left(\frac{n}{p}+1\right)} = \frac{1}{2\pi i}\int\limits_W \frac{e^{-\frac{a}{x}}}{x}\, c_n \left(x^{\frac{1}{p}}\, z\, e^{-\frac{\pi i}{p}}\right)^n dx \ ,$$

and finally, provided $|x|$ remains small enough,

$$E_p\,(a/z) = \frac{1}{2\pi i}\int\limits_W \frac{e^{-\frac{a}{x}}}{x}\sum_0^\infty c_n \left(x^{\frac{1}{p}}\, z\, e^{-\frac{\pi i}{p}}\right)^n dx \ ,$$

or

$$E_p\,(a/z) = \frac{1}{2\pi i}\int\limits_W \frac{e^{-\frac{a}{x}}}{x}\, f\left(x^{\frac{1}{p}}\, z\, e^{-\frac{\pi i}{p}}\right) dx \ .$$

The latter equation however conveys no definite meaning, unless during the integration the value of $f(x^{\frac{1}{p}}\, z\, e^{-\frac{\pi i}{p}})$ can be fixed without ambiguity. This requires that the region bounded by W contains none of the singular points t of $f(x^{\frac{1}{p}}\, z\, e^{-\frac{\pi i}{p}})$.

We will assume that in the z- plane $f(z)$ can be continued across the circle of convergence of the series $\sum\limits_0^\infty c_n\, z^n$ and that it has outside this circle a set of singular points $\alpha = A\, e^{i\beta}$. Then, taking $z = \varrho\, e^{i\theta}$, the function $f(x^{\frac{1}{p}}\, z\, e^{-\frac{\pi i}{p}})$ has in the x-plane a similar set of singular points t, given by

$$\frac{1}{t} = -\frac{\varrho^p}{A^p}\cos p\,(\theta - \beta) - i\,\frac{\varrho^p}{A^p}\sin p\,(\theta - \beta) \ .$$

In order to exclude the points t from the region delimited by the cardioid, we confine the point z in the z-plane to an area, constructed as follows. Each of the points $a = Ae^{i\beta}$ determines a curve whose equation written in polar coordinates is

$$\varrho^p = \frac{A^p}{\cos p\,(\theta - \beta)} \,,$$

and the totality of these curves divides the z-plane into a system of curvilinear polygons. In one of these polygons, which we shall designate by G_p, the origin and the circle of convergence of the series $\sum\limits_0^\infty c_n z^n$ are contained. We suppose now that the point z never leaves the interior of this polygon G_p.

In that case we constantly have

$$\frac{\varrho^p}{A^p} \cos p\,(\theta - \beta) < \frac{1}{1+\varepsilon} \,,$$

and consequently

$$\text{real part of } \left(\frac{1}{t} + \frac{1}{1+\varepsilon}\right) > 0 \,.$$

In other words, we may affirm that the points t in the x-plane are situated outside the circle with diameter $1 + \varepsilon$ and centre $x = -\frac{1}{2}(1+\varepsilon)$. Moreover, since necessarily we must suppose $|z|$ to remain finite, there is a non-evanescent minimum value of $|t|$, so that it must be possible to draw the loop W in such a manner, that all the points t remain outside, the loop thereby enclosing at the same time the circle with diameter 1 and centre $x = -\frac{1}{2}$.

The latter condition is imposed on the path W in order that during the integration we shall constantly have

$$\text{real part of } \left(\frac{1}{x} + 1\right) > 0 \,.$$

With the thus constructed loop W as path of integration the equation

$$E_p(a/z) = \frac{1}{2\pi i} \int\limits_W \frac{e^{-\frac{a}{x}}}{x} f\left(x^{\frac{1}{p}}\, z\, e^{-\frac{\pi i}{p}}\right) dx$$

retains its signification, even when the point z passes beyond the circle of convergence, if only it remains within G_p.

The first property of the function $E_p(a/z)$ is now proved at once. Multiplying by e^{-a} we have

$$\lim_{a=+\infty} e^{-a} E_p(a/z) = \frac{1}{2\pi i}\int_W \frac{1}{x} f\left(x^{\frac{1}{p}} z e^{-\frac{\pi i}{p}}\right) \lim_{a=+\infty} e^{-a\left(\frac{1}{x}+1\right)} dx$$

and hence, as

$$\lim_{a=+\infty} e^{-a\left(\frac{1}{x}+1\right)} = 0,$$

$$\lim_{a=+\infty} e^{-a} E_p(a/z) = \lim_{a=+\infty} e^{-a} \sum_0^\infty \frac{c_n z^n a^{\frac{n}{p}}}{\Gamma\left(\frac{n}{p}+1\right)} = 0 \quad . \; . \; . \; (\mathrm{I})$$

Secondly we find

$$\int_0^\infty e^{-a} E_p(a/z)\, da = \frac{1}{2\pi i}\int_W \frac{dx}{x} f\left(x^{\frac{1}{p}} z e^{-\frac{\pi i}{p}}\right) \int_0^\infty e^{-a\left(\frac{1}{x}+1\right)} dx =$$

$$= \frac{1}{2\pi i}\int_W \frac{dx}{x+1} f\left(x^{\frac{1}{p}} z e^{-\frac{\pi i}{p}}\right).$$

In the latter integral the only infinity of the subject of integration within the loop W being $x = -1 = e^{\pi i}$, the loop can be contracted into a small circle round this point and there results

$$\int_0^\infty e^{-a} E_p(a/z)\, da = f(z) \quad . \; . \; . \; . \; . \; . \; . \; . \; (\mathrm{II})$$

This equation may serve to evaluate $f(z)$ for any given point z within the region G_p, therefore we must regard G_p as the region of summability associated with the function $E_p(a/z)$.

Meanwhile BOREL indicated still a different way to calculate $f(z)$. Supposing $p = 1$, and z lying within the polygon G_1, he proved that we have

$$\lim_{a=+\infty} e^{-a} \sum_0^\infty \frac{s_n a^n}{n!} = f(z),$$

where

$$s_n = \sum_{h=0}^{h=n} c_h \, z^h = \sum_{h=0}^{h=n} u_h \, .$$

The question remains whether the function

$$\varphi_p\,(a/z) = \sum_0^{\infty} \frac{s_n \, a^{\frac{n}{p}}}{\Gamma\left(\frac{n}{p}+1\right)}$$

may be similarly used for any point z within the region G_p. That this is indeed the case we prove as follows.

It is easy to see that we can write

$$\frac{d\varphi_p}{da} - \varphi_p = \sum_0^{\infty} \frac{(s_n - s_{n-p}) \, a^{\frac{n}{p}-1}}{\Gamma\left(\frac{n}{p}\right)} \; ,$$

if we only agree to take $u_h = 0$ and $s_h = 0$ as soon as $h < 0$.

Replacing $s_n - s_{n-p}$ by

$$u_n + u_{n-1} + u_{n-2} + \ldots\ldots u_{n-p+1} = \sum_{k=0}^{k=p-1} u_{n-k} \; ,$$

we get

$$\frac{d\varphi_p}{da} - \varphi_p = \sum_{k=0}^{k=p-1} \frac{1}{z^k} \, \frac{d}{da} \sum_{n=0}^{n=\infty} \frac{u_{n-k} \, z^k \, a^{\frac{n}{p}}}{\Gamma\left(\frac{n}{p}+1\right)}$$

and

$$\int_0^{\infty} e^{-a} \left(\frac{d\varphi_p}{da} - \varphi_p\right) da = \Big[e^{-a} \, \varphi_p\,(a/z)\Big]_{a=0}^{a=\infty} =$$

$$= \sum_{k=0}^{k=p-1} \frac{1}{z^k} \left[e^{-a} \sum_{n=0}^{n=\infty} \frac{u_{n-k} \, z^k \, a^{\frac{n}{p}}}{\Gamma\left(\frac{n}{p}+1\right)}\right]_{a=0}^{a=\infty} +$$

$$+ \sum_{k=0}^{k=p-1} \frac{1}{z^k} \int_0^{\infty} e^{-a} \sum_{n=0}^{n=\infty} \frac{u_{n-k} \, z^k \, a^{\frac{n}{p}}}{\Gamma\left(\frac{n}{p}+1\right)} \, da \, .$$

Now, always supposing z to lie inside the region G_p, it is evident that $E_p(a/z)$ is related to $f(z)$ in the same manner as

$$E_p^{(k)}(a/z) = \sum_{n=0}^{n=\infty} \frac{u_{n-k}\, z^k\, a^{\frac{n}{p}}}{\Gamma\left(\frac{n}{p}+1\right)}$$

is related to

$$z^k f(z) = \sum_{n=0}^{n=\infty} u_{n-k}\, z^k\,;$$

hence we may apply equations I and II and conclude that

$$\underset{a=+\infty}{Lim}\; e^{-a} E_p^{(k)}(a/z) = 0\;,$$

$$\int_0^\infty e^{-a} E_p^{(k)}(a/z)\, da = z^k f(z)\,.$$

So it appears that we have

$$\Big[e^{-a} \varphi_p(a/z) \Big]_{a=0}^{a=\infty} = -\,u_0 + p f(z)\,,$$

or

$$\underset{a=+\infty}{Lim}\; e^{-a} \sum_0^\infty \frac{s_n\, a^{\frac{n}{p}}}{\Gamma\left(\frac{n}{p}+1\right)} = p f(z)\,, \quad . \quad . \quad . \quad . \quad \text{(III)}$$

an equation wholly equivalent to the original formula of BOREL.

Cases may occur in which the formulae I, II and III established in the foregoing have some importance. For, in asking for the value of $f(z)$ in a given point z, it may happen that this point lies outside BOREL's region of summability G_1 and that we are able by a proper selection of the integer p to find a region G_p, wherein z is contained. In that case we can replace BOREL's equations by the formulae II and III, the application of which presents scarcely more difficulties than that of the formulae for the region G_1.

Finally we may remark that equations I and II still hold if p is an arbitrarily assigned positive number. For rational non-integer values of p however, the extent of the region of summability G_p is considerably reduced, and for irrational values of p the region G_p ultimately coincides with the circle of convergence, so that the summation-formula II is no longer of any use.

Physics. — "*The Entropy of Radiation*". By J. D. van der Waals Jr. (Communicated by Prof. J. D. van der Waals.)

The entropy principle may be formulated in different ways. Strictly speaking, nothing follows from the examination of the cyclic process of Carnot but:

1st. $\int \frac{dQ}{T}$ is a total differential, if the process is reversible.

2nd. If we pass from state A to state B in a not reversible way, $\int \frac{dQ}{T}$ is smaller than when the process is reversible.

The second formulation is: The entropy tends to a maximum, i.e. the entropy always increases; and if the other conditions to which the system is subjected, allow different processes, that one in which the increase of the entropy is greatest, will take place. As we may consider every slight change as "the process", we may also say, that the fluction of the entropy is always a maximum.

To derive the second formulation from the first, we must generalize the idea entropy. We must then also attribute entropy to substances which are not in equilibrium. It being however impossible, that in a reversible way a substance is brought to a state which is not a state of equilibrium, the definition: entropy is $\int \frac{dQ}{T}$ for a reversible process, cannot be applied here. It has really been attempted to find a conception of entropy which also applies to substances which are not in a state of equilibrium.

In order that the second formulation of the principle be correct, the original conception must be extended still in another way. An entropy of radiation must be introduced. Whether a deviation from the law of Carnot might be obtained by radiation, has repeatedly been made the subject of an investigation. Bartoli[1]) imagined a cycle in which apparently a deviation occurred. Prof. Boltzmann[2]) proved however, that this contradiction may be avoided by taking into account the pressure exercised by luminous rays on a body by which they are absorbed or reflected.

In this they tried to solve only this question: Can we obtain by means of radiation a process, in which the substances yield quantities of heat, which have another ratio than would follow from

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[1]) Bartoli, Sopra i movimenti prodotti dalla luce e dal calore, Firenze, Le Monnier 1876.

[2]) Wied. Ann. XXII 1 Anno 1884. No. 5. Page 31.

the law of CARNOT? WIEN has first introduced an "entropy of radiation" [1]). He thinks it a matter of course, that radiation which can be in equilibrium with radiating bodies, and which possesses energy, must also possess entropy. He derives his arguments exclusively from the examination of reversible processes. He defines as "temperature of radiation" the temperature of a perfectly black body, which is in equilibrium with this radiation. In reversible processes, however, the quantity of heat yielded by the walls is the same as that communicated to the ether. As further according to the definition the temperatures of the walls and of the radiation are the same, it comes to the same thing whether the law of CARNOT be applied to the ether, as WIEN did, or to the walls, als BOLTZMANN did: $\int \frac{dQ}{T}$ is identical in both cases. The necessity of the conception "entropy of radiation" can therefore never be concluded from reversible processes.

E. WIEDEMANN had already pointed out the necessity of that conception for phosphorescence- and fluorescence phenomena [2]).

Yet it is clear that if the entropy principle is expressed in the second formulation, every irreversible radiation phenomenon is in contradiction with the entropy principle, if we do not attribute entropy to radiation. Every body which radiates heat into a vacuum, which heat is not at the same time absorbed by another body, would lose entropy without that at the same time at least an equal amount of entropy was gained elsewhere. Therefore the entropy principle requires, that the ether participating in the movement of radiation, is assumed to have at least as great an amount of entropy, as the radiating body has lost. Whether it is possible to find such an entropy function for radiation, cannot in my opinion, be doubted. This extension of the entropy principle is less hazardous than that in which the second formulation is derived from the first. Yet nobody will doubt whether the second formulation is correct, provided that we follow BOLTZMANN in considering the entropy principle not as an exact law but as a principle of probability.

WIEN derives, inter alia, from his considerations, the theoretical reliability of the law of STEPHAN and the relative intensity of the different wave-lengths in the light emitted by black bodies.

Another advantage of his introduction of the idea of "entropy of

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[1]) Wied. Ann. 52,1. Anno 1894. No, 5. P. 132 sequ.

[2]) Wied. Ann. 38,3. Anno 1889. No. 11. P. 485.

radiation" is, that we can ascribe a continuous existence to the entropy: when a body loses entropy by means of radiation and another gains entropy, we need not say, that in one place at least as much is created, as is lost in another place, but that the entropy has moved continuously through space from one place to another. The question about the localization of the entropy is, however, not of so much importance, as that about the localization of the energy. The constancy of this second quantity induces us to think of an identical continuance of existence, so that we postulate a perfectly continuous way of moving. This is not the case with the entropy and as the entropy of a point depends on the condition of the points round it, the entropy of a molecule may be modified by modifying its surroundings, there being no question of a continuous propagation.

For if we assume the formula of BOLTZMANN:

$$H = \int F \, log\,(F) \, d\omega$$

the amount which every molecule contributes to the entropy is $-log(F)$, as $-H$ represents the entropy. This quantity is changed momentaneously for every molecule of the group F, when one or more molecules are added to that group, there being no question of propagation. It is remarkable that if the entropy in a volume element increases in consequence of shocks, the amount with which the entropy increases must be ascribed exclusively to the molecules which have collided. For in the quantity H both F and $log(F)$ change.

The change may be represented by:

$$\int d\,F \, log\,(F) \, d\omega + \int F \, d \, log\,(F) \, d\omega.$$

The first term is the increase of the entropy of the molecules which have collided, the second term that of the other molecules. The second term, however, appears to be 0, for:

$$\int F \, d \, log\,(F) \, d\omega = \int F \frac{1}{F} \, d\,F \, d\omega = \int d\,F \, d\omega.$$

This represents the change in the total number of molecules. This number is however, not changed by collisions, and the second term is 0 [1]). If however, the entropy of the volume elements as a whole

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[1]) See BOLTZMANN, Vorlesungen über Gastheorie, 1ste Theil p. 35.

is considered, and not that of every one of the molecules separately, we may say in consequence of the entropy of radiation, introduced by WIEN: the entropy is never lost, and it propagates continuously through space. In what follows I hope to prove: Entropy originates only, when collisions (or their analogue in radiation) occur, and the new entropy is then to be found at that place where the collision has taken place.

Though much might be learned from considerations like those of WIEN, I prefer to make an attempt to obtain an insight into the nature of the entropy of radiation by considerations analogous to those of BOLTZMANN for the entropy of substances.

II.

When writing the preceding chapter, the treatises of Prof. PLANCK entitled: "Ueber irreversible Stralungsvorgänge" and his debate with Prof. BOLTZMANN in "Die Sitzungsberichte der Akademie der Wissenschaften zu Berlin, 1897, 1898 and 1899", were unknown to me. My attention was afterwards drawn to them. I found that several of the observations which I have made already occur in Prof. PLANCK's treatises. However, as my opinion differs in many respects from that of Prof. PLANCK, I think that I ought to publish the following paper, though I can oppose against the elaborate system of Prof. PLANCK only a beginning of a system according to my views. To make clear the course of my thoughts, I have left the preceding chapter unchanged. In the first place I shall have to vindicate, why I do not follow the method of treatment of Prof. PLANCK, but follow the considerations of Prof. BOLTZMANN on the molecular thermal movement also for the ethereal movement of radiation. For this purpose I shall put the views of the entropy principle of Prof. BOLTZMANN and Prof. PLANCK in sharp contrast; or at least what seems to me to be the view of Prof. PLANCK, for he does not expressively state his opinion.

Prof. PLANCK's meaning seems to me to be the following:

The basis of his considerations is that the entropy principle is correct, that is to say that the entropy can only increase.

Now many processes which occur in nature, are not elementary e. g. all thermal phenomena can only be treated adequately by applying strict mechanic laws to the separate molecules. In order to find an exact law of nature, it will be necessary to consider an elementary process which is ruled by strict mechanic laws. Now the entropy can change in one direction only, the cause of which must be found in an elementary process, which can take place in one direction only.

In this way quite a different idea of reversibility is introduced as that which was originally deduced from the cycle of CARNOT. The reversibility according to CARNOT means, if we consider more closely the mechanism of the movement of heat, that all states, through which the system has passed, are states of equilibrium. These states of equilibrium now, are nothing but a particular kind of stationary states, namely such as can exist, without continual change taking place necessarily anywhere outside the system. So e. g. a gas between two plates, one kept at 100° by means of steam and the other at 0° by means of melting ice, is in a perfectly stationary state, which however is no state of equilibrium, as on one plate steam is continually condensing and on the other ice melting.

It is easy to see that this idea has little in common with the idea of irreversibility of Prof. PLANCK. Many processes are irreversible according to CARNOT, reversible according to Prof. PLANCK, e. g. thermal processes which are brought about by the movement of the molecules. In these processes Prof. PLANCK grants the reversibility according to his definition. As these processes however, increase the entropy, it seems to me, that Prof. PLANCK ought not to have tried to find a process, which is irreversible according to *his* definitions but an explanation, why processes, which are irreversible according to CARNOT can only cause increase of entropy. This observation of mine would seem fallacious only to him who wanted to explain all thermal processes not by molecular motion and collisions, but either by radiation or by an elementary strictly irreversible process of which we have as yet not the least idea. Now we shall investigate the question whether there is really an elementary strictly irreversible process.

Prof. BOLTZMANN denies this positively.

As well in the ordinary mechanics (provided heat and other internal movement be introduced as kinetic energy) as in all ether phenomena no process occurs that could not take place in an opposite direction. If a movement fulfils the equations of LAGRANGE and those of MAXWELL, the same applies to a movement which arises from the former by reversing all velocities and all magnetic forces.

This observation seems to me to be quite decisive. Yet the consideration of all processes is not equally justified. The movement of a HERTZ's vibrator, which is damped because of the emission of radiation, may be thought to take place in opposite direction, so that a wave converges from the infinite space where it has everywhere the same phasis, exactly into the same point. Yet we are not justified in assuming, that this second movement occurs in nature. On this Prof. PLANCK's considerations are based. He thinks that he has found his perfectly irreversible process in radiation which falls on a resonator. He makes this process really irreversible by excluding a certain number of movements as not occurring. In reality Prof. PLANCK's ideas differ less from those of Prof. BOLTZMANN than he thinks. For the latter calls a great many movements possible, but very improbable, and assumes justly, that such improbable movements may occur both in phenomena of molecular movement and in phenomena of radiation.

Prof. BOLTZMANN's considerations seem to be chiefly as follows. As basis of his considerations he takes the reversibility of all processes, as well mechanical as electrical and magnetical ones. From this follows that a process, in which the entropy increases, might also take place in the opposite direction, so that the entropy decreased. Apparently this is in contradiction with the experiment which teaches us, that only those processes occur, in which the entropy increases. To explain this apparent contradiction, Prof. BOLTZMANN argues as follows:

If we know exactly the initial conditions of a system with n degrees of freedom, i.e. the n generalised coordinates and their fluctions at a given moment, and if we know the laws of all the forces, acting on the system, we can calculate the state of the system at any moment. If however we know at a given moment only $n - 1$ of the coordinates and their fluctions, we can in general calculate nothing for a later moment. The want of knowledge of one of the $2\,n$ necessary data, makes not only that one coordinate indetermined for the future, but all the coordinates. If we consider a gas as a system with many degrees of freedom, the condition would be exactly determined only then, if at a given moment we know exactly the coordinates and their fluctions for every molecule separately. As we however never know them, we can never say how the condition in the next moment will be. Perfectly general laws for movement of heat can therefore not be drawn up.

By varying the coordinates of the separate molecules, we can however obtain a great number of systems, all of which fulfil the conditions, which are required to call the system in question a gas or a solid substance with a certain temperature and under a certain pressure and which differ only in the coordinates of the separate molecules. The number of these systems is infinite. Now Prof.

Boltzmann has proved that for the vast majority of those systems, the state after a given time is of course not perfectly determined, but yet fulfils certain conditions, that namely the mean density and the mean kinetic energy in every volume element will be such that we may speak again of a solid or a gas of a certain temperature and under a certain pressure. Of course this is not proved for the great majority of all systems *occurring in nature*, but for all *imaginable* systems which answer to our idea "substance of a certain temperature and under a certain pressure". If we suppose all these different systems to be equally probable, we may say that it is highly improbable that we meet with a phenomenon, in which the entropy increases with a measurable amount. The supposition of Prof. Boltzmann that these systems are equally probable, is not new. Every one who has written on kinetic gas theory could not but make this supposition though in a somewhat different formulation, in order to calculate the mean number of collisions and such like quantities. The fact that observations show that the entropy always increases, justifies the assumption that this supposition agrees with reality. Convinced of the correctness of these considerations of Prof. Boltzmann, I wanted to treat the entropy of radiation in a similar way. The H theorem of Prof. Boltzmann is closely connected with the distribution of velocities according to Maxwell. Therefore I thought that I had in the first place to find the analogue of it for the distribution of the electric forces in a space, in which a great number of radiating molecules are to be found. This distribution will be treated in the following chapter.

First some observations on an, in my opinion, essentiel consequence of the considerations of Prof. Boltzmann, viz that the entropy increases only in consequence of collisions.

To show this we take the following process into consideration:

The walls inclosing a quantity of gas are suddenly removed at the moment t, so that the gas spreads in an infinite vacuum. We leave the molecular attraction out of account. If we take the gas at a high degree of rarefaction and if the volume in which it was enclosed is supposed to be not too large, many molecules will move away without any collision. In order that we may apply Boltzmann's H theorem, we must have a large quantity of molecules. The assumption that after the moment t not a single molecule collides, may be in opposition to this requirement. Yet we may examine what might be the consequence of the assumption that all molecules moved away with the velocity which they had at the moment

t, without changing it by collisions. It is easy to show, that the entropy would then remain constant.

Let us first think the gas enclosed in a small cube with a centre O, the axes being taken parallel to the sides. We get

$$H = \int\!\!\int\!\!\int\!\!\int\!\!\int\!\!\int F \, log\, (F)\, dx\, dy\, dz\, d\xi\, d\eta\, d\zeta$$

ξ η ζ representing the components of the velocities of the molecules. The first three integrals for x y and z must be taken between the limits $-\frac{1}{2}a$ and $+\frac{1}{2}a$, where a represents the edge of the cube, and the other three for ξ η and ζ between $-\infty$ and $+\infty$. If the volume of the cube was 0, the velocity of the molecules which had reached after one second the point $P\,(x'\,y'\,z')$ at a distance r from O would also be r and their density $a^3\,F\,(x'\,y'\,z')$.

By assuming this density as being the real one, we shall make a slight error. For the velocity we must however take into account that the velocity of molecules, which reach P after one second, starting from different points of the cube, is different.

The probability that the components of the velocity of a molecule which has reached point P, are enclosed between the limits:

$$x' + x = \xi' \text{ and } x' + x + dx = \xi' + d\xi'$$

$$y' + y = \eta' \text{ and } y' + y + dy = \eta' + d\eta'$$

$$z' + z = \zeta' \text{ and } z' + z + dz = \zeta' + d\zeta'$$

x, y and z representing the coordinates of the point of the cube, from which the molecule has started, is:

$$\frac{dx\, dy\, dz}{a^3} = \frac{d\xi'\, d\eta'\, d\zeta}{a^3}$$

we find for H after one second:

$$H' = \int\!\!\int\!\!\int\!\!\int\!\!\int\!\!\int a^3\, F' \frac{1}{a^3}\, log\left(a^3\, F' \frac{1}{a^3}\right) dx'\, dy'\, dz'\, d\xi'\, d\eta'\, d\zeta'$$

$$= \int\!\!\int\!\!\int\!\!\int\!\!\int\!\!\int F'\, log\, (F')\, dx'\, dy'\, dz'\, d\xi'\, d\eta'\, d\zeta'$$

F' is obtained, as we have seen, by substituting r in F for the velocity; r represents the distance from an arbitrary point to the origin.

The integrals with respect to x, y and z must here be taken between $-\infty$ en $+\infty$, those with respect to ξ, η and ζ between $-\frac{1}{2}a$ and $+\frac{1}{2}a$. Therefore H' is equal to H, the only difference is that the coordinates have been interchanged with the velocities. The unity of time being arbitrary H will remain also constant after an arbitrary time. H changes only if the molecules which are moving away, cannot reach infinity, but come in collision with a new wall and are arranging themselves into a state of stationary movement in the new volume.

The great importance which I think ought to be attached to the collisions, made me look for its analogue in radiation. For this purpose I have had to make a supposition on the nature of radiating molecules. I have namely imagined them as HERTZ's vibrators all of the same period. In this case the emitted radiation also has everywhere the same period. Its amplitude varies from point to point and changes with the time. As collision of a special kind I consider the action of an alternating electric force of a determinate direction, intensity and phasis on a molecule, which is in a vibration, the direction, amplitude and phasis of which are also determinate. According to this, every molecule is always in collision.

This view agrees with an observation of Prof. PLANCK, who says more generally [1]:

„Durch die Strahlungsvorgänge im freien Felde kann also keine Entropieänderung des Systems hervor gerufen werden. Dagegen bewirkt jeder Resonator im allgemeinen eine Entropieänderung der ihm treffenden Strahlenbündel."

III.

Law of the distribution of Electrical forces.

Concerning the nature of radiating molecules there are principally two conceptions. The first is that a source of light has a periodical movement, which gives rise to more or less regular vibrations in the ether. The other conception is that the molecules bring about perfectly irregular disturbances of the ether, which get a seeming periodicity from the apparatus by means of which we observe. Possibly both these suppositions are partly true and in some sources

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[1] Berliner Sitzungsberichte XXV 18 Mai 1899 pag. 467.

of light the regular, in others the irregular ways of movement are more prominent. As my considerations will be simplest for a gas, and we are there most inclined to think of vibrations in the molecules, I have chosen the first conception; and that in very simplified suppositions, hoping that these may be extended for processes such as really occur in nature. I imagine namely a great number of molecules spread in space which I suppose as vibrating, all with exactly the same period. I leave out of account the change of the period caused by the DOPPLER effect. I suppose that for those molecules vibrations in the direction of the x, y and z-axis are on an average equally represented, while also all phases equally probable.

These suppositions are sufficient for finding something about the distribution of the forces, without our having to determine whether or no all molecules have the same amplitude; and if not, how the distribution of the amplitudes will be.

Let us now consider a volume element $d\tau$. The action of it at a certain distance will be only determined by its electrical moment and the way in which that changes, and not by the way in which that moment is spread over the element.

If the moments of the molecules now had the most probable distribution, i. e. if all directions and phases were exactly equally represented, the moment of the element would be always 0 and no radiation would take place. The most probable distribution, however, is itself highly improbable, and generally a deviation will be found. This deviation is the cause of radiation. Let us assume that the unity of volume contains n molecules. Let us represent the components of their vibration by:

$$a_x = a_{x1} \cos. \frac{2\pi t}{T} + a_{x2} \sin. \frac{2\pi t}{T}$$

$$a_y = a_{y1} \cos. \frac{2\pi t}{T} + a_{y2} \sin. \frac{2\pi t}{T}$$

$$a_z = a_{z1} \cos. \frac{2\pi t}{T} + a_{z2} \sin. \frac{2\pi t}{T}$$

and let us call the number of the molecules per unity of volume, the amplitudes of which are contained between the limits:

a_{x1}, a_{x2}, a_{y1}, a_{y2}, a_{z1} and a_{z2} and

$a_{x1} + da_{x1}$, a_{x2}, da_{x2}, $a_{y1} + da_{y1}$, $a_{y2} + da_{y2}$, $a_{z1} + da_{z1}$ and $a_{z2} + da_{z2}$,

$F(a_{x1}\, a_{x2}\, a_{y1}\, a_{y2}\, a_{z1}\, a_{z2})\, da_{x1}\, da_{x2}\, da_{y1}\, da_{y2}\, da_{z1}\, da_{z2}$ or $F d\omega$.

The group, the amplitudes of which have the same values, but all the opposite sign, will be about as numerous. These two groups together contain $\pm 2F d\omega$ molecules. If the most probable distribution prevailed, these two groups would have exactly the same number of molecules and would furnish together a moment 0.

If we have an event, which may take place in two directions, the probability for one direction being p and that for the other q (where $p + q = 1$) and if this event occurs a very great number (n) of times, the calculus of probabilities teaches that the chance, that of these n events the number which occurs in one direction is between $np + \nu$ and $np + \nu + d\nu$, is represented by:

$$\frac{1}{C\sqrt{\pi}} e^{-\frac{\nu^2}{C^2}} d\nu .$$

In this C is equal to $\sqrt{2npq}$ and is called modulus.

If we apply this to the $2F d\omega\, d\tau$ molecules, then $p = q = \frac{1}{2}$.

The probability that the deviation, which one of the groups shows from the most probable value, lies between ν and $\nu + d\nu$, is:

$$\frac{1}{\beta\sqrt{\pi}} e^{-\frac{\nu^2}{\beta^2}} d\nu$$

where $\beta = \sqrt{F\, d\omega\, d\tau}$.

Of the $2\, F d\omega$ molecules one group has a deviation of $+ \nu$, so that it amounts to $F d\omega + \nu$, the other group has a deviation of $- \nu$ and amounts to $F d\omega - \nu$. The difference between the two groups is then $2\, \nu$ and the amount they contribute to the moment of the volume element is $[2\, \nu a_{x1}]$.

If we put:

$$[2\, \nu a_{x1} = m_{x1}]$$

in which the brackets indicate that also a corresponding expression for the y and z components and for the coefficients of $\sin\frac{2\pi t}{T}$ is meant, then we may represent the probability that the two groups in consideration contribute to the moment of the volume element an amount, the amplitudes of which lie between

$$[m_{x1}] \text{ and } [m_{x1} + dm_{x1}]$$

by

$$\frac{1}{\gamma\sqrt{\pi}} e^{-\frac{m_{x1}^2}{\gamma^2}} dm_{x1}$$

where

$$\gamma = 2\, a_{x1}\, \beta.$$

Now we are going to seek the probability that the total moment M of the volume element i. e., the sum of the amounts contributed by the separately considered groups of molecules, has amplitudes which lie between:

$$[M_{x1}] \text{ and } [M_{x1} + dM_{x1}].$$

According to the calculus of probabilities the probability for such a sum is again represented by a function of the same form as the separate terms, while the modulus is the root of the sum of the squares of the moduli of the separate terms. So:

$$\delta = \sqrt{\tfrac{1}{2} \int\!\!\int\!\!\int\!\!\int\!\!\int\!\!\int 4 a_{x1}^2\, F d\omega\, d\tau}.$$

If we take the integrals between the limits $-\infty$ and $+\infty$, the factor $\frac{1}{2}$ must not be omitted, because we have to take only half of all the groups: for if we take a group with definite amplitudes, that one with equal amplitudes, but of opposite sign has been taken into account at the same time.

For the other quantities M_{x2}, M_{y1}, M_{y2}, M_{z1} and M_{z2} of course the same formula holds good. Now we have still to prove that the chances for these quantities are independent of one another. To this purpose we draw vectors from point O, which have the quantities M_{x1}, M_{y1} and M_{z1} as components. Along the axes the density of the final points of these vectors is the same as in the distribution of velocities of MAXWELL. If a large M_{y1} was probably accompanied by a large M_{x1}, the distribution in space would not be that of MAXWELL. The choice of the axis is however perfectly arbitrary, and the distribution along every line passing through O, must be the same as along the x-axis. From this follows that the distribution is really the same, as that which MAXWELL found for the velocities, i.e. that the chances of the quantities M_{x1}, M_{y1} and M_{z1} are independent of each other. In a corresponding way we may prove this for M_{x1} en M_{x2}, M_{y1} and M_{y2}, M_{z1} and M_{z2}.

If we represent the mean of the squares of all quantities a_{x1} by $\overline{a_{x1}^2}$, we get:

$$\delta = \sqrt{2n}.\sqrt{\overline{a_{x1}^2}}$$

and

$$M_{x1}^2 = n\ a_x^2,$$

The electric and the magnetic forces of the ether vibrations, emitted by the element are proportionate to $[M_{x1}.]$. The emitted energy is therefore proportionate to $[M_{x1}^2]$. This energy proves to be on an average the sum of the quantities of the energy, which every molecule would emit, if it were alone in space.

Let us now examine what would be the distribution of the electric and the magnetic forces, the components of which we represent by:

$$f = f_1 \ cos. \frac{2\pi t}{T} + f_2 \ sin. \frac{2\pi t}{T}$$

$$g = g_1 \ cos. \frac{2\pi t}{T} + g_2 \ sin. \frac{2\pi t}{T}$$

$$h = h_1 \ cos. \frac{2\pi t}{T} + h_2 \ sin. \frac{2\pi t}{T}$$

$$L = L_1 \ cos \frac{2\pi t}{T} + L_2 \ sin. \frac{2\pi t}{T}$$

$$M = M_1 \ cos. \frac{2\pi t}{T} + M_2 \ sin. \frac{2\pi t}{T}$$

$$N = N_1 \ cos. \frac{2\pi t}{T} + N_2 \ sin. \frac{2\pi t}{T}$$

For this we apply the following formula [1]):

$$f = - V^2 \left\{ \frac{\partial^2 \chi_x}{\partial x^2} + \frac{\partial^2 \chi_y}{\partial x \partial y} + \frac{\partial^2 \chi_z}{\partial x \partial z} \right\} + \frac{\partial^2 \chi}{\partial t^2}$$

and

$$L = 4\pi V^2 \left\{ \frac{\partial^2 \chi_y}{\partial z\, \partial t} - \frac{\partial^2 \chi_z}{\partial y\, \partial t} \right\}$$

$$\chi_x = - \frac{1}{4\pi V^2} \int \frac{M_x}{r} dr, \quad \chi_y = - \frac{1}{4\pi V^2} \int \frac{M_y}{r} dr, \quad \chi_z = - \frac{1}{4\pi V^2} \int \frac{M_z}{r} dr$$

where M represents the moment of a volume-element at the moment $t - \frac{r}{V}$, so that:

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[1]) LORENTZ Arch. Neerl. XXV 5. 1892 pag. 429.

$$\chi_x = -\frac{1}{4\pi V}\int\frac{1}{r}\left\{M_{x1}\cos.\frac{2\pi}{T}\left(t-\frac{r}{V}\right)+M_{x2}\sin.\frac{2\pi}{T}\left(t-\frac{r}{V}\right)\right\}d\tau$$

and
$$f=\frac{1}{4\pi}\int\left[\frac{\partial^2}{\partial x^2}\frac{1}{r}\left\{M_{x1}\cos.\frac{2\pi}{T}\left(t-\frac{r}{V}\right)+M_{x2}\sin.\frac{2\pi}{T}\left(t-\frac{r}{V}\right)\right\}+\right.$$

$$+\frac{\partial^2}{\partial x\partial y}\frac{1}{r}\left\{M_{y1}\cos.\frac{2\pi}{T}\left(t-\frac{r}{V}\right)+M_{y2}\sin.\frac{2\pi}{T}\left(t-\frac{r}{V}\right)\right\}+$$

$$+\frac{\partial^2}{\partial x\partial z}\frac{1}{r}\left\{M_{z1}\cos.\frac{2\pi}{T}\left(t-\frac{r}{V}\right)+M_{z2}\sin.\frac{2\pi}{T}\left(t-\frac{r}{V}\right)\right\}-$$

$$\left.-\frac{1}{V^2}\frac{\partial^2}{\partial t^2}\frac{1}{r}\left\{M_{x1}\cos.\frac{2\pi}{T}\left(t-\frac{r}{V}\right)+M_{x2}\sin.\frac{2\pi}{T}\left(t-\frac{r}{V}\right)\right\}\right]d\tau$$

In this the influence of absorption has been neglected. In a complete theory we should have to calculate it by examining to what influence the vibration of every molecule is subjected by the radiation of every other molecule. Then it would be necessary to take into account the influence of the damping, which the vibrating molecules experience, and the quite unknown influence of the collisions. Here I shall confine myself to assume that the disturbances, when they have propagated over the unity of length, are reduced to $e^{-\mu}$ of their original amount. Then we have to multiply with $e^{-\mu r}$ every term under the integral sign in the expression for f.

For points for which r is great compared with the wave length, we may write by approximation:

$$f=-\frac{1}{4\pi}\left(\frac{2\pi}{TV}\right)^2\int\frac{e^{-\mu r}}{r}\left[\left\{M_{x1}\cos.\frac{2\pi}{T}\left(t-\frac{r}{V}\right)+M_{x2}\sin.\frac{2\pi}{T}\left(t-\frac{r}{V}\right)\right\}\frac{x^2}{r^2}+\right.$$

$$+\left\{M_{y1}\cos.\frac{2\pi}{T}\left(t-\frac{r}{V}\right)+M_{y2}\sin.\frac{2\pi}{T}\left(t-\frac{r}{V}\right)\right\}\frac{xy}{r^2}+$$

$$+\left\{M_{z1}\cos.\frac{2\pi}{T}\left(t-\frac{r}{V}\right)+M_{z2}\sin.\frac{2\pi}{T}\left(t-\frac{r}{V}\right)\right\}\frac{xz}{r^2}-$$

$$\left.-\left\{M_{x1}\cos.\frac{2\pi}{T}\left(t-\frac{r}{V}\right)+M_{x2}\sin.\frac{2\pi}{T}\left(t-\frac{r}{V}\right)\right\}\right]d\tau.$$

So the modulus for the probability, that $[f_1]$ lies between the limits $[f_1]$ and $[f_1+df_1]$, becomes:

$$\varepsilon = \frac{1}{4\pi}\left(\frac{2\pi}{TV}\right)^2 \delta \sqrt{\int \frac{e^{-2\mu r}}{r^2} \left\{ \left(\frac{y^2+z^2}{r^2}\right)^2 + \left(\frac{xy}{r^2}\right)^2 + \left(\frac{xz}{r^2}\right)^2 \right\} d\tau}$$

$$= \frac{\pi}{\lambda^2} \delta \sqrt{\int \frac{e^{-2\mu r}}{r^2} \frac{y^2+z^2}{r^2} d\tau}.$$

In the same way we find for L:

$$L = -\int e^{-\mu r} \left[\frac{\partial^2}{\partial y\, \partial t} \frac{1}{r} \left\{ M_{z1} \cos \frac{2\pi}{T}\left(t - \frac{r}{V}\right) + M_{z2} \sin \frac{2\pi}{T}\left(t - \frac{r}{V}\right) \right\} \right.$$

$$\left. - \frac{\partial^2}{\partial z\, \partial t} \frac{1}{r} \left\{ M_{y1} \cos \frac{2\pi}{T}\left(t - \frac{r}{V}\right) + M_{y2} \sin \frac{2\pi}{T}\left(t - \frac{r}{V}\right) \right\} \right] d\tau$$

or by approximation:

$$L = -\frac{2\pi}{T} \frac{2\pi}{TV} \int \frac{e^{-\mu r}}{r} \left[\frac{y}{r} \left\{ M_{z1} \cos \frac{2\pi}{T}\left(t - \frac{r}{V}\right) + M_{z2} \sin \frac{2\pi}{T}\left(t - \frac{r}{V}\right) \right\} \right.$$

$$\left. - \frac{z}{r} \left\{ M_{y1} \cos \frac{2\pi}{T}\left(t - \frac{r}{V}\right) + M_{y2} \sin \frac{2\pi}{T}\left(t - \frac{r}{V}\right) \right\} \right] d\tau$$

and for the modulus of the corresponding chance:

$$\eta = \left(\frac{2\pi}{T}\right)^2 \frac{1}{V} \delta \sqrt{\int \frac{e^{-2\mu r}}{r^2} \frac{y^2+z^2}{r^2} d\tau}.$$

The reasoning, according to which these formulae have been derived, is correct only when we may choose volume elements, which contain many molecules and which are yet small compared with a wave-length and with r. It does not hold for the immediate surroundings of a point. Yet the not approximated formulae for $[f_1]$ and $[L_1]$ hold also for the immediate surroundings, provided we neglect the volume of the molecules. If we imagine an element $dx\, dy\, dz$ or $d\tau$ at the distance r from the point P, then the probability that we should find a molecule in it, is $n\, d\tau$. The chance, that we should find a molecule in it with a_{x1} lying between a_{x1} and $a_{x1} + da_{x1}$, is $F_1(a_{x1})\, da_{x1}\, n\, d\tau$.

If we imagine a region $\Delta x\, \Delta y\, \Delta z$, which contains many (p) elements $d\tau$ and which is yet small compared with the wave-length and r, then the chance, that this region has a moment $[M_{x1}]$ is the sum of the chances of the different ways, in which that moment may be brought about. The chance, that the volume element $d\tau$ contains no molecule is the chance, that all the n molecules of the unity of volume lie outside the element. For one molecule this change is $1 - d\tau$, so for the n molecules $(1 - d\tau)^n$. Now the moment M_{x1} may be brought about by the fact that in q elements $d\tau$ we have no molecule, in $p - q - 1$ we have a molecule, every one of which has an arbitrary amplitude a_{x1} and in the last element with the amplitude ${}_pa_{x1} = M_{x1} - \Sigma a_{x1}$. The chance of being brought about in this way, is:

$$(1 - d\tau)^{nq} (nd\tau)^{p-q} F_1 ({}_1a_{x1}) F_1 ({}_2a_{x1}) \ldots F_1 ({}_{p-q-}a_{x1}) F_1 (M_{1x1} - \Sigma a_{x1})$$

$$d ({}_1a_{x1}) d ({}_2a_{x1}) \ldots d ({}_{p-q-}a_{x1}) d M_{x1}.$$

We find the total change for an amplitude between M_{x1} and $M_{x1} + dM_{x1}$ by first integrating with respect to ${}_1a_{x1}$, ${}_2a_{x1} \ldots {}_{p-q-1}a_{x1}$ between the limits $-\infty$ and $+\infty$, and by adding the results for all values of q.

As we have to do this for the case in which $p = \infty$, we execute this addition by multiplying with dq and by then integrating with respect to q between the limits 0 and ∞. These formulae hold always, independent of the size of $\Delta x \Delta y \Delta z$, and as we have found for it for a region with many molecules

$$\frac{1}{\delta \sqrt{\pi}} e^{-\frac{M_{x1}^2}{\delta^2}} \text{ where } \delta = \sqrt{\tfrac{1}{2} n \Delta x. \Delta y. \Delta z}.$$

this formula will also hold if $\Delta x \Delta y \Delta z$ is so small that the chance that it contains a molecule, is slight.

In this we have assumed, that the fact, that at a certain point P a definite moment $[M_{x1}]$ prevails, has no influence on the chance for the moment of the immediately surrounding points. This would be true only if the molecules themselves had no extension. If however point P lies in a molecule, which has extension, the surrounding points will also have moments of the same direction and the same phasis as P. If this circumstance however, causes a deviation from the here derived law of probability, it will probably be very small for gases.

Our result shows that in the unity of volume the total region in which f_1 is contained between the limits f_1 and $f_1 + df_1$ is:

$$\frac{1}{\varepsilon\sqrt{\pi}}\;{}^{-\frac{f_1^2}{\varepsilon^2}}\;df_1$$

and that the changes for f_1, f_2 g_1, g_2, h_1 and h_2 are independent of one another.

This does not completely determine the condition: it is left unsettled, how the total region is spread over the unity of volume; whether it probably consists of comparatively few regions which are not so very small, or of a great many very small regions. In order to find something about this, we should have to calculate the probable value of $\left[\frac{\partial f_1}{\partial x}\right]$. In the same way we might also try to find the probable value of $\left[\frac{\partial f_1}{\partial t}\right]$. Whereas $\left[\frac{\partial f_1}{\partial x}\right]$ may be deduced from the suppositions which we have already made, new suppositions would be necessary, in order to find $\left[\frac{\partial f_1}{\partial t}\right]$. It would be namely necessary, to make suppositions about the causes of change of $[a_{x1}]$. The significance of these quantities will appear from the following chapter.

At first I had thought that the name "entropy of the ether" would be preferable to that of "entropy of radiation." The name introduced by WIEN "entropy of radiation," seems however, preferable to me. At the absolute zeropoint matter has an entropy $-\infty$. Now both the formulae, that of WIEN and that of PLANCK, give for space without radiation 0 as the quantity of entropy; and this result seems correct to me. In order to maintain the analogy between the two kinds of entropy, it seems best to me, to ascribe the entropy not to the ether but to the radiation. A space, where no radiation takes place, can consequently not contain entropy of radiation.

If we speak of entropy of the ether, it would probably have a form like the following:

$$\int F([f_1])\,log\;F\,[df_1].$$

Probably however the entropy will be represented by a form like the following:

$$\int \varphi([f_1])\,F([f_1])\,log\,(\varphi F).\,[df_1]$$

in which φ represents the density, i.e. it has the same function as n in the formula of BOLTZMANN:

$$H = \int F \log (F) d\omega \quad \text{where: } F = \frac{n}{\alpha\sqrt{\pi}} e^{-\frac{c^2}{x^2}}$$

Possibly this φ is nothing but the energy per unity of volume, which quantity we are most inclined to call "density of radiation."

For the distribution of the magnetic forces the entropy will consist of another term formed in a similar way. Possibly however we shall have to find the entropy not from the electric and the magnetic forces separately, but from the vectors of POYNTING.

We find therefore the analogue of matter at the absolute 0-point not in a space without radiation, but in absolutely regular movement, e.g. in a plain wave of monochromatic light, everywhere with the same amplitude. Let us represent this wave by:

$$f = f_0 \cos. \frac{2\pi}{T}\left(t - \frac{y}{V}\right)$$

$$g = 0, \qquad\qquad h = 0.$$

Here we must take into consideration, that in this case f_1 and f_2 are not independent of each other, so that we cannot simply add the entropy for these two terms. Probably we have to diminish the amplitude everywhere with:

$$f_0 \cos. \frac{2\pi y}{\lambda} \text{ and } f_0 \sin. \frac{2\pi y}{\lambda}$$

and we have to take for F the chance that the remaining amplitude lies between certain limits, i.e.

$$F = \frac{1}{c\sqrt{\pi}} e^{-\frac{f'^2_1}{c^2}} \text{ where } c = 0 \text{ and } f'_1 = f_1 - f_0 \cos. \frac{2\pi y}{\lambda}\ .$$

This is analogous to the way, in which we prove for a gas of $0°$, which moves as a whole, that the quantity H of BOLTZMANN becomes ∞.

If we put for φ the mean energy, we find:

$$H = \int_{-\infty}^{+\infty} \tfrac{1}{2} f_1^2 \frac{1}{c\sqrt{\pi}} e^{-\frac{f_1'^2}{c^2}} \left\{ -lc - \tfrac{1}{2}\, l\pi - \frac{f'^2_1}{c^2} \right\} df_1' = \infty$$

So the entropy is $-\infty$.

Mathematics. — Prof. W. KAPTEYN presents a supplement to his communication of the Meeting of November 25, 1899: *"On some special cases of* MONGE's *differential equation".*

In my last communication was mentioned sub I that the equation $r - \lambda s = 0$ possesses two intermediate integrals, if λ is given by the relation

$$\lambda = \frac{\psi(p)}{q - \varphi(y\,p)},$$

in which supposition these intermediate integrals were deduced. However a closer examination shows that this result represents only a particular case. In the most general one $\mu = \frac{1}{\lambda}$ presents itself in the form

$$\mu = qx\frac{\partial U}{du} - q\frac{\partial U}{\partial p} + x\frac{\partial U}{\partial y} - e^{-U}\left\{\int e^{U}\left(\frac{\partial^2 U}{\partial p\,\partial y} + \frac{\partial U}{\partial p}\frac{\partial U}{\partial y}\right)\right\}du + W(p,y),$$

where $U = U(u\,p\,y)$ and $W(p,y)$ denote arbitrary functions of u, p, y and p, y respectively, whilst u stands for $z - px$.

The corresponding intermediate integrals are

$$qe^{U} + \int e^{U}\frac{\partial U}{dy}du + \int W(p.y)\,dp = f(y)$$

$$xe^{U} - \int e^{U}\frac{\partial U}{\partial p}du + \int W(p,y)\,dy = f(p)$$

By putting

$$U = -\int\frac{dp}{\psi(p)}, \qquad W = e^{-\int\frac{dp}{\psi(p)}}\frac{\varphi(y,p)}{\psi(p)}.$$

the first mentioned case reappears, as is easily demonstrated.

Anthropology. — *"A new graphic system of craniology"* by Dr. P. H. Eykman, at Scheveningen. (Communicated by Prof. C. Winkler.)

For a rough comparison of skulls, we often use three measurements, viz.: length, breadth and height.

Because the review of these three is still too difficult, Schmidt, at Leipsic, proposed using the relative instead of the absolute measures, which he obtained by multiplying the last with $\frac{300}{L+B+H}$. The sum of the relative becomes thus constant; that is: 300; and he then really only works with two instead of three respectively independent proportions, because the third is always equal to 300 minus the other two relative measurements. If two are known, then the third is also definite and in an ordinary diagram, you could, by one point, find out the relative proportions of the skull.

For practice this method is insufficient, because the third measurement, although it can be calculated, is not shown in the diagram and so escapes our notice.

I have discovered a method, giving a graphic representation in a plane, showing three measurements that suffice, to denote that their sum is constant, and at the same time indicated by one point.

We start from a trihedral angle (fig. 1), of which the ribs PQ, PR and PS represent a triple ordinate-system.

By a single point d in space, we can in this manner show three absolute measurements at the same time.

Suppose now we draw a plane, that crosses the three ribs at the same length, going through such a graphic point d, it would be easy to prove, that the sum of the three absolute measurements is equal to the length of one rib; viz.:

$$Pe + Pg + Pb = PR = PQ = PS.$$

If we suppose the rib to be 300, then this secant plane, that has the form of an equilateral triangle, will be the geometrical place of all graphic points, of which the sum of the three ordinates = 300; viz.: all points of the formula of Schmidt are in this triangle.

Supposing there were planes parallel to the three sides of the trihedral angle, you could call them planes of measurement, and then these planes would show on the equilateral triangle, systems of smaller equilateral triangles, that in their turn could serve for determining the measurement, so that we could do without the trihedral angle itself.

Fig. 2 represents the equilateral triangle with omission of the trihedral angle.

As soon as you eliminate one of the three measurements (Length, Breadth and Height), the stereometrical ordinate-system will of course alter into a diagram in a plane.

Instead of the three ordinates:

$$Pb\,(=hd),\quad Pe\,(=cd)\ \text{ and }\ Pg\,(=ad),$$

i.e. the three perpendiculars, let down from the graphic point d to the sides of the trihedral angle, now come the perpendicular lines dj, dl and dk, let down from the same point to the sides of the equilateral triangle QRS.

This will present no difficulty; for the sum of these perpendiculars is constant (or = the height of the triangle) and in future we will reckon this as 300, instead of the rib of the trihedral angle.

This triangular diagram has this advantage over the rectangular, that all the three relative measurements are represented on it; by means of which the eye can compare them better, as all three come out equally right.

HELMHOLTZ in his Physiologische Optik, just refers to the triangular diagram, in connection with LAMBERT's Farbenpyramide:

„Jeder Schnittpunkt einer dieser Liniën mit der Ebene des Dreiecks, würde den Ort der entsprechenden Farben in diesen anzeigen, und zwar würde die Vertheilung der einzelnen Farben darin genau der durch Schwerpunktsconstructionen herstellbaren Ordnung entsprechen. In jeder solche Ebene würden aber nur Farben gewisser Helligkeit angeordnet sein, welche durch die Summe der Werthe $(x + y + z)$ gegeben ist."

Let the perpendicular dj, drawn on the basis QS, signify the relative height; the perpendicular dk the relative breadth, and dl the relative length; then we shall be more conversant with the subject by the following:

all points, drawn in a line parallel to the basis, have the same relative height;

all points, in a line parallel to QR (resp. RS.) have equal relative breadth (resp. rel. length);

if there be a point in the perpendicular R, drawn on the basis QS, the length and breadth are equal to each other. Mutatis mutandis the same also concerns the perpendiculars, drawn from Q and S on the opposite sides.

if there were a point in the intersection of the three perpendiculars, all three of the measurements would be mutually equal. For a skull this would signify a *mathematical roundhead*, but this does not occur in reality.

if we draw lines, that we will call radii, from R to the basis, we shall see in each radius the points, of which the proportion of the Breadth and Length is constant;

e. g. by Rp is $B : L = 9 : 11$

» Rq » $B : L = 2 : 3$.

Skulls, that, seen *from above*, are conformable, lie in the same radius of R;

a radius, drawn from S to QR, combines the points, of which the proportion of the height to the length is constant;

e. g. by Ss is $H : L = 9 : 11$

» Sr » $H : L = 2 : 3$.

Skulls, that, seen *from the side*, are conformable, lie in the same radius of S;

by a radius, drawn from Q to RS, the proportion of the height to the breadth is constant;

e. g. by Qt is $H : B = 9 : 11$

» Qu » $H : B = 2 : 3$.

Skulls, that, seen *from the back*, are conformable, lie in the same radius of Q.

To draw a graphic point in the diagram, is very simple. For a skull rel. $L = 120$; rel. $B = 90$ and rel. $H = 90$, we find the point by taking the intersection of the lines 120 L and 90 B, which is then naturally the intersection for 90 H.

If we draw in the figure the five skulls, which TOPINARD describes as differing most in form:

	rel. L.	rel. B.	rel. H.
A Parisian	116.1	93.6	90.3
A Savoyard	111.4	101.3	87.3
Amelander	123.2	96.6	80.2
N. Caledonian	122.5	82.9	94.6
Soudanese Negro	126.6	81.8	91.6

we see (fig. 2), as was to be expected, that they are all rather near to each other, and that the greater part of the figure remains unused. The place that the skulls occupy, is shown in the figure by a broad outline; the rest of the triangle we omit, and draw the place itself with larger measurements; this was the case in fig. 3.

Here we see in an equilateral triangle at regular spaces from each other, 38 lines parallel to the basis.

The basis is marked with 75 *H*; each of the lines with a higher number and the top with 115 *H*; these are the measuring lines for the height.

We draw lines parallel to *QR* for the relative breadth, marked 80 *B* to 120 *B*; in a similar way we draw lines for the relative length parallel to *RS*, marked 105 *L* to 145 *L*.

To facilitate this matter, the same radii given in fig. 2 are also given in fig. 3. The lines of this figure can serve for a great number of skulls.

On a rather large scale I applied this method for the first time on: „*Eine anthropologisch-historische Studie über siebenhundert Schädel aus den elsässischen Ossuariën von* Dr. Med. EDMUND BLIND."

Of the 701 skulls, that this list contains, 164 were deducted, because by all these, the three measurements were not shown. Of the remaining 537 the relative measurements were calculated accurately to a decimal and the points were indicated, as is shown in fig. 4; these are printed on transparent paper and agree with the lines, shown in fig. 3.

The points are drawn in their exact place, but so, that, where two points come partly or wholly together, this is avoided, by the points being drawn next to one another.

On consideration, we soon notice, that there is a certain centre of accumulation perceptible, limited by 84 *H* — 89 *H* and 96 *B* — 99 *B*, round which the points, slightly running out in all directions, are grouped.

It is also my intention to draw diagrams of other large groups of skulls and to subject them to a similar comparison.

Scheveningen, Dec. '99.

Botanics. — Prof. J. W. Moll presents a communication of Miss T. Tammes at Groningen, entitled: „*Pomus in Pomo*".

By Professor C. A. J. A. Oudemans a monstrous apple was given to the Botanical Laboratory of the University of Groningen. This apple is originary from Dr. A. C. Oudemans, who got it accidentally in 1894. Within the apple is a second, quite loose from the external. In an added writing of Maxwell T. Masters he tells us, that he has often seen similar apples, but always the inner one joined to the external.

In the literature of teratology we meet now and then with descriptions of cases where within a fruit a smaller one is found. The greater number of these cases relates to the genus Citrus; but the abnormality occurs with other plants also.

So mention is made of some Cruciferae [1]), where the pod contains internally a smaller one; further, of so called fructus in fructu of Gentiana lutea [2]), Carica Papaya [3]), Passiflora alata [3]), Passiflora Alpinia [3]) and Piper nigrum [4]). Usually the communication is limited to one or mostly two cases; with the Citrus-species [5]) on the contrary, the phenomenon is by no means rare. It seems to occur so often in this genus that double oranges are known in the Canaries by the name of „Narangas pregnadas" [6]); whilst also at Nizza such fruits can be bought as „oranges doubles" [7]).

The descriptions of the internal fruit are not always in accordance with one another. In some cases the internal fruit has seeds, in others not. It is also described with and without a fruit-wall; the phenomenon seems not always to be quite the same and of its explication relatively very little is known.

The described apple is in alkohol and is here figured, in natural

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[1]) The Gard. Chron. 1882. Part I. p. 10 and p. 601.

[2]) Bull. Soc. Botan. de France. 1878. p. 252.

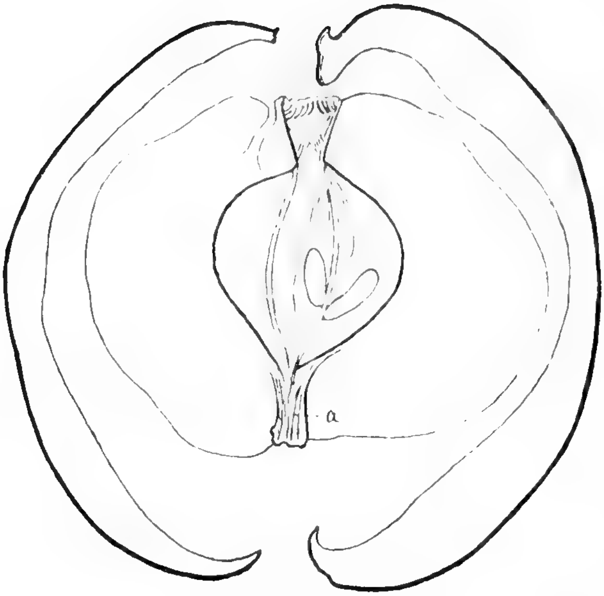
[3]) Flora Jahrg. 73, 1890. p. 332.

[4]) B. Torr, B. C., vol. 18. New-York, 1891. p. 151.

[5]) Jäger, Ueber die Missbildungen der Gewachse 1814. p. 222, und Verh. Naturhist. Ver. Rheinlande, 1860. p. 376.

[6]) Hanausek, Z. Oest. Apoth. 1888, No. 16.

[7]) Levende Natuur 1899—1900. No. 2.



size, in longitudinal section. The apple is composed of an envelope, which, probably at the cutting, has fallen into three parts, and an inner apple, cut longitudinally and of which the halves are quite loose from the envelope.

The thickness of the layer of the outer apple differs from a few m.m. to about 1 c.m. The inner-side of it cannot be distinguished by the naked eyefrom the common fruit-flesh. On the top are in the usual way fragments of the calyx; but at the base no peduncle is to be found. When fitting the parts together an opening remains at that spot. The internal apple is flat globular, the section from base to apex is ± $4^1/_2$ c.m. long, the vertical section ± 6 c.m. This apple has no separate peel. The fruit-flesh seems to differ from that of the external one; for in the alkohol-material it is softer and of lighter colour. This portion, also, wears on its summit a dried, hard, dark-coloured part, which in everything resembles the apex of a normal apple. The whole apple being cut through longitudinally the core is visible. This core is of normal structure. At the base it passes in the usual way into the peduncle *a* which here, as is the case with many apples and pears, is continued in the interior of the apple till near the core, rather markedly separated from the fruit-flesh. The peduncle does not stick out of the fruit-flesh of the inner apple, yet, it must have been somewhat longer, as through the envelope, it must have been united with the branch.

Microscopically the external apple presents at the outside an epidermis with thick cuticle, under which some layers of cells with rather thick walls. The parenchyma, which follows inwardly is a very loose tissue with great intercellular spaces. The cells are more or less isodiametrical, whilst the walls are thin and, in accordance with the jodine-sulphuric-acid reaction, consist of cellulose. The inside of this envelope shows no separate differentiation; the parenchyma extends unchanged until this inside.

The structure of the inner apple accords in so far with that of the envelope, that it is also composed of a loose parenchyma of about isodiametrical cells, whose thin walls show cellulose reaction. The whole tissue is however filled up with a mycelium, the hyphae of which are in some places so numerous that in the glycerine-preparation the parenchyma cells can only be found with much trouble. The cellulose reaction, in which the hyphae are coloured yellow by jodine-kaliumjodine whilst the parenchyma cells grow dark blue, renders the latter distinctly visible. The mycelium is not everywhere equally compact. At the outside the hyphae are much more numerous than more inwardly; they form by their conglomeration at the surface a kind of layer which, on nearer view, is even visible to the naked eye. In all portions of the core, even in the seeds, the hyphae are to be found. In the interior of the endocarp the mycelium is also very compact and there the hyphae are of a stronger structure than in the surrounding fruit-flesh.

As follows from the above description this apple not only deviates from the normal one by its monstrous structure, it moreover presents another curiosity: the presence of a fungus in the inner part, and the absence of it in the envelope. To my opinion this fact explains the monstrosity. I think that the fungus has grown at first in the interior of the quite normal apple, and using some constituents of it as food, has more and more extended itself. The portion sucked out by the fungus has had a disposition for shrivelling and the tension between the healthy and the sick part of the fruit-flesh has finally become so strong that on the limit of both a splitting has originated, so that the apple was divided into two parts; an outer normal part and an inner one full of hyphae. The greater accumulation of hyphae at the surface of the inner portion of the apple has then probably taken place after the division, as the fungus will by preference develop there, where, in consequence of the splitting, a space filled with air was present. With this explanation the following facts perfectly agree. The remains of the calyx and other flower-parts at the top of the inner apple fit precisely in the opening which exists between the dry fragments of the outer portion when these fragments are joined together. These remains have evidently formed one whole, so that there can be here no question of a flower within another. The longitudinal section of a normal apple shows clearly that it is quite well possible that the dried part at the apex might divide itself into two concentric portions; the inner member of which, wearing chiefly the stamens, would belong to the central body of the apple and the circular exterior to the envelope. On a nearer inspection of the different portions of the described apple it is evident that such has undoubtedly been the case here, and it is, moreover, to be observed in the figure. At the top of the envelope there are only fragments which remind of the calyx, whilst, the top of the inner apple wears, besides a few remnants of the calyx, the whole circle of dried stamens.

How the fungus has entered the apple; from whence the growth of the mycelium has begun; when the severing of the two parts has taken place, — these are questions not to be answered with the help of this one object. But the case appeared to me remarkable enough to describe it in short, whilst it will be of importance henceforth in the appearance of similar monstrosities, to pay attention to the presence of fungi.

Chemistry. — "*On the Theory of the Transition Cell of the third kind*". By Dr. Ernst Cohen. (First part.) (Communicated by Prof. H. W. Bakhuis Roozeboom.)

1. The theory of the transition cell of the third kind, to which van 't Hoff [1]) first drew attention, has not yet been considered.

In a former paper [2]) I have pointed out that it may be verified by means of Jaeger's [3]) measurements, but that a number of experimental data needed for the complete calculation are still lacking.

In what follows I propose to develop in the first place the thermodynamic theory of these elements, then to describe the experiments which have been made for the determination of the quantities required in the calculations, whilst, finally, the results of theory and experiment will be compared with one another.

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[1]) van 't Hoff, Vorlesungen über die Bildung und Spaltung von Doppelsalzen, Leipzig (1897), S. 29. Also: Vorlesungen über theoretische und physikalische Chemie, Erstes Heft. S. 179. — Ernst Cohen, Ueber eine neue (vierte) Art Umwandlungselemente, Zeitschr. für phys. Chemie, 25 (1898) 300.

[2]) Zeitschrift für phys. Chemie 25 (1898), 300. — Maandblad voor Natuurwetenschappen, 22 (1898) 17.

[3]) Wiedemann's Annalen, Bd. 63 (Jubelband) (1897) 354.

The elements considered consist of two cells, coupled in opposition, and constructed as follows:

Electrode, reversible with respect to the anion.	Saturated solution of a salt *S* in contact with the *stable* solid phase of the salt.	Electrode, reversible with respect to the kathion.

and

Electrode, reversible with respect to the anion.	Saturated solution of the salt *S* in contact with the *metastable* solid phase of the salt.	Electrode, reversible with respect to the kathion.

2. The temperature coefficient of the transition element will first be calculated at the transition temperature itself, on the supposition that the salt in the element is zinc sulphate ($Zn\,SO_4 . 7\,H_2O$ and $Zn\,SO_4 . 6\,H_2O$).

We will set out from the equation [1])

$$E = q\,\frac{P - T}{P} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

Where E is the E. M. F. of the element in calories, q the heat evolved by the change which gives rise to the current, P the absolute transition temperature of the change which occurs in the element and T the temperature of the element.

Differentiating (1) with respect to T we find:

$$\frac{dE}{dT} = -\,\frac{q}{P} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

At the transition temperature, the change which takes place in the element during the passage of 96540 coulombs may be represented by the equation:

$$\tfrac{1}{2}\left\{\frac{a}{a-6}\,Zn\,SO_4 . 6\,H_2O + \frac{a}{(a-6)(a-7)}\,Zn\,SO_4 . a\,H_2O = \right.$$

$$\left. = \frac{a}{a-7}\,Zn\,SO_4 . 7\,H_2O \right\} \quad . \; . \; . \; . \; . \; . \quad (3)$$

In this equation a is the number of molecules of water associated

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[1]) VAN 'T HOFF-COHEN, Studien zur chemischen Dynamik (1896), S. 247 u. 260.

with one molecule of $ZnSO_4$ in the saturated solution of $ZnSO_4 . 6\ HO$ at the temperature P[1]). The value of q in equation (2) is therefore to be taken as the heat of transformation of $Zn SO_4 . 7\ H_2O$.

3. To determine a the solubility of $Zn SO_4 . 6\ H_2O$ (or $Zn SO_4 . 7\ H_2O$) at the transition temperature must be known. We shall also find that the solubilities of the two salts at other temperatures (below the transition temperature) are required in order to calculate the E. M. F. of the transition-element at these temperatures. I therefore give at once the results of the determinations, which will be used in subsequent calculations.

The zinc sulphate employed was obtained from MERCK; it was quite neutral to congo-red paper. Its purity was attested by the fact that CLARK-cells set up with it gave exactly the same E.M.F. as the standards of the Physikalisch-Technische Reichsanstalt at the same temperature.

Determinations of the solubility of $Zn SO_4 . 7\ H_2O$ (the stable system below 39°) and of $Zn SO_4 . 6\ H_2O$ (the metastable system) were made in the usual way by means of the shaking apparatus of NOYES [2]). By taking special precautions which I have described elsewhere [3]) it was possible to determine the solubility of the metastable system down to — 5°.

In the following table (I) the results obtained are given, along with the figures found by CALLENDAR and BARNES [4]) for the solubility of the salt with seven molecules of water of crystallisation which agree very well with my own.

That the determinations of POGGIALE, MULDER, ROSCOE and SCHORLEMMER, ETARD and other authors are faulty is thus confirmed [5]).

The saturated solutions were evaporated in shallow platinum dishes on the water-bath. $Zn SO_4 . 1\ H_2O$ is formed, its composition remaining unchanged even after prolonged heating.

CALLENDAR and BARNES have also adopted this method. Since however they say in their paper: "They were then evaporated to dryness at 100° C., and the percentage of $Zn SO_4$ in each case was

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[1]) At the transition temperature the saturated solutions of the two salts $Zn SO_4 . 6\ H_2O$ and $Zn SO_4 . 7\ H_2O$ have the same concentration!

[2]) Zeitschrift für phys. Chemie, 9 (1892) 606.

[3]) Zeitschrift für phys. Chemie, 31 (1899). Jubelband S. 169.

[4]) Proceedings Royal Society, 62, 147.

[5]) See COMEY, A dictionnary of chemical solubilities (1896, London, Macmillan and Co.), p. 458.

calculated, *assuming* the residue to be the monohydrate", without proving that this was really the case by separate experiments I first made sure of this point.

a. Of a solution containing 57.20 grams of $ZnSO_4$ to 100 grams of water, 5 9390 grams were evaporated.

The weight of the residue after 24 hours was 2.3986 grams.

Assuming that the composition of the residue was $ZnSO_4 . 1 H_2O$ the original solution must have contained 57.20 grams $ZnSO_4$ to 100 grams of water.

After remaining seven days and nights on the water bath the $ZnSO_4 . 1 H_2O$ lost 3,8 mgrms., or $^1/_7$ pCt. of its weight.

b. Of a solution containing 65.84 grams of $ZnSO_4$ to 100 grams of water, 6.9124 grams were evaporated.

After 16 hours the residue weighed 3.0506 grams.

From this 65.84 grams $ZnSO_4$ to 100 grams water is calculated.

After remaining for eight days and nights on the water-bath the residue had lost 4 mgrms. or $^1/_7$ pCt. of its weight.

The method adopted is therefore quite trustworthy.

All the measurements were made with the temperatures rising, that is to say the salt and water were maintained for a long time at a lower temperature than that at which the solubility was to be determined. This was necessary since I had observed that the very viscid solutions readily remain in a supersaturated condition.

TABLE I.

	Solubility of $ZnSO_4 . 7 H_2O$.				Solubility of $ZnSO_4 . 6 H_2O$.			
Temp.	1st Determination.	2nd Determination.	Mean, COHEN.	CALLENDAR and BARNES.	1st Determination.	2nd Determination.	Mean, COHEN.	CALLENDAR and BARNES.
— 5°	39.33	39.27	39.30	—	47.08	—	47.08	—
0°.1	41.94	41.92	41.93	41.85	49.53	49.44	49.48	—
9°.1	47.11	47.07	47.09	46.96	—	54.20	54.20	—
15°.0	50.83	50.94	50.88	50.74	57.09	57.20	57.15	—
25°.0	57.94	57.87	57.90	57.95	63.74	—	63.74	63.74*
30°.0	—	—	—	61.92	65.80	65.84	65.82	65.65*
35°.0	66.59	66.63	66.61	66.61	67.99	—	67.99	67.91*
39°.0	70.00	70 09	70.05	70.05	—	70.08	70.08	70.0

All the figures are grams of $ZnSO_4$ in 100 grams of water.

Between — 5° and the transition point the solubility of $Zn\,SO_4 . 7\,H_2O$ is well represented by the equation:

$$L_1 = 41.80 + 0.522\,t + 0.00496\,t^2$$

whilst the equation which I have deduced from the determinations of CALLENDAR and BARNES between 39°.9 and 50°.2, viz.:

$$L_2 = 59.34 + 0.0054\,t + 0.00695\,t^2$$

holds good, according to my determinations, to 25°. The figures, marked in the table with asterisks are calculated from this expression.

From the above interpolation formulae the following table (II), which will be used subsequently, is obtained.

In it A is the number of molecules of water to one molecule of $Zn\,SO_4$ in the saturated solution of the system $Zn\,SO_4 . 7\,H_2O$, whilst a is the same quantity for the system $Zn\,SO_4 . 6\,H_2O$.

TABLE II.

Temperature	A	a
39°.0	12.79	12.79
35°.0	13.54	13.18
30°.0	14.47	13.65
25°.0	15.46	14.16
15°.0	17.65	15.67
9°.1	19.08	16.53
0°.1	21.43	18.11

4. The calculation of $\frac{dE}{dT}$ (equation 2) and also of E requires a knowledge of the value of q.

At the transition temperature, q is the heat of fusion of $Zn\,SO_4 . 7\,H_2O$. This quantity may be determined in two ways,

a. By extrapolation from THOMSEN's figures.
b. Experimentally.

a. Determination of q by extrapolation.

The change undergone by $Zn\,SO_4 . 7\,H_2O$ at 39° may be represented by equation (3) on p. 335.

According to the solubility determinations in table II, the value to *a* at 39° is 12.79.

Equation (3) therefore becomes:

$$1.1\ Zn\,SO_4 . 7\,H_2O = 0.941\ Zn\,SO_4 . 6\,H_2O + 0.162\ Zn\,SO_4 . 12.79\,H_2O.$$

According to THOMSEN [1]):

The heat of solution $Zn\,SO_4 . 7\,H_2O - Zn\,SO_4 . 400\,H_2O = -4260$ *cal.*

The heat of solution $Zn\,SO_4 . 6\,H_2O - Zn\,SO_4 . 400\,H_2O = -843$ *cal.*

Heat of dilution $Zn\,SO_4 . 20\,H_2O - Zn\,SO_4 . 200\,H_2O = +390$ *cal.*
(THOMSEN l. c. p. 37).

Heat of dilution $Zn\,SO_4 . 20\,H_2O - Zn\,SO_4 . 50\,H_2O = +318$ *cal.*

From the last figures we find by extrapolation:

Heat of dilution $Zn\,SO_4 . 12.79\,H_2O - Zn\,SO_4 . 20\,H_2O =$

$$= \frac{318}{30}(20 - 12.79) = +76.3 \ cal.$$

Therefore heat of dilution

$$Zn\,SO_4 . 12.79\,H_2O - Zn\,SO_4 . 200\,H_2O = 390 + 76.3 = +466.3 \ cal.$$

Since further, the heat of dilution

$$Zn\,SO_4 . 200\,H_2O - Zn\,SO_4 . 400\,H_2O = +10 \ cal.$$

(THOMSEN, l. c. p. 91).

we find:

Heat of dilution $Zn\,SO_4 . 12.79\,H_2O - Zn\,SO_4 . 400\,H_2O = +476$ *cal.*

The heat evolved by the change represented by equation (3) is therefore:

$$-1.1 \times 4260 + 0.941 \times 843 - 0.162 \times 476 = -3970 \ cal.$$

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[1]) Thermochemische Untersuchungen, III, 138.

The heat evolved by the fusion of one molecule of $ZnSO_4 . 7H_2O$, q, is

$$q = -\frac{3970}{1.1} = -3609 \text{ calories.}$$

b. Experimental determination of q.

To determine q, the heat of solution of $ZnSO_4 . 7H_2O$ in 393 mol. H_2O (final concentration therefore $ZnSO_4 . 400 H_2O$) was first determined just below 39°, and then the heat of solution of the system which is formed from $ZnSO_4 . 7H_2O$ above 39° in the same quantity of water. The difference between these quantities of heat is the value of q required.

In order to keep the water in the calorimeter at 39° it was surrounded with a metallic mantle with double walls which in its turn was wrapped in felt. Water at about 60° was poured into this mantle.

The $ZnSO_4 . 7H_2O$ was weighed out in thin walled flasks which were then sealed up and kept for some days in a thermostat at 39°.0. From this they were transferred immediately to the calorimeter. When the heat of solution of the system

$$(0.941\ ZnSO_4 . 6H_2O + 0.162\ ZnSO_4\ 12.79\ H_2O)$$

was to be determined the flasks, filled with $ZnSO_4 . 7H_2O$, were placed in a thermostat at 42° for 14 days and nights after which they were kept in a thermostat at 39°.1 for some days. As a control other flasks were treated in the same way for a shorter time; both evolved the same amount of heat when dissolved, a proof that the desired condition had been attained.

a. Determination of the heat of solution of $ZnSO_4 . 7H_2O$ — $ZnSO_4 . 400H_2O$ at 39°.

$ZnSO_4 . 7H_2O$ used = 20.333 gr.
Water value of calorimeter etc. = 530 gr.

$$t_1 = 13.699$$
$$t_2 = 13.120 \qquad \Delta t = -0.579.$$

$$\text{Heat of solution} = \frac{287.44}{20.333} \times 530 \times -0.579 \times 0,970 = -4219 \text{ cal.}$$

The specific heat of the final solution was 0.970.

The second determination gave — 4212 cal.
As the mean of the two experiments we will take
— 4215 cal. (at 39°)
whilst THOMSEN gives — 4260 cal. (at 18°)

β. Determination of the heat of solution of the system formed from $Zn\,SO_4 . 7\,H_2O$ — $Zn\,SO_4 . 400\,H_2O$ (at 39°).

$Zn\,SO_4 . 7\,H_2O$ used $= 20.366$ gr.
Water value of calorimeter etc. $= 530$ gr.

$$t_1 = 16.301$$
$$t_2 = 16.232 \qquad \Delta t = -0.069$$

$$\text{Heat of solution} = \frac{287.44}{20.366} \times 530 \times -0.069 \times 0.970 = -500\ cal.$$

A second determination gave — 516 cal.
As mean we will take — 508 cal.

From the determinations described under α and β that heat of fusion of $Zn\,SO_4 . 7\,H_2O$ is therefore —3752 cal. (39°), whilst from THOMSEN's figures we obtained, by extrapolation, —3609 cal. (18°).

The agreement is satisfactory when it is considered that similar and even greater differences exist between the direct determinations of the heat of solution of simple substances made by BERTHELOT and THOMSEN, the cause of which it is not easy to conceive [1]).

As the mean value of q we will take — 3680 cal.

5. Introducing the values found into the equation

$$\frac{dE}{dT} = -\frac{q}{P}$$

and expressing them in electrical units, we find;

$$\left(\frac{dE}{dT}\right)_{39^\circ} = -\frac{3680}{23.09}\,\frac{1}{312} = -0.51\ Millivolts.$$

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[1]) As one of the many examples which might be advanced in support of this, I take here the heat of solution of $Pb\,(NO_3)_2$ which is, according to BERTHELOT, — 4.1 K., according to THOMSEN, — 3.8 K.

The following table of the E. M. F.'s of CLARK-cells containing solid $ZnSO_4 . 7 H_2O$ or $ZnSO_4 . 6 H_2O$ is given by JAEGER [1]) in his memoir. In the last column I have added the E. M. F.'s of our transition element.

TABLE III.

Temperature.	E.M.F. in millivolts. $ZnSO_4 . 7H_2O$	E.M.F. in millivolts. $ZnSO_4 . 6H_2O$	E.M.F. Transition cell in millivolts.
0°	1449	1434	15
10°	1439	1427	12
20°	1427	1418	9
30°	1414	1409	5
39°	1400	1400	0

From these figures the temperature coefficient is

$$\left(\frac{dE}{dT}\right)_{39^\circ} = -\frac{5}{9} = -0{,}55 \text{ millivolt,}$$

whilst the thermodynamic calculation gave — 0,51 millivolt; the agreement is, thus, very satisfactory.

In a subsequent paper I shall show that the E. M. E. of our transition cell at other temperatures may be calculated by thermodynamics.

Amsterdam, University Chemical Laboratory.
December 1899.

Chemistry. — "*On the nitration of dimethylaniline dissolved in concentrated sulphuric acid*". By Dr. P. VAN ROMBURGH. (Communicated by Prof. A. P. N. FRANCHIMONT.)

Some years ago [2]) I had the honour of communicating to the Academy the results of an investigation of two new dinitro-derivatives of dimethylaniline obtained by dissolving this base (1 mol.) in

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[1]) WIEDEMANN'S Annalen 63 (1897), p. 356.

[2]) Zittingsverslag 23 Februari 1895.

twenty times its weight of concentrated sulphuric acid, and allowing 2 mols. of nitric acid, also dissolved in sulphuric acid, to act on the solution so obtained at a low temperature and pouring the mixture onto ice. Different observations made during the often repeated nitrations led me to doubt whether the dinitration really took place in the concentrated sulphuric acid solution, or whether, more probably, the reaction leading to the formation of the two nitroproducts took place in the mixture of acids when diluted with ice water. Further investigation of the course of the reaction actually brought to light that the nitration in concentrated sulphuric acid solution, even in presence of excess of nitric acid, does not go further than the formation of the mononitro-compound.

If a cooled mixture of 104 gr. nitric acid of 50 pCt., or 60 gr. of 86 pCt., and 300 gr. sulphuric acid be added in small quantities to a solution of 60 gr. dimethylaniline in 1 kg. of concentrated sulphuric acid, cooled to 0°, the temperature of the mixture rises at first with each addition. When half of the nitric acid has been added, however, no further rise of temperature is observed on adding the remaining half. When all the nitric acid has been added it is clear from the smell of the mixture that it contains free nitric acid. If, after half an hour, the half of the liquid is poured into $1^1/_4$ kg. of ice water (a mixture of equal parts of water and ice) the temperature at the end of the experiment is 30° C., a yellow crystalline product (the dinitro-compound melting at 176°) is obtained and after addition of soda to the filtered acid liquid the red isomeric compound (melting point 112°). If a cooled solution of 25 grams of dimethylaniline in $^1/_2$ kg. of sulphuric acid is added to the other half of the nitration liquid the rise of temperature is again clearly observable. On pouring the mass, after some time, into $2^1/_2$ litres of ice water a mixture of para-and metanitrodimethylaniline with a little of Mr. MERTENS' 1. 2. 4. dinitrodimethylaniline is obtained, such as is also produced according to GROLL [1]) when dimethylaniline dissolved in concentrated sulphuric acid is nitrated with one molecule of nitric acid.

When the nitration mixture containing one molecule of dimethylaniline and two molecules of nitric acid is poured into a mixture of ice and soda, dinitro-compounds are formed only in very small quantity or not at all.

From these experiments it may be concluded that, in the solu-

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[1]) Berl. Ber. 19. 198.

tion in concentrated sulphuric acid the nitration does not go further than the metamononitrocompound, so that the entry of the second nitro group must occur after the admixture of water.

I pointed out previously (loc. cit) that the two dinitrocompounds may also be prepared by dissolving the metanitrocompound in an excess of very dilute nitric acid.

I now found that by dissolving 1 gram of metanitrodimethylaniline in a mixture of 26 grams of sulphuric acid and 50 grams of water, cooled to 30°, and adding 0.85 grams nitric acid of 50 pCt, a paste of the yellow dinitro-compound melting at 176° is obtained whilst, by means of sodium carbonate, the red isomeric is separated from the filtrate. These relative quantities are exactly those found in the liquid obtained by pouring the nitration mixture into the quantity of water prescribed.

The small quantity of the dinitrodimethylaniline of MERTENS which is produced shows that in nitrating dimethylaniline by the method of GROLL the meta-compound is formed almost exclusively in the concentrated sulphuric acid solution and that the para-compound is most probably formed in the liquid after dilution with water by the action of unused nitric acid on dimethylaniline which has escaped nitration.

When para-nitrodimethylaniline (1 mol.) is dissolved in concentrated sulphuric acid and 1 mol. of nitric acid is added to the solution, the dinitro-compound of MERTENS is found alone after pouring the mixture into water; no nitro-group has taken up the meta position with regard to the amino-group.

Chemistry — "*On the formation of Indigo from Indigoferas and from Marsdenia tinctoria*". By Dr. P. VAN ROMBURGH. (Communicated by Prof. A. P. N. FRANCHIMONT).

The interesting communication which Prof. BEYERINCK made to the meeting of Sept. 30th last, from which it appears that the indigo yielding plants belong to two, physiologically quite distinct groups induce me to invite attention to some observations which I made some years ago during an investigation of indigo-yielding Indigoferas and of Marsdenia tinctoria which was published in the "Verslagen van 's Lands Plantentuin". I would add one remark. Owing to my other affairs I was unable to devote as much time to these researches as I could have wished and they are therefore of a more or less preliminary nature. When I found, on the occasion of a meeting with Mr. HAZEWINKEL, Director of the Indigo Experimental Station at Klaten, that our researches were tending in many ways in the same direction, I terminated mine for the time being and I am postponing the publication of various results until Mr. HAZEWINKEL shall have ended his researches, which are in many respects of importance, and published the results of them.

In the "Verslag" for 1891/2 it is stated that preliminary investigations into the preparation of indigo showed that the extraction of the leaves with water at the temperature prevailing here is not accompanied by evolution of gas during the time which in Java is considered needful to extract the constituents which yield the colouring matter from the plant viz: 6—7 hours. Later, for example in a day, this does occur. The gas evolved consists of carbon dioxyde and a gas which burns with a colourless flame, very probably hydrogen.

What compound exists in the aqueous extract of the indigoleaves is not yet made out with certainty. It had a distinctly acid reaction [1]) and shows the so called indicanreaction very beautifully when it is shaken with hydrochloric acid, chloroform and air.

The filtrate obtained after treating the extract with excess of lead acetate gives a yellow precipitate [2]) with ammonia, stated by SCHUNCK to be characteristic of indican.

Since indigowhite is said to be insoluble in acid liquids, it is not very probable that this substance is present in the aqueous extract of the indigoleaves. A dilute solution of indigowhite in lime water behaves also in many respects quite differently from the extract.

If the indigoleaves are extracted with dilute acetic acid (1 pCt.) instead of with water, the extract yields indigoblue abundantly when shaken with air, especially if ammonia is added."

According to Mr. v. LOOKEREN CAMPAGNE [3]) the liquid produced by the so called fermentation is alkaline and contains indigowhite in solution. In the "Jaarverslag van 's Lands Plantentuin" for 1893, the following is to be found:

"The solution obtained by extracting indigoleaves with water for 7 hours has again been the subject of an investigation, a few of the results of which will be indicated here. The liquid contained free

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[1]) That the extract of the indigo-leaves in acid is very easily shown by running it into a solution of potash coloured red by phenolphthaleïn. The reaction is also successful with a solution of blue litmus. (Note of 1892).

[2]) I have found, subsequently, that an extract of the leaves of *Indigofera galegoïdes*, which contains a substances resembling amygdalin, also gives a yellow coloured precipitate in which, however, the glucoside has no part.

[3]) Verslag omtrent onderzoekingen over Indigo, 1893, 16.

or very loosely combined carbon dioxide [1]) in very large quantity, which may be driven out not only by warming but also by a current of gas free from oxygen [2]).

The substance which yields indigoblue on oxidation may be extracted from the solution by means of chloroform either with or without addition of acetic acid. When the chloroform solution, which has a light greenish yellow colour, is evaporated by blowing a current of air into it, a greenish coloured residue is obtained which is partially soluble in water. The aqueous solution, which possesses a splendid fluorescence, gives indigoblue at once when shaken with air and ammonia; indigoblue is also formed by exposure to the air, and very rapidly when warmed.

An extract of the leaves of *Marsdenia tinctoria*, which is also very distinctly acid to litmus, behaves in a similar way. It has not yet been possible to obtain the substance which yields the indigoblue in a state fit for analysis, nor to prepare crystallized derivatives of it."

The fact that the indigo-yielding substance is formed from the leaves by dilute organic acids was confirmed by Messrs. VAN LOOKEREN CAMPAGNE and VAN DER VEEN in 1895 [3]); notwithstanding the insolubility in acids it is still taken for indigowhite. The solubility of the indigowhite in the extract is explained, by these investigators, by the formation of an unstable compound with substances which yield indigored and indigorubin on oxidation. The ready oxydation of the substance which is extracted by chloroform, in presence of mineral acids or of alkaline carbonates, shows, according to the same authors, that we are not dealing with indoxyl.

In 1897 I again took up my researches, and in the "Verslag" for that year the following is to be found:

"If Indigoleaves (Guatemala or Natal) or leaves of *Marsdenia tinctoria* are placed in an atmosphere of chloroform or carbondioxide they retain their green colour. If, after some time, they are brought in contact with the air, they quickly become bluish, proving that the indican in the dead leaves, which had probably escaped from the cells in the form of a solution, had been decomposed.

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[1]) If carbon dioxide is passed into a solution of indigowhite in lime water until the lime is converted into bicarbonate, the whole of the indigo is precipitated and no indigoblue can be obtained from the filtrate by means of air and ammonia. (Note of 1893.).

[2]) If the current of gas is passed through the liquid for a long time, it is well to mix it with chloroform vapour in order to render living organisms, which might give rise to carbon dioxide during the experiment, inactive.

[3]) Landwirtsch. Versuchsstationen. XLVI, 249.

The presence of a soluble enzyme, capable of decomposing the glucoside, has not so far been proved with certainty [1]).

The many attempts which have been made to separate such a soluble compound have so far given no result. On the other hand it was possible to show that the leaves contain, either a substance of this kind which is so firmly retained that it may be regarded as practically insoluble, or else they carry an insoluble substance which has the power of decomposing a solution of indican so that the substance which on oxidation yields indigo, is set free.

If indigoleaves are steeped in water for 7 hours and the sherry-coloured liquid, which contains the decompositionproduct which yields indigo on oxydation, is then displaced by distilled water containing chloroform, it is found that after several repetitions of this treatment, the displaced liquid yields no more indigo. The dried leaves are again washed several times with water containing chloroform and then placed in contact with a solution of indican [2]) to which chloroform is added; after two hours this gives, when shaken with air, an abundant separation of indigo. If the leaves are now again thoroughly washed, they are still able to decompose a sterilized solution of indican. This may be repeated several times with the same leaves, even when they have been in contact with chloroform water for more than a month.

The washed leaves may be dried over sulphuric acid without losing this property.

The property of decomposing a solution of indican in an hour is retained after extracting the fresh leaves with ether, alcohol, acetone or chloroform.

By treating the leaves, dried in this way, with dilute acids or bases or with glycerine, it has not sofar been possible to obtain

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[1]) VAN LOOKEREN CAMPAGNE, Verslag omtrent onderzoekingen over Indigo, p. 13. contented himself with a *reductio ad absurdum*, a kind of proof which is somewhat unusual in researches of this nature.

[2]) Such a solution of indican is prepared, according to ALVAREZ (C. R. 105, 287) by placing indigoleaves in small quantities at a time in boiling water. Quantitative determinations show that the decomposition of indican is very small when the time of contact is short. Mr. LOHMANN, assistent for the examination of tea, found that such a solution of indican yields indigo in contact with emulsin and air; this agrees with older, vague statements that indican is decomposed by enzymes. The specimens of emulsin in the laboratory were insoluble in water. In the mean time it appeared from a publication of the Indigo-experimental-station at Klaten that Mr. HAZEWINKEL was experimenting with soluble enzymes in the preparation of indigo, this observation was therefore not followed further. (Note of 1897).

a solution of the substance which decomposes the indican. The dried leaves of *Indigofera galegoïdes*, as also some other kinds of leaves with which experiments were made, were incapable of producing the decomposition, so that it appears to be a specific property of some indigo yielding plants. These researches, which proceed slowly, will be continued, as also those on the substance which on oxidation gives rise to indigo; this substance may also be extracted by carbon tetrachloride."

Finally in the recent "Verslag" for 1898:

"Investigations on the composition and properties of a red compound, which is obtained by evaporation of the chloroform solution of the liquid decompositionproduct of indican from Indigoferas which yields indigo, progress but little owing to lack of time. MARCHLEWSKI and RADCLIFFE (Chem. Centralbl. 1898, II, 204), consider indican to be the glucoside of indoxyi. The properties of the decomposition product which yields indigo on oxidation, and which has already been shown here not to be identical with indigowhite, agree, to some extent, well with those of indoxyl. Since Mr. HAZEWINKEL, Director of the Experimental Station at Klaten is occupied with this matter, I have not followed it further."

Physics. — Dr. E. VAN EVERDINGEN JR.: "*The* HALL-*effect and the increase of resistance of bismuth in the magnetic field at very low temperatures*" I (continued). (Communication N°. 53 (cont.) from the Physical Laboratory at Leiden, by Prof. H. KAMERLINGH ONNES.)

5. In the Proceedings of October 28, 1899, p. 221, I expressed the hope that the measurement of the HALL-effect at the boiling-point of liquid oxygen would yield a more decisive answer to the question as to whether or no this phenomenon has a maximum at low temperatures. This measurement has now been made, though as yet only for one strength of field, and the answer is certainly a decided negative, as will appear from § 7.

6. *The liquid oxygen bath.* For pouring out the liquid oxygen we used the vessel without a vacuum-wall, described and drawn in § 2 of this communication, but somewhat altered for this purpose after the manner of Prof. KAMERLINGH ONNES' cryostat [1]). Besides

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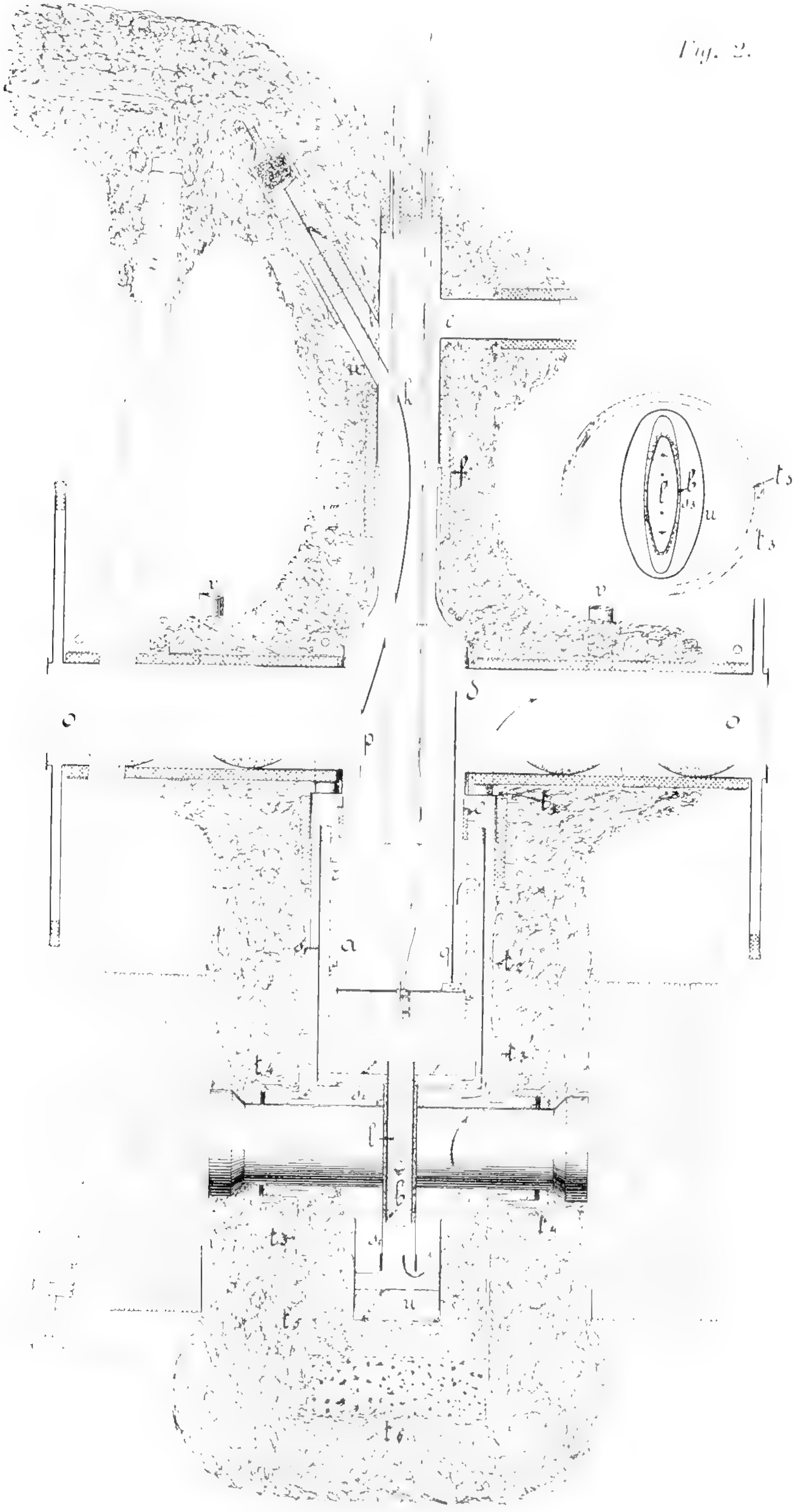
[1]) See Communication N°. 51, Proc. 30 Sept. '99. p. 126. Comm. Phys. Lab. Leiden N°. 51, p. 3.

E. VAN EVERDINGEN Jr. The HALL-effect and the increase of resistance of bismuth in the magnetic field at very low temperatures. (I) continued.

Fig. 2.



lengthening the wooden receptacle a and the glass tube d, a double jacket was added to lead off the cold vapours, which in this manner largely screen the liquid from heat. Moreover observing-glasses were used to watch the liquid streaming out.

The whole apparatus is drawn in fig. 2, whilst fig. 1 may serve to further elucidate it. The lengthened wooden receptacle a, the paper vessel b, the caoutchouc-ring c, the glass-tube d, the **T**-piece e, the caoutchouc-tube f and the plate carrier l were mentioned in § 2 of this paper. The steel capillary tube k is now introduced into the **T**-piece through the oblique side tube w, from which it is wholly insulated by means of wood and caoutchouc, the horizontal side-tube now leading towards a safety-tube immersed in mercury. The supply of liquid oxygen from the oxygen-spiral in the ethylene boiling flask [1] can be shut off by the cock [2] z, by means of a long wooden stem; before entering the capillary tube the liquid passes through a small filter. The tube k ends in front of the observing-tubes [3] o, which are fastened by means of a copper case and sealing-wax to the tube d; the jet of liquid meets a jet-catcher [4] p suspended by means of fiddle strings to d, and spreads out in a fan over this tube. In order to indicate the level of liquid in a, a float q with a stem was used, which latter ends at the level of the observing-glasses.

The cold vapours leave a through the holes r, six in number, and stream downwards in the annular space between a and b on one side and the jacket s_1—s_3 on the other side. s_1 is a circular cylinder of compressed paper, fastened to the border of a, s_2 a wooden bottom with an oval hole, into which an oval cylinder of paper s_3 has been glued; the minor axis of this is only a little wider than b, but sufficient space is left along the major axis for the vapour to escape [5]. The latter then rises in the space limited by the jacket $t_1 \dots t_6$. t_1 is a copper rim, joined to the case of the observing-tubes and fitting on the glass-cylinder t_2, to which it is fastened by means of a caoutchouc-tube and brass tightening bands. t_3 is a wooden cylinder with holes provided with flanges to admit the pole-pieces; a tight fit is obtained here by means of a leather washer, screwed on by the wooden nuts t_4. t_5 is again a glass-cylinder and t_6 a cork stopper. In order to prevent the cold vapours

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[1] Proc. 29 Dec. '94, p. 172. Comm. N°. 14, p. 17.

[2] See Communication N°. 51. Proc. 30 Sept. '99, p. 129, Comm. N°. 51, p. 9.

[3] ib. p. 130. Comm. N°. 51, p. 10.

[4] ib. p. 127, glass C. Comm. N°. 51, p. 5.

[5] See transverse section, drawn in the figure on the right hand side of e.

from flowing immediately to the bottom and to diminish the conduction of heat from below, another little vessel *u* of compressed paper with a wooden bottom has been placed under and around s_3. The space left beneath the pole pieces has been filled up with wool. In the rim t_1 six holes have been made, connected with the copper tubes *v*, four of which lead off the gaseous oxygen, whilst two have been shut with a stopper and serve as a safety arrangement.

In order to obtain the room wanted for these jackets between the coils of the electromagnet, it was necessary to considerably lengthen the pole-pieces. For weak currents this did not much diminish the strength of the field; for strong currents the loss was considerable.

During the experiment all parts of the apparatus except the observing-glasses were wrapped in wool. The receptacle *a* was completely filled with liquid oxygen, and as an additional precaution liquid was even allowed to flow out until a considerable quantity had passed through the holes *r* and had collected in *u*. The apparatus stood this well; especially the compressed paper, which appears to be a very suitable material for this work.

7. *The* HALL-*effect at the boiling point of liquid oxygen.*

For the HALL coefficient *R* in a magnetic field of 4400 C. G. S. units the value **41,4** was found. Hence the product *RM* is **182000**. Before, at a temperature of 10° C., *R* was found to be 11,0. This does not wholly agree with the value 10,15, which may be obtained by interpolation from the table given in § 3 of this paper for the field 4400 and the temperature 10° C. Recently PERROT [1]) has noticed, that the thermo-electric constants of crystalline bismuth showed irregular variations with time, which he at first was inclined to ascribe to the influence of repeated heating and cooling; this however appeared later [2]) not to be the case. In order to see whether perhaps something of that kind really happened in consequence of the strong cooling in my experiments, I repeated the determination of the HALL-coefficient *R* at 10° C. shortly after the experiment in liquid oxygen, and found 11,1. The difference from the value of *R* 11,0, determined immediately before the experiment is too small to be worth attention. As formerly I have also not noticed continuous variations with time in electrolytic bismuth, I think we

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[1]) Arch. d. Sc. phys. et nat. (4) 6 p. 105 and 229, 1898.

[2]) 〃 〃 〃 〃 〃 〃 (4) 7 p. 149, 1899.

must rather describe the difference between the values found now and formerly to an uncertainty in the knowledge of the resistance in the circuit of the HALL-current [3]), which is required for the calculation of R. For, as the variations of this resistance appeared only after some time, the resistance was not measured during the experiments of the first determinations in § 3. With the determinations now published the resistance was measured twice during the experiment and was found to be constant. Therefore we retain the value 11,0 for 10° C.

The value at — 90° C. for a magnetic field of 4400 is found by interpolation to be 17,1 and is for the same reason not quite certain.

T_{abs}	R	$\frac{C}{T}$	$C'r$
283	11,0	11,0	11,0
183	17,1	17,0	12,7
91	41,4	34,2	22,2

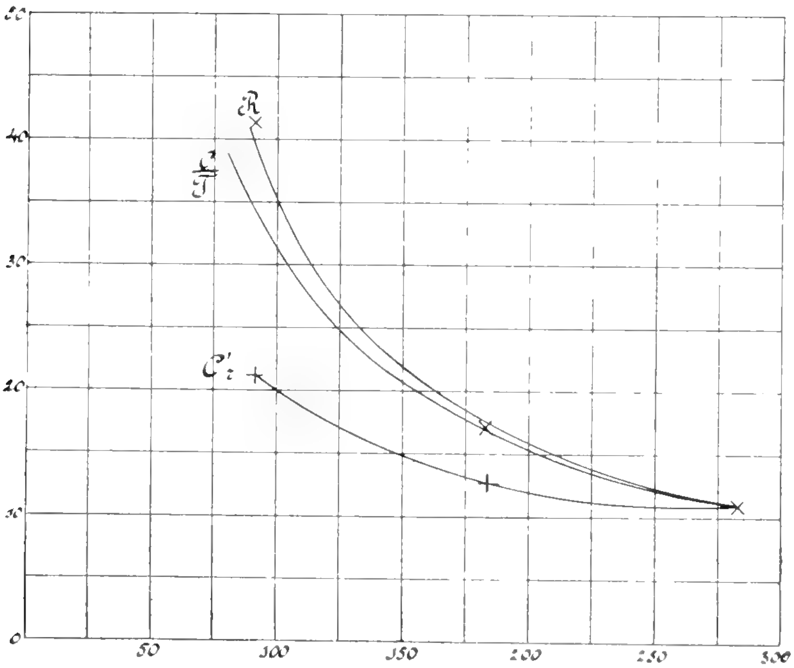

Fig. 3.

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[3]) See § 3.

This however interferes little with the value of the following, in which for the sake of comparison besides the absolute temperatures T and the corresponding values of R the values $\frac{C}{T}$ are also given, where C has been chosen so as to make the value at 10° C. equal to 11,0. Further in the values $C'r$, where r represents the resistance of electrolytic bismuth in a field of 4400 C.G.S. units, taken from observations by FLEMING and DEWAR [1]), C' is likewise chosen to make the value 11,0 at 10° C.

Fig. 3 gives a graphical representation of these numbers. It is evident that the HALL-coefficient increases much more rapidly than the resistance and a little more rapidly than $\frac{C}{T}$. Hence no evidence of an approach towards a maximum can be found.

In order to give a clearer view of the meaning of a HALL-coefficient 41,4 we will calculate the tangent of the angle through which the equipotential lines were turned in this experiment. For this it is necessary to know the resistance of the bismuth at — 182° C. in the magnetic field. As this resistance has not yet been measured for the plate, we take as a preliminary value $2{,}46.10^5$, taken from FLEMING and DEWAR. We then find for the tangent the value **0,740**.

For the sake of comparison a list is appended of the values of this tangent for some of the metals with the largest HALL-coefficients, all of them for a magnetic field of 4400.

Bismuth	— 0,740
Nickel	— 0,083
Antimony	+ 0,021
Tellurium	+ 0,017
Iron	+ 0,004

As it may safely be assumed, that the HALL phenomenon has never been observed in a field of greater intensity, higher than 20.000 C. G. S. units, it appears that the value 0,740 is the largest ever obtained.

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[1]) Proc. Roy. Soc. 60 p. 73, 1896.

(January 24, 1900.)

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday January 27, 1900.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 27 Januari 1900 Dl. VIII).

CONTENTS: "The determination of the Apex of the Solar motion". By Prof. J. C. KAPTEYN, p. 353. — "On twisted quintics of genus unity". By Prof. JAN DE VRIES, p. 374. — "The cooling of a current of gas by sudden change of pressure". By Prof. J. D. VAN DER WAALS, p. 379. — "The direct deduction of the capillary constant σ as a surface tension". By H. HULSHOF (Communicated by Prof. J. D. VAN DER WAALS), p. 389. — "Determination of the latitude of Ambriz and of San Salvador (Portuguese West-Africa)". By C. SANDERS (Communicated by Dr. E. F. VAN DE SANDE BAKHUYZEN), p. 398. — "Methods and Apparatus used in the Cryogenic Laboratory. II. Mercury pump for compressing pure and costly gases under high pressure". By Prof. H. KAMERLINGH ONNES, p. 406. — "Lipolytic ferment in human ascitic fluid". By Dr. H. J. HAMBURGER, p. 406. — "The action of strong nitric acid upon the three isomeric chloro-benzoic acids and some of their derivatives. By Dr. P. J. MONTAGNE (Communicated by Prof. A. P. N. FRANCHIMONT), p. 407. — "The alleged identity of red and yellow mercure oxide" (II). By Dr. ERNST COHEN (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM), p. 407. — "Determination of the decrease of the vapour tension of solutions by determining the rise of the boiling point". By Dr. A. SMITS (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM), p. 407. — Erratum, p. 408.

The following papers were read:

Astronomy. — "*The determination of the Apex of the Solar motion.*" By Prof. J. C. KAPTEYN.

1. *Fundamental hypothesis.*

It is usually taken for granted that the best known determinations of the direction of the solar motion in space are based on the following hypothesis:

Hypothesis H. The peculiar proper motions of the fixed stars have no preference for any particular direction.

In reality however this is not quite correct; at a closer investigation we find that neither the method of **Airy**, nor that of **Argelander** is entirely based on this hypothesis, and yet these two were almost without exception used in all modern determinations of the position of the Apex.

Finding the distribution of the proper motions in regard to the great circles drawn through the position of the Apex as determined by these methods unsatisfactory, **Kobold** concludes that we must drop the hypothesis H, as not agreeing sufficiently with the facts. Such a conclusion however cannot be accepted until at least one computation has been made, which is completely founded on this hypothesis.

This has given rise to the following investigation, in which I have tried to develop a method satisfying this condition. After having explained the method I shall give a short criticism of those of **Airy**, **Argelander** and **Kobold**, which criticism however lays no claim whatever to being complete.

2. *Meaning of the letters and simple relations.*

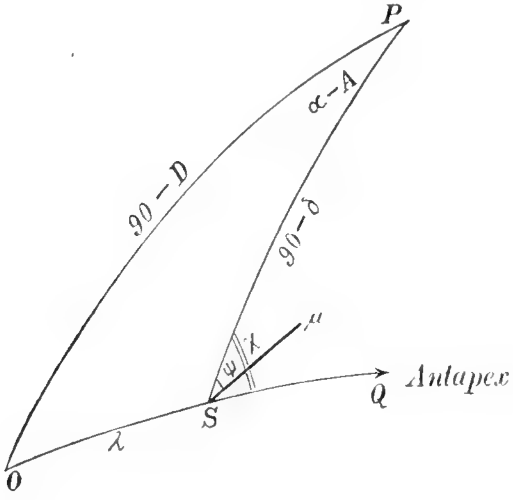

Fig. 1.

O the Apex;
P the Pole of the Equator;
S an arbitrary Star;
A and D the coordinates of the Apex O;
α and δ the coordinates of the Star S;
$\lambda = OS =$ the angular distance of the Star to the Apex;
$\mu = S\mu$ the observed motion of S;
SQ the direction towards the Antapex = direction of the parallactic proper motion;

$\psi = PS\mu =$ angle made by the total proper motion μ with the declination circle;
$\chi = PSQ =$ angle made by parallactic proper motion with the declination circle;
$\upsilon =$ component of total proper motion in direction SQ;
$\tau =$ component at right angles to the former (sign same as that of $\sin(\chi-\psi)$);
(1) $p = \chi-\psi = \mu SQ =$ angle made by μ with the parallactic proper motion;
$h =$ linear motion of the solar system in space;
$\varrho =$ distance of the star to the solar system.

We have:

(2) $\frac{h}{\varrho} \sin\lambda =$ parallactic proper motion of star S;

Moreover let:

ν (fig. 2) $=$ peculiar proper motion of S;
α' the angle made by this peculiar proper motion with the parallactic.

We then have the following relations:

$$\upsilon = \mu\cos(\chi-\psi) = \mu\cos p \tag{3}$$

$$\tau = \mu\sin(\chi-\psi) = \mu\sin p \tag{4}$$

$$\left.\begin{aligned} \frac{\partial\upsilon}{\partial A} &= -\tau\frac{\partial\chi}{\partial A} \\ \frac{\partial\upsilon}{\partial D} &= -\tau\frac{\partial\chi}{\partial D} \end{aligned}\right\} \tag{5}$$

$$\left.\begin{aligned} \frac{\partial\tau}{\partial A} &= \upsilon\frac{\partial\chi}{\partial A} \\ \frac{\partial\tau}{\partial D} &= \nu\frac{\partial\chi}{\partial D} \end{aligned}\right\} \tag{6}$$

3. *Stars in a very limited part of the sky.* First we consider only a group of stars lying so close together that we can practically assume that they are all at the same point of the sky.

We have to express that these stars satisfy the hypothesis *II*.

The very first condition, the one which I shall here use exclusively, resulting from this hypothesis is this, that the sum of the projections of the peculiar proper motions on any direction is equal to *zero*.

This can also be expressed as follows: the resultant of the peculiar proper motions must be equal to *zero*.

If we project the proper motion ν (fig. 2) on

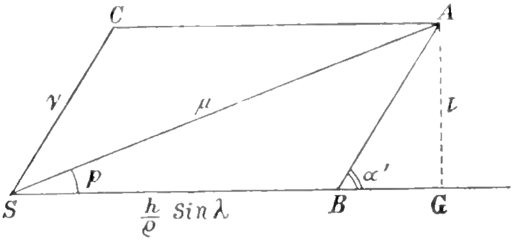

Fig. 2.

the direction SG to the Antapex and at right angles to it, this condition is expressed by the equations:

$$(7) \quad \Sigma\, \nu \cos \alpha' = 0 \qquad \Sigma\, \nu \sin \alpha' = 0\ .$$

Now along with the peculiar proper motion each star has a parallactic motion $\frac{h}{\varrho} \sin \lambda$, in the direction of SG to the Antapex. Consequently the entire proper motion μ of each star has for components

$$v = \nu \cos \alpha' + \frac{h}{\varrho} \sin \lambda \qquad \tau = \nu \sin \alpha'$$

so that if we take the sum for all the stars of the group we obtain, according to the conditions (7).

$$(8) \quad \Sigma\, v = \sin \lambda\, \Sigma \frac{h}{\varrho} \qquad \Sigma\, \tau = 0.$$

The resultant of all the total proper motions μ is directed along SG, from which we conclude at once that the sum of the projections of the motions μ on this direction is greater than on any other. If therefore the direction in which the Antapex is situated as seen from the group of stars under consideration is unknown, it can be derived from the observed proper motions by the fact that for this direction

$$(9) \quad \Sigma\, v \text{ must be maximum.}$$

It is easy to see that for a group of stars as that here considered, this condition is equivalent to the second condition of (8)

$$(10) \quad \Sigma\, \tau = 0$$

This latter however is not so easily extended to all parts of the sky.

4. *Influence of the different distances of the stars.* For a group of stars at one point of the sky it is easy to derive from condition (9) or (10) the direction to the Antapex. We can arrive at a result however, at least theoretically more accurate, by modifying that condition (without throwing up the principle).

It is easy to see at once that if we have stars of greatly differing distances to the sun, the stars whose distance is very large (and whose proper motion is therefore as a rule very small) will influence the result much less than stars at a smaller distance (and with as a rule greater proper motion).

If we start from the principle that one and the same irregularity in the distribution of the linear, peculiar proper motions must have the same effect on the accuracy of the direction to the Antapex for stars at a greater distance and for those at a smaller distance, it is easy to show that not the condition (9) but

$$(11) \quad \Sigma\, \rho\, v \text{ maximum.}$$

must be satisfied.

This one would certainly be preferable to (9), if the distances of the stars were known. This being however the case for so very few objects we are forced to adhere to the theoretically less valuable condition (9).

Fortunately however the objection, arising from the predominating influence of the stars nearest to the sun, may be met to a great extent.

5. *Grouping according to amount of proper motion.*

This may be done by grouping the stars into classes included between pretty narrow, determined limits of the proper motion. The separate results for these groups will finally be combined into a single one, taking due account of their probable errors. We will first have to show however that for such groups of stars the condition (9) is still satisfied, for from considerations as were given in Astr. Nachr. N⁰. 3487 Page 100 etc. (and which for the sake of brevity we must omit here) follows, that, for groups as are meant here, the distribution of the peculiar proper motions will *certainly no longer satisfy Hypothesis II.*

This is easily done. For it is seen at once that, whereas the former of the conditions (7) ceases in general to be satisfied by such groups, the condition

$$\Sigma\, \nu \sin \alpha' = 0$$

will still hold. We immediately conclude to this from reasons of symmetry. Now as $\nu \sin \alpha' = \tau$, we shall also still have $\Sigma\, \tau = 0$ and the condition (9) will be satisfied which is equivalent to it.

Consequently there can be no objection to the grouping in classes of determined proper motions. With this the only advantage which condition (11) might have over (9) disappears in a great measure. In what follows we shall therefore entirely neglect the conditions (11).

6. *Stars scattered about the whole sky or any considerable part of it.*

So every region of the sky gives a condition of the form (9). These might all be combined to *one* condition

$$(12) \quad \Sigma\, \upsilon \text{ maximum}$$

where the sum is to be extended to the stars available in all parts of the sky. In that way however not the most *accurate* determination of the position of the Apex will be obtained.

To arrive at a more advantageous combination the following problem is to be solved:

Given that for the various parts of the sky the accidental deviations from Hypothesis *II* are equal, to combine the conditions (12), which hold for the separate zones of constant λ, in such a way that the effect of those deviations on the coordinates of the Apex which have to be determined, be a minimum.

The solution of this problem which gives rise to no particular difficulties, shows that the $\Sigma\, \upsilon$ of each region must be multiplied by its corresponding value of $\sin \lambda_0$ before they are combined into a single sum.

Consequently for the whole sky we shall *not* have to satisfy the condition (12), but

$$(\mathrm{I}) \quad \Sigma\, \upsilon \sin \lambda_0 \text{ maximum.}$$

7. *Second form of the method.*

As has already been remarked the objection, that by using (I) the large proper motions exercise a very predominant influence, may be avoided by a grouping into classes of different proper motion. This can be done in still another way.

By substituting the value (3) for v in (I) it becomes

$$\Sigma \mu \cos p \sin \lambda_0 \text{ maximum.}$$

As this holds also for stars whose proper motion is included between determined limits, it also holds for stars with absolutely the same proper motion $\mu = \mu_1$. For such a group the condition becomes

$$\text{(II)} \quad \Sigma \cos p \sin \lambda_0 \text{ maximum}$$

and as each value of the proper motion leads to such a condition, it must also be satisfied by all the stars together.

The equations for the coordinates of the Apex, obtained in this way contain only the *directions* and are entirely independent of the *amount* of the proper motion.

It seems to me however that the condition (I), at least if it is applied to stars whose proper motions are included between pretty narrow limits, is preferable to (II) especially for this reason, that the former is a more direct consequence of hypothesis H on which the investigation is based.

8. *Derivation of the Apex from the condition* (I).

To determine the coordinates of the Apex in such a way that condition (I) is satisfied, the differential quotients in regard to A and D of $\Sigma v \sin \lambda_0$ must disappear. Consequently we have with the aid of (5)

$$\text{(13)} \quad \Sigma \tau \frac{\partial \chi}{\partial A} \sin \lambda_0 = 0 \qquad \Sigma \tau \frac{\partial \chi}{\partial D} \sin \lambda_0 = 0$$

which for stars at *one* point of the sky is reduced to the *single* equation $\Sigma \tau = 0$, as of course was to be expected.

Let A_0 and D_0 be approximate values of A and D and dA, dD the required corrections of these. All the quantities computed with the aid of these approximate values will be distinguished by means of an appended $_0$.

So v_0 and τ_0 will represent the projections of the proper motion μ on the great circle through the star and the approximate position of the Apex and at right angles to it.

We thus have in the equation (13)

$$\tau = \tau_0 + \left(\frac{\partial \tau}{\partial A}\right)_0 dA + \left(\frac{\partial \tau}{\partial D}\right)_0 dD = \tau_0 + v_0\left(\frac{\partial \chi}{\partial A}\right)_0 dA + v_0\left(\frac{\partial \chi}{\partial D}\right)_0 dD$$

$$\frac{\partial \chi}{\partial A} = \left(\frac{\partial \chi}{\partial A}\right)_0 + \left(\frac{\partial^2 \chi}{\partial A^2}\right)_0 dA + \left(\frac{\partial^2 \chi}{\partial A\,\partial D}\right)_0 dD$$

Evidently these equations hold only as long as we do not approach the Apex or the Antapex within distances of the order of dA and dD where the terms of a higher order may not be neglected. It will be best therefore to exclude entirely the stars close to the approximate position of the Apex. This cannot cause any considerable loss of weight. I find e. g. that of the stars of BRADLEY only a fourteenth part have $\sin\lambda < 0.40$ and less than one eighth part have $\sin\lambda < 0.50$.

The first of the equations (13) now becomes

$$dA\,\Sigma\left\{v_0\left(\frac{\partial \chi}{\partial A}\right)_0^2 + \tau_0\left(\frac{\partial^2 \chi}{\partial A^2}\right)_0\right\}\sin\lambda_0 +$$

$$+\,dD\,\Sigma\left\{v_0\left(\frac{\partial \chi}{\partial A}\right)_0\left(\frac{\partial \chi}{\partial D}\right)_0 + \tau_0\left(\frac{\partial^2 \chi}{\partial A\partial D}\right)_0\right\}\sin\lambda_0 = -\,\Sigma\,\tau_0\left(\frac{\partial \chi}{\partial A}\right)_0\sin\lambda_0$$

The quantities τ must be in all parts of the sky as often *positive* as *negative*. According to what we have discussed this is an immediate consequence of the hypothesis H (compare form. (10)).

So $\Sigma\,\tau\left(\frac{\partial^2 \chi}{\partial A^2}\right)_0$ will already disappear for limited parts of the sky. The same holds *à fortiori* for the sum extended over the whole sky.

$\Sigma\,\tau_0\left(\frac{\partial^2 \chi}{dA^2}\right)_0$ differs from the preceding sum only in the quantities τ being computed with an approximate Apex, the coordinates of which need still the corrections dA and dD. This quantity will thus be of the order of dA and dD and may be neglected in the coefficient of dA. The same holds for all quantities containing τ_0 in the coefficients of dA and dD. So the above equation is reduced to the former of the two following ones, in which the sums are indicated with the notation used in the theory of least squares:

$$(14)\quad\left\{\begin{aligned}&\left[v_0\sin\lambda_0\left(\frac{\partial \chi}{\partial A}\right)_0^2\right]dA + \left[v_0\sin\lambda_0\left(\frac{\partial \chi}{\partial A}\right)_0\left(\frac{\partial \chi}{\partial D}\right)_0\right]dD = -\left[\tau_0\sin\lambda_0\left(\frac{\partial \chi}{\partial A}\right)_0\right]\\&\left[v_0\sin\lambda_0\left(\frac{\partial \chi}{\partial A}\right)_0\left(\frac{\partial \chi}{\partial D}\right)_0\right]dA + \left[v_0\sin\lambda_0\left(\frac{\partial \chi}{\partial D}\right)_0^2\right]dD = -\left[\tau_0\sin\lambda_0\left(\frac{\partial \chi}{\partial D}\right)_0\right]\end{aligned}\right.$$

The second of these equations is derived in quite the same way as the first.

9. *Derivation of the Apex from condition* (II).

The maximum conditions are:

$$\Sigma \sin p \sin \lambda_0 \frac{\partial \chi}{\partial A} = 0 \qquad\qquad \Sigma \sin p \sin \lambda_0 \frac{\partial \chi}{\partial D} = 0 \ ,$$

in which we put:

$$\sin p = \sin p_0 + \cos p_0 \left(\frac{\partial \chi}{\partial A}\right)_0 dA + \cos p_0 \left(\frac{\partial \chi}{\partial D}\right)_0 dD$$

$$\frac{\partial \chi}{\partial A} = \left(\frac{\partial \chi}{\partial A}\right)_0 + \left(\frac{\partial^2 \chi}{\partial A^2}\right)_0 dA + \left(\frac{\partial^2 \chi}{\partial A \, \partial D}\right) dD \ .$$

The first of the equations thus becomes:

$$dA \, \Sigma \left\{ \cos p_0 \sin \lambda_0 \left(\frac{\partial \chi}{\partial A}\right)_0^2 + \sin p_0 \sin \lambda_0 \left(\frac{\partial^2 \chi}{\partial A^2}\right)_0 \right\} +$$

$$+ \, dD \, \Sigma \left\{ \cos p_0 \sin \lambda_0 \left(\frac{\partial \chi}{\partial A}\right)_0 \left(\frac{\partial \chi}{\partial D}\right)_0 + \sin p_0 \sin \lambda_0 \left(\frac{\partial^2 \chi}{\partial A \, \partial D}\right)_0 \right\}$$

$$= - \, \Sigma \sin p_0 \sin \lambda_0 \left(\frac{\partial \chi}{\partial A}\right)_0 .$$

Here again, for quite similar reasons as in the equations of the preceding article, the terms with $\sin p_0$ in the coefficient of dA and dD may be neglected, they being of the order of dA and dD. The equation is thus reduced to the former of the two following ones (the second is found in the same way as the first):

$$(15) \left\{ \begin{array}{l} \left[\cos p_0 \sin \lambda_0 \left(\frac{\partial \chi}{\partial A}\right)_0^2\right] dA + \left[\cos p_0 \sin \lambda_0 \left(\frac{\partial \chi}{\partial A}\right)_0 \left(\frac{\partial \chi}{\partial D}\right)_0\right] dD = - \left[\sin p_0 \sin \lambda_0 \left(\frac{\partial \chi}{\partial A}\right)_0\right] \\ \left[\cos p_0 \sin \lambda_0 \left(\frac{\partial \chi}{\partial A}\right)_0 \left(\frac{\partial \chi}{\partial D}\right)_0\right] dA + \left[\cos p_0 \sin \lambda_0 \left(\frac{\partial \chi}{\partial D}\right)_0^2\right] dD = - \left[\sin p_0 \sin \lambda_0 \left(\frac{\partial \chi}{\partial D}\right)_0\right] \end{array} \right.$$

10. AIRY's *method.*

In his derivation of the position of the Apex and the amount of the linear proper motion of the sun, AIRY starts from the idea, that the peculiar proper motions having no preference for any particular directions, may be treated entirely as errors of observation.

Hence each star gives two equations of condition between h, A and D, expressing that the observed proper motions projected on two mutually perpendicular directions are equal to the projections on those same directions of the parallactic proper motions. AIRY chooses for the two directions the parallel and the declination circle.

To get a clear insight into the *character* of AIRY's solution it is preferable however to choose for these directions the direction of the star towards the Antapex and the great circle through the star at right angles to the former.

Doing this his equations of condition get the form

$$(16) \quad \tau = 0$$

and

$$(17) \quad v = \frac{h}{\varrho} \sin \lambda \ .$$

So we can say that by AIRY's method A, D and h are determined in such a way that all the equations (16) and (17) are satisfied in the best way possible. Now as AIRY and every one who has applied his method, have solved these equations by least squares, this determination comes in reality to the choosing of A, D and h in such a way that both

$$(18) \quad \Sigma\, \tau^2 \text{ minimum}$$

$$(19) \quad \Sigma \left(\frac{h}{\varrho} \sin \lambda - v\right)^2 \text{ minimum.}$$

The former of these does not contain the unknown quantity h and only leads to a determination of A and D. The second gives the three unknown quantities, so that we arrive at two independent determinations of A and D and one of h. I will here discuss the two conditions (18) and (19) separately.

11. *The condition $\Sigma\, \tau^2$ minimum.*

The minimum conditions are (with the aid of (6)):

$$(20) \quad \Sigma\, \tau\, v \frac{\partial \chi}{\partial A} = 0$$

$$(21) \quad \Sigma\, \tau\, v \frac{\partial \chi}{\partial D} = 0 \ .$$

For stars all situated at the same point of the sky, they are reduced to this one

$$(22) \quad \Sigma\, \tau\, v = 0$$

differing from the condition

$$\Sigma \tau = 0$$

which we have found as a necessary consequence of hypothesis *H*. This proves sufficiently that in reality AIRY's method (at least if his equations of condition are treated with least squares) does not agree with hypothesis *H*.

A few examples will show this still more clearly and will at the same time prove that the application of conditions (9) and (18) may lead to *very considerably* different solutions.

1st *example* (see fig. 3). In each of the two points of the celestial sphere *S* and *S'* we find two stars. The proper motions *SA* and *SB* of the two stars in *S* are equal and we will begin by assuming that their directions form an obtuse angle. The same holds for the stars in *S'*.

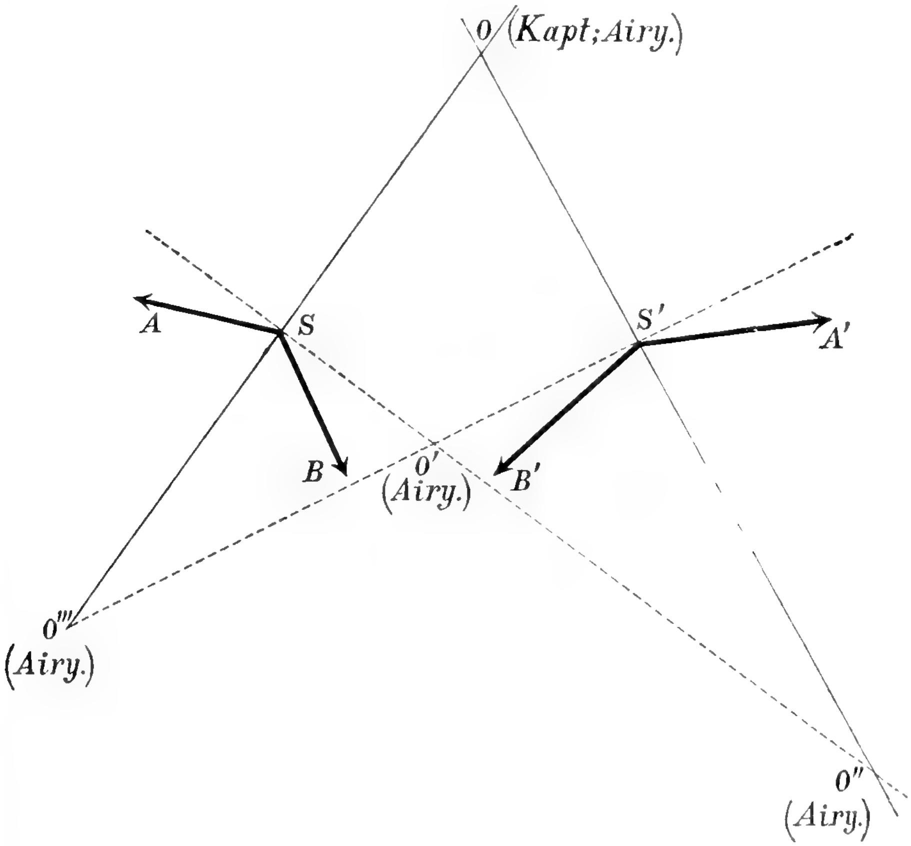

Fig. 3.

We see at once that the direction which causes the $\Sigma \tau$ [1]) of the proper motions of the stars in S to disappear is the bisectrix SO of the angle ASB. Likewise the line which in S' makes $\Sigma \tau = 0$ will be the bisectrix $S'O$ of $A'S'B'$.

From the given proper motion we conclude therefore, according to the method proposed by me, to a position O of the Apex.

On the other hand the direction which makes minimum the $\Sigma \tau^2$ of the proper motions of the stars in S is evidently the line SO' at right angles to the bisectrix; likwise in S' the line satisfying this condition is the line $S'O'$ at right angles to $S'O$.

According to the condition $\Sigma \tau^2$ min. of AIRY we conclude therefore to a position for the Apex (or Antapex) in O'.

If we leave the angle ASB unchanged, but reduce $B'S'A'$ in such a way, that the bisectrix does not change place, then in the moment that that angle passes through 90° the Apex (Antapex) according to AIRY's determination, will suddenly leap over from O' to O'', where it remains when the angle $B'S'A'$ is still more reduced. If the angle $B'S'A'$ had retained its original value ($> 90°$) and angle ASB had been reduced in the above stated way, the Apex would have leaped from O' to O'''. If then again we had reduced $A'S'B'$, at the moment of this angle passing through 90°, the Apex (Antapex) would have leaped from O''' to O.

In the nature of the problem there seems to be no reason whatever for such leaping [2]) and in our determination the Apex remains where it is notwithstanding the changes introduced.

Moreover it seems very little plausible indeed to assume for the Apex one of the positions O', O'', O'''.

The place determined according to both methods coincides evidently only when both angles are acute.

2nd example (see fig. 4). For stars in the region S let the line

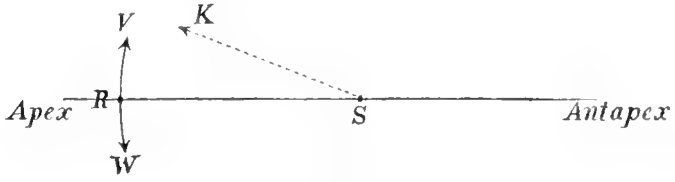

Fig. 4.

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[1]) According to the statement in § 3 the condition for stars at one point of the sky is equivalent to $\Sigma \tau = 0$.

[2]) There are still many other cases in which the condition (18) leads to discontinuous changes in the Apex for continuous changes of the data of the problem.

to the Apex be determined by a number of proper motions (not shown in the figure) which, to avoid complication, we shall suppose to be all direct. If now one more star be added, whose proper motion SK makes an acute angle with the line towards the Apex (which therefore is retrograde) we easily see that according to the condition $\Sigma\, r^2$ min. (AIRY) the line SR towards the Apex will have to be turned somewhat more into the direction RV, whilst the condition (10) demands a movement in the direction RW[1]).

12. *The condition* $\Sigma \left(\frac{h}{\varrho} \sin\lambda - v\right)^2$ *minimum.*

The equations of condition are of the form

$$(23) \qquad \frac{h}{\varrho} \sin\lambda = v$$

They contain the distances which are as a rule unknown. This is certainly the chief objection to the use of these equations. They seem therefore much more suitable to give information about mean parallaxes of definite groups of stars when once the Apex is known, than to assist in determining the position of the Apex itself.

For the calculations according to AIRY's method different ways have been followed to escape the difficulty arising from the unknown distances. One of the commonest practices (STUMPE, PORTER, etc.) is to divide the stars into groups included between narrower or wider limits of proper motion and then to assume the distance of the stars of each group to the sun to be the same.

If this be true in the mean of great numbers of stars for different parts of the sky, it might seem for a moment that we might really derive trustworty values of dA, dD and the mean value of $\frac{h}{\varrho}$ from a treatment of the equations (23). Meanwhile we must bear in mind that at all events a new hypothesis has been introduced, viz., that the mean parallax of stars with equal proper motion in different parts of the sky, is the same. If this is not the case the position obtained for the Apex too will be in general erroneous.

However there is another and decisive objection to the use of equations (23) if we have grouped the stars according to their proper

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[1]) A practical advantage of our method over AIRY's may still be mentioned here: In AIRY's method the large proper motions have a much more predominant influence on the results even than in ours: This is easy to see from the normal equations to be given in art. 15.

motions, viz: that these equations for groups of stars included between determined, arbitrary limits of the proper motion, howsoever numerous the stars may be, *are certainly in general not true*[1]).

This is evident from the argument given in Astron. Nachr. N°. 3487, pages 100—102, to which we must refer here. The error committed will certainly be *different* in general for regions with different λ even in the case that the proper motions are equal.

So not only do derivations such as those of STUMPE (Astron. Nachr. N°. 3000) and many others, give entirely illusory determinations for the secular parallax of the stars (as I already tried to show in Astr. Nachr. N°. 3487) but neither can the determination of the position of the Apex be defended. It may even be anticipated with great probability that the error must change systematically with the amount of the proper motion, so that the regular change found by STUMPE in the declination of the Apex for his various groups has nothing particularly surprising.

Other writers as i. a. L. STRUVE attribute determined parallaxes to stars of determined magnitude. The last decisive objection disappears here, but not the first. It runs as follows: we assume that at least the mean parallax of the stars of determined magnitude is everywhere in the sky the same. For the galaxy and outside it I have already tried to show, some years ago, (Verslag Kon. Akad. Jan. 1893) that this is probably *not* the case.

To sum up, according to the preceding, AIRY's method comes to the determination of the coordinates of the Apex and the linear motion of the sun in such a way that the conditions (18) and (19) are satisfied.

The first condition does not contain the distances but does not in general satisfy the conditions $\Sigma\, \tau = 0$ for stars in one and the same part of the sky, which must be considered as the principal condition derivable from the hypothesis H. The second condition contains the distances which are in general unknown. This causes the introduction of hypotheses which are more or less probable, and which may easily exercise an injurious influence on the determination of A and D. Particularly the grouping according to proper motion must be absolutely objected to in the application of AIRY's method, because implicit suppositions are introduced which are *certainly* not realized.

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[1]) It is even not permissable to exclude stars with very small proper motion.

13. *Method of* ARGELANDER.

In this method each star gives an equation of condition of the form

$$(24) \quad p = 0 \qquad (\text{weight } \sin^2 \lambda_0)$$

They are treated with least squares. So in reality A and D are determined by the condition

$$(25) \quad \Sigma\, p^2 \sin^2 \lambda_0 \text{ minimum,}$$

giving the minimum conditions

$$(26) \quad \Sigma\, p \sin^2 \lambda_0 \frac{\partial \chi}{\partial A} = 0 \qquad \Sigma\, p \sin^2 \lambda_0 \frac{\partial \chi}{\partial D} = 0.$$

For a single region of the sky the two are reduced to this *one*

$$(27) \quad \Sigma\, p = 0,$$

so that here neither the condition furnished by hypothesis II is satisfied.

The objection to the method of ARGELANDER consists chiefly in this that the retrograde proper motions have too great an influence.

Let for instance the proper motions $\mu_1\ \mu_2\ \mu_3\ \mu_4$ (belonging to stars in the same region of the sky) make with an assumed direction towards the Antapex angles of $+20°, +10°, -10°, -20°$. As long as we know only these proper motions the assumed direction towards the Antapex, both according to my method and to that of ARGELANDER, will be the most probable. If however a proper motion μ_5 is added, making with the assumed direction towards the Antapex an angle of 170°, this direction, according to ARGELANDER's method will have to be corrected by 34°, whereas according to our method that correction will be only 2°.1 in the same direction. Since long it has been remarked moreover that in ARGELANDER's method too, discontinuous changes in the place of the Apex may be caused by continuous changes of the proper motions.

The following example will prove this clearly.

In a definite region of the sky there are n stars whose proper motion is in perfectly the same direction. This common direction is assumed as the approximate direction towards the Antapex. We now add *one* star, making with that direction the angle

$$p_0 = 180 - \omega$$

where ω is a very small quantity. If this is neglected, it follows from (27) that the direction towards the Antapex has to be corrected by

$$-\frac{180^\circ}{n+1}.$$

If however for the added star we had

$$p_0 = 180 + \omega = -(180 - \omega)$$

then we should have found for that correction

$$+\frac{180}{n+1}.$$

So there is a leap of $\dfrac{360^\circ}{n+1}$.

There is again no foundation for such a leap in the nature of the problem, and it does not appear in our solution.

14. *Method of* KOBOLD *(Bessel).*

I need but say a few words of this method, as KOBOLD himself clearly states that his method is not based on hypothesis *H*.

He determines the Apex of the motion of the sun in such a way that the great circle of which the Apex is the pole, approaches as closely as possible to the pole of the proper motions of all the stars.

To satisfy this condition he makes

$$\Sigma \cos^2 Q \text{ minimum},$$

where Q represents the distance from the Apex of the pole of a proper motion. Expressed in the quantities used by us, the condition is

$$(28) \quad \Sigma \sin^2 \lambda \sin^2 p \text{ minimum}.$$

This is satisfied if we write down for each star an equation of condition

$$(29) \quad \sin \lambda \sin p = 0$$

and then solve the whole of these equations with least squares.

This method cannot be tested by the condition (10). It is namely a peculiarity of this method, that whereas, according to the other methods, from stars of one part of the sky, only a *direction* can be derived, in which the Apex must be situated, we find by KOBOLD's method a *complete* determination of the position of that point.

Its position is no other than that of the group of stars itself. In the choice of the position of the Apex each region votes as it were for itself. Every line passing through this region thus passes through the Apex too, so that at the same time the condition (10) is satisfied and it is not.

This peculiarity of the method together with this second (which exists for stars of *one* part as well as for stars of *all* parts of the sky) that for the direction of the motion of an arbitrary number of stars we may substitute a diametrically opposite motion without the slightest effect on the coordinates of the Apex, appears to me sufficient to declare the method unsuitable *for the determination of the direction of the motion of the sun.*

15. *Abridged calculation.*

It is a very common practice in the derivation of the coordinates of the Apex, to abridge the work of computation by taking the mean of the proper motions of a greater or smaller number of stars situated close together. I wish to point out that in this way the result, derived by means of the various methods, will approach in general to those which will be found by the method proposed here. So, far from having been more or less impaired by this abridged calculation, the results must have gained considerably in accuracy.

It must be borne in mind however that in this way, in all methods except in that proposed by me, the principle is sacrificed, at least in part.

The proof of what has been advanced here will be best given by writing out in full and in a similar form for the various methods, the equations of condition and the normal equations ensuing from these. I begin by giving them.

a. *Method of* AIRY (as modified).

I leave out of consideration condition (19), this being the only one dependent on the distances.

As

$$r = r_0 + \left(\frac{\partial r}{\partial A}\right)_0 dA + \left(\frac{\partial r}{\partial D}\right)_0 dD = r_0 + v_0 \left(\frac{\partial \chi}{\partial A}\right)_0 dA + v_0 \left(\frac{\partial \chi}{\partial D}\right)_0 dD$$

the equations (16) become

$$(30) \quad v_0 \left(\frac{\partial \chi}{\partial A}\right)_0 dA + v_0 \left(\frac{\partial \chi}{\partial D}\right)_0 dD = - r_0$$

which, treated with least squares, give the normal equations:

$$(31)\quad\left\{\begin{aligned}&\left[v_0^2\left(\frac{\partial\chi}{\partial A}\right)_0\right]dA+\left[v_0^2\left(\frac{\partial\chi}{\partial A}\right)_0\left(\frac{\partial\chi}{\partial D}\right)_0\right]dD=-\left[r_0\,v_0\left(\frac{\partial\chi}{\partial A}\right)_0\right]\\&\left[v_0^2\left(\frac{\partial\chi}{\partial A}\right)_0\left(\frac{\partial\chi}{\partial D}\right)_0\right]dA+\left[v_0^2\left(\frac{\partial\chi}{\partial D}\right)_0^2\right]dD=-\left[r_0\,v_0\left(\frac{\partial\chi}{\partial D}\right)_0\right]\end{aligned}\right.$$

They are of course identical with the equations (20) and (21) if in the reduction of these we treat the quantities $\frac{r_0}{v_0}$ as quantities of the order of dA and dD.

b. Method of ARGELANDER.

If we reduce to unity of weight, the equations of condition (24) may be writen

$$(32)\quad p\ sin\ \lambda_0=0$$

or by writing

$$p=p_0+\left(\frac{\partial p}{\partial A}\right)_0 dA+\left(\frac{\partial p}{\partial D}\right)_0 dD=p_0+\left(\frac{\partial\chi}{\partial A}\right)_0 dA+\left(\frac{\partial\chi}{\partial D}\right)_0 dD$$

$$(33)\quad sin\ \lambda_0\left(\frac{\partial\chi}{\partial A}\right)_0 dA+sin\ \lambda_0\left(\frac{\partial\chi}{\partial D}\right)_0 dD=-p_0\ sin\ \lambda_0\,,$$

which lead to the normal equations:

$$(34)\quad\left\{\begin{aligned}&\left[sin^2\lambda_0\left(\frac{\partial\chi}{\partial A}\right)_0^2\right]dA+\left[sin^2\lambda_0\left(\frac{\partial\chi}{\partial A}\right)_0\left(\frac{\partial\chi}{\partial D}\right)_0\right]dD=-\left[sin^2\lambda_0\left(\frac{\partial\chi}{\partial A}\right)_0 p_0\right]\\&\left[sin^2\lambda_0\left(\frac{\partial\chi}{\partial A}\right)_0\left(\frac{\partial\chi}{\partial D}\right)_0\right]dD+\left[sin^2\lambda_0\left(\frac{\partial\chi}{\partial D}\right)_0^2\right]dD=-\left[sin^2\lambda_0\left(\frac{\partial\chi}{\partial D}\right)_0 p_0\right]\end{aligned}\right.$$

which again will be identical with (26), if we treat the quantities p_0 as of the order of dA and dD.

c. Method of KOBOLD.

By introducing

$$sin\ \lambda=sin\ \lambda_0+cos\ \lambda_0\left(\frac{\partial\lambda}{\partial A}\right)_0 dA+cos\ \lambda_0\left(\frac{\partial\lambda}{\partial D}\right)_0 dD$$

$$sin\ p=sin\ p_0+cos\ p_0\left(\frac{\partial\chi}{\partial A}\right)_0 dA+cos\ p_0\left(\frac{\partial\chi}{\partial D}\right)_0 dD$$

the equations of condition (29) become

$$\left\{\cos\lambda_0\sin p_0\left(\frac{\partial\lambda}{\partial A}\right)_0+\sin\lambda_0\cos p_0\left(\frac{\partial\chi}{\partial A}\right)_0\right\}dA+\left\{\cos\lambda_0\sin p_0\left(\frac{\partial\lambda}{\partial D}\right)_0+\sin\lambda_0\cos p_0\left(\frac{\partial\chi}{\partial D}\right)_0\right\}dD=-\sin\lambda_0\sin p_0 \tag{35}$$

which give the normal equations:

$$\left\{\begin{aligned}
&\left[\left\{\cos\lambda_0\sin p_0\left(\frac{\partial\lambda}{\partial A}\right)_0+\sin\lambda_0\cos p_0\left(\frac{\partial\chi}{\partial A}\right)_0\right\}^2\right]dA+\\
&+\left[\left\{\cos\lambda_0\sin p_0\left(\frac{\partial\lambda}{\partial A}\right)_0+\sin\lambda_0\cos p_0\left(\frac{\partial\chi}{\partial A}\right)_0\right\}\left\{\cos\lambda_0\sin p_0\left(\frac{\partial\lambda}{\partial D}\right)_0+\sin\lambda_0\cos p_0\left(\frac{\partial\chi}{\partial D}\right)_0\right\}\right]dD\\
&\qquad=-\left[\left\{\cos\lambda_0\sin p_0\left(\frac{\partial\lambda}{\partial A}\right)_0+\sin\lambda_0\cos p_0\left(\frac{\partial\chi}{\partial A}\right)_0\right\}\sin\lambda_0\sin p_0\right]\\
&\left[\left\{\cos\lambda_0\sin p_0\left(\frac{\partial\lambda}{\partial A}\right)_0+\sin\lambda_0\cos p_0\left(\frac{\partial\chi}{\partial A}\right)_0\right\}\left\{\cos\lambda_0\sin p_0\left(\frac{\partial\lambda}{\partial D}\right)_0+\sin\lambda_0\cos p_0\left(\frac{\partial\chi}{\partial D}\right)_0\right\}\right]dA+\\
&\qquad+\left[\left\{\cos\lambda_0\sin p_0\left(\frac{\partial\lambda}{\partial D}\right)_0+\sin\lambda_0\cos p_0\left(\frac{\partial\chi}{\partial D}\right)_0\right\}^2\right]dD\\
&\qquad=-\left[\left\{\cos\lambda_0\sin p_0\left(\frac{\partial\lambda}{\partial D}\right)_0+\sin\lambda_0\cos p_0\left(\frac{\partial\chi}{\partial D}\right)_0\right\}\sin\lambda_0\sin p_0\right]
\end{aligned}\right. \tag{36}$$

Let us now assume, as was supposed above, that we take the mean of the proper motions of the stars situated closely together and continue working with these as if they were real proper motions. The effect of thus taking means of a considerable number of motions will of course be, that the peculiar motion, which takes place in various directions, is eliminated for the greater part, so that the mean proper motion found will, with some approximation, represent the mean parallactic motion for the region under consideration.

If we distinguish the values obtained by taking means by dashes over the letters, then we will evidently have for the various regions, with greater or smaller approximation (cf. (8)):

$$\bar{v}=\overline{\frac{h}{\rho}\sin\lambda} \qquad \bar{\tau}=0$$

and consequently

$$tg\, p=\frac{\bar{\tau}}{\bar{v}}=0$$

If first we take only zones of constant λ_0 and if farthermore we assume that the mean secular parallax $\frac{h}{\rho}$ is, with some approximation, the same for stars in various parts of the sky, we shall see at once that the effect of taking the mean for various parts of the sky in such a zone of constant λ_0, is this, that the different $\bar{v}$'s will become equal with some approximation, whilst moreover for such a zone, as indeed for the whole sky, $\bar{\tau}$ and $\bar{p}$ become *small* quantities.

If therefore we introduce into the equations (31) of AIRY:

$$(37)\quad \left\{ \begin{aligned} &\lambda = \text{constant} \\ &v_0 = \bar{v} = \text{constant} \\ &\tau_0 = \bar{\tau} \end{aligned} \right.$$

they will become

$$\bar{v}^2 \left[\overline{\left(\frac{\partial\chi}{\partial A}\right)^2}\right] dA + \bar{v}^2 \left[\overline{\left(\frac{\partial\chi}{\partial A}\right)\left(\frac{\partial\chi}{\partial D}\right)}\right] dD = -\bar{v}\left[\overline{\tau\frac{\partial\chi}{\partial A}}\right]$$

$$\bar{v}^2 \left[\overline{\frac{\partial\chi}{\partial A}\,\frac{\partial\chi}{\partial D}}\right] dA + \bar{v}^2 \left[\quad \overline{\left(\frac{\partial\chi}{\partial D}\right)} \quad\right] dD = -\bar{v}\left[\overline{\tau\frac{\partial\chi}{\partial D}}\right]$$

These equations are identically the same as those into which our equations (14) are transformed, if in these too we introduce the values (37).

So zones of the same λ will furnish approximately the same results if treated according to both methods. Hence the combination of all these partial solutions will certainly not lead to strongly deviating results.

A still closer correspondence may be expected between the results of ARGELANDER's method and the results of the second form of that proposed by us, when by taking means, all the angles are first made small.

For if we neglect quantities of the order.

$$p^2\, dA \;,\quad p^2\, dD \;,\quad p^3$$

we may write in the second member of the equations (34) $p_0 = \sin p_0$, so that those equations become, if here again we take a zone of constant λ_0,

$$\sin^2 \lambda_0 \left[\overline{\left(\frac{\partial\chi}{\partial A}\right)^2}\right] dA + \sin^2 \lambda_0 \left[\overline{\frac{\partial\chi}{\partial A}\,\frac{\partial\chi}{\partial D}}\right] dD = -\sin^2 \lambda_0 \left[\overline{\sin p\,\frac{\partial\chi}{\partial A}}\right]$$

$$\sin^2 \lambda_0 \left[\overline{\frac{\partial\chi}{\partial A}\,\frac{\partial\chi}{\partial D}}\right] dA + \sin^2 \lambda_0 \left[\overline{\left(\frac{\partial\chi}{\partial D}\right)^2}\right] dD = -\sin^2 \lambda_0 \left[\overline{\sin p\,\frac{\partial\chi}{\partial D}}\right]$$

which equations are identical with (15) if we introduce in them the same suppositions.

So, here again we find, that zones of identical λ_0 will lead to approximately the same results in the two methods. What holds for each of the zones separately, must also hold with some approximation for the final results.

For **Kobold**'s method the approximation will be somewhat less satisfactory. For here we must neglect terms of the order

$$p\,dA, \quad p\,dD, \quad p^2$$

to gain our end.

If we do this, the equations (36) will become

$$2\,sin^2\lambda_0\left[\overline{\left(\frac{\partial\chi}{\partial A}\right)^2}\right]dA + 2\,sin^2\lambda_0\left[\overline{\frac{\partial\chi}{\partial A}\,\frac{\partial\chi}{\partial D}}\right]dD = -\,2\,sin^2\lambda_0\left[\overline{sin\,p\,\frac{\partial\chi}{\partial A}}\right]$$

$$2\,sin^2\lambda_0\left[\overline{\frac{\partial\chi}{\partial A}\,\frac{\partial\chi}{\partial D}}\right]dA + 2\,sin^2\lambda_0\left[\overline{\left(\frac{\partial\chi}{\partial D}\right)^2}\right]dD = -\,2\,sin^2\lambda_0\left[\overline{sin\,p\,\frac{\partial\chi}{\partial D}}\right]$$

which are again identical with our equations (15) if we introduce in them the same suppositions. Zones of identical λ treated according to both methods giving approximately identical results, this must lead here also to pretty nearly the same final results.

The calculations of **Kobold** (Astr. Nachr. N^0. 3592) confirm this conclusion. The solution which he makes with mean proper motions is the only one which is in a somewhat tolerable agreement with what others have found, calculating with other methods but also with mean values of the proper motions.

Kobold finds $A = 262°.8$ $D = +\,16°.5$

L. **Struve** finds $A = 273°.3$ $D = +\,27°.3$

After all that has been said the conclusion is pretty obvious that what, perhaps more than anything else, must hinder us in accepting the methods used until now for the derivation of the direction of the solar motion is this: that quantities are treated as small ones, which in reality are *not* small[1]).

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[1]) From an utterance of Prof. **Newcomb** I conclude that he too ascribes the deviating result of **Kobold** to the reason here stated.

16. *Values of the differential quotients used in the preceding articles.*

The following formulae may serve for the various differential quotients used in the preceding equations.

(For the meaning of the letters see fig. 1).

$$\frac{\partial \chi}{\partial A} = -\frac{\cos D \cos O}{\sin \lambda}$$

$$\frac{\partial \chi}{\partial D} = \frac{\cos \delta \sin \chi}{\cos D \sin \lambda}$$

$$\frac{\partial \lambda}{\partial A} = -\cos \delta \sin \chi$$

$$\frac{\partial \lambda}{\partial D} = -\cos O$$

where χ, λ and O are to be computed by

$$\sin \lambda \sin \chi = \sin (\alpha - A) \cos D$$

$$\sin \lambda \cos \chi = \cos (\alpha - A) \cos D \sin \delta - \sin D \cos \delta$$

$$\sin \lambda \sin O = \sin (\alpha - A) \cos \delta$$

$$\sin \lambda \cos O = -\cos (\alpha - A) \cos \delta \sin D + \sin \delta \cos D.$$

A few observations of Prof. JAN DE VRIES and Prof. J. A. C. OUDEMANS were answered by the lecturer.

Mathematics. — "*On twisted quintics of genus unity.*" By Prof. JAN DE VRIES.

1. By central projection a twisted curve of order five and genus unity can be transformed into a plane curve of order five with five nodes. Consequently in each point of space meet *five* chords or bisecants of the twisted curve R_5.

If the centre of projection is taken on R_5 a curve of order four with two nodes is obtained. From this ensues that through each point of R_5 *two* trisecants may pass.

2. The bisecants that meet a given right line l form a surface

A, on which l is a fivefold line. Ten chords lying in every plane through l the scroll A is of order *fifteen*.

Besides the fourfold curve R_5 the scroll A contains a double curve of which we shall determine the order.

If the points A_i $(i = 1, 2, 3, 4, 5)$ lie in a plane with l then the fifteen points $B \equiv (A_i A_k\ ,\ A_l A_m)$ belong to the above mentioned curve.

In order to find how many points B are lying on l we assign the point common to l and $A_i A_k$ to the points common to l and the right lines $A_l A_m$, $A_m A_n$ and $A_n A_l$; hereby we create a correspondence (15,15) between the points of l. Two corresponding points only then coincide when a point B lies on l. In the correspondence there are still thirteen other points which differ from B agreeing with such a point; so B represents *two* coincidences. Hence l contains fifteen points B and the above mentioned double curve is of order *thirty*.

3. If l has a point S in common with R_5 then A_{15} breaks up into the quartic cone, with centre S, standing on R_5 and into a surface A_{11}, on which R_5 is a threefold curve, l remaining a fivefold line. Moreover by a very simple deduction it is shown that now the double curve is of order *eight*.

4. If l becomes a bisecant b the surface A_{15} contains two quartic cones. The remaining scroll A_7 has the fourfold line b and the double curve R_5. The double curve (B) disappears here.

By assigning each of the three points of R_5 lying with b in the same plane to the chord connecting the other two, the chords of the scroll A_7 are brought into projective relation with the points of R_5.

So any plane section of A_7 is, just as R_5, of *genus unity* and must have fourteen nodes or an equivalent set of singularities. This curve has five double points on R_5 and a fourfold point on b. Evidently the missing three double points can only be represented by a threefold point derived from a threefold generator of A_7, i.e. from the trisecant of the twisted curve.

So a bisecant will be cut only by **one** *trisecant.*

5. As b meets in each of its points of intersection with the curve two trisecants, the *trisecants* of R_5 form a *scroll* T_5 of order *five* of which R_5 is a double curve. Evidently T_5 can have no other double curve, so this surface is also of *genus unity*.

Two bisecants meet a trisecant t in each of its points whilst each plane through t contains a chord. All these bisecants form a cubic scroll Δ_3 with double director t. The single director u is evidently a unisecant of R_5. On the scroll Δ_{11} determined by u of course t is a part of the above mentioned double curve.

Each of the double points of the involution determined on u, by the generators of Δ_3 procures coinciding chords; consequently u is the section of two double tangent planes.

6. A conic Q_2 having five points in common with R_5 is not intersected by a trisecant in a point not lying on R_5, for in its points of intersection with R_5 it has ten points in common with T_5. The surface Γ formed by the conics Q_2, the planes of which pass through the line c, is intersected by each trisecant in three points; so Γ is a cubic surface.

The right line c meets five trisecants lying on Γ_3, hence also five bisecants belonging to this surface. As c is intersected by the conic Q_2 of Γ_3 in an involution, there are two conics Q_2 touching it. When c becomes a unisecant then its point S on R_5 is a double point of Γ_3. Besides c still five right lines of Γ_3 pass through S, two of which are trisecants; the remaining three must be bisecants completed to degenerated conics Q_2 by the other trisecants resting on c.

If c becomes a chord, Γ_3 has two double points, each of which supports two bisecants belonging to Γ_3 and two trisecants also lying on the surface. If finally c is a trisecant, Γ_3 becomes the above mentioned surface Δ_3.

So: *All conics Q_2 intersecting two times a given right line form a cubic surface.*

7. *The conics Q_2 passing through any given point P form a cubic surface Π_3 with double point P.*

For only one conic Q_2 passes through P and the point S on R_5, as PS is a single line on the cubic surface Γ_3 determined by PS. From this ensues that R_5 is a single curve of the surface Π_3, so that this is intersected by a trisecant in three points. And as a right line through P has in general with only one conic Q_2 two points in common, one of which is lying in P, P is a double point of Π_3.

On this surface lie the five bisecants meeting in P, moreover the five trisecants by which they are completed to conics. The quadratic cone determined by these five chords intersects Π_3 in a right line p, on which the mentioned trisecants rest; so p has no point in common with R_5. Moreover any given right line through P determining only one conic Q_2 of Π_3, the planes of the conics Q_2 on Π_3 must form a pencil; the planes of the above mentioned degenerated conic Q_2 pass through p, so p is the axis of the pencil. The remaining ten right lines of Π_3 are evidently unisecants of R_5.

8. The axis p determined by P cannot belong to a second surface Π_3, for the five trisecants resting on p determine together with p the bisecants intersecting each other in P.

If P lies on R_5, p is quite undeterminate.

The point P being taken on a trisecant t, through that point two bisecants pass forming with t conics Q_2; the axis p coincides with t, which follows as a matter of course from this, that Π_3 becomes the surface Λ_3 belonging to t.

9. If P describes the right line a_1, the locus of the axis p is a *cubic scroll* Δ_3, of which a_1 is the linear director. For if P' and P'' are the points common to a_1 and Q_2, then this conic lies on the surface Π_3' and Π_3'' belonging to P' and P''; so its plane contains the corresponding axes p' and p''.

To Δ_3 evidently belong the five trisecants resting on a_1; in the points common to R_5 and these trisecants R_5 is cut by Δ_3. They moreover meet the *double director* a_2 of Δ_3.

These trisecants lie at the same time on the scroll Δ_3' having a_2 as linear director; on this surface a_1 is the double director.

The right lines a_1 *and* a_2 *correspond mutually to one another.* If a_1 is itself an axis, each plane through this right line contains only *one* axis p differing from a_1. In that case the surface Δ_3 becomes a scroll of CAYLEY and a_2 coincides with a_1.

In the correspondence (a_1, a_2) *each axis is consequently assigned to itself.* This also relates to all trisecants, as each of these must be regarded as an axis of each of its points.

10. The five trisecants cut by a_1 and by a_2 also lie on the surface Γ_3 determined by a_1; so this contains the right line a_2 as well.

Therefore both axes p' and p'' lying with a_1 in a plane ω cut each other in the point O common to a_2 and the conic Q_2 determined by ω.

From the mutual correspondence between a_1 and a_2 we conclude that Γ_3 also contains all the conics Q_2, the planes of which pass through a_2. Five bisecants belonging to Γ_3 rest on a_2.

If according to a well known annotation we call the five trisecants consecutively b_3, b_4, b_5, b_6 and c_{12}, then the five bisecants resting on a_1 are indicated by c_{13}, c_{14}, c_{15}, c_{16} and b_{12}, and a_2 meets the bisecants c_{23}, c_{24}, c_{25}, c_{26} and b_1.

It is easy to see that the remaining ten right lines of Γ_3 viz. a_3, a_4, a_5, a_6, c_{34}, c_{35}, c_{36}, c_{45}, c_{46}, c_{56} have each *one* point in common with R_5.

11. Let P be any point of the conic Q_2 meeting a_1 in P' and P''. Now the axes p and p' must intersect each other on Q_2; so p will pass through the point O common to p' and p''.

Consequently the axes p lying in a plane ω pass through a point O of conic Q_2 determined by ω.

As O has been found to describe the line a_2 if ω revolves about a_1, O and ω are focus and focal plane in relation to a linear complex of rays of which a_1 and a_2 are conjugate lines, the axes p and the trisecants t being rays.

12. The conics Q_2 which cut R_5 in P and P' forming a cubic surface, a right line l having α points in common with R_5 meets the $(3-\alpha)$ conics Q_2 through P and P'.

So R_5 is a $(3-\alpha)$-fold curve of the surface Φ, containing the conics Q_2 which pass through P and rest on l. As a trisecant can meet none of those conics in a point not on R_5, Φ is a surface of order $3\,(3-\alpha)$.

Of the $3\,(3-\alpha)$ points common to Φ and the β-secant m $\beta\,(3-\alpha)$ lie on R_5. The remaining $(3-\alpha)\,(3-\beta)$ points of intersection determine as many conics Q_2 resting on l and on m and passing through P as well.

From this we conclude again that all the conics Q_2 cut by l and m will form a surface Ψ, on which R_5 is a $(3-\alpha)\,(3-\beta)$-fold curve. Then however Ψ must be a surface of order $3\,(3-\alpha)\,(3-\beta)$.

If we now notice that a γ-secant n is cut by Ψ in $(3-\alpha)\,(3-\beta)\,\gamma$ points lying on R_5, thus in $(3-\alpha)\,(3-\beta)\,(3-\gamma)$-points not lying on this curve, it is evident that *three right lines having respectively α, β and γ points common with R_5 determine* $(3-\alpha)\,(3-\beta)\,(3-\gamma)$ *conics Q_2 resting on these lines.*

So any three bisecants meet one conic Q_2 only.

13. Let C_2 be a conic having *no* point in common with R_5.

The surface Π_3, with its double point P on C_2, cuts this curve still in four points P'; consequently C_2 is a fourfold curve of the locus Σ of the conics Q_2, each having two points in common with C_2.

The conic Q_2 lying in the plane Φ of C_2 belongs six times to the section of Σ and Φ.

Moreover as each bisecant of R_5 lying in Φ determines a conic Q_2 of Σ, this surface is of order $4 \times 2 + 6 \times 2 + 10 = 30$.

Through the point S_k of R_5 lying in Φ ten conics Q_2 of Σ_{30}, pass, viz. the four conics determined by the chords $S_k S_l$ and the conic Q_2 to be counted six times containing all the points S_k. So R_5 is a tenfold curve.

If C_2 breaks up into two right lines l and m intersecting each other in P the locus consists of the cubic surface Π_3 belonging to P and the surface Ψ_{27} formed by the conics Q_2 resting on l and m. And now according to 12. the curve R_5 is a ninefold curve of Ψ_{27} and according to 7. a single curve on Π_3; so in accordance with what was mentioned above it is a tenfold curve of $\Sigma_{30} \equiv \Psi_{27} + \Pi_3$.

As C_2 and R_5 have α points in common, we find in a similar way that the conics Q_2 which meet C_2 in two points not situated on R_5 form a surface of order ${}^3/_2 (4-\alpha)(5-\alpha)$, where R_5 is a curve of multiplicity ${}^1/_2 (4-\alpha)(5-\alpha)$, C_2 being a $(4-\alpha)$-fold line.

14. We shall still determine the number of conics Q_2 resting on the α-conic C_2, the β-conic D_2 and the γ-conic E_2.

The surface Γ_3 of the conics Q_2, cutting R_5 in P and P', and C_2 have $(6-\alpha)$ points in common. So R_5 is a $(6-\alpha)$-fold curve of the locus of the conic Q_2, passing through P and meeting C_2; so this surface is of order $3(6-\alpha)$.

Of its sections with D_2 a number of $(6-\alpha)(6-\beta)$ are not situated on R_5, which proves that R_5 is a $(6-\alpha)(6-\beta)$-fold curve of the surface of the conics Q_2 resting on C_2 and D_2; so this latter surface is of order $3(6-\alpha)(6-\beta)$.

Consequently there are $(6-\alpha)(6-\beta)(6-\gamma)$ *conics* Q_2, *having a point in common with each of the conics* C_2, D_2, E_2.

In particular any three conics Q_2 *are cut by one conic* Q_2 *only.*

Physics. — “*The cooling of a current of gas by sudden change of pressure.*” By Prof. J. D. van der Waals.

If a gas stream under a constant high pressure is conducted through a tube, so wide that we may neglect the internal friction, and this stream is suddenly brought under a smaller pressure, either by means of a tap with a fine aperture, or, as in the experiments of Lord Kelvin and Joule by means of a porous plug, the temperature of the gas falls. For a small difference in pressure of the gas before the tap and the gas behind the tap the amount has been determined by the experiments of Kelvin and Joule. They represent the cooling $T_1 - T_2$ for air in the empiric formula:

$$T_1 - T_2 = k \frac{p_1 - p_2}{T_1^2} \, .$$

By means of the equation of state we calculate for this cooling [1]), again on the supposition that p_1 and p_2 are small:

$$T_1 - T_2 = \frac{2}{m} \, \frac{273}{c_p} \left(\frac{2\,a}{1 + \alpha\, t_1} - b \right) \left(p_1 - p_2 \right) .$$

In this formula p_1 and p_2 are expressed in atmospheres, m is the molecular weight, c_p the specific heat at a constant pressure for the gas in a rarefied state.

If in the equation of state a is a function of the temperature, and is to be represented by $a \dfrac{273}{T}$, we should find, if T_1 and T_2 do not differ much, and p_1 and p_2 are small:

$$T_1 - T_2 = \frac{2}{m} \, \frac{273}{c_p} \left[3\,a \left(\frac{273}{T_1} \right)^2 - b \right] \left(p_2 - p_1 \right) .$$

It is still doubtful, which of those two formulae better represents the observations of Kelvin and Joule. It is remarkable how different a value we find for this cooling, as for everything which relates to quantities of heat, if a is a function of the temperature. The accurate knowledge of this process has of late proved to be more necessary than before, as Linde has applied this process for obtaining very low temperatures and as in Linde's apparatus this way of expansion is made use of to obtain liquid air.

Let us represent the energy per unity of weight of the gas under the pressure p_1 by ε_1. Let the specific volume be v_1 and the temperature T_1. For the gas under the pressure p_2 we represent these quantities by ε_2, v_2, T_2. Then the process is represented by the formula:

$$\varepsilon_1 + p_1 v_1 - p_2 v_2 = \varepsilon_2 \quad . \; . \; . \; . \; . \; . \; . \quad (1)$$

or

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[1]) Die Continuität etc., IIte Auflage Seite 123.

$$\varepsilon_1 + p_1 v_1 \quad = \varepsilon_2 + p_2 v_2$$

With the symbol $\chi = \varepsilon + pv$ chosen by GIBBS, we may represent the process shortly by

$$\chi_1 = \chi_2 \ .$$

The vis viva of the progressive motion may be neglected, if the velocity of the motion is small. Moreover the section of the tube before- and after the tap may be chosen in such a way, that the velocity may be considered as invariable. We may therefore represent by ε the thermodynamic energy of a gas, being in equilibrium.

From the equation: $\left(\frac{\partial \varepsilon}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p$ we find, if we assume as equation of state: $p = \frac{RT}{v-b} - \frac{a\,f(T)}{v^2}$:

$$\varepsilon = \varphi(T) - \frac{a}{v}\left[f(T) - Tf'(T)\right] .$$

The meaning of $\varphi(T)$ we find from $c_v = \left(\frac{\partial \varepsilon}{\partial T}\right)_v$, from which follows:

$$c_v = \varphi'(T) + \frac{a}{v}\,Tf''(T) \ .$$

The meaning of $\varphi'(T)$ is therefore the value of the specific heat at $v = \infty$, which we shall represent by $c_{v=\infty}$. If we think the substance in a very rarefied state to consist of molecules, which do not change with the temperature, we may put $c_{v=\infty} = \varphi'(T) =$ constant and so $\varphi(T) = Tc_{v=\infty}$. The quantity ε is:

$$\varepsilon = Tc_{v=\infty} - \frac{a}{v}\left[f(T) - Tf'(T)\right] .$$

If we write:

$$pv = RT + RT\frac{b}{v-b} - \frac{a}{v}f(T) \ ,$$

the value of χ becomes as follows:

$$\chi = (c_{v=\infty} + R)T - \frac{a}{v}\Big[2f(T) - Tf'(T)\Big] + RT\,\frac{b}{v-b}$$

or

$$\chi = c_{p=0}\,T \quad - \quad \frac{a}{v}\Big[2f(T) - Tf'(T)\Big] + RT\frac{b}{v-b}\,.$$

Making use of this value of χ, we deduce from $\chi_1 = \chi_2$ the following formula:

$$c_p\,(T_1 - T_2) = \left\{\frac{a}{v_1}\Big[2f(T_1) - T_1 f'(T_1)\Big] - \frac{RT_1\,b}{v_1 - b}\right\} -$$

$$- \left\{\frac{a}{v_2}\Big[2f(T_2) - T_2 f'(T_2)\Big] - \frac{RT_2\,b}{v_2 - b}\right\}.$$

If we want to keep a and b at the value which they have in the equation of state, in which the pressure of one atmosphere is chosen as the unity of pressure and the volume which the unity of weight of the gas occupies under that pressure and at 0° as unity of volume, this last formula assumes the following form:

$$c_p\,(T_1 - T_2) = \frac{2}{m}\,273\left\{\frac{a}{v_1}\Big[2f(T_1) - T_1 f'(T_1)\Big] - \frac{RT_1 b}{v_1 - b}\right\} -$$

$$- \frac{2}{m}\,273\left\{\frac{a}{v_2}\Big[2f(T_2) - T_2 f'(T_2)\Big] - \frac{RT_2 b}{v_2 - b}\right\}.$$

Let us think v_2 so great that the quantities $\dfrac{a}{v_2}$ and $\dfrac{RT_2\,b}{v_2 - b}$ or $\dfrac{(1+a)(1-b)(1+\alpha t_2)\,b}{v_2 - b}$ may be neglected, then the cooling is determined by the value which $\dfrac{a}{v_1}\Big[2f(T_1) - T_1 f'(T_1\Big] - \dfrac{RT_1 b}{v_1 - b}$ possesses. If at given T_1 we make the value of v_1 pass through all the values from $v_1 = \infty$ to $v_1 = b$, and if we think T_1 chosen in such a way that:

$$a\Big[2f(T_1) - T_1 f'(T_1)\Big] > (1+a)(1-b)(1+\alpha t_1)\,b\,,$$

the value of the expression:

$$\frac{a}{v_1}\Big[2f(T_1) - T_1 f'(T_1)\Big] - \frac{RT_1 b}{v_1 - b}$$

will begin with zero; then this expression will obtain a positive value, which rises to a maximum; after which it will diminish again and after having passed through zero, it may even become negative.

It appears from this remark, that at a given value of T_1 we may give to v_1, and so also to p_1 such a value that the cooling has its maximum value; or in other words there is a most advantageous value for p_1 in LINDE's apparatus. The existence of such a most advantageous value follows of course by no means from the approximated empiric formula of Lord KELVIN and JOULE, which is generally used to explain the LINDE-process. Yet the existence of a most advantageous way of working has been observed, but it is ascribed to a quite different cause. So we read in „La liquéfaction des gaz. J. CAURO, pag. 33" about this what follows: „Comme „la production frigorifique de l'appareil dépend de la différence de „pression $p_1 - p_2$ avant et après l'écoulement et que, d'un autre „côté, le travail de compression est fonction du quotient de ces „mêmes pressions $\left(\frac{p_1}{p_2}\right)$, il est clair, que l'avantage est d'avoir une „grande différence de pression, mais en même temps un rapport „aussi faible que possible entre ces mêmes pressions."

In this phrase very great importance is attached to the quantity of heat, which is developed when the gas, returning under the pressure p_2, is again compressed to its original pressure p_1 — and this heat is in fact, considerable, and the more considerable the smaller p_2 is at given p_1. It is even greater than the heat which is annihilated when the pressure is lowered to p_2. But in the apparatus of LINDE the arrangement is such, that the developed heat is given out in quite a different part of the apparatus, from that where the cold is produced; and the gas heated by compression loses this heat before it reaches the cooling-spiral, so for instance by passing through the cooling mixture, which serves to dry the gas. And if this were not sufficient for taking away the heat which is produced by compression, it would not be difficult to find more efficacious means.

But in the quoted phrase the usual mistake has been made, against which I will warn here, viz. to put the cooling proportional to $(p_1 - p_2)$ — or to expect at any rate that the cooling will always increase with the increase of $p_1 - p_2$.

In order to find the condition which must be fulfilled that the cooling be maximum, we may consider χ_1 as function of T_1 and p_1 and χ_2 as function of T_2 and p_2. The value of T_1 we think as being given; also the value of p_2. We get from:

$$\chi_1 = \chi_2$$

$$\left(\frac{\partial \chi_1}{\partial p_1}\right)_{T_1} dp_1 = \left(\frac{\partial \chi_2}{\partial T_2}\right)_{p_2} dT_2.$$

If T_2 is to be a minimum and therefore the cooling a maximum, then $\left(\frac{\partial \chi_1}{\partial p_1}\right)_{T_1}$ and therefore also $\left(\frac{\partial \chi_1}{\partial v_1}\right)_{T_1}$ must be 0.

Therefore:

$$\left(\frac{\partial \varepsilon_1}{\partial v_1}\right)_{T_1} + \left[\frac{\partial (p_1 v_1)}{\partial v_1}\right]_{T_1} = 0$$

or

$$\frac{a}{v_1^2}\left\{2 f(T_1) - T_1 f'(T_1)\right\} = \frac{RT_1}{(v_1 - b)^2}.$$

If a is thought to be constant, this equation becomes:

$$\frac{2a}{v_1^2} = \frac{(1+a)(1-b)(1+\alpha t_1)}{(v_1-b)^2}.$$

If, however, a is taken as $a\,\frac{273}{T}$, as **Clausius** does for CO_2 we find:

$$\frac{3a}{v_1^2} = \frac{(1+a)(1-b)(1+\alpha t_1)^2}{(v_1-b)^2}.$$

In order to avoid needless calculations, I shall in what follows only examine the consequences if a is put constant.

Then we find:

$$\left(\frac{v_1}{v_1 - b}\right)^2 = \frac{2a}{(1+a)(1-b)(1+\alpha t_1)} = \frac{27}{4}\,\frac{T_\varkappa}{T_1}.$$

If we had sought the value of v, for which the value of pv is a minimum, we had obtained:

$$\left(\frac{v'}{v' - b}\right)^2 = \frac{27}{8}\,\frac{T_\varkappa}{T_1}.$$

From this appears that the value v_1, for which a maximum value is obtained, is the same as that for which pv has a minimum value at a temperature equal to half T_1.

If we had calculated the value of v_1 for which the cooling is 0, always on the supposition that $\frac{a}{v_2}$ and $\frac{b}{v_2 - b}$ may be neglected, we should have found:

$$\frac{v_1}{v_1 - b} = \frac{2a}{(1+a)(1-b)b(1+\alpha t_1)} = \frac{27}{4}\frac{T_\kappa}{T_1},$$

while we obtain for the value v_1, for which pv_1 has again the limiting value RT_1:

$$\frac{v'}{v' - b} = \frac{a}{(1+a)(1-b)b(1+\alpha t_1)} = \frac{27}{4}\frac{T_\kappa}{T_1}.$$

Here again we arrive at the result, that the value of v_1, for which the cooling $= 0$, is the same as that for which pv has again the limiting value at a temperature of $\frac{T_1}{2}$.

Through this remark we are able to conclude also to the circumstances of the discussed cooling, if we know the course of pv.

Thus we find both the minimum product of pv and the value of $pv = RT$ at $v = \infty$ if $T = \frac{27}{8} T_\kappa$ — and we find the maximum cooling and the cooling $= 0$ also if $v = \infty$ at a temperature which has twice this value. This means for the product pv that it is found greater than RT for every finite value of v — and for the cooling that it is negative for every value of v. At $T > \frac{27}{4} T_\kappa$ the consequence of the process, in which $\chi_1 = \chi_2$, will be that the gas is heated when it flows out. As for hydrogen we may put $T = 40°$, the gas will be heated at $T > 270°$, so this must have been the case in the experiment of Lord KELVIN and JOULE [1]). As the experiment was made at $t = 17°$ or $T = 290°$, only a slight increase of temperature may have been observed, if we have determined the limits of the temperature correctly. If a is considered as a function of the temperature, these limits are rendered by other ratios. But the existence of such a limit of the temperature is beyond doubt.

When T is lowered, the value of v becomes smaller, as well for the maximum cooling, as for the limit between cooling and heating.

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[1]) See also KAMERLINGH ONNES, Verslag Kon. Akad. Febr. 1895.

If we put e.g. $T = 2\,T_\varkappa$, which is the case for air that is cooled somewhat below 0° centigrade, we find for the value of v for the maximum cooling $2{,}2\,b$, and for the value of v for a cooling $= 0$ an amount $= \frac{27}{19}\,b$. For $T = T_\varkappa$ these values have decreased to $^5/_3\,b$ and $\frac{27}{23}\,b$.

By elimination of T we find for the locus of the points of maximum cooling in the p, v diagram:

$$p = \frac{a}{b}\;\frac{2\,v - 3\,b}{v^2}\;.$$

If we put $\frac{1}{v} = \varrho$ (density), we find the parabola:

$$p = \frac{a}{b}\,(2\,\varrho - 3\,b\,\varrho^2),$$

which yields $p = 0$ for $\varrho = 0$ and for $\varrho = \frac{2}{3}\,\frac{1}{b}$. The maximum value of p, which is found for $\varrho = \frac{1}{3\,b}$, is equal to $\frac{a}{3\,b^2}$ or to $9\,p_\varkappa$. For air (which we treat here for simplicity's sake as a single substance) this minimum pressure amounts to $9 \times 39 = 351$ atmospheres.

To the existence of such a parabola for the points, where pv has a minimum value, has been concluded by BELTRAMI from the observations concerning pv of AMAGAT.

For the points, for which the cooling $= 0$, we find:

$$p = \frac{a}{b}\;\frac{2\,v - b}{v^2}$$

or

$$p = \frac{a}{b}\,(2\,\varrho - b\,\varrho^2).$$

So also a parabola in the p, ϱ diagram.

By elimination of v_1 we get a relation between p_1 and T_1, which has the following form:

$$p_1 = 27\,p_\varkappa \left[1 - \sqrt{\frac{4}{27}\,\frac{T}{T_\varkappa}}\right] \left[3\sqrt{\frac{4}{27}\,\frac{T}{T_\varkappa}} - 1\right].$$

We find the maximum value of p_1 at $T = 3\,T_\varkappa$, and as has been mentioned before, it is equal to $9\,p_\varkappa$. So for air $9 \times 39 = 351$.

For $T = 2\,T_\varkappa$ we find $p_1 = 304$ atmospheres, and for
$T = T_\varkappa$ $\quad p_1 = 100$ "

The constant value which has been chosen in the apparatus of **Linde**, may be considered as an arithmetical mean of the most advantageous pressure at the beginning and that at the end of the process.

But at the same time we may conclude from the circumstance that p_1 is a function of T_1, that an apparatus, which would work theoretically perfectly, should be able to regulate the pressure p_1 according to the temperature which reigns in the inner spiral.

The numeric values of the pressure, and the limits of the temperature which have been found, will be different according to the equation of state which is used. But though we cannot warrant the absolute accuracy of the numeric values in consequence of the inaccuracies of the equation of state, yet we may prove, that from every equation of state, which properly accounts for the course of the product pv, as found experimentally, the existence of a pressure, for which the cooling is equal to 0, follows, and so also the existence of a pressure, for which the cooling has a maximum value. For as long as $p_1 v_1 < p_2 v_2$, the resulting external work will promote cooling. This influence is greatest for a pressure, at which $p_1 v_1$ has a minimum value. If $p_1 v_1$ is again equal to $p_2 v_2$, the cooling has the same value as it has in case of perfectly free expansion. But if the pressure is still higher, $p_1 v_1$ rises above $p_2 v_2$, and approaches infinitely to a limiting value which is ∞, so that every cooling which would be the immediate result of free expansion, may be neutralized by that of $p_1 v_1 - p_2 v_2$. Only if we should assume also an infinite value for the cooling caused by free expansion, the above reasoning would not be convincing. But then, nobody will assume this.

We may represent the maximum cooling in the following simple form:

$$T_1 - T_2 = \frac{2}{m}\,\frac{273}{c_p}\,\frac{2a}{b}\left(\frac{b}{v_1}\right)^2$$

or

$$T_1 - T_2 = \frac{2}{m}\,\frac{273}{c_p}\,\frac{2a}{b}\left\{1 - \sqrt{\frac{4}{27}\,\frac{T_1}{T_\varkappa}}\right\}^2$$

or

$$T_1 - T_2 = \frac{27\,T_\varkappa}{2\,m\,c_p}\left\{1 - \sqrt{\frac{4}{27}\,\frac{T_1}{T_\varkappa}}\right\}^2.$$

From this we find at $T_1 = 2\,T_\varkappa$ the value 55°.

Properly speaking we ought to subtract a certain amount from this 55°, because the opposed p_2 may not be neglected. Let us put it at $0{,}265 \times 20$. Then we may at $T_1 = 2\,T_\varkappa$ put the cooling at 50°, if the opposed pressure amounts to 20 atm. and p_1 has the most advantageous value. According to the approximating formula we should find somewhat more than 75°.

For decreasing values of T_1 the maximum value increases, as $\left\{1 - \sqrt{\frac{4}{27}\frac{T_1}{T_\varkappa}}\right\}^2$ increases with T_1.

If we write:

$$\frac{T_1 - T_2}{T_\varkappa} = \frac{27}{2\,m\,c_p}\left\{1 - \sqrt{\frac{4}{27}\frac{T_1}{T_\varkappa}}\right\}$$

it appears that if $\frac{T_1}{T_\varkappa}$ has the same value, $\frac{T_1 - T_2}{T_\varkappa}$ has also the same value for all gases for which $m\,c_p$ has the same value, and this is the case for all those whose molecules contain two atoms.

If we write:

$$\frac{m\,c_p\,(T_1 - T_2)}{T_\varkappa} = \frac{27}{2}\left\{1 - \sqrt{\frac{4}{27}\frac{T_1}{T_\varkappa}}\right\}^2$$

we conclude, that at the same value of $\frac{T_1}{T_\varkappa}$ the heat annihilated by the expansion is for all substances an equal fraction of $T_\varkappa$ of T_1, and so of the vis viva of the progressive motion.

It need scarcely be observed that if the expansion could have taken place in an adiabatic way, the cooling would have been much more considerable.

From the equation of state:

$$\left(p + \frac{a}{v^2}\right)\left(v - b\right) = RT\ ,$$

follows for the course of the isentropic line:

$$\left(p + \frac{a}{v^2}\right)\left(v - b\right)^\varkappa = C\,,$$

in which $\varkappa$ represents the value of $\left(\frac{c_p}{c_v}\right)$ at infinite rarefaction.

By elimination of p we find $T\,(v - b)^{\varkappa - 1} = C_1$.

If we take $T_1 = 2\,T_k$ and for v_1 the value for the greatest cooling according to the process $\chi_1 = \chi_2$, so $v_1 = 2{,}2\,b$, and for v_2 a value, which corresponds to $p_2 = 20$ atm., then even by this one expansion the air would have been cooled already far below the critical point. Lord Rayleigh has already pointed out, that the process of Linde might be improved by causing the expanding gas to perform more work. It remains therefore desirable to find an arrangement, by which the expansion approaches more nearly an isentropic process than is the case in the apparatus of Linde.

Physics. — Prof. J. D. van der Waals presents for the proceedings a communication of Mr. H. Hulshof at Delft, on: "*The direct deduction of the capillary constant σ as a surface-tension.*"

The amount of the capillary tension and the capillary energy, as found by Prof. van der Waals in his Théorie Thermodynamique de la capillarité, may also be determined directly. The existence of capillary tension is undoubtedly the consequence of molecular attraction. Therefore we shall have to examine the influence of molecular attraction in the capillary layer, i.e. we shall have to determine the value of the molecular pressure for an arbitrary point of the capillary layer. The equation of state gives $a\varrho^2$ for the value of the molecular pressure; the equation of state, however, comprises only those cases, in which the distribution of matter is homogeneous. As the molecular pressure is the direct consequence of the attraction, which the particles exercise on one another and is therefore determined in a point by the condition of the surroundings, it may be expected that for not homogeneous distribution of matter the molecular pressure in different directions will have different values. The existence of capillary tension is to be ascribed to the fact, that in the capillary layer the molecular pressure in the direction of the surface of the liquid is different from that in the direction normal to the surface.

When the matter is homogeneously distributed the molecular pressure per surface element do is equal to the force with which all the matter on one side of the plane in which do is situated, attracts in the direction towards this plane the material cylinder with do as base, situated on the other side of the plane. In the capillary layer we can also define the molecular pressure in the same way.

Therefore we shall determine the molecular pressure in a point A of the capillary layer:

a. in the direction normal to the surface of the liquid;

b. in the direction parallel to the surface.

a. Through A we lay a plane parallel to the surface of the liquid. The force with which the layer of a thickness du, parallel to the separating layer, at a distance u below the plane laid through A, attracts the unity of mass f, h_1 cM above this plane, is:

$$-d\,\psi\,(u+h_1),$$

on the supposition that the examined layer has the unity of density. The density in a layer parallel to the surface of the liquid is the same everywhere. We give therefore, the density as a function of the distance from the plane laid through A. If we call the normal h and take as positive direction that one turned towards the vapour phasis, so that $h=0$ is situated in the homogeneous liquid phasis, the density of the layer with a thickness du will be:

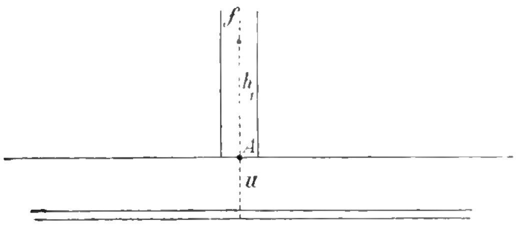

Fig. I

$$\varrho - u\frac{d\varrho}{dh} + \frac{u^2}{1.2}\frac{d^2\varrho}{dh^2} - \text{etc.}$$

where ϱ, $\frac{d\varrho}{dh}$, $\frac{d^2\varrho}{dh^2}$ have the values which these quantities have in point A. For all layers below the plane through it, the attraction is:

$$\int_{u=0}^{u=\infty} - \left(\varrho - u\frac{d\varrho}{dh} + \frac{u^2}{1.2}\frac{d^2\varrho}{dh^2}\right) d\,\psi\,(u+h_1).$$

Let us imagine in f not the unity of mass, but let us consider there a volume-element with a thickness of dh_1 and for the sake of simplicity with a base of 1 cm.^{2} instead of do. The density of this volume-element being:

$$\varrho + h_1 \frac{d\varrho}{dh} + \frac{h_1^2}{1.2}\frac{d^2\varrho}{dh^2} + \text{etc.}$$

the attraction which is to be calculated may be represented by:

$$\int_0^\infty \left(\varrho + h_1\frac{d\varrho}{dh} + \frac{h_1^2}{1.2}\frac{d^2\varrho}{dh^2}\right) dh_1 \int_{u=0}^{u=\infty} -\left(\varrho - u\frac{d\varrho}{dh} + \frac{u^2}{1.2}\frac{d^2\varrho}{dh^2}\right) d\,\psi\,(u+h_1)$$

$$\int_{u=0}^{u=\infty} -\varrho\, d\,\psi\,(u+h_1) = \varrho\,\psi\,(h_1)$$

$$\int_{u=0}^{u=\infty} u\frac{d\varrho}{dh}\, d\,\psi\,(u+h_1) = \left[u\frac{d\varrho}{dh}\,\psi\,(u+h)\right]_{u=0}^{u=\infty} - \frac{d\varrho}{dh}\int_{u=0}^{u=\infty}\psi\,(u+h_1)\,du$$

The integrated term is zero for the two limits.

$$\int_{u=0}^{u=\infty} -\frac{u^2}{1.2}\frac{d^2\varrho}{dh^2}\, d\,\psi\,(u+h_1) = \left[-\frac{u^2}{1.2}\frac{d^2\varrho}{dh^2}\,\psi\,(u+h_1)\right]_{u=0}^{u=\infty} +$$

$$+\frac{d^2\varrho}{dh^2}\int_{u=0}^{u=\infty}\psi\,(u+h_1)\,u\,du$$

The integrated term is here also zero for the two limits.
The integral becomes therefore:

$$\int_0^\infty \Big(\underset{(1)}{\varrho} + \underset{(2)}{h_1\frac{d\varrho}{dh}} + \underset{(3)}{\frac{h_1^2}{1.2}\frac{d^2\varrho}{dh^2}}\Big)\, dh_1 \Big[\underset{(1')}{\varrho\,\psi\,(h_1)} - \underset{(2')}{\frac{d\varrho}{dh}\int_{u=0}^{u=\infty}\psi\,(u+h_1)\,du} +$$

$$+ \underset{(3')}{\frac{d^2\varrho}{dh^2}\int_{u=0}^{u=\infty}\psi\,(u+h_1)\,u\,du}\Big]$$

$$\int_0^\infty \varrho\, dh_1\, \varrho\,\psi\,(h_1) = \varrho^2\int_0^\infty \psi\,(h_1)\,dh_1 = a\varrho^2 \quad . \quad . \quad . \quad . \quad (1)\ (1')$$

$$-\int_0 \varrho\, dh_1 \frac{d\varrho}{dh} \int_{u=0}^{u=\infty} \psi(u+h_1)\,du = -\varrho\frac{d\varrho}{dh}\int_0^\infty dh_1 \int_{u=0}^{u=\infty}\psi(u+h_1)\,du =$$

$$+\varrho\frac{d\varrho}{dh}\int_0^\infty dh_1\int_{u=0}^{u=\infty} d\,\pi(u+h_1) \quad . \quad , \quad (1)\ (2')$$

We put $\psi(u)\,du = -d\pi(u)$ and suppose, as is usually done that $\pi(\infty)$ is equal to zero. The latter expression may be transformed into:

$$-\varrho\frac{d\varrho}{dh}\int_0^\infty \pi(h_1)\,dh_1 = \left[-\varrho\frac{d\varrho}{dh}h_1\pi(h_1)\right]_0^\infty - \varrho\frac{d\varrho}{dh}\int_0^\infty h_1\,\psi(h_1)\,dh_1$$

The integrated term is zero for the two limits.

$$\int^\infty \varrho\,dh_1\frac{d^2\varrho}{dh^2}\int_{u=0}^{u=\infty}\psi(u+h_1)\,u\,du = -\varrho\frac{d^2\varrho}{dh^2}\int_0^\infty dh_1\int_{u=0}^{u=\infty} u\,d.\,\pi(u+h_1) =$$

$$= -\varrho\frac{d^2\varrho}{dh^2}\int_0^\infty dh_1\Big[u\,\pi(u+h_1)\Big]_{u=0}^{u=\infty} + \varrho\frac{d^2\varrho}{dh^2}\int_0^\infty dh_1\int_{u=0}^{u=\infty}\pi(u+h_1)\,du \quad \ldots \quad (1)\ (3')$$

Here too the integrated term is zero for the two limits.
We put $\pi(x)\,dx = -d\chi(x)$ and suppose as usual that $\chi(\infty)=0$. The latter expression may be transformed into:

$$-\varrho\frac{d^2\varrho}{dh^2}\int_0^\infty dh_1\int_{u=0}^{u=\infty} d.\,\chi(u+h_1) = -\varrho\frac{d^2\varrho}{dh^2}\int_0^\infty dh_1\Big[\chi(u+h_1)\Big]_{u=0}^{u=\infty} =$$

$$= \varrho\frac{d^2\varrho}{dh^2}\int_0^\infty \chi(h_1)\,dh_1 = \varrho\frac{d^2\varrho}{dh^2}\Big[h_1\,\chi(h_1)\Big]_0^\infty + \varrho\frac{d^2\varrho}{dh^2}\int_0^\infty h_1\,\pi(h_1)\,dh_1.$$

The integrated term is zero for the two limits; so the expression becomes:

$$\varrho\frac{d^2\varrho}{dh^2}\int_0^\infty \pi(h_1)\,d.\frac{h_1^2}{2} = \varrho\frac{d^2\varrho}{dh^2}\left[\pi(h_1)\frac{h_1^2}{2}\right]_0^\infty + \varrho\frac{d^2\varrho}{dh^2}\int_0^\infty\frac{h_1^2}{2}\,\psi(h_1)\,dh_1$$

The integrated form is again zero for the two limits.

$$\int_0^\infty h_1 \frac{d\varrho}{dh}\,\varrho\,\psi(h_1)\,dh_1 = \varrho\frac{d\varrho}{dh}\int_0^\infty h_1\,\psi(h_1)\,dh_1 \quad . \quad . \quad . \quad (2)\,(1')$$

$$\int_0^\infty - h_1\frac{d\varrho}{dh}\,dh_1\frac{d\varrho}{dh}\int_{u=0}^{u=\infty}\psi(u+h_1)\,du = -\left(\frac{d\varrho}{dh}\right)^2\int_0^\infty h_1\,dh_1\int_{u=0}^{u=\infty}\psi(u+h_1)\,du =$$

$$= \left(\frac{d\varrho}{dh}\right)^2\int_0^\infty h_1\,dh_1\int_{u=0}^{u=\infty} d\,.\,\pi(u+h_1) = \left(\frac{d\varrho}{dh}\right)^2\int_0^\infty h_1\,dh_1\Big[\pi(u+h_1)\Big]_{u=0}^{u=\infty} =$$

$$= -\left(\frac{d\varrho}{dh}\right)^2\int_0^\infty h_1\,dh_1\,\pi(h_1) = -\left(\frac{d\varrho}{dh}\right)^2\int_0^\infty \pi(h_1)\,d\,.\,\frac{h_1^2}{2} =$$

$$= -\left(\frac{d\varrho}{dh}\right)^2\left[\pi(h_1)\frac{h_1^2}{2}\right]_0^\infty - \left(\frac{d\varrho}{dh}\right)^2\int_0^\infty\frac{h_1^2}{2}\,\psi(h_1)\,dh_1 \quad . \quad . \quad (2)\,(2')$$

The integrated form is zero for the two limits.

$$\int_0^\infty \frac{h_1^2}{1.2}\frac{d^2\varrho}{dh^2}\,dh_1\,\varrho\,\psi(h_1) = \varrho\frac{d^2\varrho}{dh^2}\int_0^\infty\frac{h_1^2}{2}\,\psi(h_1)\,dh_1 \quad . \quad . \quad (3)\,(1')$$

$$\int_0^\infty h_1\frac{d\varrho}{dh}\,dh_1\int_{u=0}^{u=\infty}\frac{d^2\varrho}{dh^2}\,\psi(u+h_1)\,u\,du = \frac{d\varrho}{dh}\frac{d^2\varrho}{dh^2}\int_0^\infty h_1\,dh_1\int_{u=0}^{u=\infty}\psi(u+h_1)\,u\,du\,.\,(2)(3')$$

This expression has the dimension $\int_0^\infty h_1^3\,\psi(h_1)\,dh_1$ and will be neglected by us as well as (3) (2') and (3) (3').

For the molecular pressure in the direction normal to the surface of the liquid we find therefore:

$$a\varrho^2 - \varrho\frac{d\varrho}{dh}\int_0^\infty h_1\,\psi(h_1)\,dh_1 + \varrho\frac{d^2\varrho}{dh^2}\int_0^\infty\frac{h_1^2}{2}\,\psi(h_1)\,dh_1 + \varrho\frac{d\varrho}{dh}\int_0^\infty h_1\,\psi(h_1)\,dh_1 -$$

$$-\left(\frac{d\varrho}{dh}\right)^2\int_0^\infty\frac{h_1^2}{2}\,\psi(h_1)\,dh_1 + \varrho\frac{d^2\varrho}{dh^2}\int_0^\infty\frac{h_1^2}{2}\,\psi(h_1)\,dh_1$$

or

$$a\varrho^2 + \varrho\frac{d^2\varrho}{dh^2}\int_0^\infty h_1^2\,\psi(h_1)\,dh_1 - \left(\frac{d\varrho}{dh}\right)^2\int_0^\infty \frac{h_1^2}{2}\,\psi(h_1)\,dh_1$$

We put $\int_0^\infty h_1\,\psi(h_1)\,dh_1 = c_1$ and $\int_0^\infty h_1^2\,\psi(h_1)\,dh_1 = c_2$, therefore the expression for the molecular pressure is transformed into:

$$a\varrho^2 + c_2\,\varrho\frac{d^2\varrho}{dh^2} - \frac{c_2}{2}\left(\frac{d\varrho}{dh}\right)^2$$

If we add to this molecular pressure the external pressure p_1, we may equate this sum to $p+a\varrho^2$, if p represents the pressure, which belongs to a homogeneous phasis with the density ϱ.

$$p_1 + a\varrho^2 + c_2\,\varrho\frac{d^2\varrho}{dh^2} - \frac{c_2}{2}\left(\frac{d\varrho}{dh}\right)^2 = p + a\varrho^2$$

$$p_1 - p = -c_2\,\varrho\frac{d^2\varrho}{dh^2} - \frac{c_2}{2}\left(\frac{d\varrho}{dh}\right)^2$$

This relation is the same as has been deduced by Prof. VAN DER WAALS.

b. We shall now calculate the molecular pressure in the direction of the surface of the liquid. For this purpose we suppose a plane laid through A, normal to the capillary layer, and in A a cylinder with a thickness do normal to that plane. The matter in the cylinder has everywhere the same density. The unity of mass in c acts on the unity of mass in S with a force $\varphi(r)$, if r represents the distance Sc. The component of this force in the direction normal to PQ is $\varphi(r)\cos Sca$ or $\varphi(r)\frac{dr}{dz}$ if we call the direction ab the direction z.

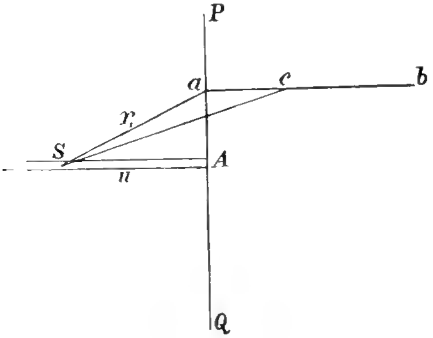

Fig. 2.

The material cylinder $ab \perp PQ$, with a thickness do' and with a unity of density acts therefore on the unity of mass in S with a force, of which the component in the direction $\perp PQ$ is:

$$do' \int\limits_{r=r_1}^{r=\infty} \varphi(r) \frac{dr}{dz}\, dz = do' \int\limits_{r_1}^{\infty} \varphi(r)\, dr = do' \zeta(r_1),$$

where we assume that $d \,.\, \zeta(r) = -\varphi(r)\, dr$ and $\zeta(\infty) = 0$.

Let us now imagine in the plane PQ a system of polar coordinates with A as origin and the line $\perp$ to the paper as fixed axis. We take as surface element $y\, dy\, d\varphi$. Let the density in A be ϱ, then in an arbitrary point of the plane PQ the density is:

$$\varrho + \frac{d\varrho}{dh}\, y \sin\varphi + \frac{1}{2} \frac{d^2\varrho}{dh^2}\, y^2 \sin^2\varphi + \ldots .$$

It is easy to see that if the terms $\varrho + \frac{d\varrho}{dh}\, y \sin\varphi$ alone existed, the attraction which the substance right of PQ would exercise on the unity of mass in the direction $\perp PQ$, would be the same as in case of a homogeneous density ϱ and therefore:

$$\varrho\, \psi(u).$$

We have still to add to this attraction:

$$\int\limits_{y=0}^{y=\infty} \int\limits_{\varphi=0}^{\varphi=2\pi} \frac{1}{2} \frac{d^2\varrho}{dh^2}\, y^2 \sin^2\varphi\, y\, dy\, d\varphi\, \zeta(r) .$$

$$\int\limits_{0}^{2\pi} \sin^2\varphi\, d\varphi = \pi$$

and so the expression becomes:

$$\frac{1}{2} \frac{d^2\varrho}{dh^2} \int\limits_{0}^{\infty} \zeta(r)\, \pi\, y^3\, dy = \frac{1}{4} \frac{d^2\varrho}{dh^2} \int\limits_{r=u}^{r=\infty} 2\pi\, \zeta(r)\, (r^2 - u^2)\, r\, dr$$

for $r^2 = u^2 + y^2$ and so $r\, dr = y\, dy$.

For this latter expression we may also write:

$$-\frac{1}{4}\,\frac{d^2\varrho}{dh^2}\int\limits_{r=u}^{r=\infty}(r^2-u^2)\,d\,\psi(r)=$$

$$=\left[-\frac{1}{4}\,\frac{d^2\varrho}{dh^2}\,(r^2-u^2)\,\psi(r)\right]_{r=u}^{r=\infty}+\frac{1}{2}\,\frac{d^2\varrho}{dh^2}\int\limits_{r=u}^{r=\infty}\psi(r)\,r\,dr\;.$$

This integrated term is zero for the two limits.
So we find for the component of the attraction ⊥ P_1Q:

$$\varrho\,\psi(u)+\frac{1}{2}\,\frac{d^2\varrho}{dh^2}\int\limits_{u}^{\infty}\psi(r)\,r\,dr$$

and therefore for the attraction of the cylinder:

$$do\int\limits_{0}^{\infty}\varrho\,du\left[\varrho\,\psi(u)+\frac{1}{2}\,\frac{d^2\varrho}{dh^2}\int\limits_{u}^{\infty}\psi(r)\,r\,dr\right]$$

and for the molecular pressure in the direction of the capillary layer:

$$\int\limits_{0}^{\infty}\varrho\,du\left[\varrho\,\psi(u)+\frac{1}{2}\,\frac{d^2\varrho}{dh^2}\int\limits_{u}^{\infty}\psi(r)\,r\,dr\right].$$

This expression becomes:

$$\varrho^2\int\limits_{0}^{\infty}\psi(u)\,du-\frac{1}{2}\,\varrho\,\frac{d^2\varrho}{dh^2}\int\limits_{0}^{\infty}du\int\limits_{u}^{\infty}r\,d\,\pi(r)\;.$$

The latter term may be transformed into:

$$-\frac{1}{2}\,\varrho\,\frac{d^2\varrho}{dh^2}\int\limits_{0}^{\infty}du\,\Big[u\,\pi(u)\Big]_{u}^{\infty}+\frac{1}{2}\,\varrho\,\frac{d^2\varrho}{dh^2}\int\limits_{0}^{\infty}du\int\limits_{u}^{\infty}\pi(r)\,dr=$$

$$=\frac{1}{2}\,\varrho\,\frac{d^2\varrho}{dh^2}\int\limits_{0}^{\infty}u\,\pi(u)\,du+\frac{1}{2}\,\varrho\,\frac{d^2\varrho}{dh^2}\int\limits_{0}^{\infty}\chi(u)\,du\qquad=$$

$$=\frac{1}{2}\,\varrho\,\frac{d^2\varrho}{dh^2}\int\limits_{0}^{\infty}u\,\pi(u)\,du+\left[\frac{1}{2}\,\varrho\,\frac{d^2\varrho}{dh^2}\,u\,\chi(u)\right]_{0}^{\infty}+\frac{1}{2}\,\varrho\,\frac{d^2\varrho}{dh^2}\int\limits_{0}^{\infty}u\,\pi(u)\,du\;.$$

The integrated term is zero for the two limits and so we keep:

$$\frac{1}{2}\varrho\frac{d^2\varrho}{dh^2}\int_0^\infty 2\,u\,\pi(u)\,du = \left[\frac{1}{2}\varrho\frac{d^2\varrho}{dh^2}u^2\,\pi(u)\right]_0^\infty + \frac{1}{2}\varrho\frac{d^2\varrho}{dh^2}\int_0^\infty u^2\,\psi(u)\,du\,.$$

Also this integrated term is zero for the two limits.

We find therefore for the molecular pressure in the direction of the capillary layer:

$$\varrho^2\int_0^\infty \psi(u)\,du + \tfrac{1}{2}\varrho\frac{d^2\varrho}{dh^2}\int_0^\infty u^2\,\psi(u)\,du$$

or

$$a\,\varrho^2 + \frac{c_2}{2}\varrho\frac{d^2\varrho}{dh^2}\,.$$

The pressure in consequence of the attraction has therefore another value in the direction of the capillary layer than in the direction normal to this layer. In the direction of the capillary layer a surplus of molecular pressure will exist in consequence of the attraction. This surplus will amount to:

$$a\,\varrho^2 + \frac{c_2}{2}\varrho\frac{d^2\varrho}{dh^2} - a\,\varrho^2 - c_2\,\varrho\frac{d^2\varrho}{dh^2} + \frac{c_2}{2}\left(\frac{d\varrho}{dh}\right)^2$$

or

$$-\frac{c_2}{2}\varrho\frac{d^2\varrho}{dh^2} + \frac{c_2}{2}\left(\frac{d\varrho}{dh}\right)^2.$$

This surplus of pressure taken over a surface ⊥ to the bordering layer whose length in the direction of the capillary layer is 1 cm. and whose breadth is equal to the thickness of the capillary layer, furnishes the value of the capillary tension:

$$\int\left\{-\frac{c_2}{2}\varrho\frac{d^2\varrho}{dh^2} + \frac{c_2}{2}\left(\frac{d\varrho}{dh}\right)^2\right\}dh\,,$$

which integral is to be taken over the whole thickness of the capillary layer.

We may make also another representation to ourselves of the capillary tension. Let us bear in mind that the thermal pressure $\vartheta = \frac{R\,T}{V-b}$ in any point has the same value in all directions. If now in consequence of the molecular attraction the molecular pressure has different values in different directions, the condition, which is thereby brought about, may be compared with a condition where the pressure has a different value in different directions. If we call the quantity which is to be considered as the pressure in the direction $\perp$ to the capillary layer, p_1 and that in the direction of the capillary layer, the following formula would hold:

$$p_1 + a\varrho^2 + c_2\varrho\frac{d^2\varrho}{dh^2} - \frac{c_2}{2}\varrho\left(\frac{d\varrho}{dh}\right)^2 = p_2 + a\varrho^2 + \frac{c_2}{2}\varrho\frac{d^2\varrho}{dh^2}$$

or

$$p_1 - p_2 = -\frac{c_2}{2}\varrho\frac{d^2\varrho}{dh^2} + \frac{c_2}{2}\left(\frac{d\varrho}{dh}\right)^2.$$

This difference in pressure taken over a surface normal to the bordering layer, with a length of 1 cm. and a breadth equal to the thickness of the capillary layer, furnishes the value of the capillary tension:

$$\int(p_1-p_2)\,dh\ .$$

The work which is to be performed for enlarging the surface with 1 cm.², the temperature remaining constant, so the capillary energy is:

$$\sigma = \int(p_1-p_2)\,dh = \int\left\{-\frac{c_2}{2}\varrho\frac{d^2\varrho}{dh^2} + \frac{c_2}{2}\left(\frac{d\varrho}{dh}\right)^2\right\}dh\ .$$

With the aid of this latter consideration we can easily show that the capillary energy is equal to the amount with which the thermodynamic potential of the bordering layer, taken over a cylinder whose section is 1 cm.² and whose height is equal to the thickness of the capillary layer, exceeds the thermodynamic potential of the same mass in the homogeneous vapour- or liquid-phasis.

Astronomy. — "*Determination of the latitude of Ambriz and of San Salvador (Portuguese West-Africa).*" By C. SANDERS (Communicated by Dr. E. F. VAN DE SANDE BAKHUYZEN).

During a several years' residence on the West coast of Africa I spent as much as I could of my leisure in making observations for determining geographical positions. Till now, besides a rather inaccurate theodolite, which did not allow to read beyond full minutes, I had at my disposal only a sextant. Recently however, after consulting with Dr. E. F. VAN DE SANDE BAKHUIJZEN who for a long time already has rendered me valuable assistance in my endeavours to obtain useful results, I have bought a portable universal instrument, by means of which I hope that my future observations will attain a higher degree of accuracy.

Yet, among the earlier observations there are already some, of which the publication may prove desirable, with a view to the great uncertainty which still exists about the exact position of several places on the South-West coast of Africa.

I will here communicate my observations for the determination of the latitude of Ambriz and of San Salvador, both in Portuguese West-Africa.

I. *Determination of the latitude of Ambriz.*

The observations were made with a sextant of **WEGENER** with vernier on which can be read 10″, and an artificial horizon; besides I used a mean time chronometer. Observations referred to the sea-horizon, together with some made by means of the small theodolite mentioned above, are not communicated, because they are far less accurate.

The errors of graduation of the sextant were determined by Dr. **KAISER** at Leiden as follows:

at 0°	0″0	at 70°	+ 22″5
10	+ 5.5	80	+ 23.5
20	+ 9.5	90	+ 24.0
30	+ 13.0	100	+ 24.5
40	+ 16.0	110	+ 24.5
50	+ 18.7	120	+ 24.5
60	+ 21.0		

Before each set of observations I tested the adjustment of the mirrors and the telescope. If small deviations were found, they were immediately corrected. The index error was always determined before the observations by 4 till 6 pointings on the direct images; in the case of solar observations they were equally distributed over both limbs. This determination was often repeated in the same manner after the observations.

I assumed for the eastern longitude 13° 8′ or expressed in time 52 m. 32 sec. This value was deduced from determinations of the time (measurements of 8 till 10 altitudes near the *prime* vertical) and a comparison of the so found local time with that of Greenwich, as given by the chronometers on board several ships that touched at this port. The English Admiralty-chart (corrected up to 1897) gives also 13° 8′ for the Eastern longitude of Ambriz.

As provisional value of the latitude I assumed 7° 50′ south.

The observations were made before the old factory of the „Nieuwe Afrikaansche Handelsvennootschap" and consist of the three following series:

1. *Circummeridian altitudes of the sun on May* 10, 1893.

For the reduction of the observations I used the following formula:

$$\varphi = \delta - z + \frac{\cos\varphi\cos\delta}{\sin(\delta-\varphi)} \cdot \frac{2\sin^2\frac{1}{2}t}{\sin 1''} - \frac{\cos^2\varphi\cos^2\delta}{\sin^2(\delta-\varphi)}\,\mathrm{cotg}\,(\delta-\varphi)\frac{2\sin^4\frac{1}{2}t}{\sin 1''}$$

z represents the northern zenith distance, whereas southern latitude is regarded negative. The term depending on $2\sin^6\frac{1}{2}t$ could be neglected, as its influence, even in the case of the greatest hour angles, was too small.

The following corrections and daily rates of the chronometer were found:

March	18	1893	+ 46m 56s 50	
				— 0s 24
April	12	"	+ 46 50.40	
				— 0.23
May	3	"	+ 46 45.48	
				— 0.39
June	3	"	+ 46 33.26	

That I might use a constant value for the declination of the sun, the hour-angles were reckoned from the instant of the maximum altitude, computed from the formula:

$$t_0 = 0.255\frac{d\delta}{dt}(\mathrm{tang}\varphi - \mathrm{tang}\delta)$$

in which t_0, the hour-angle of the maximum altitude, is expressed in seconds of time and $\frac{d\delta}{dt}$ stands for the variation of the sun's declination in one hour, expressed in seconds of arc.

The observed altitudes were corrected for refraction, parallax and semidiameter. The places of the sun etc. were taken from the Connaissance des Temps.

For the time of the observations and the used part of the sextant we find :

Corr. chronometer to mean loc. time	$+ 46^{m} 43^{s}4$
Indexcorrection sextant	$- 1' 55''$
Corr. for error of graduation	$+ 25''$
Temperature	27° C.
Barometer	760 m.M.
Mean loc. time of transit of sun, T	$11^{h}56^{m}13^{s}$
Hour-angle of maximum altitude, t_0	$- 4^{s}5$
Declination of the sun for $T + t_0$	$+ 17° 41' 43''5$

The separate observations and their results are given in the following table, which needs no further comment.

Limb	Chron. time.	Hour-angle.	Reading Sext.	Latitude.
l	$10^{h}53^{m}40^{s}$	$- 15^{m}45^{s}1$	127° 45′ 40″	− 7° 50′ 3″6
u	54 55	14 30.1	128 54 50	49 53.2
l	56 14	13 11.1	127 56 20	49 59.1
u	57 1.5	12 23.6	129 2 30	50 4.4
l	57 37.5	11 47.6	128 1 10	50 2.3
u	58 20	11 5.1	129 7 30	49 45.4
l	59 2	10 23.1	128 5 30	50 5.5
u	59 40	9 45.1	129 11 20	49 48.8
l	11 0 17.5	9 7.6	128 8 50	50 10.3
u	1 6.5	8 18.6	129 15 5	49 47.7

Hence:

Latitude from lower limb	− 7° 50′ 4″2
" " upper limb	49 51.9
Mean value	− 7° 49′58″0
Difference upper limb—lower limb	+ 12″3

Examining these results and also those of the 2nd series given below, it appears clearly that there is a perceptible constant personal error in esteeming the contact of the two images of the sun, and its mean value as deduced from the two series is 5″.3 If we correct the separate results for this amount, we obtain as mean error of a single pointing

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± 5″.8 and as mean error of the final result ± 1″.8. We must also take into account however the error made in determining the index correction, which influences all the observations equally. If we assume that for this determination 5 pointings were made (compare above) and accordingly take the mean value of its error to be $\pm 5''.8 \times \sqrt{1/5} = \pm 2''.6$, the total mean error of the result becomes ± 3″.2.

Moreover, as the observations are not arranged symmetrically with respect to the meridian, an error in the correction of the chronometer also influences the final result. Probably this error is not large, as the rate of the chronometer was pretty regular in the period considered. Also the results from the first and the last pair of observations, viz. 58″.3 and 58″.6, agree well inter se. An error in the chronometer correction of 2^s would result in a variation of 3″.5 in the latitude.

2. *Circummeridian altitudes of the sun on May* 14, 1894.

The observations were reduced in the same way as those of May 10, 1893. The sun's places etc. were now taken from the Nautical Almanac; they are based on the same elements and values as those of the Conn. d. T. The following corrections and daily rates of the chronometer were found:

Jan. 12	1894	$+ 43^m\ 44^s76$	
			$- 0^s80$
April 26	„	$+ 42\ \ 21.30$	
			$- 0.99$
May 22	„	$+ 41\ \ 55.60$	
			$- 2.01$
July 13	„	$+ 40\ \ 11.20$	

For the time of the observations and the used part of the sextant we find:

Corr. of the chronometer	$+ 42^m\ 3^s6$
Index correction sextant	$- 1'\ 50''$
Correction for error of graduation	$+ \ \ 25''$
Temperature	27°
Barometer	760 mM.
Mean loc. time of transit of sun, T	$11^h\ 56^m\ 9^s4$
Hour angle of maximum altitude, t_0	$- 4^s4$
Declination of the sun for $T + t_0$	$+ 18°\ 41'\ 10''1$

The separate observations and their results follow here:

Limb.	Chron. time.	Hour angle.	Reading Sext.	Latitude.
l	11h 2m 41s	— 11m 20s 4	126° 10′ 20″	— 7° 50′ 5″3
u	3 30	10 31.4	127 16 20	50 1.2
l	4 17	9 44.4	126 14 50	50 8.8
u	5 18	8 43.4	127 21 10	49 58.7
l	6 9	7 52.4	126 19 50	49 54.1
u	6 54	7 7.4	127 25 10	49 43.0
l	7 42	6 19.4	126 22 20	50 9.7
u	8 24	5 37.4	127 27 40	49 46.8
l	9 5	4 56.4	126 24 40	50 3.9
u	9 42	4 19.4	127 29 0	50 0.0
l	21 3	+ 7 1.6	126 21 10	50 6.0
u	21 42	7 40.6	127 23 10	50 9.3
l	22 16	8 14.6	126 18 5	50 22.1
u	22 50	8 48.6	127 20 30	50 12.4
l	23 29	9 27.6	126 15 30	50 11.0
u	24 45	10 43.6	127 15 40	50 3.5
l	25 33	11 31.6	126 9 20	50 17.8
u	26 9	12 7.6	127 11 25	49 59.7
l	26 46	12 44.6	126 5 50	50 1.8
u	27 26	13 24.6	127 7 0	49 57.9

Hence:

Latitude from lower limb	— 7° 50′ 8″05
" upper "	49 59.25
Mean result	— 7° 50′ 3″6
Difference upper limb—lower limb	+ 8″8

The value now found for the personal contact error agrees fairly well with that found from the first series.

If again we correct the separate results for the mean value of this error, viz. 5″.3, we now get as mean error of one pointing ± 8″.3

and for the mean of all ± 1″.9. If we add to this as mean error of the index correction $\pm 8''.3 \times \sqrt{1/5} = \pm 3''.7$, the total mean error becomes ± 4″.1. The uncertainty in the correction of the chronometer may be perhaps a little larger than for May 10, 1893, although the acceleration found after May 22 has probably not begun before that date, about which time the colder season began. But at any rate, through the symmetrical arrangement of the observations, an error of this kind will influence only very slightly the final result.

In reality the observations for index error will as a rule be preciser than the altitude determinations with the mercurial horizon and, if on the other hand we take into consideration the possible uncertainty of the chronometer correction, then I don't think the precision of my observations is overrated, if we assume ± 5″ as mean error both of the result of May 10 1893 and of that of May 14,1894.

3. *Meridian altitudes of the sun and of α Crucis.*

In the third place I measured several times the greatest altitude of the sun and once that of *α* Crucis.

The observations on the sun were always made on the lower limb, as in this way the maximum altitude from the mercurial horizon is easiest and most accurately measured; the images of the lower limb namely are separating before the culmination.

Here follow the observations and their results. The column „Corr." gives the sum of the index correction and the correction for errors of graduation. The declinations and the semidiameter and parallax of the sun were taken for 1893 from the Connaissance des Temps, for 1894 from the Nautical Almanac.

Date.	Object.	Reading.	Corr.	Temp.	Barom.	Latitude.
May 7 1893	Sun L. L.	129° 56′ 50″	— 1′ 30″	29°	759.5	— 7° 50′ 6″7
〃 8 〃	〃 〃	129 24 20	1 30	29	758	50 4.4
〃 9 〃	〃 〃	128 52 20	1 30	28	759	50 4.2
〃 10 〃	〃 〃	128 21 0	1 30	27	760	50 1.5
June 2 〃	〃 〃	119 20 15	1 31	27	761	50 1.1
May 10 1894	α Crucis.	70 12 0	1 13	25.5	760.4	50 9.6
〃 14 〃	Sun L. L.	126 28 20	1 30	27	760	49 57.0

The results from the altitudes of the sun still remain to be corrected for the personal error; applying for this the value found previously, we obtain as final results :

May	7	1893	— 7° 50′ 1″4
〃	8	〃	49 59.1
〃	9	〃	49 58.9
〃	10	〃	49 56.2
June	2	〃	49 55.8
May	10	1894	50 9.6
〃	14	〃	49 51.7
		Mean	— 7° 49′ 59″0

As it is difficult to form an opinion about the relative precision of the observation of α Crucis and those of the sun, the same weight is given to all of them. The mean error of an observation is then found to be ± 5″.6, that of the mean ± 2″.1.

The results from the 3 series now must be combined. Although for the last series a smaller mean error was found, it did not seem advisable to assign to it a greater weight than to the others. For it is possible that for this kind of solar observations the personal error differs perceptibly from that in the determination of circummeridian altitudes.

So we have :

Series	I	— 7° 49′ 58″0
〃	II	63.6
〃	III	59.0
	Mean	— 7° 50′ 0″2

The three series agree fairly well inter se, and as final result for the latitude of the place of observation we may take :

— 7° 50′ 0″

which value will probably be exact within a few seconds.

The reduction of the latitude to that of the harbour light amounts, according to the map of "Port Ambriz" on the English Admiralty chart : "Cape-Lopez-bay to St. Paul de Loanda", to + 12″ ± 2″ (the map is not graduated), and so the latitude of the harbour light is found to be :

— 7° 49′ 48″

The value given on the Admiralty chart is : — 7° 52′ 9″ and accordingly 2′ 21″ too much south.

II. *Determination of the latitude of S. Salvador do Congo.*

A few observations have been obtained about the latitude of San Salvador, the old capital of the former kingdom of Congo. They were made before the factory of the "N. Afrik. Handelsvenn.", situated about 1 K.M. north of the centre of the hill on which the town is built (562 m. above the sea-level).

Only the following meridian altitudes were observed.

Date.	Object.	Reading.	Corr.	Temp.	Bar.	Latitude.
May 8 1895	Sun L. L.	132° 49′ 10″	— 1′ 10″5	27°	714	— 6° 15′ 18″2
〃 10 〃	〃	131 45 20	1 16	27.5	714	15.3
〃 11 〃	α Crucis.	67 31 50	1 13	22	713.5	26.1

If to the results from the observations of the sun we apply the correction + 5″.3, the mean result for the latitude becomes:

—6° 15′ 16″

with an uncertainty of perhaps 10″ or still more.

Dr. CHAVANNE (Map of JUSTUS PERTHES 1886) found for the latitude of San Salvador (the hill extends over a few kilometers only)

— 6° 20′ 10″

and for the longitude 14° 47′ 18″ East of Greenwich. Very probably there is also an error in the longitude of more than 20′, the true eastern longitude being smaller.

Physics. — "*Methods and Apparatus used in the Cryogenic Laboratory. II. Mercury pump for compressing pure and costly gases under high pressure*". By Prof. H. KAMERLINGH ONNES.

(Will be published in the Proceedings of the next meeting).

Physiology. — "*Lipolytic ferment in human ascitic fluid*". By Dr. H. J. HAMBURGER.

(Will be published in the Proceedings of the next meeting.)

Chemistry. — Prof. A. P. N. FRANCHIMONT presented to the library the dissertation of Dr. P. J. MONTAGNE, entitled: "*The action of strong nitric acid upon the three isomeric chloro-benzoic acides and some of their derivates*".

(Will be published in the Proceedings of the next meeting.)

Chemistry. — "*The alleged identity of red and yellow mercure oxide*" (II). By Dr. ERNST COHEN (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

(Will be published in the Proceedings of the next meeting.)

Chemistry. — "*Determination of the decrease of the vapour tension of solutions by determining the rise of the boiling point*". By Dr. A. SMITS (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

(Will be published in the Proceedings of the next meeting.)

(February 21, 1900.)

E R R A T U M.

Page 103 formula 2, 3 read as follow:

$$\mathfrak{B} = \frac{P - P'}{P_1 - P_1'} = \frac{p - p'}{p_1 - p_1'} \cdot \frac{1 + (p + p')\left(\frac{273}{T}\right)^2 \left(a - b\,\frac{T}{273}\right)}{1 + (p_1 + p_1')\left(\frac{273}{T}\right)^2 \left(a_1 - b_1\,\frac{T}{273}\right)}$$

$$\mathfrak{B} = B \left\{ 1 + \left(\frac{273}{T}\right)^2 \left[(p + p')\left(a - b\,\frac{T}{273}\right) - (p_1 - p_1')\left(a_1 - b_1\,\frac{T}{273}\right) \right] \right\}$$

Page 104 Table I read as follow:

x	B	$\mathfrak{B}$	$\mathfrak{B}_1(1-x)+\mathfrak{B}_2 x$	x'
0	1.5328	1.5258		
0.2082	1.3057	1.3019	1.3075	0.2135
0.3000[1]	1.2052	1.2024	1.2112	0.3084
0.4192	1.0826	1.0809	1.0862	0.4243
0.5077	0.9884	0.9877	0.9934	0.5131
0.6498	0.8399	0.8398	0.8444	0.6541
0.7085	0.7799	0.7802	0.7828	0.7110
1	0.4765	0.4771		

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday February 24, 1900.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 24 Februari 1900 Dl. VIII).

CONTENTS: "A simple and rapid method for preparing neutral Pikro-carmine". By Prof. J. W. VAN WIJHE, p. 409. — "The Entropy of Radiation" (II). By J. D. VAN DER WAALS JR. (Communicated by Prof. H. G. VAN DE SANDE BAKHUYZEN), p. 413. — "On rational twisted Curves". By Prof. P. H. SCHOUTE, p. 421. — "Lipolytic ferment in Ascites-liquid of man". By Dr. H. J. HAMBURGER, p. 428. — "Methods and Apparatus used in the Cryogenic Laboratory. II: Mercury pump for compressing pure and costly gases under high pressure". By Prof. H. KAMERLINGH ONNES (with 7 plates), p. 437. — "The alleged identity of red and yellow mercuric oxide" (Part II). By Dr. ERNST COHEN (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM), p. 458. — Prof. A. P. N. FRANCHIMONT presents Dr. P. J. MONTAGNE's dissertation: "The action of hydrogen nitrate upon the three isomeric chloro-benzoic acids and some of their derivatives", p. 461. — "The Enantiotropy of Tin" (IV). By Dr. Dr. ERNST COHEN (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM), p. 464 (with one plate). — "On Phenomena on the sun considered in connection with anomalous dispersion of light". By Prof. W. H. JULIUS, p. 467. — "On the formation of trisubstituents of benzol form disubstituents". By Prof. A. F. HOLLEMAN (Communicated by Prof. C. A. LOBRY DE BRUYN), p. 468. — "Enquiries into the system $Tl\,NO_3 + Ag\,NO_3$". By Dr. C. VAN EYK (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM), p. 468.

The following papers were read:

Anatomy. — Prof. J. W. VAN WIJHE describes: "*A simple and rapid method for preparing neutral Pikro-carmine*".

By many it will no doubt be deemed unnecessary trouble to add another to the manifold prescriptions for the preparation of pikrocarmine. Most investigators who use it, will be content with one of the well-known methods of preparation which they have been in the habit of following, as was also the case with me, until, about a year ago, the stain disappointed me.

This happened during the study of young embryonic tissue, which had been blackened by osmic acid and had afterwards been bleached.

The ordinary means to tinge nuclei: haematoxylin, alum-carmine and different aniline-stains produced a diffuse colouring, whereas only after having been for about fourteen days in pikro-carmine the nuclei became visible.

Then however the protoplasm of the cells had disappeared; it could not be otherwise than dissolved in the alkaline pikro-carmine, and it seemed only natural rather to take a neutral solution of this tincture. I tried different prescriptions, but I was not successful in finding a neutral solution: a moist red litmuspaper hung in the bottle above the liquid, was tinged blue after a few hours.

Paul Mayer in his article: "Ueber Pikrocarmin" [1]) says not to believe that: "Carmin in einer ganz neutralen Flüssigkeit, die noch dazu eine relativ grosse Menge pikrinsauren Salzes enthält, gelöst bleiben kann" (l. c., p. 19). He examined pikro-carmine from the anatomical laboratory at Munich and from the Collège de France, moreover liquid and solid samples of Grübler and different solid samples of Merck.

The pikro-carmine is a solution of two solids: picrate of ammonium and ammoniumcarmine — the discoverer Ranvier believed it to be a chemical combination, but this is an assertio gratuita — and now it is (leaving the alkaline reaction out of the question), a deficiency of most prescriptions that they cannot specify the relative proportion of these elements and leave it to the inconstancy of chance.

This is the case with all prescriptions in which bacteria from the air are called to aid, according to the method followed in the Collège de France [2]), moreover the preparation then lasts several months, and, as experience has taught me, there is considerable danger of obtaining a totally useless product.

Because of the difficulties just mentioned and others besides, Paul Mayer says at the end of his article (l. c., p. 28): „Das Facit wäre also: das Pikro-carmin gehört zu den Färbmitteln, die eine bewegte Vergangenheit hinter sich haben, und von denen man möglichst wenig Aufhebens mehr machen sollte."

Pikro-carmine can however not yet be considered out of date as a stain in microscopical technics, and I have been successful in preparing in a simple way a liquid, which may practically be called neutral, at the same time containing fully known quantities of picrate of ammonium and ammoniumcarmine. The method can

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[1]) Paul Mayer, "Ueber Pikrocarmin", Zeitschrift für wissenschaftliche Mikroskopie und mikroskopische Technik. Bd. 14, 1897.

[2]) See A. Bolles Lee, The Microtomist's Vademecum, fourth Ed. 1896, p. 153.

partly be considered as a modification and simplification of HOYER's prescription [1]) running thus:

Take 25 cc. [2]) of an old strong [3]) solution of carmine in ammonia and pour it carefully in 100 cc. of strong alcohol (of circa 96 pCt.), a voluminous precipitate of ammoniumcarmine now forms itself. Filter after half an hour or longer, rinse the precipitate on the filtrum with 100 cc. strong alcohol and dry it for 24 hours in a thermostate of 40—45° C. [4]).

If the solution was old enough a dark red, nearly black crumbled mass is obtained, which is easily rubbed down to a powder thoroughly and clearly soluble in distilled water or in picrate of ammonium of whatever strength. If picric acid is added to the solution, a precipitate is immediately formed; the picrate of ammonium may therefore not contain free picric-acid which was the case with a certain quantity which I received from MERCK [5]).

The relative proportion of ammoniumcarmine and picrate of ammonium, which, as a rule, seemed to me most favourable for staining was as 1 : 2. In order to obtain a liquid, which would at the same time fix the tissues to some extent (as pikrocarmine is expected to bring about), I took a 1 pCt. solution of picrate of ammonium, — i.e. a nearly concentrated solution [6]) and added thereto $^1/_2$ pCt. ammoniumcarmine.

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[1]) HOYER, Beiträge zur histologischen Technik, Biologisches Centralblatt, Bd. 2, 1882. Following the somewhat lengthy prescription of HOYER, I was not successful in obtaining a powder quite soluble in water. Besides a good deal of carmine is lost.

The "Pikrocarmin nach HOYER" of GRÜBLER must, according to the List of Prices, be dissolved with ammonia, and could therefore not be used for my purpose.

[2]) These and other quantities are of course taken ad libitum, the statement is for the convenience of those who may want to follow the prescription.

[3]) At first I dissolved 30 gr. carmine in 100 cc. not diluted ammonia of circa 10 pCt. Afterwards I found out that the carmine dissolves better in ammonia diluted with the double quantity of distilled water.

[4]) The filtered liquid is thrown away. After evaporation a tough red substance is obtained, which, when thoroughly dried forms a coherent, hard mass, soluble in alcohol as well as in water. With alcohol the watery solution gives no precipitate.

In the same manner it appears that the solution of *carminic acid* in ammonia consists of two kinds of ammoniumcarmine, one of which can be precipitated by strong alcohol, but the other cannot.

[5]) A sample, which I received from GRÜBLER was excellent on the contrary. Picrate of ammonium can easily be prepared. For instance 9 gr. picric-acid are dissolved in 100 cc. alcohol of circa 96 pCt. adding 15 cc. ammonia and evaporating on the thermostate at about 60°.

[6]) In winter crystals are formed in the 1 pCt. solution of picrate of ammonium.

To prevent the stain from crystallising in winter, it can be diluted with half the quantity of distilled water.

The solution was not neutral however, although both ingredients were perfectly dry. Although they were dried for a whole week in a temperature of 45°, a moist red litmuspaper hung in the bottle above the liquid, turned blue after some time. Probably free ammonia clung to the dry powders. To get rid of it a solution was boiled in a glass receiver for some time, until a red litmuspaper did not turn blue in the vapour. This was the case after boiling from a quarter to half an hour. After cooling down, the liquid looked slightly unclear, which was easily amended by filtering. The loss of volume was restored with distilled water.

The tincture was now ready; to keep it free of mould, it was needful to add an antiseptic; 1 pCt. chloral, recommended by HOYER, proved efficient.

This pikrocarmine [1]) is practically neutral, for a moist red litmuspaper hung in the closed bottle above the surface of the liquid, was not yet tinged blue after four months.

The tincture [2]) contains $^1/_2$ pCt. ammoniumcarmine and 1 pCt. picrate of ammonium, for the loss of weight in consequence of the unclearness after boiling, is so insignificant, that it cannot be taken into consideration. The preparation is finished in two days; should time be short it could even be done in one day; in which case the drying is left undone, and after a preliminary experiment, the quantity can be calculated which must be taken from the moist precipitate. The insignificant quantity of alcohol, which it contains, is of no consequence, and is moreover dispersed by boiling.

A difficulty with this method is that an *old* carmine solution in ammonia must be used. Mine was two years old. Fresh solutions, and such as well which were half a year old, produced, instead of a black, a more or less clear red ammoniumcarmine powder, which was only partly and unclearly soluble in water.

The carmine-solution must therefore "ripen", how long, I have not been able to ascertain; but two years is not too much. The question now is wherein this ripening consists and if it cannot take place at once. It is well-known that a ripe solution (from which the superfluous ammonia has been allowed to evaporate as much as possible), stains the tissues better than a fresh one, and this is very generally — amongst others by GIERKE [3]) — ascribed to the for-

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[1]) To be obtained at the address of Dr. G. GRÜBLER, Leipzig.

[2]) One drop of the tincture on the filtering-paper gives, after being dried, a brown-yellow stain with red edge. This edge is much broader with the boiled, than with the unboiled liquid.

[3]) H. GIERKE, Färberei zu mikroskopischen Zwecken, 1885, p. 14 and 15.

mation of ammonium-carbonate, the carbonic acid being resorbed from the air. There is no doubt that this resorption takes place; and expecting that the salt mentioned might cause the ripening, I added 10 pCt. carbonate of ammonium to the solution. However without the desired result, even after the solution was several months old.

I then took into consideration whether the carmine might perhaps resorb oxygen from the air, and would need to be oxygenated; and this proved to be case.

When putting together:

10 gr. carmine powder,

10 cc. ammonia,

20 cc. hydrogenperoxyd,

the mixture boiled for a short time in a glass receiver, then cooled down (for instance by letting the receiver float in water in a half-filled cylinderglass), a ripe carmine solution is obtained in a few minutes, which, treated in the above-mentioned way, produces fully 9 gr. [1] of an almost black ammoniumcarmine, which is entirely, sometimes a little unclearly, soluble in water.

Instead of boiling with hydrogen-peroxyd an equal quantity of a 1 pCt. solution of kaliumpermanganate can be taken as well, although in this case the oxygenation is easily carried too far.

Physics. — "*The entropy of radiation*" (II). By J. D. VAN DER WAALS JR. (Communicated by Prof. H. G. VAN DE SANDE BAKHUYZEN).

IV.

Distribution of the vibrations of the molecules.

In the second part of his "Vorlesungen über Gastheorie" Prof. BOLTZMANN discusses the way in which the intramolecular energy is distributed over the different molecules. He finds that the chance

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[1] If *dry* carmine has been used. But carmine as it is sold, frequently contains 10 pCt. or more water, though it may seem to be dry.

that a molecule belongs to a certain group, may be represented by:

$$A_1 \, e^{-2hE_1} \, dp_1 \, dp_2 \, . \, . \, . \, dp_\mu \, dq_1 \, dq_2 \, . \, . \, . \, dq_\mu .$$

In this A_1 and h are constants, E_1 the energy of the intramolecular motion, $p_1 \, . \, . \, . \, p_\mu$ the coordinates, which determine that motion and $q_1 \, . \, . \, . \, q_\mu$ the momenta corresponding to those coordinates.

From this would follow, that the chance that the amplitude a_{x1} of the vibration of a molecule is contained within certain limits, is represented by:

$$\frac{1}{\beta \sqrt{\pi}} \, e^{-\frac{a_{x1}^2}{\beta^2}} \, da_{x1}.$$

However we cannot accept this result without further proof. The motion, which we are considering, and which is the cause of radiation, is necessarily damped, so that between two collisions a molecule has lost part of its intramolecular energy; moreover the molecule has absorbed energy from the field. For such a motion the proof of Prof. BOLTZMANN does no longer hold.

In order to find the distribution of the amplitudes we shall have to take into consideration two causes of change: the collisions and the electric forces.

First I shall examine the influence of the electric forces, and then inquire whether the collisions of the molecules will modify the distribution brought about by the electric forces. I shall make the same assumptions about the construction of a molecule as Prof. LORENTZ did[1]), i. e.:

a. I assume every molecule to contain an ion charged with electricity.

b. That ion has a position of equilibrium in the molecule, from which it can move in all directions, and to which it is driven back with a force, proportional to the deviation.

c. The mass of the ion is so small compared to that of the rest of the molecule, that when the molecule is vibrating, the ion alone may be considered to move.

d. The remaining part of the molecule is charged opposite to the charge of the ion and that in such a way that, when the ion is in its position of equilibrium, the electric forces, exercised by

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[1]) Arch. Neerl. XXV, 5, 1892.

the ion, are entirely destroyed by the remaining part of the molecule. From these assumptions we find for the equation of motion of an ion [1]):

$$m\,\frac{d^2x}{dt^2} = -\,\mathrm{f}(x-x_1) + 4\,\pi\,V^2\,\frac{d^2x}{dt^2}\int\varrho_0\,\omega\,d\tau + \frac{e^2}{V}\,\frac{d^3x}{dt^3} + 4\,\pi\,V^2\,e\,f +$$

$$+\,e\left(\frac{dy}{dt}\,N - \frac{dz}{dt}\,M\right).$$

Here m represents the mass of the ion, f a constant factor, x the coordinate of the ion, x_1 that of the position of equilibrium of the ion, e the electric charge.

The term $-\,\mathrm{f}\,(x-x_1)$ is due to the fact that an ion has a position of equilibrium, towards which it is driven back. The second and third term of the right hand side indicate the influence of the electric forces exercised by the molecule itself. The second term may be transferred with the negative sign to the left hand side; it is evident that it gives then an apparent change of the mass of the ion. If we represent by m the mass of the ion, modified in such a way, we may leave this term further out of account. The third term has always the sign opposite to that of the velocity and explains the damping, which a vibrating particle experiences in consequence of the fact that part of the energy is radiated into space. The three last terms express the forces exercised by the surrounding molecules on the ion. Prof. LORENTZ has pointed out that the fourth term is great compared to the fifth and sixth. For f we shall take the electric force, as it is in the position of equilibrium of the ion. The force $4\,\pi\,V^2\,e\,f$, which we take then into consideration, acts on the ion and on the rest of the molecule with the same amount but in an opposite direction, and has therefore only influence on the vibration of the molecule. On the other hand, the forces which we neglect:

$$4\,\pi\,V^2\,e\,\frac{df}{dx}(x-x_1) + e\left(\frac{dy}{dt}\,N - \frac{dz}{dt}\,M\right)$$

would also give a progessive motion to the centre of gravity of the molecule. Afterwards I hope to discuss the influence of these forces.

For the external force f we shall write:

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[1]) LORENTZ, loc. cit. equation I § 90 in connection with equations 111 and 112.

$$f_1 \cos\frac{2\pi t}{T} + f_2 \sin\frac{2\pi t}{T}$$

and we shall take constants for f_1 and f_2. As a molecule is actually subjected to an alternating electric force, the amplitude and the phasis of which vary with the time, we get in this way a solution which will hold with approximation for a short time only; but which will yet be sufficient to conclude from the condition at a given moment to that of a short time Δt after. The equation which we have to solve, is therefore reduced to:

$$m\frac{d^2x}{dt^2} = -\mathfrak{f}(x-x_1) + \frac{e^2}{V}\frac{d^3x}{dt^3} + 4\pi V^2 e\left(f_1 \cos\frac{2\pi t}{T} + f_2 \sin\frac{2\pi t}{T}\right)$$

or if we put $a_x = e\,(x-x_1)$:

$$m\frac{d^2a_x}{dt^2} = -\mathfrak{f}\,a_x + \frac{e^2}{V}\frac{d^3a_x}{dt^3} + 4\pi V^2 e^2\left(f_1 \cos\frac{2\pi t}{T} + f_2 \sin\frac{2\pi t}{T}\right)$$

The solution of this is:

$$a_x = \left(a'_{x1}\cos\frac{2\pi t}{T} + a'_{x2}\sin\frac{2\pi t}{T}\right)e^{-kt} + b_{x1}\cos\frac{2\pi t}{T} + b_{x2}\sin\frac{2\pi t}{T}\,.$$

By substituting in the equation for $m\dfrac{d^2a_x}{dt^2}$ this value of a_x and by equating the coefficients of

$$e^{-kt}\cos\frac{2\pi t}{T}\,,\quad e^{-kt}\sin\frac{2\pi t}{T}\,,\quad \cos\frac{2\pi t}{T} \text{ and } \sin\frac{2\pi t}{T}$$

separately to zero, we find the following four equations:

$$a_{x1}\,m\left(\frac{4\pi^2}{T^2} - k^2\right) - \mathfrak{f}\,a_{x1} + \frac{e^2}{V}a_{x1}\left(-k^3 + 3k\frac{4\pi^2}{T^2}\right) + 2\,a_{x2}\,m\,k\frac{2\pi}{T} + \frac{e^2}{V}a_{x2}\left[3\,k^2\frac{2\pi}{T} - \left(\frac{2\pi}{T}\right)^3\right] = 0$$

$$a_{x2}\,m\left(\frac{4\pi^2}{T^2} - k^2\right) - \mathfrak{f}\,a_{x2} + \frac{e^2}{V}a_{x2}\left(-k^3 + 3\,k\frac{4\pi^2}{T^2}\right) - 2\,a_{x1}\,m\,k\frac{2\pi}{T} + \frac{e^2}{V}a_{x1}\left[-3\,k^2\frac{2\pi}{T} + \left(\frac{2\pi}{T}\right)^3\right] = 0$$

$$b_{x1}\, m \frac{4\pi^2}{T^2} - \mathfrak{f}\, b_{x1} - b_{x2} \frac{e^2}{V}\left(\frac{2\pi}{T}\right)^3 + 4\pi V^2 e^2 f_1 = 0$$

$$b_{x2}\, m \frac{4\pi^2}{T^2} - \mathfrak{f}\, b_{x2} + b_{x1} \frac{e^2}{V}\left(\frac{2\pi}{T}\right)^3 + 4\pi V^2 e^2 f_2 = 0 .$$

From the first and the second equations follows:

$$m\left(\frac{4\pi^2}{T^2} - k^2\right) - \mathfrak{f} + \frac{e^2}{V}\left(-k^3 + 3k\frac{4\pi^2}{T^2}\right) = 0$$

$$2mk + \frac{e^2}{V}\left(3k^2 - \frac{4\pi^2}{T^2}\right) = 0 .$$

from which T and k may be calculated.

a'_{x1} and a'_{x2} are constants which may be arbitrarily chosen. The quantities b_{x1} and b_{x2} are not arbitrary, but are determined from the third and the fourth equations as follows:

$$b_{x1} = \frac{4\pi V^2 e^2\left[\left(m\frac{4\pi^2}{T^2} - \mathfrak{f}\right) f_1 + \frac{e^2}{V}\left(\frac{2\pi}{T}\right)^3 f_2\right]}{\left(m\frac{4\pi^2}{T^2} - \mathfrak{f}\right)^2 + \frac{e^4}{V^2}\left(\frac{2\pi}{T}\right)^6}$$

$$b_{x2} = \frac{4\pi V^2 e^2\left[-\frac{e^2}{V}\left(\frac{2\pi}{T}\right)^3 f_1 + \left(m\frac{4\pi^2}{T^2} - \mathfrak{f}\right) f_2\right]}{\left(m\frac{4\pi^2}{T^2} - \mathfrak{f}\right)^2 + \frac{e^4}{V^2}\left(\frac{2\pi}{T}\right)^6}$$

We shall represent this by:

$$b_{x1} = p f_1 + q f_2 \qquad b_{x2} = -q f_1 + p f_2$$

The quantity b depends therefore only on the accidental value of the amplitude of the electric force on the point where it happens to be, and not on the accidental value of the amplitude of the vibration of the molecule.

$$b_{x1}^2 + b_{x2}^2 = (p^2 + q^2)\,(f_1^2 + f_2^2) .$$

The amplitude of b_x is therefore $\sqrt{p^2 + q^2}$ times or $4\pi V^2 e^2$ times the amplitude of f. Moreover the phasis of b_x is f. As however all phases occur equally frequently the distribution of the quantities $[b_{x1}]$ will be the same as that of the quantities $[f_1]$, so that the chance that b_{x1} is contained within certain limits may be represented by:

$$\frac{1}{\zeta\sqrt{\pi}} e^{-\frac{b_{x1}^2}{\zeta^2}} db_{x1} \quad \text{where} \quad \zeta = 4\pi V^2 e^2 \varepsilon \;{}^{1}).$$

In order to find the distribution of the vibrations we may reason as follows. Starting from a certain initial condition the molecules will entirely lose their original vibrations by radiation. The vibrations in the direction of the X-axis, which they absorb from the field, are dependent on the f-component of the vibrations of the ether, and not on the g- and h-component. As the f-, g- and h-components are independent of each other, also a_x, a_y and a_z, caused by them, must be independent of each other, and as all directions occur with the same frequency, the distribution of the a's must also be that of MAXWELL. The chance that the quantity a_{x1} is contained within given limits, may therefore be represented by:

$$\frac{1}{\beta\sqrt{\pi}} e^{-\frac{a_{x1}^2}{\beta^2}} dx_{x1}\,.$$

In order to arrive at this result the solution of the differential equation for a_x is not necessary. In this way however the condition is not yet perfectly determined. From the value found for a_x appears that if a molecule were exposed to an electric wave of constant intensity, it would have assumed the amplitude b after an infinite time. If a molecule is placed in a region where the amplitude of the electric force has a definite value, it will have been for some, though it be a short, time in a region, where the amplitude of the electric force did not differ much from that definite value. So it will have already assumed part of the amplitude b. The probability of the action of a force f on a molecule with a vibration a_x cannot be simply represented by:

$$\frac{1}{\varepsilon^2\pi} e^{-\frac{f_1^2+f_2^2}{\varepsilon^2}} \frac{1}{\beta^2\pi} e^{-\frac{a_{x1}^2+a_{x2}^2}{\beta^2}} df_1\, df_2\, da_{x1}\, da_{x2}\;,$$

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[1]) Proc. Roy. Acad., Dec. 1899. Pag. 322.

as would be the case if electric force and vibration were independent of each other; but these quantities are dependent on one another. If the above expression held true for the probability of the action, the way of motion would satisfy conditions, exactly corresponding to those which Prof. BOLTZMANN assumes for the case of molecular thermal motion, in order that the motion may be called "molecular-irregulated." [1]) In reality however, the way of motion is here molecular-regulated or as I would call it partially regulated. Totally regulated the condition would be, if the a_{x1} was entirely determined by f; if e.g. a_{x1} had everywhere assumed the value b_{x1}. The way of motion will be regulated in a higher degree as the quantity

$$\left[\frac{df_1}{dt}=\frac{\partial f_1}{\partial t}+\frac{\partial f_1}{\partial x}\frac{dx}{dt}+\frac{\partial f_1}{\partial y}\frac{dy}{dt}+\frac{\partial f_1}{\partial z}\frac{dz}{dt}\right]$$

is smaller. Here $\frac{\partial f_1}{\partial t}$ represents the fluction of f_1 in a point which does not move from its place, $\frac{df_1}{dt}$ the total fluction of the quantity f_1 for a molecule which moves with a velocity, the components of which are $\frac{dx}{dt}$, $\frac{dy}{dt}$ and $\frac{dz}{dt}$.

I have however not yet succeeded in finding the law according to which the motion is regulated.

At first sight it may seem strange that the condition of maximum-entropy should possess a certain order, whereas for the case of the molecular thermal motion of a gas we consider the total irregularity as condition for the maximum-entropy. In order to solve this seeming contradiction we must take notice of the fact that we are here concerned with the action of forces. Now we know that the action of external forces which varies so slowly from point to point that they may be thought constant throughout regions which though small, are still measurable and contain many molecules (e.g. gravity), causes the density to be not everywhere the same in the condition of maximum-entropy, so that we have „molar regulation." But then it is not to be wondered at that the electric forces of radiation, which cannot be thought constant throughout regions of measurable dimensions, should cause a "molecular-regulation".

Even though we had succeeded in determining the regulation in con-

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[1]) „Molekular-ungeordnet." BOLTZMANN, Gastheorie I. Pag. 21.

sequence of the electric forces, we should not have found the true condition. The influence of the collisions may probably not be neglected. If the mutual collisions of the molecules took place in a perfectly irregular way, they would undoubtedly lessen the degree of regulation, and render the condition nearer irregular. The way of motion is however not only partially regulated with regard to the action of the electric forces on the molecules, but also with regard to the mutual collisions of the molecules. In order to explain this we consider two molecules which have come very near to each other. The forces exercised by the surrounding molecules will be about the same for both, and will tend to bring their internal motion more and more into syntony. Moreover each of the molecules absorbs part of the energy emitted by the other. On account of these two causes a partial regulation is brought about in the collisions of the molecules, of which it seems impossible to me to determine the influence without special hypotheses on the mechanism and even the form of the molecules, for which as yet all data are wanting.

There is however another difficulty which makes me doubt whether the considerations of Prof. BOLTZMANN on the internal motion are applicable to the motion which causes radiation.

For according to Prof. BOLTZMANN the internal energy would increase in proportion to that of the progressive motion of the molecules, i. e. with the temperature. According to the law of STEFAN the emitted energy is proportional to the fourth power of the temperature. These two results can only be brought into harmony by assuming that the absorption decreases strongly with the rise of the temperature.

Properly speaking the law of STEFAN holds good for the total quantity of emitted light and may perhaps only be applied for cases where a continuous spectrum is emitted. The wavelength, which has the greatest intensity depends however for a continuous spectrum on the temperature, so that for the light of a fixed wave-length the law of STEFAN does not hold good. The displacement of the predominating wave-length is however not so great, that the law of STEFAN could not be applied with approximation.

Let us assume that actually the internal energy increases proportional with the temperature, and so the quantity δ[1]) with the root of the temperature. Let us represent two temperatures by T_1 and T_2, the intensities of light emitted at that temperature by I_1 and I_2 and

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[1]) Proc. Royal Acad. of Sciences, Dec. 1899. Pag. 319.

the corresponding quantities δ and ε [1]) by δ_1 and δ_2 and by ε_1 ε_2, then we have, neglecting the molecules which surround a point immediately:

$$\frac{T_1^4}{T_2^4} = \frac{I_1}{I_2} = \frac{\varepsilon_1^2}{\varepsilon_2^2} = \frac{\delta_1^2 \int \frac{e^{-2\mu_1 r}}{r^2} \frac{y^2+z^2}{r^2}\, d\tau}{\delta_2^2 \int \frac{e^{-2\mu_2 r}}{r^2} \frac{y^2+z^2}{r^2}\, d\tau}$$

or

$$\frac{T_1^3}{T_2^3} = \frac{\int \frac{e^{-2\mu_1 r}}{r^2} \frac{y^2+z^2}{r^2}\, r^2\, dr \sin\varphi\, d\varphi\, d\theta}{\int \frac{e^{-2\mu_2 r}}{r^2} \frac{y^2+z^2}{r^2}\, r^2\, dr \sin\varphi\, d\varphi\, d\theta} = \frac{\int_0^\infty e^{-2\mu_1 r}\, dr}{\int_0^\infty e^{-2\mu_2 r}\, dr} = \frac{1/\mu}{1/\mu.}$$

Prof. LORENTZ [2]) has deduced, that μ (his quantity α) is inversively proportional to the root of the temperature. And though both the way in which I have arrived at the conclusion that the absorption is inversely proportional to the third power of the temperature, and that in which Prof. LORENTZ found that it is inversely proportional to the root of the temperature, are but rough approximations yet these results differ too much, to attribute this only to the neglections.

Therefore an incorrect assumption must have been made somewhere. And if so I should doubt in the first place the correctness of the assumption, that for all internal motions the increase of the energy must be proportional to the energy of the progressive motion. I should therefore suppose that in collisions there are influences felt which cause the energy of the internal motions, which bring about radiation, to increase more at a rise of the temperature than the energy of the progressive motion of the molecules.

Mathematics. — "*On rational twisted curves*". By Prof. P. H. SCHOUTE.

1. Let P_1, P_2, P_3, P_4, . . . be successive points of a given twisted curve R; then we may consider the centre of circle $P_1 P_2 P_3$ lying in plane $P_1 P_2 P_3$ as well as that of sphere $P_1 P_2 P_3 P_4$. When the

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[1]) Proc. Royal Acad. of Sciences, Dec. 1899. Pag. 322.

[2]) Versl. Kon. Akad. v. Wet. April 1898, Dl. VI, blz. 559.

points taken on the curve coincide in a same point P, the limit of the first point is the centre C_p of the circle of curvature, that of the second point the centre S_p of the sphere of curvature, i. e. the centre of spherical curvature of R in P. If P describes the given curve R, then C_p and S_p describe twisted curves related to R, of which the latter is also the cuspidal edge of the developable enveloped by the normal planes of R; this locus of centres S_p of spherical curvature may be indicated by the symbol R_s.

From the wellknown theorem according to which the line of intersection c of two planes α, β, perpendicular to the intersecting lines a and b, is a normal to the plane γ of these lines a and b, ensues that reversely the osculating planes of R are also perpendicular to the corresponding tangents of R_s. These osculating planes of R however, not passing at the same time through the points of contact of the corresponding tangents of R_s, are not normal planes of R_s and so the relation between the curves R and R_s is generally not reciprocal. A wellknown striking example derived from transcendent twisted curves, where this reciprocity really exists, is the helix or curve formed by the thread of a screw; moreover for this curve the two loci of the points C_p and S_p coincide.

Let us go a step farther and suppose that $P_1, P_2, P_3, P_4, P_5, ..$ are successive points of a given curve R, which is contained in a four-dimensional space, but not in a three-dimensional one, which curve we therefore call a "wrung curve"; then besides the centres of the circle and sphere of curvature the centre H_p of the hypersphere of curvature appears, which is the limit of the hypersphere $P_1\, P_2\, P_3\, P_4\, P_5$, when the five determining points coincide in point P of the given curve. A third locus has then to be dealt with, and so we can extend these considerations to a space with any given number of dimensions.

In the following pages we wish to deduce the characteristics of the locus R_h of the centre of hyperspherical curvature of the highest rank in relation with the general rational wrung curve R^n_s of degree n, which *is* contained in a space with s dimensions but *not* in a space with $s-1$ dimensions.

2. "The row of characteristic numbers from class to degree of "the locus R_h of the centres of hyperspherical curve of the highest "rank belonging to the general rational wrung curve in R^n_s is

$$\text{“}3n-2, \quad 2(3n-3), \quad 3(3n-4), \; . \; . \; . \quad s(3n-s-1).\text{”}$$

To prove this we represent R^n_s by the equations

$$x_i = \frac{\alpha_i}{\nu}, \qquad (i = 1, 2, \ldots s) \quad \ldots\ldots \quad (1)$$

on rectangular axes, where the symbols $\alpha_1, \alpha_2, \ldots \alpha_s$ and ν indicate polynomia of degree n in a parameter t.

If the equations

$$\frac{\alpha_i}{\nu} = a_i + \frac{\beta_i}{\nu}, \qquad (i = 1, 2, \ldots s)$$

represent the result of the division of the s polynomia α_i by ν, where the s quantities a_i are independent of t and the s new polynomia β_i contain t in the degree $n-1$ at most, then it is clear that the transformation of the system of coordinates to parallel axes corresponding to the formulae

$$x_i = \xi_i + a_i, \qquad (i = 1, 2, \ldots s)$$

simplifies the original representation (1) of R^n_s into

$$\xi_i = \frac{\beta_i}{\nu}, \qquad (i = 1, 2, \ldots s) \quad \ldots\ldots \quad (2)$$

We repeat that this simplification consists in the fact that the s polynomia β_i ascend only to the degree $n-1$ in t.

If moreover β'_i and ν' represent the differential-coefficients of β_i and ν according to t, then

$$\nu \sum_{i=1}^{s} (\beta'_i \nu - \beta_i \nu') \xi_i = \sum_{i=1}^{s} (\beta'_i \nu - \beta_i \nu') \beta_i \quad \ldots \quad (3)$$

represents the normal space with $s-1$ dimensions of R^n_s in the point (2) with the value t of the parameter.

This equation is of degree $3n-2$ in t, which proves what was asserted. For the envelope of a space of $s-1$ dimensions, the equation of which contains a parameter to the degree k, has for characteristic numbers:

$$k, \quad 2(k-1), \quad 3(k-2), \ldots \quad s(k-s+1).$$

By means of the general theorem now proved we find from $n = 2$ to $n = 10$ the following table for the general rational twisted curve of minimum order:

$s = n = 2$ . . . 4, 6,
$s = n = 3$ . . . 7, 12, 15,
$s = n = 4$ . . . 10, 18, 24, 28,
$s = n = 5$ . . . 13, 24, 33, 40, 45,
$s = n = 6$ . . . 16, 30, 42, 52, 60, 66,
$s = n = 7$ . . . 19, 36, 51, 64, 75, 84, 91,
$s = n = 8$ . . . 22, 42, 60, 76, 90, 102, 112, 120,
$s = n = 9$ . . . 25, 48, 69, 88, 105, 120, 133, 144, 153,
$s = n = 10$ . . . 28, 54, 78, 100, 120, 138, 154, 168, 180, 190.

The first line of this table says that the evolute of a general conic is a curve of class four and order six, the second that the locus R_s of the general skew cubic R_3^3 is a twisted curve of class seven, rank twelve and order fifteen, etc.

If as usual we consider the coefficients $u_1, u_2, u_3 \ldots u_s$ of the equation $\Sigma u_i \xi_i = 0, (i = 1, 2, \ldots s)$ as the tangential coordinates of the space with $s-1$ dimensions represented by that equation, we find from (3) for the normal space

$$u_i = -\frac{\nu(\beta_i' \nu - \beta_i \nu')}{\sum_{i=1}^{s} \beta_i (\beta_i' \nu - \beta_i \nu')}, \quad (i = 1, 2, \ldots s), \quad . \quad (4)$$

which representation of R_h in space of s dimensions is dualistically opposite to that given for R_s^n. We write it in the abridged form:

$$u_i = \frac{\tau_i}{\tau_0}, \quad (i = 1, 2, \ldots s) \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

3. The degree of the equation (3) or that of the forms τ of (5), all in t, can lower itself in particular circumstances. These, apparently of five kinds, can be reduced to the following two cases:

a). The equation $\nu = 0$ has equal roots.

b). The equations $\beta_i = 0, (i = 1, 2, \ldots s)$ have common equal roots.

We shall now consider the influence of each of those suppositions on the class of the locus R_h.

3^a. If $t = t_1$ is a k-fold root of $\nu = 0$, this value is at the same time a $k-1$-fold root of $\nu' = 0$ and each of the forms τ of (5), and so (3) too, is divisible by $(t-t_1)^{k-1}$. The curve R_h is then of class $3\,n - k - 1$.

By the substitution of $t - t_1 = \frac{1}{t'}$ the case of the k-fold root t_1 of $\nu = 0$ assumes an apparently different form. It transforms the equations (2) into

$$\xi_i = \frac{\gamma_i}{\mu}, \quad (i = 1, 2, \ldots s), \quad \ldots \ldots \quad (6)$$

where the s forms γ_i represent polynomia of degree n in t' without constant term, whilst μ contains t' to the degree $n-k$ only; so it leads to the case that $\mu = 0$, considered as an equation of degree n, possesses a k-fold root $t' = \infty$. Then the s forms $\tau_i, (i = 1, 2, \ldots s)$ of (5) become polynomia of degree $3\,n - 2\,k - 1$ in t', whilst τ_0 ascends to degree $3\,n - k - 1$ in t'. Then the corresponding equation (3) is also of degree $3\,n - k - 1$ in t' and so R_h remains of class $3\,n - k - 1$ as it should do.

In passing we draw attention to the fact that the degree of μ being lower than n it will be impossible to lower at the same time the degree of all the s polynomia γ_i by a transformation of coordinates to parallel axes, as this would include at the same time the possibility to lower the order of R^n_s.

The particular case treated here refers to the position of the points of R^n_s at infinity. If ν is divisible by $(t-t_1)^k$ the point at infinity of the curve belonging to t_1 will count k times among the n points of intersection of the curve with the space at infinity with $s-1$ dimensions containing all points at infinity of the space with s dimensions.

So we find for $s = n = 3$:

"The class of the locus R_s of a skew ellipse or a skew hyperbola is seven, whilst this number passes into six with the parabolic hyperbola and into five with the skew parabola."

What we find here agrees with the wellknown results for $s = n = 2$. Although through any point P of the plane of an ellipse or hyperbola four normals of this curve pass, we can fall from this point three normals only on the parabola, as the line connecting P with the point P_∞ at infinity of the parabola must be considered as an improper normal. Any point P of space is situated in seven normal planes of a skew ellipse or skew hyperbola, but only in six normal planes of a parabolic hyperbola and in five normal planes of a skew parabola, as the plane through the connecting line PP_∞ of P with the point of contact P_∞ at infinity with the plane V_∞ at infinity, perpendicular to the tangent p_∞ of the curve in P_∞, represents one improper normal plane for the last but one, and the coincidence of two improper normal planes for the last.

Of course the particularity treated here can appear more than once. If $\nu = 0$ contains the roots $t_1, t_2, \ldots\ldots t_p$ respectively $k_1, k_2, \ldots k_p$ times, where each of the p quantities k exceeds unity, the class of R_h is represented by $3n + p - 2 - \sum\limits_{j=1}^{p} k_j$.

3^b. If $t = t_1$ is a common k-fold root of the s equations $\beta_i = 0$, then this value is at the same time a common $k-1$-fold root of the s equations $\beta'_i = 0$ and the s forms of τ_i (5) are divisible by $(t-t_1)^{k-1}$, whilst τ_0 contains the factor $(t-t_1)^{2k-1}$; then again (3) is divisible by $(t-t_1)^{k-1}$ and the curve R_h is of class $3n - k - 1$.

By the substitution of $t-t_1 = \frac{1}{t'}$ the case treated here presents itself in an apparently different form. It leads to the equations (6), where now the s forms γ_i represent polynomia of degree $n - k + 1$ in t' without constant term and μ is a general form of degree n in t'. Regarded as equations of degree n in t', the s equations $\gamma_i = 0$ contain the common $k-1$-fold root $t' = \infty$ and the common simple root $t' = 0$. The s terms τ_i, $(i = 1, 2, \ldots s)$ become polynomia of degree $3n - k - 1$ in t', whilst τ_0 ascends only to degree $3n-2k-1$ in t'. The corresponding equation (3) is then as above of degree $3n - k - 1$.

Apparently besides the cases treated up till now where the equation (3) lowers its degree, another entirely new case can be pointed out, namely that where the $s + 1$ equations $\beta'_i = 0$, $\nu' = 0$ have a common k-fold root $t = t_1$. It is easy to see however that this apparent new case forms but a special case of what was treated above. If we start from the equations (1), because after all we shall directly have to transform the coordinates to parallel axes, then we have

$$\alpha'_i = (t - t_1)^k \varphi_i^{(n-k-1)}\ , \quad (i = 1, 2, \ldots s)\ , \quad \nu' = (t - t_1)^k \varphi_0^{(n-k-1)}\ ,$$

when the s symbols $\varphi_i^{(n-k-1)}$ and $\varphi_0^{(n-k-1)}$ represent polynomia of degree $n-k-1$ in t. From this ensues by integration

$$\alpha_i=(t-t_1)^{k+1}\psi_i^{(n-k-1)}+b_i,\ (i=1,2,\ldots s),\ \nu=(t-t_1)^{k+1}\psi_0^{(n-k-1)}+b_0,$$

in which the quantities b_i and b_0 denote constants. So the transformation of coordinates to parallel axes characterized by the formulae

$$x_i=\xi_i+\frac{b_i}{b_0},\quad (i=1,\ 2,\ \ldots\ s)$$

finally gives

$$\xi_i=\frac{(t-t_1)^{k+1}\chi_i^{(n-k-1)}}{\nu},\quad (i=1,\ 2\ \ldots\ s),$$

by which we alight on the case that the s equations $\alpha_i=0$ belonging to (1) have a common $k+1$-fold root t_1, whilst ν moreover after being diminished by a constant quantity b_0 is divisible by $(t-t_1)^{k+1}$.

The particularity treated here appears only in the case when the curve R_s^n has singular points of a definite character. So the simplest case of a common double root t_1 of the s equations $\beta_i=0$ implies that the origin of each of the spaces of coordinates $\xi_i=0$ represents two of the n points of intersection with R_s^n, which with a view to the equality of the values of the parameter belonging to those points only then takes place when R_s^n shows a cusp in this point. We see at the same time that we have not generally enough enunciated the case sub 3^b). For from this appears that the particularity will come in as soon as R_s^n has a cusp anywhere. So the case sub 3^b) ought to run: "The equations $\alpha_i=0$, $(i=1,2,\ldots s)$ have common equal roots or a transformation of coordinates to parallel axes can call forth this particularity."

Of course the case may present itself that t_1 is a common equal root of the s equations $\beta_i=0$, but that the degree of multiplicity in relation to those equations differs. If t_1 is a k_1-fold root of $\beta_1=0$, a k_2 fold root of $\beta_2=0$, etc, then for k we must take the smallest number k_i.

If it happens p times that a transformation of coordinates to parallel axes implies the particularity indicated here, and if $k_1, k_2, \ldots k_p$ are the smallest numbers k for each of the corresponding values t_1, t_2, . . . t_p of t, then $3n+p-2-\sum_{r=1}^{p} k_i$ will indicate the class of R_h.

4. In the preceding number we have dealt with the class of R_h only, without taking the other characteristic numbers into consideration. We now immediately add that the rule according to which the envelope of a space with $s-1$ dimensions, the equation of which contains a parameter to degree k, is characterized by the numbers

$$k, \qquad 2(k-1), \qquad 3(k-2), \; \ldots\ldots \; s(k-s+1)$$

in general needs some modifications as soon as one of the abovementioned particular cases appears. In the very simplest case of the parabola we find e. g. for the characteristic numbers, class and order, of the evolute 3 and 3, but not 3 and 4 as might be expected for $k=3$. So in general in each of the particular cases treated here the numbers k, $2(k-1)$, $3(k-2)$, etc. must be treated as upper limits.

In a following paper we shall revert to this last point.

Physiology. — "*Lipolytic ferment in ascites-liquid of man*". (Remarks on the resorption of fat and on the lipolytic function of the blood). By Dr. H. J. HAMBURGER.

(Read January 27, 1900.)

In an essay published in the year 1880 CASH [1]) has contradicted the opinion that the emulsion of fat already takes place in the intestinal lumen. For he was never successful in separating an emulsion from the contents of the intestines by centrifugal force. And he did not much wonder at this: for the small intestine has an acid reaction, and with acid reaction no fat-emulsion can be produced.

This opinion of CASH does not seem quite correct to me. Giving to animals a meal containing much fat, HEIDENHAIN has found [2]), and so have I myself many a time, that a creamy surface can be taken off the mucosa of the small intestine, which, examined microscopically, contains small fat-globules. Nevertheless this layer

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[1]) Archiv f. Physiol. 1880. S. 323.

[2]) PFLÜGER's Archiv. 1888, supplement, S. 93.

has an acid reaction. That acid reaction can be coexistent with exquisite emulsions, has been proved by J. Munk, who obtained emulsions by mixing pure fatty acid with a little Na_2CO_3-solution. Another question is however whether the emulsion is already found so finely divided in the intestinal lumen as later on in the chyle-vessels. This now is certainly not the case. Even in the epithelium-cells and in the adenoid tissue of the villi relatively large globules of fat are found, and it is only in the chyle that it appears in its peculiar dust-shape.

It can scarcely be doubted that in the lymph of the villi a cause must exist which brings about the transition of fat to the form of dust.

In order to test this supposition it would be well to gather chyle, undo it by means of a Chamberland's candle of particles of fat and afterwards shake the clear liquid with fat. It is however scarcely possible to obtain the necessary quantities of chyle for the purpose.

I happened to learn that in the Hospital of the Utrecht University a patient was treated, whose abdomen contained a large quantity of ascites-liquid, which had the appearance of chyle. Professor Talma kindly put it at my disposal.

Upon close microscopical investigation however the liquid showed not a single particle of fat and it soon appeared that the observed opalescence proceeded from a mucoid substance which was first described by Hammarsten [1]) and the existence of which was later on confirmed by different medical men [2]).

As regards its composition, the liquid contained 1.939 pCt. solids, consequently less than normal lymph; in which, as is well known, circa 4 pCt. solids are present. It contained 1.715 pCt. albumen, 0.0808 pCt fat, and 0.0564 pCt. soap.

The extraordinary insignificant quantity of fat proved that this was not a case of real chylous ascites, as one could have believed at first sight.

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[1]) O. Hammarsten. Ueber das Vorkommen van Mucoïdsubstanzen in Ascitesflüssigkeiten. Autoreferat in Maly's Jahresber. f. Thierchemie, über das Jahr 1890. S. 417.

[2]) S. und A. L. Paykul. Beiträge zur Kenntniss der Chemie der serösen Exsudate. Ref. Jahresber. f. Thierchemie, über das Jahr 1892. S. 558.

G. Lion. Communication d'un cas d'ascite laiteuse ou chyleuse. Arch. de méd. expériment. 1894, p. 826.

Ceconi, Ueber einen Fall milchig getrübten nicht fetthaltigen Ascites. Italiaansch in Riforma mediche, 1897, no 51. Ref. Maly's Jahresber. f. Thierchemie, über das Jahr 1897. S. 190.

It was proved by laparatomy that the patient was suffering from cirrhosis hepatis and slight chronic peritonitis.

Although the liquid was not chylous, we have nevertheless examined it in the proposed direction, because lymph from other parts of the body seems likewise to have the property to divide fat into the smallest grains. Think of GIMBERT's [1]) experiments; he repeatedly injected into the human body, not only without harm, but with favourable influence on the general condition 25—30 gr. olive—oil with 1 : 15 creosote. The experiments of LEUBE should also be remembered [2]). He was encouraged by the experience made with respect the human body, that subcutaneous injections of camphorated oil applied even in large quantities, can be borne without disad vantage, and consequently tried subcutaneous injections of fat on dogs and thus obtained a considerable deposit of fat in different parts of the body.

Finally I quote the experiments of J. L. PRÉVOST [3]) according to which the oil injected into the lymphbag of frogs, appears as tiny globules in the circulation.

It must be taken for granted that the fat can undergo a minute division in the tissue spaces; otherwise mortal emboli, for instance in the lung-capillaries, would undoubtedly have followed these experiments. With regard to this it is interesting on the other hand that DAREMBERG [4]) by subcutaneous injections on rabbits and Guinea pigs, caused death.

Furthermore 50 cc. of the ascites-liquid with 5 cc. of lipanine were shaken together. In this manner an emulsion was formed, which, by standing motionless and also by centrifugalizing separated itself into two layers. The upper layer examined microscopically, showed large fatglobules; the lower one, particles as tiny as dust, similar to those that are found in chyle and also in milk, the cream having been taken off by centrifugalizing. After that the lower layer was removed and once more centrifugalized. It remained however equally untransparent.

Why had the emulsion separated itself into two layers?

Is it because the oil contained two different kinds of fat, of which the one gives an emulsion *as fine as dust*, but not the other

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[1]) Compt. rend. de la Soc. de Biol. T. 40, 1889, p. 733.

[2]) Sitzungsber. der physik. med. Gesellsch. zu Würzburg. 1895. S. 1 no. 5.

[3]) Travaux du laboratoire de thérap. expérim. de l'Univers. de Genève, II. 1896, p. 44.

[4]) Compt. rend. de la Soc. de Biol. T.40, 1889, p. 702.

one? Or were the conditions not favourable for a thorough dust-emulsion of the *whole* mass of fat?

In order to decide this question the uppermost layer (large drops of fat) was taken off by means of a pipette and shaken anew with fresh ascites-liquid. Centrifugal force was again applied and once more a separation into two layers was visible. Both layers contained fat; now the undermost layer even contained more fat than at the beginning of the experiment and the microscope only showed the dustshape. From this it was evident, that the part of the fat, which, with the first experiment was separated in the shape of globules into an uppermost layer, had been transformed into fat in the shape of dust by shaking with fresh ascites-liquid.

That which had not passed into dust was shaken again with fresh ascites-liquid, and now at length all the fat had been turned into the shape of dust.

That with the first shaking-experiment the fat only partly passed into dustform, does not find its cause in an eventual difference in the relative condition of the different kinds of fat in the oil, but can be explained from the conditions of the experiment. It has indeed been proved that a perfect dust-shaped emulsion can be obtained *at once*, if only the shaking is continued for a long time and with a relatively large quantity of ascitesliquid.

I have further considered whether a peculiar quality of the ascites-liquid must account for this. Therefore the experiment was repeated with another albuminous liquid, viz. with bloodserum. 30 cc. horse-serum were mixed with 5 cc. lipanine and the mixture strongly shaken for one hour. The emulsion was next centrifugalized, and thereby divided itself into two layers, a lower one with fat in dust-shape, an upper one with tiny fatglobules.

The latter was removed, vigorously shaken with 30 cc. of the fresh serum and after that centrifugalized again; once more two layers were obtained; the lower one however now contained much more fat than with the first shaking. After having been shaken third time with 30 cc. serum, all the fat was brought into the form of dust. Shaking 150 cc. serum with 5 cc. lipanine for four hours, brought about the perfect dust-shaped emulsion. This emulsion could now no more be divided into two layers by centrifugalizing. We thus did not find any specific quality in our ascites-liquid with regard to the dispersion of the fat, for the same occurred with the blood-serum.

Transferring these facts to normal life — which does not seem too hazardous in this case — it can be imagined, that the lymph of the villi in its *motion*, causes the little fatglobules, already in a state of thorough division, to pass into the shape of dust. Surely this lymph-current works slowly, but it should be considered, that the time at its disposal is not short; 30 hours after a rich meal has been taken the chyle still carries away fat.

As is well known COHNSTEIN and MICHAËLIS have pointed out in two interesting publications [1]), that, when blood has been mixed with chyle-fat and air is then carried through the mixture, the fat disappears, and a combination dissoluble in water takes its place. We were interested to know, when blood is mixed with our artificial chyle (dust-shaped emulsion of lipanine in ascites-liquid) and a current of air was made to pass through, whether a disappearance of fat would likewise be observed.

To this purpose 240 cc. of the ascites-liquid with 15 cc. lipanine were shaken for $1^1/_2$ hour. After centrifugalizing, the undermost of the two layers is removed, which contains the fat exclusively in dust-form.

Of the artificial chyle attained in this manner:

(1) 75 cc. was mixed with 25 cc. horse-blood rich in erythrocytes [2]). For 23 hours a current of air is allowed to pass through under a temperature of ± 16° C.

(2) 75 cc. of the artifical chyle are mixed with 25 cc. blood. *No* current of air is allowed to pass through.

The liquids (2) are mixed just before drying takes place.

At the same time exactly the same experiments are performed with dust-shaped lipanine-*serum*-emulsion, consequently:

(3) 75 cc. of a dust-shaped lipanine-serum-emulsion are mixed with 25 cc. horse-blood, and through this mixture air is allowed to pass through for 23 hours (the same current of air as under (1).

(4) 75 cc. of the dust-shaped lipanine-serum-emulsion are mixed with 25 cc. of blood. *No* current of air passes through.

The liquids (4) are mixed just before drying takes place.

(1), (2), (3) and (4) are placed into two small receptacles, mixed with 20 gr. of pure sand and being stirred, dried in a temperature of 80°. After having been pulveriged, extraction with ether, free of water, in a Soxhlet apparatus for 48 hours.

From (1) . . . . 0,244 gr. ether residu
" (2) . . . . 0,475 gr. " "
were be obtained.

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[1]) Sitzungsber. der Preussischen Akademie der Wissensch. 1896. S. 171; more circumstantially in PFLÜGER's Archiv. B. 65, 1897 S. 76; B. 69, 1897, S. 473.

[2]) Such blood is obtained by leaving defibrinated horse-blood to itself and by pipetting off the serum after the red blood-corpuscles have settled down.

By this we have proved, that by letting the air stream through the mixture of blood and lipanine-ascites-emulsion a considerable transformation of fat takes place.

From (3) 0.371 gr. Ether residu is obtained
〃 (4) 0.283 gr. 〃 〃 〃 〃

From these two numbers it is evident that by letting a current of air pass through a mixture of blood and *dust-shaped* lipanine-*serum*-emulsion, no transformation of fat takes place.

These numbers even rather tend in the opposite direction.

After all these experiments it must be taken for granted, *that the lipolytic ferment was not present in the blood, nor in the serum, but existed in the ascites-liquid.*

The question could now be examined, whether the presence of blood is really required for the transformation of fat and whether it is not sufficient to pass air through the lipanine-ascites-emulsion.

To reply to this question, 80 cc. of a lipanine-ascites-emulsion (75 cc. ascites-liquid + 5 cc. lipanine) were shaken for 3 hours and submitted to a current of air for 20 hours. After that the fat-contents were determined, which took place at the same time with a portion of the same emulsion, not having been treated with a current of air.

80 cc. lipanine ascites-emulsion treated with air contained 4.300 gr. of fat
80 cc. 〃 〃 〃 *not* 〃 〃 〃 〃 4.252 〃 〃 〃

The passing through of air only, has consequently not given cause to transformation of fat.

This result agrees with that of Cohnstein and Michaëlis. These investigators also found in their experiments with true chyle, that without the presence of red blood-corpuscles, the passing through of a current of air was not able to cause a transformation of fat.

Repetition of the experiment.

This experiment was performed in the same manner as the foregoing; the only difference being that instead of 24 hours, the current of air was only allowed to pass for $12^1/_2$ hours, under room-temperature, and instead of horse-blood, ox-blood was used.

(1) 75 cc. of dust-shaped lipanine-ascites-emulsion + 25 cc. ox-blood. Current of air for $12^1/_2$ hours; after that the liquid is mixed with sand, dried an extracted with ether. Ether-extract 0.064 gr.

(2) 75 cc. of the dust-shaped lipanine-ascites-emulsion are mixed with 25 cc. ox-blood, although not before a current of air has been led through the mixture (1) during 12½ hours. After intermixing, the liquid is treated at the same time and in the same way as in (1). Only here, as has been mentioned, no air is allowed to pass through. Ether-extract 0.186 gr.

(3) 75 cc. of the dust-shaped lipanine-ascites-emulsion produce an ether-extract of 0.219 gr.

(4) 75 cc. of dust-shaped lipanine-*serum*-emulsion are mixed with 25 cc. ox-blood. Current of air for 12½ hours. Dried with sand, extracted with ether. Ether-extract 0.359 gr.

(5) The same as experiment (4), however without the current of air. Ether-extract 0.364 gr.

(6) 75 cc. of the dust-shaped lipanine-serum-emulsion. Ether-extract 0.369 gr.

It appears from (1) and (2), that in passing air through the mixture of blood and dust-shaped lipanine-ascites-emulsion (artifical chyle), fat disappears.

On comparing (2) with (3) it appears that also when a current of air is not passed through, a little fat is analysed. As the experiments of COHNSTEIN and MICHAËLIS have pointed out, and we have been able to confirm, this transformation takes place in consequence of the drying of the emulsion in presence of blood and air.

It appears from (4) and (5), that the passage of air through the mixture of dust-shaped lipanine-*serum*-emulsion and blood, causes *no* transformation of fat, which is confirmed by the result of (6).

Two repetitions of the experiment.

Ox-blood was now again taken; duration of the passage of air 28 and 18 hours. Room-temperature.

(1) 75 cc. dust-shaped lipanine-ascites-emulsion + 25 cc. ox-blood. Passage of a current of air through the mixture for 18 hours. After that dried with sand and extracted with ether. Ether-extract in the two experiments 0.215 Gr. and 0.114 Gr.

(2) 75 cc. of the dust-shaped lipanine-ascites-emulsion are mixed with 25 cc. ox-blood, after air has been conducted through the former mixture for 18 hours; after mixture the whole mass is treated instantaneously, consequently at the same time with (1), for the determination of fat. This experiment is therefore similar to (1); with the exception that no air is conducted through. Ether-extract 0.498 and 0.288 Gr.

(3) 75 cc. of the dust-shaped lipanine-ascites-emulsion give from 0.562 and 0.315 Gr.

(4) 75 cc. of the dust-shaped lipanine-serum-emulsion are mixed with 25 cc. oxen-blood. Passage of air for 18 hours. Drying with sand, extraction by means of ether, free of water. Ether-extract 0.401 and 0.312 Gr.

(5) Same experiment (4), but without passage of air. Ether-extract 0.394 and 0.321 Gr.

(6) Passage of air through 75 cc. of the dust-shaped lipanine-ascites-emulsion. Ether-extract 0.567 Gr.

On comparing (1) and (2) it appears again, that by passing air through the mixture of blood and dust-shaped lipanine-ascites-emulsion, disappearance of fat takes place.

On comparing (2) and (3) it appears that by non-conduction of air, some fat is transformed as well. This transformation occurs whilst the drying is going on, as long as the temperature still remains below the transformation-temperature of the ferment.

(4) and (5) show, that conduction of air through the mixture of blood and dust-shaped lipanine-*serum*-emulsion, causes *no* transformation of fat, which is confirmed by the results drawn from (6).

Finally the comparison of (6) and (3) proves, that without the aid of blood, the passing through of air is not efficient to make the fat disappear. Considering the results of the different experiments, there is no doubt, that in the examined ascites-liquid a substance exists which appears able to transform fat, and which, with the aid of bloodcorpuscles and with access of oxygen, performs the change.

COHNSTEIN and MICHAËLIS are of opinion that this substance, with which they obtained such a transformation of the chyle-fat, is contained in the blood which was used by them.

Closely considering their experiments it strikes us that they have no right to maintain this conclusion. For when they observe that after mixing blood with chyle, *fat* disappears from the latter, it is notwithstanding possible, that the ferment is not present in the blood, but in the chyle. It must seem strange that the authors have not considered this possibility, because *no* fat disappeared from the mixtures of *milk* and blood and from *codliver-oil*-emulsions with blood. The authors have tried to explain this latter fact by taking for granted, that the fat would be present in the chyle in a more finely divided condition. Meanwhile this explanation does not seem satisfactory to the investigators themselves, and it cannot be correct, for as was mentioned above, fat also appears in milk in dust-shape. The fat of the so-called undermilk (the undermost of the two layers in which the milk is separated when contrifugalized), consists exclusively of dust-particles; it amounts to about $^1/_{20}$ of the total quantity of fat.

Also from emulsions of codliver-oil with Na_2CO_3, a portion can always, by centrifugalizing, be separated as emulsion in dust shape.

It would perhaps be possible — also in connection with what we found in our ascites-liquid — to find the explanation of their negative result with milk and codliver-oil, in the fact, that neither in milk and codliver-oil, nor in blood a lipolytic ferment was present, but that it was present in the chyle; hence the transformation of fat in a mixture of blood and chyle.

To my regret I was obliged to cut short my investigation on this subject. Although I am fully aware that these results are incomplete in many ways, it seemed expedient to me to publish them at present, as for some time I shall not have the opportunity to pursue this subject, and I wished to stir up other inquirers to the use of ascites-liquid for the study of the lipolytic ferment. The mucoid ascites-liquid can be had in such abundance (repeatedly more than 8 Liter of liquid were removed from the abdominal cavity of the patient), that it will afford a better and more extensive opportunity for the study of the nature and the effects of the lipolytic ferment, than most other animal ferments.

The above mentioned researches have given the following results:

1. It is possible to make from lipanine (acid olive oil) a perfect dust-shaped emulsion. This has not only been successfully performed with the aid of the examined mucoid ascites-liquid, but also with ordinary horse-blood-serum.

2. This fact seems to indicate, that during life, the transition into dust-shape of the small fat globules, which still exist in the adenoid tissue of the villi, is caused by the continuous motion of the lymph of the villi.

3. The opalescent, non-fatcontaining, mucoid ascites-liquid examined by us, contains a lipolytic ferment, which possesses the power to transform dust-shaped fat. For this transformation the presence of bloodcorpuscles and also access of air is necessary.

4. The contention of COHNSTEIN and MICHAËLIS, that the lipolytic ferment discovered by them, originates from the blood, has not been proved. Their and my experiments rather show, that the ferment is a constituent of the chyle.

Physics. — Communication N°. 54 from the Physical Laboratory at Leiden by Prof. H. KAMERLINGH ONNES: "*Methods and Apparatus used in the Cryogenic Laboratory II: Mercury pump for compressing pure and costly gases under high pressure*".

(Read January 27, 1900.)

§ 1. At the meeting of January 25, 1896 I read the description of a compressor which has been repeatedly used for researches in the Physical Laboratory. As the reproduction of the drawings belonging to this description was very expensive I had to delay their publication. To the description of the cryogenic laboratory by Prof. MATHIAS[1]) a diagram was added which could serve as a preliminary illustration to § 3 of Comm. 14 (Dec. '94). Of late only I had the opportunity to prepare the complete set of drawings for zincographical reproduction. These enable me to now describe more fully the way in which I have availed myself of CAILLETET's happy idea of a mercury pump in order to obtain a compressor of great use in researches with compressed gas.

The compression with mercury has two advantages. If a liquid is brought into the pump cylinder of a compressor, we may thereby eliminate the clearancespace, if the gas does not dissolve perceptibly in this fluid under high pressure. For in this case, the gas which is formed during exhaustion from the residual liquid in the pump-cylinder will partly fill the latter and its disturbing influence will be greater or less, as the difference between the exhaustion and forcing pressures is greater or less. Therefore with most liquids only small differences of pressure between the sucking and compression sides will be permissible, and if a higher degree of pressure is required we shall have to apply compressions in successive pump-cylinders as in the BROTERHOOD compressor (Comp. Comm. N°. 51 § 3).

If however mercury is used, there is no objection to raising the gas at once from its normal or even its exhausted condition to more than 100 atmospheres, if desired[2]).

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[1]) E. MATHIAS, Le laboratoire cryogène de Leyde. Rev. Gen. de Sciences, 1896, pag. 381.

[2]) The sudden compression causes a great generation of heat (as in the case of the fire pump) notwithstanding the considerable cooling by the walls and the mercury. A mixture which is easily exploded should not be compressed by the pump, as it might be ignited by the heating. This occurred once, when methane and oxygen became mixed by accident. The manometer was smashed and flung away, a flash of fire burst from one of the outlets, and on opening the pump, several parts were found to be burned. The explosion fortunately occurred without any personal accident.

In the second place the gas enclosed between pure mercury and steel cannot become contaminated by volatile substances which it might otherwise absorb from the liquid in the pump-cylinder or from the lubricant used for this cylinder.

These advantages are of especial importance if we must compress moderately large quantities of pure or costly gases, and for this purpose an apparatus of the same dimensions as that of CAILLETET is indispensable in a laboratory.

That the compressor (to be described below) answers its purpose in all respects, may be proved by the fact that it has been frequently used during the last eight years, without having undergone the slightest change, or giving the least trouble. The improvements made upon the original CAILLETET pump in former years (especially in '88) were rendered necessary by repeated disappointments, which so often disagreeably interrupted the progress of my work that I almost despaired of ever obtaining a mercury pump easily handled and perfectly trustworthy.

In considering the apparatus we must bear in mind that it has grown by gradual improvement from the CAILLETET-pump, and also that traces of less successful modifications have remained. It would be possible to design now *a priori* a compressor that from the point of view of mechanical design would be of better shape and construction owing to the greater harmony of its dimensions. I hope that a mechanical engineer will feel himself drawn to the solution of this problem. I was satisfied in having an apparatus which worked well from a physicist's point of view, and, in the same manner and after this design every other CAILLETET-pump can be successfully modified.

§ 2. Fig. 1 Pl. I. shows CAILLETET's original compressor so that we may compare the two compressors together. Fig. 1 is a section, figs. 2 and 3 show the manner in which the gas to be compressed is admitted through the sucking-cock λ into the pump-cylinder.

Pl. III is a diagramatic representation of the new compressor with the accessories belonging to it. The purpose of this plate is to explain the way in which the different parts work. These are for the greater part drawn on the same scale in a simplified but yet recognizable manner, while the connections are entirely diagramatical. The real form of these parts, so far as they are not sufficiently represented in this plate, may be seen on Pls. IV, V and VI figs. 1 and 2, while figs. 1, 3 and 2 of Pl. II show the actual arrangement of the different parts of the foremost and the hindmost halves in front elevation, and of the whole in side elevation [1]).

We now come to a more complete explanation of the desirability of the most important changes [2]). A survey of these has been given in § 3 Comm. No. 14 (Dec. '94), to which a reference should be made in the first place.

𝔄 1. It was necessary to arrange that air can not get into the pump tube through the packing (comp. δ, Pl. I fig. 1).

𝔄 2. The piston can not be damaged through insufficient lubrication and hence cause the packing to fail to give adequate closure.

𝔄 3. The mercury can not be soiled by the lubricant.

When the latter occurs the scum which gathers near the forcing-valve, keeps back the high pressure gas below this and enables mercury and then gas to leak back from the reservoir under high pressure. Therefore it is of the greatest importance that the mercury remains quite clean. My principal desire in most of the changes was to enable me to accomplish this.

It was possible to attain all these requirements by transferring the plunger, which by moving upwards in Cailletet's compressor causes the compression of the gas (comp. α fig. 1, Pl. I) to a separate compression tube C' Pl. III. From this through a wide connecting tube d, as shown in the diagram, it moves the mercury in the pump-cylinder e up and down. The lubricant used was glycerine, which gives a sufficient lubrication and yet as is the case with vaseline and more especially oils, does not unite with mercury by agitation to a butterlike substance (see especially 𝔄 3).

Contact of the mercury with the packing is wholly avoided by introducing a layer of glycerine above the mercury, which can be done now that the packing is above and not under the mercury.

The stuffing box b is entirely immersed in glycerine, so that the pump can only suck in glycerine, if the packing does not fit tightly; should however air enter it might cause the pump to stop working but could not mix with the experimental gas. This could only take place if the mercury and the glycerine were entirely forced

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[1]) The resemblance of the forms makes it easy to find our way on the drawings, moreover the letters have been chosen so that the letter itself indicates a distinct part of the apparatus, the annexed numeral a certain detail of that part, and following numerals details of that detail.

[2]) Some of the newly added pieces were constructed with much care by Mr. J. W. Giltay (formerly Kipp & Sons); to Messrs. Kouw and Curvers, mechanics at the laboratory I owe my best thanks for the extreme care with which they have assisted me in these alterations.

over to the sucking-side but against this the necessary precautions have been taken.

𝔅. 1. If the packing of the plunger is to produce no difficulties it is necessary that it should give a good closure with little friction, for which reason I have replaced Cailletet's packing by a collar packing.

𝔅. 2. It is also necessary that the plunger should remain perfectly smooth (comp. 𝔄. 2), which can only be obtained in the long run when a perfectly rectilinear motion independent of the packing is secured. This is facilitated by the use of guides and rods and by modifying the beam accordingly.

𝔅. 3. The moving of the mercury should be slow only, (from 20 to 60 up and down movements per minute); to obtain this and also to allow the pump to be regularly worked by hand, the crank is connected to the shaft which makes 60 revolutions per minutes (with an electromotor up to 90) by means of chain gearing.

ℭ. During compression, the pump-cylinder must always be entirely filled with mercury, so that the high pressure gas remaining behind in the clearance space, shall not make exhaustion impossible when the mercury recedes.

Each time that the mercury presses the gas through the forcing valve into the reservoir of compressed gas, the gas takes some mercury with it. In Cailletet's pump to make up for this loss, some mercury is admitted into the sucking chamber from the reservoir above *v* (Pl. 1 fig. 2). But after some time there is an uncertainty about the quantity of mercury in the high-pressure reservoir of the pump, more especially in consequence of the leakage of mercury from the apparatus, which is unavoidable with the construction of this pump.

If too much mercury is admitted into this reservoir, it would overflow into the apparatus in which the compressed gas is forced.

In the newly constructed pump the quantity of mercury to be used is measured precisely once for all and is not liable to diminish. Moreover a capillary connection has been contrived between the reservoir of compressed gas and the pump-cylinder, through which a quantity of mercury which can be exactly regulated, can flow back from the former into the pump body, so that during every compression there is a small excess of mercury in the latter.

𝔇. 1. A perfectly rectilinear up and down motion is desirable in order to ensure a satisfactory fit of the forcing valve, which separates the pump reservoir from the pump cylinder.

𝔇. 2. In finishing the upper end of the pump chamber we must bear in mind that compressed gas must not remain behind in scratches, holes or other irregularities of the walls, as this could have the same influence as any air-bubbles which might be kept back by dirt gathered near the pressing valve, if we had not taken the necessary precautions to prevent this as described in 𝔄. 3. For it is not unusual for all the gas from the pump cylinder to be compressed to less than 1 c.c. when forced through the pressing-valve. In addition all the parts must remain free from rust, and hence only perfectly dry gas can be admitted into the pump. By means of the precautions taken (comp. also 𝔅 1 and 𝔄 1) it is possible to obtain a vacuum, which in the pump cylinder is a primary necessity if the exhaust is to be satisfactory.

𝔇. 3. Into this vacuum again the gas must be so admitted during the exhaust, that no air can possibly enter, that the mercury cannot be contaminated, and that the inflow of the gas is not hindered, while even under the highest pressure nothing must leak back from the pump-cylinder towards the exhaust-side.

In CAILLETET's original pump this is attained by a cock, which is opened and shut at the right moments by means of levers moved by blocks (comp. Pl. I) fastened to a disk on the shaft of the pump. Such a cock cannot work without being lubricated and a little of the lubricant might come on to the surface of the mercury, and the pump could then no longer be used (comp. 𝔄 3). We cannot be certain that the cock will remain properly lubricated after some time, and in lubricating air might come in which could contaminatie the gas. Besides it is difficult to keep the cock channel free from the lubricant and therefore large enough.

And yet CAILLETET had good reason for using this cock. For an ordinary valve will generally give either an insufficient closure with the various pressures, at which a good closure is required, or it will stick at the highest pressure, so that it does not admit gas into the pump-cylinder during the next exhaust.

In order therefore to replace that cock by a valve, which would avoid this lubrication, we had to contrive (as remarked in Comm. N^{0}. 14) a special construction which would satisfy the above mentioned requirements without being liable to the difficulties offered by ordinary valves. The valve described in § 3 enables us at least as far as it is concerned, to work with the pump uninterruptedly, for as long as is required. It is only rarely that the exhaustion fails, and then it suffices to let the pump rest a few moments in the exhaust position in order that the valve may again become loosened.

𝔈. 1. We must always expect the possibility of the mercury returning, or what sometimes could be worse, of the already compressed gas returning into the apparatus, from which it is taken, in consequence of leakage along forcing and suction valves, especially when the working of the pump is interrupted for some time for one reason or other. This returning of the mercury might cause great disturbances and even accidents. In Cailletet's original pump a feeding valve (*u* Pl. I fig. 1) has sometimes been used but afterwards this has been again removed. When this small ebonite valve came into use, and was closed by a pressure of for instance 100 atmospheres, it thereby stuck and the pump was stopped working. It could not then be started again without very complicated operations, if we did not wish to lose gas or to have it contaminated with air. Moreover this valve was an obstruction to the easy entrance of the gas into the cylinder.

In the newly constructed compressor a safety-feeding-valve (comp. g_{10} Pl. III) has been constructed which in ordinary circumstances lies loosely under its support but is raised and pressed against this by the mercury, as soon as this forces its way towards the exhaust side, while the valve can be loosened from the support from the outside, after having been pressed against it by high pressure, without opening the pump.

𝔈 2. At the same time we can avail ourselves of this valve for closing the pump at the exhaust-side, and this is always done as soon as we stop the working of the pump.

When started again after an interruption or stoppage with the valve closed, the pump begins to exhaust the sucking-chamber as far as the valve, and then by opening this we can again make the connection with the exhaust-tube.

𝔈. 3. As with the least contamination of the mercury (and especially when small splinters of iron or other particles of hard material are in the pump) the valves cease to be perfectly closed, part of the mercury may flow over to the exhaust-side. In order to prevent this from getting into the apparatus, from which the gas is taken, an antechamber g_6 (Pl. III) is made, which if necessary can contain the whole quantity of mercury which is above the exhaust-valve in the pump cylinder.

𝔉. The compressed gas must be entirely freed from mercury. The spreading of the gas jet in the dome shaped reservoir, in which (in Cailletet's pump) it is compressed before it is admitted into the outflow pipe is partly useful to this end.

𝔉. 1. It appeared however an advantage to add a spray catcher and separating plate.

𝔉. 2. Further separation is promoted by passage through a small cylinder k_{11} (Pl. III) in which the current of gas is once more forced to change its direction, while

𝔉 3. the last traces of mercury are removed by a mercury-filter k_3 (Pl. III) in which the mercury is brought into contact with copper and gold-leaf.

𝔊. In order to be warned when the mercury passes over into either the chamber g_6 or into the overflowvessel k_3, and to observe the position of the mercury in the compression tube C', insulated contacts are taken through the steel walls, of which those in g_6 and k_3 are permanently connected with an electric bell, while that in C only makes contact through a control switch.

𝔋. The above indicates what is necessary for sucking in the pure gas at the exhaust-side and for forcing it out at the pressure-side under high pressure and free from mercury.

In order to be able to work regularly with the pump we must still contrive some additional apparatus. Among these are:

𝔋. 1. A number of cocks, several of which are united together on a cock-board, which also gives

𝔋. 2. an opportunity for measuring not only the tension in the reservoir of the pump (as in Cailletet's pump), but also that in the apparatus in which the gas is being compressed.

𝔋. 3. A safety-valve, which bursts whenever the pressure becomes high enough to endanger one of the pieces of apparatus which are under pressure and joined on to the pump.

𝔋. 4. a safety-tube on the exhaust-side, for protecting the apparatus to be connected with it,

𝔋. 5. a connection with the air-pump so that the compressor and all the accessories can be exhausted before pure gas is admitted into them.

The operations which are made with the pump, may be arranged under three different heads, which we can find for ourselves from the diagram if we connect I, II and III with the exhaust-tube of the pump. But before treating of these three operations we will first describe the pump itself more in detail.

§ 3. *α*. *Packing of the compression-tube* (see Pl. IV). The piston-rod or plunger A'_3 moves in a lignum vitae coating b_3 fitting in a cavity turned in the compression-tube C'_0. Before working the wood it is thoroughly soaked in glycerine [1]. On this coating rests a leather collar b_{41}, which has been made by pressing it, when moist, into a mould made specially for it. When the pressure below the leather collar increases, the inner part of this is pressed against the steel rod, and hence the higher the pressure the better the closure. If however the plunger moves upwards and the vacuum occurs in the compression-tube, which vacuum with closed suction-valve can amount to 10 cm. of mercury (comp. Pl. III), the closure would be prevented owing to the pressure from without; therefore the leather ring must be pressed artificially against the piston-rod (comp. § 2 𝔄 1). For this purpose we have placed in the leather collar an india-rubber ring b_{42}, which presses the collar against the plunger, when the packing-ring is tightened.

The packing-compressor b_{21} with the lining b_{22} is pressed down by the nut b_1, screwed on to the forcing-cylinder. In this nut also a wooden lining b_{31} is screwed, through which the plunger runs.

In order to keep the packing entirely under the glycerine (comp. § 2 𝔄 1) a small cup b_{12} is placed on the nut b_1 which is entirely filled with glycerine and which communicates by two tubes b_{13} and and b_{14} and grooves b_{32} in the nut with the space between the nut and the cylinder b_{15} and also with the space between the packing-compressor and the plunger. The air in this space can escape through the longer tube while the space is being filled by the glycerine through the other tube.

The screw-threads b_{16} between the cylinder-wall C_1 and the nut b_1 are filled with wax in order to prevent the glycerine from leaking away along them.

If the apparatus is out of use for some time, the glycerine is removed to prevent it from attracting water and hence causing rust, while the wooden linings are kept in glycerine.

In screwing off the nut the glycerine which flows out is caught in the cup V_{12}, fitting on the support V_{10}. The glycerine is removed from the compression cylinder by means of a pipette and blotting paper. The mercury (7 KG.) is left in the pump.

For the preparation of the apparatus exactly measured quantities of glycerine are poured into the forcing cylinder (70 c.c.) and into the cup b_{12}.

To introduce the glycerine into the closed pump the packing is

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[1] It is first immersed in glycerine and turned nearly to its proper dimensions, it is again soaked for some time in glycerine and then turned to its correct size. Reserve pieces are kept in stock.

loosened under decreased pressure, while to remove the glycerine one of the contacts is loosened a little under pressure. If the exact quantity of glycerine is present, and if during the exhaust the switch belonging to the contact C'_3 is pressed down (§ 2 𝔖), the bell is not heard, if the same is done with the switch belonging to C'_5 the bell must always be heard, but with the switch belonging to C'_4 the bell is only heard for a moment. Pl. V fig. 2 shows a high-pressure-proof contact with platinum-point.

β. Up and down motion of the plunger. The plunger A'_3 together with the cross-arm A'_2 (comp. also Pl. II fig. 3) and the rod A which is directed upwards are forged of one piece of steel. The rod moves through a guide block V_{20} (comp. § 2 𝔅. 2) which consists of two parts V_{21} and V_{22} screwed upon each other and is connected to the frame V_0 through the arm V_{20}.

The lubricating oil which flows from the guide-block is caught in the cup A'_4 which fits loosely on the cross-piece, and so cannot soil the glycerine (comp. § 2 𝔄. 3).

The side arms of the cross piece A'_2 are moved up and down by drawing rods S_{41}. These are coupled to a ring S_3 sliding round the smooth cylinder C'_0 (comp. § 2 𝔅. 2); the levers S_1 in moving up and down can turn on the bolts S_{34} with which they are fastened to the ring S_3.

The beam consists of two symmetrical curved levers being wider towards the side of the compression-tube, and enclosing it (comp. Fig. 3 Pl. II and Pl. IV to the left, upper view of the ring), while the two parts where they are coupled to the connecting rod or with the hinge S_2, fit immediately against the smooth sides of the rods S_{41}.

The piece S_3, consisting of the halves S_{31} and S_{32} screwed against each other (comp. upper view Pl. IV) leaves room when moving up and down for the contact-screws C'_3 C'_4 C'_5. For greater security it is covered with a small plate S_{30} in which is a small lubrication-hole leading to the lubrication-canals S_{31} and S_{32}.

γ. Transferring of the motion, gearing. In this connection fig. 1, 2 and 3, of Pl. II must be consulted, on which no letters are placed for the sake of clearness.

The connecting rod *t*, Pl. IV is moved by the crank U_{11} U_{12} U_{13} on which is a ratchet wheel with ratchet and ratchetsupport to render a backward movement impossible.

This improvement is especially useful when the pressure-valve leaks, but also when we stop the pump and put the plunger in the lowest position in order to reduce the possibility of leakage as much as possible.

The fly-wheel is connected on one side of the crank with a pin, on the other side a toothed wheel is fastened which receives the motion by a chain from a second toothed wheel on the shaft proper. This shaft runs in a supporting piece fixed tightly by means of strong screws to the frame and strengthened by a separate oblique stay.

The wheel is drawn in the figures of Pl. II on the shaft over which the leather belt runs to an additional shaft worked by a steam engine. In the Leiden laboratory this latter shaft is on the wall opposite the pump. Instead of the steam engine we can also employ an electromotor of 1 H. P. (75 K.G.M. per sec.) by means of a large and lightly built wheel of 1 meter diameter and the same additional shaft. Finally there is an arrangement for placing a handle on the shaft of the pump, so that one or two men can turn this at the proper speed (§ 2 𝔅 3).

δ. *Compression tube and the communication of the mercury of the compression tube and the pump cylinder.* The thick-walled forcing cylinder C'_0 rests with its base C'_{60} on the frame V, screwed on to it tightly with four bolts C'_7 the exact position being determined by four pins C'_{72}.

A direct connection with the pumpcylinder was made impossible owing to the frame and the crank.

Therefore, a little above the bottom of the cylinder a bored tap with screw-thread C'_8 is forged on, on which the thick-walled bent connection-tube $d_0\, d_2$ (see Pl. III, VI fig. 1 and Pl. II) is fastened by the nut d_1. The **T**-piece d_2 forms a junction between the elbow d_0 and the double bent tube d_3, which is fastened with the nut d_4 on the pump proper e_{00} (Pl. V) this being itself provided with a screw-thread.

The nut d_1 rests on the tube by means of a collar d_{03} forged on to d_{00} and a closure is obtained by the washer d_5. The fastening of the nut d_4 was a little more complicated. On the tube d_{30} is screwed a ring d_{31} above which is placed an india-rubber ring d_6 and a plate d_{33}, which can be pushed over the screw-thread of d_{30}, this being slightly rounded off towards the upper end by the addition of a rounded ring d_{34}. The india-rubber ring is thus completely enclosed and in tightening the nut d_4 this india-rubber gives a perfect closure.

The **T**-piece d_{20} (Pl. VI fig. 1) is screwed on the two tubes d_0 and d_3, so that the bend of the former becomes of the required form, the proper thickness is then given to the leather packings d_{71} and d_{81} the closure being obtained by securing nuts d_{91} and d_{92}.

The passage for the mercury, is interrupted in the **T**-piece by two bends d_{201} and d_{202}, opening into a space d_{203}, which space is closed by a tap provided with packing d_{23} and also with an opening with its screw d_{24} and accompanying packing.

It is used during the cleaning of the pump to run off mercury, for which purpose the **T**-piece is held downwards; moreover drops of glycerine if they are carried along by the mercury can gather in d_{203} and be drawn off through d_{24}. It is seldom necessary to dismount the double bent tube. A great convenience of the above mentioned arrangements is that the mercury can always remain in the pump and hence the introduction of dust or splinters is not to be feared.

ε. *The pump body e* with its water circulation e_9 (Pl. III and V) is in the main the same as CAILLETET's. Here also the head e_4 is hermetically fitted on the pump body by means of a leather ring while a layer of mercury renders the closure of this packing perfect [1]). The iron basin e_1 is arranged to prevent the mercury being spilt [2]).

ζ. *Connection of pump-cylinder and pressure-reservoir.* The steel capillary i is fixed at both ends in the cocks i_1 and i_2. The latter is adjusted at the height of the suction-valve. At first the communication was made for convenience along d_{24}, but it is evident that the leaking of gas into the pump-cylinder, whenever the cock is not shut in time, may cause great inconvenience.

The cocks i_1 i_2 are constructed according to the Leiden model of high-pressure cocks. In order that they should work satisfactorily it is most important that everything should be very accurately prepared on the lathe, so that the point of the pin i_{230}, which is hardened, fits quite centrally into the conical hole i_{21}. When the pivot is loosened, the gas must be able to move freely along i_{231}, and therefore the space left should not be too small. The screw-thread i_{232} must not cut the packing when the cock is entirely open, and hence the pivot i_{233} must have the full thickness out of which the screw is

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[1]) The packing is tightened by means of a key with a very long handle.

[2]) The floor in the neighbourhood of the pump is arranged so that any mercury spilt can be easily collected.

cut and fit precisely in the small ring i_{25}. A little below the washer case the screw-thread must end in a cylindrical boring corresponding with the part of i_{233} projecting outside the packing. The packing itself is pressed into a conical space and care must be taken that new layers of leather (or cork) are always added in time, before the packing-compressor i_{26} is screwed too far down by the nut i_{27}. On placing the cock in the apparatus, care must be taken that the point is directed towards that side, where the removal of the packing, which these cocks especially permit, could offer difficulties. To show that the position of the cock may not be altered the handle is taken away from the head of the pin.

As usual the capillary i_0 is fastened into the overpipes with screw-threads and marine-glue.

When the cock i_2 is open the boring i_{21} communicates with the cock i_1. In the boring i_{101} of this cock is a filter consisting of closely packed platinum-wires i_{104} enclosed in a small case with sieve-shaped bottom i_{103} and with a rim and washer i_{102} resting on the cock itself. The satisfactory working of the filter depends on the pump being thoroughly cleaned, an operation which is rarely necessary with my construction, and which therefore can be done with the utmost care.

With one of the cocks i we regulate, with the other we shut entirely, a thing which should not be forgotten if the work is stopped for a moment. Moreover these two cocks are required for removing the capillary from the pump when necessary without interrupting the work. If everything goes well we can see the capillary moving regularly between two positions (like a Bourdon spring) under the influence of the alternating pressure.

The boring i_{11} communicates with the boring i_{02} in the pump body. To adjust the cock i_1 to this so that the packing can be tightened while the cock remains perfectly stationary (which the space at our disposal renders necessary in view of the capillary connected with it) a cylinder shaped lengthening piece i_{12} with flange is forged on i_{10}. It is fastened in the boring e_{02} by means of a bored conical joint with a thread i_{17}, which is in two pieces, held together by pegs.

In the boring e_{02} an ebonite cap e_8 with packing is fastened, so that, when as much mercury as possible has run through i, a layer remains to assist the closure of e_4 in e_{00}.

η. *Forcing-valve with accessories.* The steel pressure-valve (Pl. V fig. 1) rests on the support e_2 which is screwed in the upper-end of the boring in the pump-body. This upper-end is provided with a very finely finished screw-thread in which the thread on the valve support fits very tightly (comp. § 2 𝔇 2). The lower end of the boring in this steel support is turned out smooth and trumpet shaped, so that during compression bubbles of gas cannot remain behind (comp. § 2 𝔇 2). The support fits on the pump body with the help of the enclosed washers e_{22}.

The conical part of the valve-pin e_{31} is ground with the utmost care on the support e_{23}, when it is moved it is guided (comp. § 2 𝔇 1) by a cylinder e_{32} sliding up and down in the cylindrical opening e_{24}, in which cylinder pieces are cut away along the lines of movement. The spring e_{78} and the pin e_{74} prevent the lengthening piece e_{33} from moving too much upwards.

Moreover a slightly bent asbestos plate e_{34} may be screwed in the valve between e_{31} and e_{33}, which in some cases secures a better closure, but this means is not always applied.

The upper part of the spray-catcher e_{70} is supported by the cylinder e_{751} screwed on to e_2. The superabundant mercury pressed through the forcing-valve rises in this cylinder. The gas escapes through the openings e_{752} and is directed downwards by the second cylinder e_{76} (comp. § 2 𝔉 1).

The plate e_{71} prevents the penetration of mercury into the upper part of the dome (comp. § 2 𝔉. 1). After applying the second jacket no mercury drops were ever found on the plate. The outlet tubes e_5 and e_6 for the gas from the head are, as in the case of CAILLETET's apparatus, provided at their upper extremities with flat ends in order to screw them on the washers in the bottom. The cock e_{41} through which we can allow the gas to flow out, without using the tubes e_5 and e_6, is not now used because of the troublesome mercury-mist, which is produced on opening at high pressure.

O. Exhaust-valve. (For the different sections and details of the valve-box and accessories see Pl. V fig. 1.) The steel valve-box f is fixed against the flat side of the pump body (comp. Pl. III), in which the boring coincides with the boring f_1 in the valve-box. They are fastened together by bolts, running through the holes f_2 and screwed in the holes e_{01} in the pump body. Between the flat sides of the exhaust valve-box and of the pump-body india-rubber sheeting (45 mg. per cm^2.) is laid over the grooves f_{21} which are useful in making a good closure. The support of the suction-valve f_3 is screwed in the piece f, while the closure takes place at the packing f_4. The valve support is provided with numerous fine holes f_6. The valve-pin f_5 which is carefully ground on the valve-support, is guided in it by means of the cylindrical rod f_{50} while the conical part f_{51} closes the openings in the valve-support. The valve-pin is constantly pressed against the valve-support by the small spring f_{57} and the small pin f_{56}. The valve-support can be screwed out by means of the doubly interrupted ring f_{31}, which is turned out of it. An india-rubber plate f_{53} is fastened on the valve-pin by means of the screw f_{52}; a four-armed steel spring f_{54} presses the edges of the india-rubber plate lightly against the valve support. It requires then some excess of pressure on the forcing-side to press the steel valve tightly on to the valve support. Should this happen at high pressure the india-rubber sheet rests simply on a flat surface formed by the upper part of the valve-cone and the upper-side of the valve-support. The screw stopper or valve-box-lid f_7 with the packing f_8 allow us to test whether the valve works well and to remove the valve-support with its valve from the valve-box.

ι. *Safetyfeeding-valve.* The valve-box and the exhaust-box f_{01} adjacent to it are formed of one piece of forged steel; the boring f_9 forms the communication between the exhausted space f_1 and f_{11}, the space left between the ring f_{31} and the valve-box-wall, and the suction-chamber f_{91} in which the gas enters from the sucking-tube g_{10}, if the valve g_2 is not closed (comp. § 2 𝔈 2).

A small cylinder g_{22} provided with two notches is connected to this valve by a rod g_{311} and peg g_{310}, on which rod is cut a screw-thread with which it can be screwed up and down through the packing g_{33} by a thread in the screwhead g_{32}. This screwhead is provided on its innerside with a thread. If the small peg g_{312} is held, then the small rod must, by the rotating motion of g_{32}, slide up and down without turning as is necessary in order to loosen it (comp. § 2 𝔈 1). The screwhead is turned by means of the disc g_{321} of g_{32}.

The lowerside of the tube g_{10} against which the safety-valve presses is rounded towards the inner side (comp. g_{101}) to ensure a better closure of the valve. The coating g_{21} of india-rubber mixed with much zinc white is tightly forced into the conical cup g_{20} [1]) and requires only little pressure to assure the closure. As a rule the valve lies on three ridges g_{41}, made on a supporting ring

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[1]) Additional valves are turned on the lathe to the correct size and kept in stock.

g_{42} (which encloses also the packing of g_1), so that the gas can always stream freely from g_{10} to f_{91}, for which purpose also grooves have been cut in the tube g_1. The stem g_{311} is usually also screwed back a few turns and the valve may still, without being hindered by the peg, be raised so far by the mercury rising suddenly that it closes the opening g_{101}.

It will be remarked that the connection between the several parts of g and f is a little more complicated than is required; this will also appear to be the case for g itself, which is explained by the remark at the end of § 1; the detailed drawing may be useful for those who wish to change a Cailletet-pump into a compressor of the Leiden pattern.

The nut g_4 (Pl. VI fig. 2) presses g_{10} closely against g_{51}. In the same way as Cailletet we use the pointed screw g_{54} to let mercury flow out into the tube g_{10} from the mercury reservoir g_{57} through the hole g_{58} and the opening g_{56}, from there it is received in the exhaust-chamber and from there again in the pump cylinder, provided these spaces are under no pressure. This screw-cock is only opened at the commencement or in the case of leakage. Generally the pump sucks gas through g_{53} from the cavity g_{52} and the chamber g_6 (see Pl. III).

The latter (comp. § 2 𝔈. 3) is made from a gun barrel, provided with the necessary steel mountings (see Pl. VI fig. 2). The gas is admitted into it by the tube g_{71}. On the joint g_{76} connected with it, several conducting tubes (I, II, and III) with nuts and packing can be screwed.

At the lower end this chamber is provided with a cock g_{65} to let out any mercury that might have run over. The upward bent tube g_{611}, which can be screwed off, must give a tight joint by a mercury layer. Even if a small quantity of mercury begins to overflow into the tube by insufficient closure of the valves the contact g_{63} gives warning immediately (comp. § 2 𝔊), while the contact g_{604} indicates that more mercury has run over than was contained in the pump cylinder above the suction-valve (see Pl. III), and hence that something is wrong with the compression-tube C'_0.

κ. *The transference of the compressed gas.* The compressed gas can escape (see Pl. III) from the reservoir through the conducting tubes k and l. If this is done slowly, very little mercury usually will be carried along. Therefore the cocks are always opened very carefully and except in urgent cases the gas is let out as slowly as it is admitted by the regular working of the pump.

The flange k_{11} (see Pl. III and Pl. V fig. 3) is fastened to the bent tube k_{10} of the main conduit by marine-glue, it is closed by means of the packing k_{12}, which is screwed on to the overflow vessel k_4 by means of the nut k_{13}. The contact k_{16} which inmediately gives warning when mercury passes over into this vessel, is constructed like C'_3 (see Pl. V fig. 2). The joint k_{15} on which the outlet tube k_{20} fits with a nut and packing, is forged on to the side of the steel vessel k_{13} which is fastened to the frame (see Pl. II fig. 2 en 1).

The steel high-pressure point-cock k_{21} (see Pl. III) which closes the forcing side of the pump is constructed in the manner explained in detail for i_1 and i_2, like k_1 it is fastened to the frame. The bent tube l_{20} which is more especially intended to enable the pressure in the head to be read on the manometer is provided with a (smaller) overflow vessel l_1; its bottom can be screwed off, but as we need hardly fear any mercury on this side, no connections to an electric bell were made. From this vessel (not shown on Pl. II as it is not fastened to the pump itself) the pressure is brought to the bronze high-pressure point-cock l_2 on the cock-board and can be transferred to the manometer N_{23} along l_3.

The steel filter-box k_3 Pl. III, whither the gas passes from the overflow-vessel, consists (Pl. V fig. 4) of a hollow cylinder k_{30}, on the joints of which the overpipes of the inlets and outlets k_{31} can be connected by nuts. The overpipes are bored trumpetshape on the side turned towards the filter-box. This contains, enclosed by rings and perforated supporting plates k_{33}, thicker brass-wires packed closely together k_{341}, secondly thinner brass-wires in k_{342}, and finally between two plates with fine sieve-holes, gold-leaf k_{343} is placed in order to remove the last traces of the mercury (comp. § 2 ℨ. 3). This filter-box is fastened to the frame of the pump (see Pl. II, fig. 2 and 1). The cocks, tubes or apparatus in which the gas is admitted after having traversed this filter need not be made exclusively of steel or other material, unattacked by mercury, nor need all soldering work be avoided, as was the case with the preceding. But then they must be placed at such a distance from the pump itself, that no contact with mercury is to be feared, which would be the case if they were in the immediate neighbourhood. The tubes connecting the pump to the cock-board, for instance, are made of iron or steel. [1]).

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[1]) The bell wires are either made of iron coated by india-rubber or are protected by iron tubes.

λ. The *safety-cap* (k_4 Pl. III) consists of a small chamber k_{40}, on the rim of which a carefully rolled thin plate of hard brass is screwed by means of a nut k_{42} and a washer. Thickness and manipulation are so arranged that explosion will occur at a given pressure, while leakage which easily occurs with the usual safety-valves is excluded.

μ. *The cockboard.* The tube k_5 (Pl. III) conducts the compressed gas to the main tube n_0 of the cock-board, carrying the arms n_{11}, n_{21} and n_{31}, so that the gas can be drawn off by four ways.

Generally the cock n_{12} admits the gas into the apparatus in which it is to be kept or used for researches, while a reservoir p is connected to the tube n_{14} which reservoir in many cases serves to maintain the pressure, when the apparatus is fastened on to the cock n_{13}.

The cock n_{41} serves to conduct the compressed gas to another apparatus or to be sampled for analysis.

The cock n_{22} allows the tension of the compressed gas to be measured on the manometer. With cocks k_{21} and l_2 closed we can also measure on the manometer the tension of the apparatus connected to n_{14} or n_{13}, and also with cock n_{22} closed and cock l_2 opened the tension of the gas in the dome of the pump. As an example: we may wish to test if the pump is working regularly (especially with the operations II and III).

By means of the cock n_{32} the pump with accessories is connected with the sucking-apparatus (comp. § 4 ν) consisting, among other things of a tube leading to an airpump and to an open bottle with a safety-tube immersed in mercury. Moreover n_{32} is used to permit gas brought under pressure, to flow back to the exhaust-side of the pump (e.g. a gas-holder) (comp. § 4 ν).

§ 4. The accessories described above may be considered as immediately belonging to the pump, now we have still to consider what is further required for the operations mentioned in § 2 and indicated on Pl. III by I, II, III.

I. To suck gas from a space under ordinary or less than atmospheric pressure.

An instance of this is the frequently occuring sucking from a gas-holder. To this end the sucking-tube g_{71} of the pump is connected to the:

v. Exhaust apparatus for ordinary pressure. (Comp. I Pl. III.) This consists entirely of glass pieces of apparatus, to which the iron sucking-tube is connected by means of india-rubber. The gas from the gasholder is filtered through cotton wool and drawn through the tube O_6 Pl. III; if the cock O_5 is in the position shown here, the gas flows immediately to the pump along O_{20} and through the glasswool, phosphoric anhydride and fused sodiumhydrate in the tube O_{21}. If we turn the cock O_5 through 180° into its usual position, the gas passes through the washbottles O_8, usually filled with pure sulphuric acid (comp. § 2 𝔇. 2). In both cases the wide safety-tube O_7 is connected, in which the mercury rises to barometric height during evacuation. The double washbottles are made so [1]) that they work in the same way with either direction of the gas-current. The bubbling of the gas through the sulphuric acid, which must remain perfectly clear, allows us, like the rising of the mercury in O_7 to test very accurately whether the suction-valve works well and also if the pump-cylinder is properly exhausted. The pump-cylinder is filled with gas of less pressure than that in the apparatus from which it flows; we can reckon to take in from 100 to 125 liters of normal gas in an hour.

Any spray from the sulphuric acid is received in the bulbs O_{31} and O_{32}; moreover the tubes are arranged so that the liquid flows back to the bottles; very fine drops that might be carried along, are retained in O_{21}.

If the compression is stopped, the gas still left in the dome e_4 is caused to flow back through the cock n_{23} along O_{20} and O_5 to O_6.

The mercury-pump and accessories are exhausted through O_4. The three-way stopcock must then be so turned that the drying tubes communicate on both sides with the air-pump. For the exhaustion of the tubing of the apparatus (e.g. gas-holder) up to O_5 we can use O_7.

II. To force compressed gas from a space of lower into one of higher pressure.

As an instance of this we may consider the transference of gas from one cylinder to another (e. g. from an almost empty one into one not quite full, a case which often occurs when we wish to raise the pressure in the latter or to have the former at our disposal). With a view to this operation the chamber g_6 is made so that it can resist if necessary the full pressure of the pump. Fig. III (Pl. III)

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[1]) Compare E. C. de Vries. Thesis for the Doctorate. Leiden 1893.

indicates the connection through a high pressure cock q_2 with a reservoir q_3, in which the pressure is read on the manometer q_{43} to be closed by the cock q_{42}. In this reservoir the gas from the cylinder q_6 which is to be forced through the regulating-cock q_5 is generally admitted so that the tension in q_6 does not rise above 10 atmospheres. With higher pressures at the beginning or at the end the pump might begin to work too heavily and the pump-cylinder become warm. Generally before commencing to force over the gas, the pump and the reservoir are exhausted through N_{32} and O_4. If the apparatus on the exhaust-side is strong enough, a safety-valve may be applied, which conducts gas when the pressure is too high on the forcing-side back to the exhaust-side (comp. § 5 C_{30}). Because the working of the mercury-pump requires constant attention, we may however trust to being warned in time by the manometer whilst the safety-cap gives final security.

III. To work in conjunction with a pump which delivers gas under pressure.

With regard to the mercury-pump itself, the conditions are the same as if compressed gas were admitted from a cylinder through q_1, and it is obvious that we may often avail ourselves of the usefulness of my compressor for this purpose. As an example of this I will consider here only the case when the auxiliary compressor is especially constructed to work together with the mercury-pump, i. e. when it transmits exactly so much gas at the highest pressure (admitted on the exhaust side of the mercury-pump), as the latter can take up. If in such a compressor the gas were also forced by means of mercury we would actually have obtained a mercury compressor with two degrees of pressure and tenfold power. With a mercury-pump after the present pattern buth on a somewhat larger scale and with a proportionate auxiliary compressor at my disposal, I should be able to bring about the long wished for circulation of liquid hydrogen in the cryogenic laboratory. In the mean time many researches do not involve the great requirements of this last problem, nor do they admit the use of a BROTHERHOOD compressor, arranged for the compression of large quantities of pure gas as described Comm. N°. § 3. For a commencement I found it sufficient to build an auxiliary compressor, which in contradistinction to the BOTHERHOOD is meant to be exhausted and in which the gas is compressed by a minimum of glycerine. Thereby in contrast with the mercury-pump the auxiliary compressor, destined to work with it could be made to run fast (at 150 revolutions per minute), and could hence be of small dimensions and inexpensive.

With pressures up to 10 atmospheres the disadvantages of the lubricant used, in connection with a drying apparatus presently to be described (in ϱ) are so unimportant that I hope before long to obtain by means of this apparatus liquid hydrogen. The vacuum pump which I considered necessary for this in Comm. N^o. 23 § 5 will soon be in regular work.

The connection, whenever the mercury pump and the auxiliary compressor work together, is shown by II (Pl. III). The mercury pump and auxiliary compressor are regularly used for the oxygen-circulation of the cryogenic laboratory (comp. comm. N^0. 14)[1], in the manner described.

The gas from the auxiliary compressor passes first through the

ϱ. *drying tower for gas under high pressure.* This is a steel bottle I (see Pl. III and Pl. VI, fig. 3. A front view of I was already given in Comm. N^0. 51, Pl. II, as D_1) closed at the upper end by means of a nut with flat sides and an overpipe with packing I_1. The tube is made very wide so as to secure a slow motion of the gas. It is designed to stand a higher possible pressure (150 atm.) than that allowable in the drying tubes described in Comm. N^0. 51 (§ 3 and fig. 6 Pl. III.)

The drying agent (phosphorous pentoxide, or sometimes sodium hydroxide) is not immediately introduced into this heavy tube, but is in a thin-walled brass tube I_4, which is so fastened in the drying tower that the gas is obliged to flow through the drying agent. It is exhausted by the pump itself, the cocks N_{23} and O_4 being used. When the tube I_4 is filled with the substance through which the gas must pass mixed with glasswool or dried asbestos, and closed at the upper and the lower ends with the sieves I_{41} and I_{42} (fastened to it by screw-threads) we may allow the rim I_{43} to rest on the wall of the drying tower itself and then screw up the bottom I_{42} by means of the bar I_{45}, which causes the packing to expand and press against the wall of I.

The bent tube I_{31} serves to let out the drops of glycerine that might be carried along from the auxiliary compressor, the cock I_{32} is used to remove them, to exhaust the apparatus, and to introduce or draw off gas.

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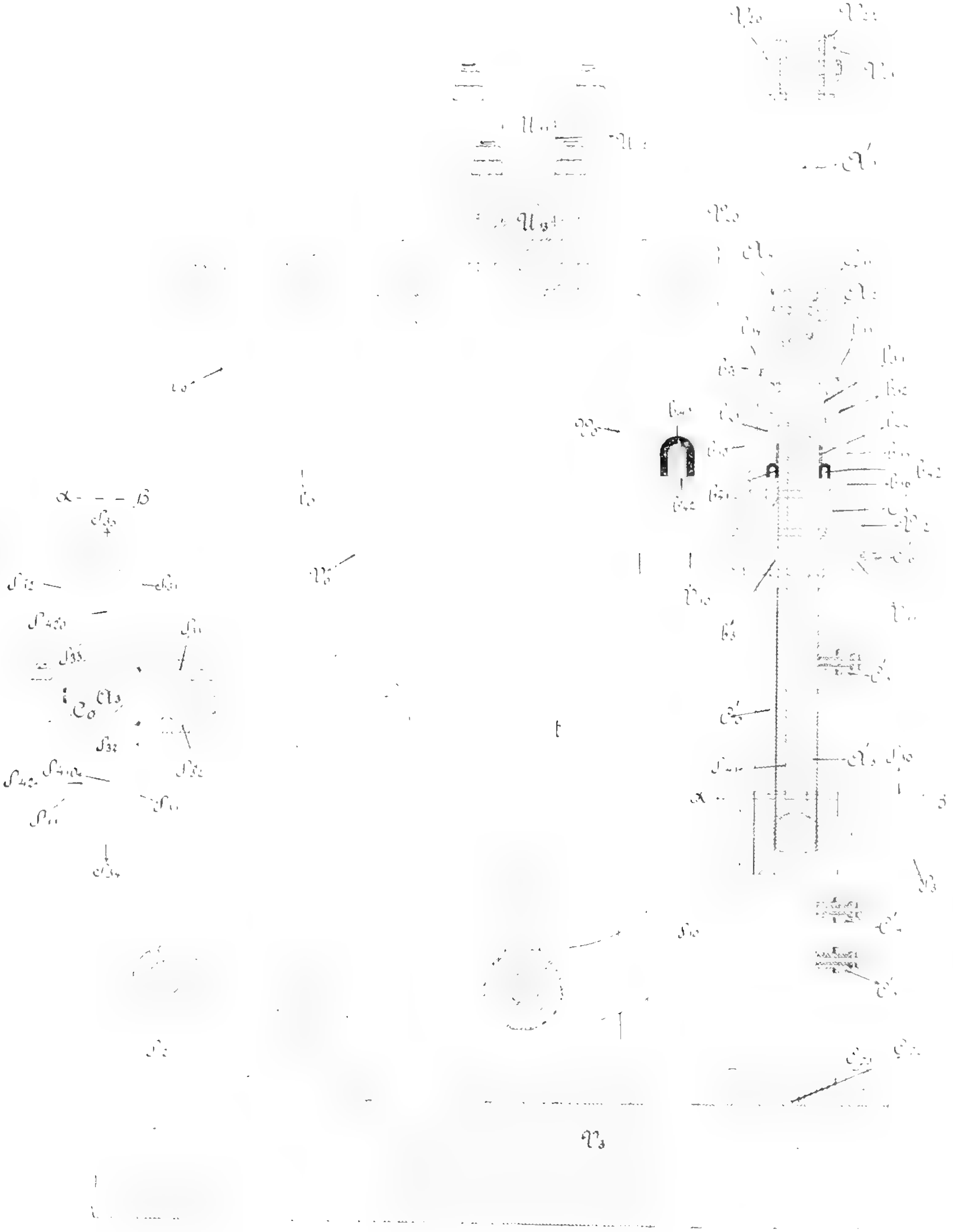
[1] Comp. Mathias l. c. Pl. 1.

H. KAMERLINGH ONNES: „Methods and apparatus used in the Cryogenic Laboratory II: Mercury pump for compressing pure and costly gases under high pressure”.

Scale 1

PLATE IV.



§ 5. *The auxiliary compressor* itself remains to be described: according to the diagram on Pl. III and the detailed drawing on Pl. VII, which also (fig. 1) gives a simplified view of the whole compressor. It was constructed for me by the Société Génevoise. To save room it is suspended on the wall below the driving-shaft (§ 2, γ at the end) with which also the mercury pump is coupled.

The plunger F is hollow and surrounds a copper tube, through which water for cooling the plunger and compressed gas is conducted, (see F_1 and F_2 on Pl. III). For admitting and drawing off the water india-rubber tubes are used which move together with the plunger and are connected to the water supply.

The packing E_1 consists of two collars E_{12} and E_{13} as in the forcing-cylinder of the mercury-pump (comp. § 3, α). They are placed in opposite directions one to shut during exhaustion, the other during compression, and are enclosed by the nut E_3 screwed against the pump-body D, in which it fits exactly, and which it holds by means of a rim E_2. The plunger is protected by wooden rings (comp. § 3, α) and a leather ring E_{15} fitting on a bronze ring E_{16}. The outer rim E_2 is filled with glycerine. In the nut is a lubricating chamber E_4, (Pl. VII fig. 3) in which glycerine is brought under pressure. The pressure is applied in the storage-bottle through the cock C_6 (see. fig. 2 and 5 Pl. VII) and the tube G_0 (fig. 2). G_{31} is used to test whether the apparatus has been completely filled with liquid. The glycerine is hindered from flowing out of this chamber by a second collar packing E_{52}, screwed on by means of the nut E_{24} and the enclosing piece E_{53}. The problem of obtaining only a small clearance gasspace and of allowing as little of the lubricant as possible to be in contact with the gas, has been solved by turning the plunger so exactly that it fits almost hermetically in the pump-cylinder, and further by making the bottom of the pump cylinder spherical, and cutting it off so that it is wedge shaped with two flat surfaces (those of the valves). The whole bottom-piece C of the pump cylinder can be removed, which facilitates the cleaning and dismounting of the valves.

The gas sucked-in is admitted into the pump cylinder through the suction-valve C_{21}, the pressure of this gas can be read on a vacuummeter B (connected with C_1), used because the auxiliary compressor also serves especially as an air pump, as for instance in the circulation of liquid oxygen evaporating under low pressure. The suction-valve is kept back by a spring and an adjusting-pin C_{23} and can be taken out of the pump by screwing off C_{24}. The gas is then forced through the compression-valve (the drawings of compression-valve and suction-valve require no further explanation) to the tube H_0, in which the pressure is indicated by the manometer, and further along H_1 to I. When the safety-valve C_{30} rises the canals C_{40} and C_{41} make a communication between the exhaust chamber behind C_{21} (fig. 4) and the forcing chamber behind C_5. This safety-valve is pressed by a long spring C_{33} with adjusting block C_{34} and adjusting pin C_{35}. The adjusting pin passes through the packingbox C_{36}, ends in a square head C_{38}, and is adjusted for a given pressure by means of a wrench. If this is done we can allow the auxiliary compressor to work whether the mercury pump takes up the compressed gas or not.

Chemistry. — "*The alleged identity of red and yellow mercuric oxide*". Part II. By Dr. ERNST COHEN (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

(Read January 27, 1900.)

1. It has been stated in my first communication [1]) that there exists between red and yellow mercuric oxide a difference in free energy 0.685 millivolts at 25.°0.

I now wish to communicate some details as to the determination of the temperature coefficient of the previously described mercuric oxide cell and discuss the thermic determinations made by VARET in 1895 [2]).

2. The E. M. F. of the mercuric oxide cell may be represented by the equation :

$$\pi = \frac{E_c}{n\varepsilon_0} + T\frac{d\pi}{dT}$$

in which π is the E.M.F. of the cell at the temperature T, E_c the chemical energy of the process taking place on the passage of ε_0 Coulombs, whilst n represents the valency of the mercury.

If π and T and also the temperature coefficient $\frac{d\pi}{dT}$ are known we can calculate E_c with the aid of the said equation.

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[1]) Proc. Royal Acad. Nov. 25, 1899, pg. 273.

[2]) loc. cit. pg. 273, note 1.

3. In order to determine experimentally $\frac{d\pi}{dT}$, the same element which had been used for the measurements at 25°,0 [1]) was immersed in a thermostat kept at 35°,0. The arrangement was quite the same as the one previously described. The standard cells (Weston and Clark) remained in the thermostat which I had used previously at 25°,0.

From time to time the E. M. F. of the mercuric oxide cell was measured in the manner previously described; after it had become constant, the measurements were continued for a number of hours. In this way was found:

E. M. F. of the mercuric oxide cell I at 35°.0.

Hours after placing in the thermostat.	E. M. F. (millivolts).
50½	0.774
69	0.774

By way of control, the whole investigation was repeated. A new element (II) was fitted up; the same chemicals were used whose preparation and purification have been fully described in the first communication.

This element was afterwards heated to 35°.0.

E. M. F. of the mercuric oxide cell II at 35°,0.

Hours after the composition.	E. M. F. (in millivolts).
220	0.772
244	0.772

4. Finally the used Weston-cell was again compared with the two Clark-cells A and B in the same manner as before,

$$\frac{E.M.F.\ \text{Clark}\ A_{25^\circ}}{E.M.F.\ \text{Weston}_{25^\circ}} = 1.3942 \quad \frac{E.M.F.\ \text{Clark}\ B_{25}}{E.M.F.\ \text{Weston}_{25^\circ}} = 1.3940\,,$$

whilst in former experiments the relations 1.3946 and 1.3945 were found.

We now find for the temperature-coefficient of the mercuric oxide cell

$$\frac{0.773-0.685}{10} = 0{,}0088 \text{ millivolts.}$$

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[1]) Proc. Royal Acad. Nov. 25, 1899, pg. 280.

If, now, we introduce into the equation

$$\pi = \frac{E_c}{n\varepsilon_0} + T\frac{d\pi}{dT}$$

or

$$E_c = n\,\varepsilon_0\left(\pi - T\frac{d\pi}{dT}\right)$$

the found values $\left(T = 298;\ \pi = 0.685;\ \frac{d\pi}{dT} = 0{,}0088\right)$ and express everything in caloric measure we find

$$E_c = -\,2 \times 23{,}09 \times 1{,}9374 = -\,89.4 \text{ calories}$$ [1]

6. Varet has determined in 1895 the heat of reaction of red mercuric oxide with hydrocyanic acid. He finds this to be 31550 calories, whilst Berthelot found 31600 for the yellow oxide. Varet then observed: "On voit que la transformation de l'oxyde "jaune de mercure en oxyde rouge ne donne lieu à aucun effet "thermique appréciable."

The difference of — 50 calories certainly does not signify much considering it is a difference between two large figures and the ordinary caloricmetric determinations are subject to rather great errors. Still I cannot help pointing out that the calculated results of — 89 calories and the experimental result obtained by Varet are of the same order, whilst our electrical measurements decidedly prove that there must exist a difference in chemical energy between the two varieties of mercuric oxide.

It is moreover somewhat illogical on the part of Varet [2] to state that no appreciable thermic effect takes place when the yellow oxide changes into the red modification, when in his paper on the different modifications of mercury sulphide, real importance is attached to the caloric value of —60 calories obtained as a difference between 240 and 300 calories.

Amsterdam, Chem. Lab. of the University.
January 1900.

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[1] Strictly taken we aught to pay attention to the difference of heat of solution of HgO in the solutions of KOH.

[2] Ann. de chimie et physique [VII] T. 8 p. 102. (1896).

Chemistry. — Professor A. P. N. FRANCHIMONT presents to the library of the Academy Dr. P. J. MONTAGNE's dissertation, entitled *"The action of hydrogen nitrate upon the three isomeric chloro-benzoic acids and some of their derivatives".*

(Read January 27, 1900.)

The contents of which he explains as follows:

MONTAGNE's work originated in experiments made by VAN ROMBURGH in 1885 and by TAVERNE in 1897 and 1898. VAN ROMBURGH had treated benzamide and its two methyl derivatives with nitric acid at the ordinary temperature and had found that, to some extent, their behaviour differed from that of the aliphatic amides and methyl-amides under the same circumstances; this together with other facts was at first ascribed to the more pronounced negative properties of the aromatic atomic group. As, however, in the nitration of aromatic substances, this also takes place in the nucleus, the question first arose whether the change of the carboxyl group into the amide or methyl-amide group had any effect on the position taken up by the nitro-group. Experience regarding the nitration of aromatic substances teaches that the NO_2 group often takes up more than one position, the greater part into one and a smaller part into another, and that this depends, among other things, on the temperature at wich the reaction takes place; when the temperature is lowered the formation of the bye-product sometimes diminishes or ceases. TAVERNE showed that the temperature and the duration of the action of the nitric acid influenced the result. If, therefore, we want to follow the effect of an alteration in the side chain it is desirable to make the experiments at the same, preferably low, temperature. The negative properties of the benzene nucleus are however changed by the entrance of a nitro-group to a degree which varies with the position taken up by the nitro-group. Since the greater or smaller negativeness of this nucleus may influence the action of the acid on the side chain, it was of importance to investigate the effect of altering the negativeness of the benzene group in some other way. MONTAGNE chose the increase of the negativeness by the introduction of chlorine and therefore investigated the action of nitric acid at zero on the three isomeric chloro-benzoic acids and also on their methyl esters, amides, methyl- and dimethylamides. Then TAVERNE had found no difference in the nitration at zero of benzoic acid and of its methyl ester, but a difference existed in the case of the amide. HOLLEMAN has only recently demonstrated by means of more accurate experiments that the nitration of the methyl ester differs somewhat from that of the acid. Whilst the negativeness of the benzene nucleus is increased by the chlorine, that of the side chain is diminished by the introduction of methyl.

It is also known in the chemistry of aromatic substances that the groups in the ortho-position exercise a greater influence on each other than others and it has been shown that this influence depends not so much on their nature as on their position, so that the same phenomenon, such as the counteracting or preventing of a reaction of one of the groups by the other, may be caused both by a negative and a positive one; phenomena of this kind, so-called sterical obstacles, might occur here and should not be lost sight of.

A score of unknown compounds wanted for, or produced during the research and which also had to be made in different ways for the purpose of identification are described in the dissertation.

Looking at the results obtained, it is first of all shown that the nitrating process (with hydrogen nitrate at zero) gave with the free chloro-benzoic acids results not greatly differing from those obtained by other methods. The chief products were at all events the same but it has not been ascertained whether their relative amount was the same. Ortho-chlorobenzoic acid gave a second mono-nitroderivative which has not been further investigated, but not a di-nitro-derivative such as obtained by HÜBNER on gently warming with fuming nitric acid.

The methyl esters yielded as chief product the esters of the same nitro-acids which were obtained from the free acids; the bye-products and their proportions have not been further investigated and no mention is made of the influence of temperature on the nitration. The results obtained in the nitration of amides and methylamides at zero agree with those obtained by TAVERNE with benzamide, phenylacetamide, phenylpropionamide and their methylderivatives in so far as the position occupied by the nitro-group is the same as in the chief product of nitration of the free acids. But TAVERNE obtained from benzamide only the *m*-nitroderivative, whilst benzoic acid yielded both the *m*- and *o*-derivatives; from phenylacetamide and phenylpropionamide only the *p*-derivative was obtained whilst the acids gave both the *p*- and *o*-compounds just as the methyl and dimethylamides.

The time required for complete nitration seems to differ greatly. It seems as if the amides and methyl-amides are nitrated less rapidly than the corresponding acids and that there exists even a difference between the derivatives of the three isomeric chloro-benzoic acids.

It also appears that the stability of the amides and methylamides of the different chloro-nitrobenzoic acids when in contact with nitric acid at zero is not the same. The most unstable are the derivatives of 4 chlorine- 3 nitrobenzoic acid which according to BETHMANN is the weakest of the three chloro-nitrobenzoic acids. It is remarkable that this acid is the only one of the three where none of the groups is in ortho-position with the side chain, and the slow action of nitric acid on the amides of the two others may perhaps be to some extent ascribed to the ortho-position of chlorine- or nitro-group, or in other words to "sterical obstacle". From the methylamides of 3 chlorine- 6 nitro- and of 4 chlorine- 3 nitro-benzoic acid, a methylnitramide was obtained, but none was got from 2 chlorine- 5 nitrobenzoic acid the only compound in which the chlorine is in the ortho position.

The result of the action of nitric acid at the ordinary temperature on the amides and their methyl derivatives was that the amides yielded, as usual, nitrous oxide and nitro-acid whilst the methylamides yielded nitrous oxide, methyl nitrate and nitro-acid; the dimethyl amides yielded nitro-acid and dimethylnitramine. The nitro-acids of the *o*- and *m*-derivatives appeared to contain a small quantity of an isomeric body. This result differs from that obtained by TAVERNE with the derivatives of phenylacetic and phenylpropionic acid which yielded a dinitro acid. The difference in stability towards nitric acid was here also apparent; and as regards the dimethylamides, a little secondary action took place, presumably oxidation of one of the methylgroups and formation of a methyl nitramide.

The dissertation also contains a table of melting points of the compounds described. It will be noticed that, as is generally the case, the melting points of the chlorides and methyl esters are lower than those of the acids and those of the amides either higher or lower; but those of the mono-methylamides are lower than those of the amides and those of the dimethylamides are lower still.

MELTING POINTS.

	ortho-comp.	meta-comp.	para-comp.
chloro-benzoic acid	140°	158°	236°.5
chloride	— 4°	liquid	16°
methyl ester	liquid	21°	43°
amide	141°	134°.5	179°
mono-methylamide	121°.5	75°	161°
dimethylamide	13°.5	61°	59°

	$2\ Cl\ 5\ NO_2$. compound	$3\ Cl\ 6\ NO_2$. compound	$4\ Cl\ 3\ NO_2$. compound
chloro-nitro-benzoic acid	165°	138°	181°.5
chloride	solid	—	51°
methyl ester	75°	48°.5	83°
amide	178°	154°	156°
mono-methylamide	174°	134°	136°.5
dimethylamide	124°.5	104°.5	113°.5

Chemistry. — "*The Enantiotropy of Tin*" (IV). By Dr. ERNST COHEN (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

1. At the 65th meeting of "Deutsche Naturforscher und Aerzte" held at Nürnberg in 1893 [1]), it was stated by H. STOCKMEIER that the roof of the post-office at Rothenburg a. T., which is made of cast tin plates was found to be corroded (suffering from "tin-plague"; compare proceedings 1899, p. 152).

After consulting the older literature on this subject, he attributed the phenomenon to the low temperature which had prevailed at Rothenburg.

STOCKMEIER, however, also communicated, that the roof of the town-hall tower adjoining the post-office which is made of flattened tin plates had remained perfectly sound although exposed to the same low temperature. To explain the phenomenon, STOCKMEIER mentions a research by LEWALD [2]) who attributes the disaggregation of tin at a low temperature, as noticed by FRITZSCHE in St. Petersburg, to its shape (blockform) and mode of manufacturing and not, as he emphatically states, to the physical properties of the "matter".

LEWALD says: "es ist nun nicht richtig zu sagen: Zinn hat die Eigenschaft bei circa — 35° C. seine Struktur zu ändern und zu zerfallen, sondern bloss Zinn, *welches in Blockformen gegossen*, zeigt dieses Verhalten."

He believes, that the tincrystals formed on cooling the cast mass get into a state of tension. "Es muss daher einen Temperaturgrad geben, bei dem die Spannung der Kristalle einen solchen Grad erreicht, dass sie zum Zerfallen der Blöcke führt."

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[1]) Verhandlungen der Gesellschaft deutscher Naturforscher und Aerzte. 65e Versammlung zu Nürnberg (11—15 Sept. 1893), S. 97.

[2]) Das Ausland 1870, S. 71 Dinglers polytechn. Journal 196 (1870) 369.

In order to prove that only cast, but not flattened tin shows the phenomenon of disaggregation, he says: „wer sich hiervon überzeugen will, der giesse sich eine Zinnstange von circa 1 Quadratzoll Querschnitt, lasse dieselbe einmal durch ein Vorkaliber eines Rundeisenwalzwerkes gehen, schneide sich ein beliebiges Stück ab, setze dasselbe einer Kälte von — 40° C. und darüber aus, und das Zinn wird *nicht* zerfallen."

2. My previous experiments [1]) had taught me that not only block tin but also powdered metal may change into the grey modification. When dealing with tin-filings, it is no longer possible to admit the existence of tensions (vaguely) believed in by Lewald. Moreover, the filings after passing into the grey modification produce such a finely divided dust that under these circumstances the existence of tensions becomes still more problematical.

The fact that grey tin, after reversion into the white modification, may again and again be changed into its original form is moreover quite opposed to Lewald's idea and proves that the corrosion of the tin is a property of the "matter" and not, as Lewald believes, a consequence of the mode of manufacturing (casting, flattening).

3. The explanation given by Stockmeier of the different behaviour of the tin roofs of the two Rothenburg buildings is, therefore, not valid when viewed in the light of my researches, and it was to be expected that the roof of the tower of the town-hall which was lined with flattened tin sheets would in course of time show corrosion. That this idea was right is proved by the following communication which I received a few days ago from Dr. Stockmeier of Nürnberg: . . . „Ich selbst habe ja gelegentlich der Naturforscherversammlung in Nürnberg, bei welcher ich über die eigentümlichen Erscheinungen der Veränderung der Zinnbedachung des Postturmes in Rothenburg vortrug, gefühlt, dass die Thatsache, wonach die Zinnbedachung des Postturmes zerstört war, die des benachbarten Rathausturmes aber intakt blieb, durch die damals eben noch als richtig anerkannten Lewald'schen Beobachtungen sehr gesucht erklärt werden musste. Allein eine andere Erklärungsweise stand damals nicht zur Verfügung.

Nachdem sich nunmehr gezeigt hat, dass auch an der Bedachung

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[1]) See Proc. Royal Acad. of Scienc. 1899, 7, 149, 281. Zeitschrift für phys. Chemie, Bd. 30. 600, (1899).

des Rathausturmes in Rothenburg an einer Stelle die Bildung der grauen Modifikation des Zinns auftritt, ohne dass unterdessen eine so tiefe Temperatur wie im Jahre 1893 *geherrscht hätte*, kann man wohl der Annahme huldigen dass durch Verwehen kleiner Teilchen des grauen Zinnes vom benachbarten Postturm auf die Bedachung des Rathausturmes, die Erscheinung vor sich ging."

Evidently there has taken place "infection".

4. I have also investigated the influence of vibrations on the change of white tin into the grey modification. I begin to state that my experiments in that direction gave me a negative result. The few communications which I wish to make as regards the method of working are intended to induce others who may be able to work under more favourable conditions than myself, to repeat the experiments.

ERDMANN [1]) and HJELT [2]) have noticed the "tin-plague" in organ-pipes. ERDMANN explains this by the vibrations to which they are subjected. Although we know now that vibrations alone cannot cause the phenomenon (above 20° this is surely impossible) it yet seemed to me worth while to try whether mechanical influences are likely to accelerate the inversion. Then it is known that a concussion or a blow can abrogate a meta-stable equilibrium. One has only to think of the crystallisation of supersaturated solutions and superfused substances [3]); also the spontaneous evolution of gas from supersaturated gaseous solutions under those circumstances [4]).

The researches of ABEL, NOBEL, CHAMPION, PELLET, BERTHELOT, THOMSEN, SPRINGMÜHL and others in the field of explosives have disclosed facts of this kind.

Wave motions and other periodical vibrations may give rise to explosions even when their intensity is comparatively small. Nitrogen iodide does not explode on a plate or string of low tune, but a high tune will cause an explosion to take place.

On the subject of explosions caused by the explosion of other substances, LOTHAR MEYER says: „Wahrscheinlich hängen diese Unterschiede von dem Rythmus der durch die Explosionen erzeugten

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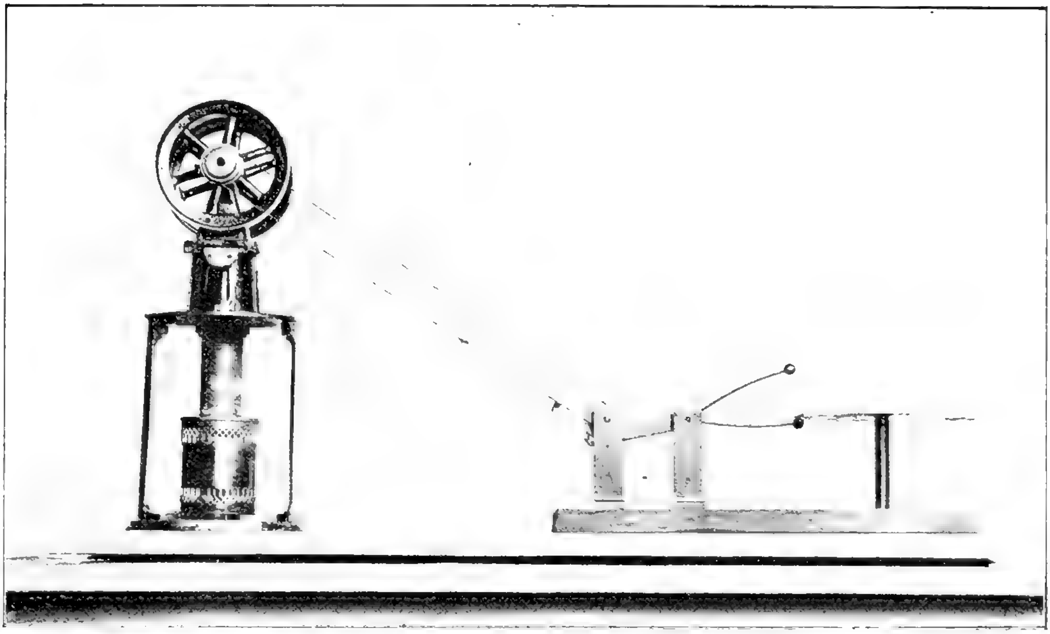
[1]) Journal für pract. Chemie. 52, 428 (1851).

[2]) Ofversigt af Finska Vetensk. Soc. förhandlin. 32.

[3]) Compare O. LEHMANN, Molecularphysik. I (1888) 189. According to OSTWALD salol is not solidified by violent motion; also compare LOTHAR MEYER, Dynamik der Atome (1883) 397.

[4]) LEHMANN, Molecularphysik 2 (1888) 117; (Zeitschrift für phys. Chemie, 22 (1897) 289; BERTHELOT, Les matières explosives 1 (1883) 130.

ERNST COHEN: The Enantiotropy of Tin (IV).



Erschütterungen in der Art ab, dass nur durch Schwingungen von bestimmter Wellenlänge die Atome in Mitschwingungen versetzt, dadurch aus ihren labilen Gleichgewichtslagen weiter als gewöhnlich hinausgeführt werden und dann in stabile Lagen übergehen."

Although this view appears somewhat vague, I as already stated, decided to subject ordinary tin to vibrations below the transition-temperature.

As I did not know whether organ pipes of a definite tune had shown a stronger corrosion than others, I chose as a source of vibration a CHLADNI plate which gave an intense rattling sound.

The accompanying reproduction of a photograph represents the apparatus:

To the right stands the iron plate kept in strong vibration by two copper hammers. These are attached to an excentric which is rapidly whirled by means of a cord, by a HEINRICI hot-air motor.

The whole apparatus which was placed in a cellar was exposed during the experiment to a temperature varying from +5° to +12°, therefore below the transition point. The plate was kept vibrating day and night for three months. The sheet of tin was attached to the plate by means of copper wire.

As already stated, no inversion of the tin had taken place.

If a place were at disposal where the temperature could be kept for a long time below zero, it would be an easy matter to make a comparative experiment by attaching to the plate a dilatometer filled with tin and comparing it to a second one, which had not been subjected to vibration.

5. Statements found in older literature and communications made to me by different colleagues induce me to study the behaviour of antimony, aluminium, manganese, silver, copper and lead from the same standpoint as tin.

Amsterdam, February 1900.
Chemical Laboratory of the University.

Physics. — *"On Phenomena on the Sun considered in connection with Anomalous Dispersion of Light"*. By Prof. W. H. JULIUS.

(Will be published in the Proceedings of the next meeting.)

Chemistry. — "*On the formation of trisubstituents of benzol from disubstituents*". By Prof. A. F. HOLLEMAN (Communicated by Prof. C. A. LOBRY DE BRUYN).

(Will be published in the Proceedings of the next meeting.)

Chemistry. — "*Enquiries into the system* $Tl\,NO_3 + Ag\,NO_3$". By Dr. C. VAN EYK (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

(Will be published in the Proceedings of the next meeting.)

(March 28, 1900.)

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING
of Saturday March 31, 1900.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 31 Maart 1900 Dl. VIII).

CONTENTS: "Determination of the decrease in the vapour tension of solutions by means of the determination of the increase in the boiling point". By Dr. A. SMITS (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM) (With one plate), p. 469. — "The formation of trisubstituted derivatives from disubstituted derivatives of Benzene". By Prof. A. F. HOLLEMAN (Communicated by Prof. C. A. LOBRY DE BRUYN), p. 478. — "Formation and transformation of the double salt of Silvernitrate and Thalliumnitrate". By Dr. C. VAN EYK (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM), p. 480. — "On Orthogonal Comitants". By Prof. JAN DE VRIES, p. 485. — "On Indigo-fermentation". By Prof. M. W. BEIJERINCK, p. 495. — "Indican — its hydrolysis and the enzyme causing the same". By J. J. HAZEWINKEL (Communicated by Prof. S. HOOGEWERFF), p. 512. — "Contribution to the knowledge of Indican". By Prof. S. HOOGEWERFF and H. TER MEULEN, p. 520. — "A special case of the differential equation of MONGE". By Prof. W. KAPTEYN, p. 525. — "On the locus of the centre of hyperspherical curvature for the normal curve of n-dimensional space". By Prof. P. H. SCHOUTE, 527. — "Equations in which functions occur for different values of the independent variable". By J. D. VAN DER WAALS JR. (Communicated by Prof. J. D. VAN DER WAALS), p. 534. — "The 14-monthly period of the motion of the Pole of the Earth from determinations of the azimuth of the meridian marks of the Leiden Observatory from 1882—1896". By J. WEEDER (Communicated by Prof. H. G. VAN DE SANDE BAKHUYZEN), p. 546. — "Considerations on Gravitation". By Prof. H. A. LORENTZ, p. 559. — "On the power of resistance of the red blood corpuscles". By Dr. H. J. HAMBURGER, p. 574. — "On the critical isotherm and the densities of saturated vapour and liquid in the case of isopentane and carbonic acid". By Dr. J. E. VERSCHAFFELT (Communicated by Prof. H. KAMERLINGH ONNES, p. 574.

The following papers were read:

Chemistry. — Prof. H. W. BAKHUIS ROOZEBOOM presents an article by Dr. A. SMITS entitled: "*Determination of the decrease in the vapour tension of solutions by means of the determination of the increase in the boiling point.*"

(Read January 27, 1900.)

Introduction.

The peculiar result obtained with the micromanometer [1]) induced me to try and determine the decrease in vapour tension by another

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[1]) Verslag Kon. Academie Jan. 2, 1897, Nov. 27 1897, Sept. 30 1899 and Proceedings Sept. 30, 1899.

method. It seemed to me there would be no particular difficulty in comparing the vapour tensions of pure water and solutions at a temperature different from 0°. I tried to gain my object by determining the difference in pressure required to equalise the boiling points of pure water and saline solutions.

In an article entitled: „An apparatus to keep the vapour tension of a boiling liquid constant,'' [1]) the apparatus is described which I will briefly call „manostat''. This manostat enables me to reduce the pressure in a certain space to any desired extent, within definite limits, and then to keep it constant within 0.5 m. m. of water. By regulating the pressure of this apparatus it is therefore possible to make all solutions show the same boiling point. To be able to accurately read off the diminution in pressure, pure water is boiled under the same condition as the solution and from its decrease in temperature may be calculated the decrease in pressure corresponding with the decrease in vapour tension of the solution.

Preliminary Experiments.

I experienced great difficulties in my preliminary work when using the apparatus of BECKMANN [2]). Firstly, because the indication of the thermometer was dependent on the degree of heating; this is chiefly due to the wrong manner in which the condensed solvent runs back into the boiling mass.

Secondly, because the actual boiling vessel was not sufficiently screened to prevent radiation, which was shown by the fact, that mild air-currents had a perceptible influence on the indication of the thermometer.

A third drawback experienced in my preliminary trials, but which was not caused by any defect in BECKMANN's apparatus was as follows:

The indication of the thermometer appeared to be dependent on the place occupied by the mercury reservoir in the column of liquid. As far as I am aware, nobody has, as yet, called attention to this fact but as will be shown presently, it is a factor which under special circumstances is to be reckoned with. On account of this, a number of published results are undoubtedly faulty.

It is plain that this phenomenon may be accounted for by the difference in pressure between the different layers of liquid, but that it should be noticed so decidedly in boiling water or in boiling

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[1]) Verslag Kon. Acad. Nov. 27 1897.

[2]) Zeitschr. f. physik. Chem. 1891.

solutions astonished me somewhat as during the boiling a certain amount of mixing takes place by the rising of the vapour bubbles. The difference in temperature between two aqueous layers of a boiling watercolumn at a distance of 1 c. m. of each other ought, theoretically, to amount to ± 0.036°. My actual experiments gave values laying between 0.015 and 0.030°. A change in the position of the thermometer had a smaller influence, when the instrument was deeply immersed in the liquid than when it was nearer the surface. This is only natural if we remember, that the vapour bubbles ascending from the bottom layers are larger in size than those of the top layers so that the mixing process in the former is less imperfect.

In any case it was shown that the "mixing" during the boiling was by no means sufficient to quite neutralize the difference in temperature between the different layers of liquid. As however the difference in temperature is partly neutralized, we are dealing here with a state of labile equilibrium.

After having tried BECKMANN's process, I applied the method proposed by S. SAKURAI [1]), because the results, obtained by W. LANDSBERGER [2]), who used this process in a slightly simplified form for the determination of molecular weights, inspired me with confidence. On further investigation however, it appeared to me that no very accurate results are obtainable by this method. As was to be expected, the boiling point of the water or of the solution depended on the temperature of the steam which was blown into it. Unless the evaporation keeps perfectly equal pace with the condensation, the pressure in the steam-generating flask is liable to constant variation and as this affects the temperature of the steam we cannot be certain of a constant boiling point. For this reason I abandoned the method.

All this induced me to have a new boiling apparatus constructed with the object of avoiding the first two sources of error arising from the use of BECKMANN's apparatus, although convinced that the third objection would still remain.

As we know by experience that a liquid boils more readily in a metallic vessel with a rough interior surface than in a glass one, in other words that, even without special precautions, the danger of overheating is smaller when using a metallic vessel instead of a glass one, a metallic vessel seemed to me preferable to one made of glass and I, therefore, decided to determine the boiling points in vessels

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[1]) Journ. of the chemical Society 63. 495.

[2]) Zeitschr. f. Anorg. Chem. 17. 423.

made of silver, which had also the advantage that they could be readily made in any desired shape. The construction of the apparatus, presently to be fully described, was entrusted on the recommendation of Prof. H. C. Dibbits, to Mr. Begeer of Utrecht, who has performed his task with great skill and ability.

Description of the Apparatus.

The actual boiling vessels consist of cylindrical silver vessels closed at one end. They have a height of 20 cm. and a diameter of 6 cm. The bottom and sides walls consist of one piece. As will be seen from the accompanying drawing (Fig. I) the top of the silver cylinder is closed with a lid through which pass the glass condensing tube *A* and the thermometer *C*. This tube, shown in the drawing on a reduced scale, has a diameter of 1 cm. and reaches inside the cylinder to a distance of 2 cm. from the bottom. The tube is sealed at the bottom, but at its side turned away from the thermometer it is provided with three openings of 1 cm. diam. Just underneath the lid, the tube has another oval opening 2.5 cm. long and turned towards the thermometer.

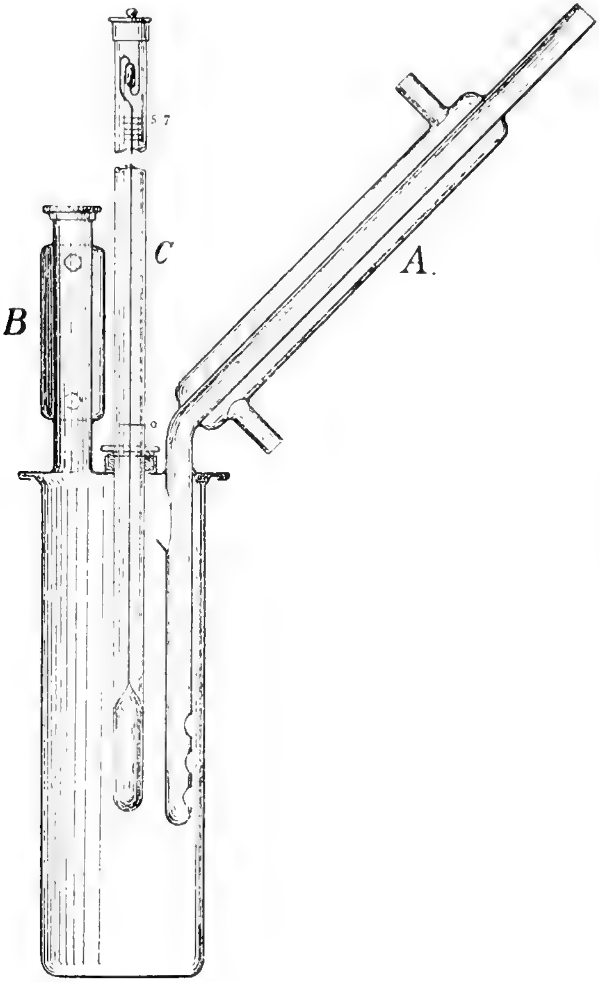

Fig. 1.

The holes below serve to allow the condensed vapour to mix with the boiling liquid, whilst the oval hole at the top serves to carry off the watervapour. The thermometer which is provided with an indiarubber ring may be connected airtight with the lid by means of a screw. The second small silver condenser *B* is 1,5 cm. wide and may also be closed at the top by means of a screw. Through this tube, salts are introduced into the apparatus. Two of these instruments are placed in a copper waterbath with two cylindrical openings from the bottom to the lid. The edges of the lids of the silvercylinders rest on the lid of the copper waterbath which is 22 cm. in height. The bottom of the silver cylinders, therefore, do not fall within the plane of the bottom of the copper waterbath. The waterbath has a diameter of 24 cm. and has besides the two cylindrical openings already mentioned, two other holes in the lid; through one of these passes a thermometer and through the other the tube of a large condenser. The arrangement is shown in Fig. II.

Both the condensing tubes *A* and *A'* are connected by means of the india-rubber tubes *a* and *a'* with the **T**piece *T*, whilst the latter may be connected with the manostat by means of the tube *m*. The heating of the waterbath takes place by means of two small luminous flames of two Bunsen-burners, whilst underneath each silver cylinder a Bunsen-burner was placed, the flame of which was so regulated that it just touched the bottom of the cylinder.

As regards the arrangement of the manostat I still have to mention that I have replaced the aspirator by a water-suction air pump. To be able to regulate the diminution in pressure in the suction-pipes, I connected it with the following arrangement consisting of a glass cylinder closed by a doubly perforated cork. Through the one hole passes one of the tubes of a **T**piece which stops just underneath the cork. Through the other hole is introduced a long glass tube which may be moved up and down with a little friction. The glass cylinder is almost filled with water. If now, the **T**piece is linked to the suctionpipe of the pump, the suction may be easily regulated by pushing the long tube more or less down into the water. This arrangement works very regularly and easily and for my purpose it is preferable to an aspirator.

The second boiling vessel filled with water serves to keep the operator well informed about the action of the manostat. A change of pressure in the apparatus of 1 mm. of water causes a change in the boiling point of ± 0.003°.

Preliminary observations with the new Apparatus.

It was first of all necessary to ascertain what kind of nucleus ought to be put into the silver cylinders to present overheating.

My first trials were made with "shot" but the result was not satisfactory as overheating could not be entirely prevented in this manner and it seemed to me desirable to choose a substance of a lower specific gravity. The choice fell on enamel grains with some silver (tetrahaedra) and experiments made with these gave very satisfactory results. With a constant pressure, the boiling point of water remained constant to 0.002°; introduction of more enamel grains had no influence on the boiling point. Secondly, it had to be ascertained in how far the indication of the thermometer depended on the height of the column of liquid above the bulb. Experiments showed that a displacement of the thermometer of 1 cm. causes a difference of 0.010—0.030° in its indications. On adding water in such quantity as to increase the depth above the bulb by 1 cm. a change of temperature was noticed which was always larger than that caused by a 1 cm. displacement of the thermometer, but the change of temperature was always smaller than 0.030°. This phenomenon may be explained by the fact that in the latter experiment the mercury bulb remains in the same liquid layer, whilst in the first experiment it was transferred to a layer of a different "mixing".

It is not a matter of astonishment that, even, when using these boiling vessels, a change in the position of the thermometer causes a change in its indication and about to the same extent as I noticed with glass vessels, if we consider that the vessels have a diameter of 6 cm. At a very small distance from the side, the influence

READINGS OF THE THERMOMETERS.

Left Thermometer.	Right Thermometer.
1.610	2.100
1.598 1 c.m. higher	2.100
1.610 ″ ″ lower	2.099
1.598 ″ ″ higher	2.100
1.578 2 ″ ″	2.100
1.553 3 ″ ″	2.099
1.550 4 ″ ″	2.100
1.550 5 ″ ″	2.100
1.550 4 ″ ″	2.099
1.552 3 ″ ″	2.099
1.576 2 ″ ″	2.099
1.598 1 ″ ″	2.099
1.610 0 ″ ″	2.099

A. SMITS. Determination of the decrease in the vapour tension of solutions by means of the determination of the increase in the boiling point.

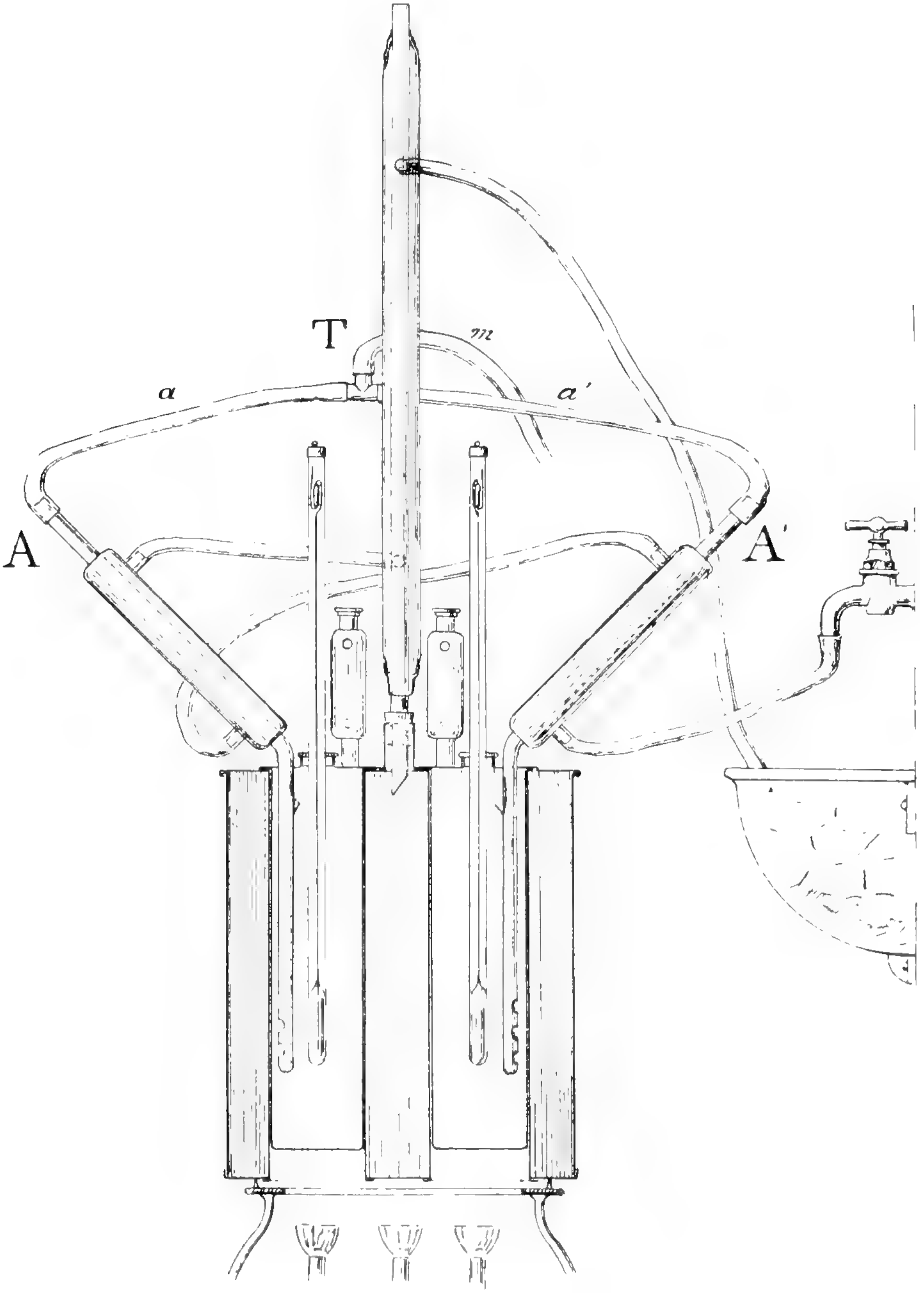

Fig. II.

of the conductivity of the silver may be perceptible, but it is not astonishing that this influence is no longer noticeable at a distance of 3cm.

In using these vessels, I again noticed that the lower down the thermometers are placed in the liquid, the smaller becomes the difference in temperature between the different liquid layers. In the following table, the thermometer on the left is displaced each time 1 cm. whilst the position of the one on the right was left unchanged.

It will be noticed from this table that, when the thermometer was raised by 3 c. m., the mercury reservoir was surrounded by vapour. It is plain, that, if we want to get different concentrations by adding salt to the water or to the solution, we must determine beforehand what will be the influence at that position of the thermometer, of a definite increase of the depth of liquid above its mercury reservoir, so as to be able to make a correction if necessary. If still more concentrated solutions are to be examined, it is desirable to avoid the correction by successively introducing into the apparatus equal quantities of solution and taking care not to alter the position of the thermometer. I next made the following experiment to compare the two BECKMANN thermometers.

Distilled water was introduced into both boiling vessels and the boiling point read off, the pressure being kept constant by means of the manostat. The pressure was then changed to such an extent, that the thermometers fell about 0.5°. After some time the thermometers were again carefully read off. This experiment was repeated at different tensions.

I herewith communicate some of the results.

	Thermometer I	Thermometer II	Difference in the Readings.
	1.457	1.195	0.262
I	0.884	0.622	0.262
	2.658	2.076	0.582
II	2.058	1.474	0.584
	2.090	1.508	0.582
III	1.614	1.030	0.584
	1.610	2.100	0.490
IV	1.285	1.775	0.490

etc.

The result was very satisfactory as the readings of the boiling points only showed a difference of at most 0.003° when the temperature was lowered to the extent of ± 0.5°. Finally it was ascertained what influence was exercised on the boiling point by the method of heating. An experiment showed that the turning of the flames either up or down, did not affect the boiling point as long as, the liquid was kept actively boiling.

Way of Experimenting.

The experiment may now be made as follows: — First of all distilled water is introduced into both boiling vessels, and also grains of enamel and silver tetrahaedra, whilst the quantity of water, intended for the vessel in which salt is afterwards to be dissolved, is being weighed. The four burners are next lit, water being allowed to flow through the large condensers A and A′. When the water boils both in the copper waterbath and the silver cylinders, the flames under the waterbath are turned low and those under the silver vessels are regulated. By means of the rubber tube *m*. the silver cylinders are connected with the manostat and the latter is set in action. To know the pressure which exists in the apparatus during this first experiment, the barometer and the watermanometer of the manostat are read off.

After a quarter of an hour, both the thermometers are read off by means of a magnifying glass and the correction with the manostat is interrupted. The burner underneath the vessel intended for the salt is removed and water is passed through the small condenser. The stopper of the small condenser may then be removed without fear of any loss of watervapour. A weighed quantity of salt is now introduced and the stopper reinserted. The burner is now replaced underneath the boiling vessel, while the water is allowed to pass for some time through the small condenser to rinse down small particles of solid matter adhering to the inside of the condenser by means of the condensed steam. After a while, the boiling vessels are again connected with the manostat and the latter is so arranged that the boiling point of the salt solution is *the same* as that of the water; the thermometers are read off at intervals. The fall observed in the thermometer which is placed in the boiling water, corresponds with the decrease in vapour tension of the solution at the temperature of the salt solutions, which is the same for every concentration.

The results of my investigation will be communicated after the close of another investigation, which I have started with Mr. **Ph. Kohnstamm** as to the question whether generally speaking the temperature of the vapour of any boiling liquid or of a solution is the same as that of the liquid.

I may mention here that H. B. HITE [1]) and H. C. JONES [2]) have succeeded in constructing an apparatus, which gives very satisfactory results with certain solvents. Both have remembered, that in the first place care must be taken that the condensing liquid shall not come in direct contact with the thermometer. The method of JONES is much preferable to HITE's method on account of its simplicity and also because it gives better results when using solvents of a high boiling point. When however I tried the process, using water as solvent, I found that the results were then not very accurate. Although in JONES' method, a displacement of the thermometer exercises little influence on the boiling point as the mercury reservoir is entirely surrounded by metal, the boiling point is sensibly influenced by the method of heating. I further found that the method of S. L. BIGELOW [3]) (heating by electricity) may give very good results in the case of non-electrolytes, if the platinum wire is not twisted into a spiral but left straight. If the wire is then passed through a small U tube the vapour bubbles do not come into contact with the mercury reservoir of the thermometer, but they ascend at both sides of the thermometer. Operating in this manner the boiling point is constant when using the same number of ampères. This method is not at all applicable in the case of electrolytes on account of electrolysis setting in. An attempt which I made, to get a constant boiling point by heating with a boiling liquid instead of a flame, ended in failure. I used liquids of different boiling points varying from 105° to 183° but did not obtain a constant boiling point in this manner.

The result of my investigation is, therefore, as follows :

The apparatus used till now for the determination of the increase in boiling point of aqueous solutions give very satisfactory results in the determination of molecularweights but they are not sufficiently delicate to study the decrease of vapour tensions. For this purpose metallic boiling vessels seem to be desirable, also an arrangement which enables us to regulate with great accuracy the pressure above the boiling solutions and to keep the same constant.

Amsterdam, Jan. 1900. *Univ. Chem. Labor.*

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[1]) Amer. Chem. J. 17, 502.

[2]) Zeit. Phys. Chem. 21 114.

[3]) Amer. Chem. J. 22 280.

Chemistry. — Prof. C. A. Lobry de Bruyn presents a communication from Prof. A. F. Holleman: "*The formation of trisubstituted derivatives from di-substituted derivatives of Benzene.*"

(Read February 24, 1900.)

As stated last year (in the Recueil) [1]) benzoic acid when nitrated at 0° yields the three possible isomers in the proportion of:

18.5 ortho : 80.2 meta : 1.3 para.

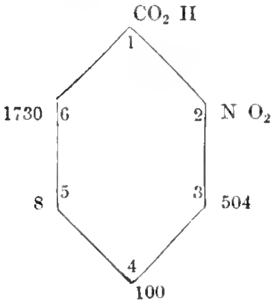
Jointly with Mr. B. R. de Bruyn, I have now found that on nitrating nitro-benzene at 0°, the three isomers are formed in the proportion of:

6.4 ortho : 93.5 meta : 0.1 para

at all events the amount of the para-compound was less than 0.2.

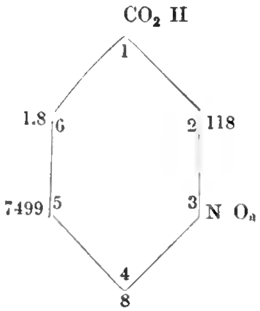
If one now examines, as far as is possible at the present time what relative proportions of the isomeric dinitroacids have been obtained by nitrating the mono-nitrobenzoic acids it appears that the compounds obtained in largest quantity are those for which the products of the above relative numbers are greatest.

In the nitration of *o*-nitrobenzoic acid the products for the still unoccupied places in the benzene nucleus are given in the formula below:



The highest figure is, therefore, in 6; acid in fact, the acid 1 : 2 : 6 is the chief product.

In the nitration of *m*-nitrobenzoic acid the products for the still unoccupied places are:



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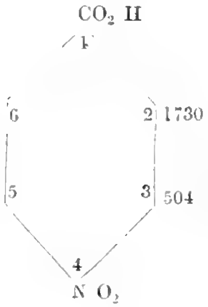
[1]) Proceedings 1899.

Looking at the great value of the product in 5, it is to be expected that the acid 1 : 3 : 5 will be the chief product, while the others will only be obtained in minute quantity. In fact the 1. 3. 5. acid is the only dinitro-acid as yet obtained.

In the nitration of p-nitrobenzoic acid the said products are:



Hübner and Stromeyer first obtained the 1. 2. 4 acid by this process and later on Claus and Halberstadt working on a larger quantity of material isolated the 1, 3, 4 acid which is no doubt formed to a smaller extent.

In the nitration of chloro-benzene at 0° a semi-solid crystalline mass is obtained; if care is taken to collect together all the products formed in the reaction this mass after being fused solidifies at 58°.9. It is known that ortho- and para-chloro-nitrobenzene are formed in this nitration; whether the meta compound is also formed in small quantities remains to be seen; at all events its presence in the nitrated mass is not stated in the literature. Since p- chloronitrobenzene melts at 82° and the ortho compound at 32°, it is evident from the solidifying point that the para compound strongly predominates, so that the relation will be: ortho little, meta traces, para very much. This, and the relation in which the three nitrobenzoic acids are formed, proves that in the nitration of ortho-chloro-benzoic acid, the acid 1 : 2 : 5 ($CO_2 H = 1$) ought to be formed in large predominating quantity together with small quantities of the acid 1 : 2 : 3 ; in the nitration of m-chlorobenzoic acid the acid 1 : 3 : 6 should be chiefly formed, the acid 1 : 3 : 2 occurring only in small and the other isomers in very trifling quantities; in the nitration of p- chlorobenzoic acid the acid 1 : 4 : 3 should be almost exclusively formed. This quite confirms the recent research of Montagne [1]).

In the literature, nothing much is said about the relative quantities of the isomers formed in the nitration of benzene derivatives ; as a rule the writers confine themselves to such statements as "chief product", or „much" of this „little" of the other isomer. With the aid of such statements it is possible to ascertain whether the above rule is of general application. This seems indeed to be the case.

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[1]) Dissertation, Leiden 1899.

This does not only apply to nitrations, but also in cases of the introduction of bromine and chlorine. I have met with many instances in which it was possible to predict which of the possible isomers would be the chief product.

The question now arises whether the relative quantities in which the isomeric trisubstituted derivatives are generated corresponds to the relation shown by the above mentioned products, or in other words whether the phenomena observed in the formation of trisubstituted derivatives may be explained quantitatively in this manner. Researches in this direction are in progress in my laboratory.

Chemistry. — Prof. H. W. Bakhuis Roozeboom presents in the name of Dr. C. van Eyk, of Breda, the following paper: "*Formation and transformation of the double salt of Silvernitrate and Thalliumnitrate.*"

(Read February 24, 1900.)

1. Silvernitrate and thalliumnitrate are rhombic at the ordinary temperature; at 159° and 142° respectively, they undergo a structural change and become rhombohedric. No records exist as to the formation of mixed crystals. Retgers (Zeit. phys. Chem. 5, 451) mentions the existence of a double salt without mentioning however whether he has obtained this from the aqueous solution or from the fused mixture. The object of this investigation was to see what kind of crystals are deposited from fused mixtures of various concentrations (varying from 100 per cent of silvernitrate to 100 per cent of thalliumnitrate) and to study the possible changes which these crystals undergo at lower temperatures.

2. Determination of the meltingpoint line.

The solidifying points of mixtures of $Tl\,NO_3$ and $Ag\,NO_3$ (varying from 0 to 100 percent) were observed and the course of the solidification was watched.

It was found that the meltingpoint line, starting from either $Tl\,NO_3$ or $Ag\,NO_3$, took a descending course with a short double salt line situated between the two branches.

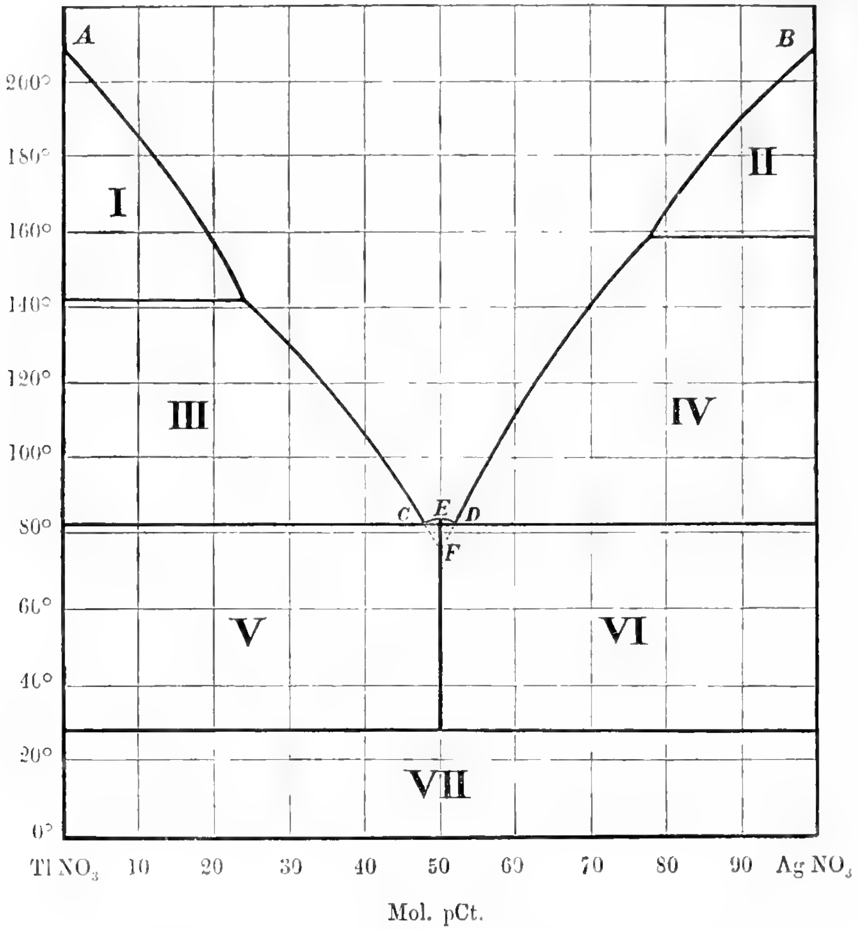
Mol. pCt. $Ag\,NO_3$	Commencement of Solidification.
100	208°.5
94	196°
90	188°.5
87	183°

Mol. pCt. Ag NO$_3$.	Commencement of Solidification.
86	181°
78.5	161°.5
7.05	140°
68	133°
62	116°
54	91°
53	85°
52	81°.6
50	82°.8
48	81°.2
47	85°
41.5	100°.6
40.5	105°
37.5	112°
30.7	129°
22.5	149°
14	173°.5
0	206°

The graphic illustration (see figure) gives a clearer view.

The points of intersection *C* and *D* of the doublesalt line with the two descending branches of the meltingpoint line cannot be readily determined, as both the lines *A C* and *B D* continue far beyond those points. For instance, the mixture with 47 mol. per cent of Ag NO$_3$ commences to solidify at 85°, crystals being deposited which are heavier than the melt. On lowering the temperature to below 80°, the crystals continue to form until all at once a large quantity of double salt separates and the temperature rises to 82°.8. The temperature at which this sudden separation takes place is not the same in every experiment; sometimes this only commences at 68°. The same takes place with mixtures containing more than 50 mol. per cent of Ag NO$_3$. From the mixture with 53 mol. per cent of Ag NO$_3$, crystals begin to form at 83°.5; these are lighter than the melt. Sometimes the formation of them may continue down to 75° or lower until all at once a large quantity of doublesalt crystals is deposited and the temperature goes up to 82°.8.

The mixture with 50 mol. per cent of Ag NO$_3$ deposits, from the commencement, crystals different from the two first. The crystals are of about the same density as the melt. In this mixture the first crystals separate at 82°8, or if supercooling takes place the temperature goes up to 82°8, which is the melting point of the double salt, as soon as crystals are deposited.



The meltingpoint *E* and the two eutectic points for doublesalt + $AgNO_3$ and double salt + $TlNO_3$ do not perceptibly differ. The short line *C E D* of the doublesalt is, therefore, almost horizontal. As a consequence of the fact that the points *C* and *D* lie so close to 50 percent, the solidification trajectory that is the series of temperatures at which solidification takes place, is very prolonged for fused mixtures containing much $AgNO_3$ or $TlNO_3$. Even in the case of these mixtures, the lines *A C* and *B D* may pass the points *C* and *D* owing to superfusion of the doublesalt. Solidification was incomplete even at 80° in the case of mixtures containing 90 percent $AgNO_3$ or 90 percent $TlNO_3$.

If the doublesalt did not form of its own accord, the eutectic point *F* where the melt solidifies to a conglomerate of $AgNO_3$ + $TlNO_3$ would be noticed at about 75°.

3. The course of the meltingpoint line admits of two possibilities as regards the nature of the crystals which separate from the melt

containing from 0 to 48 mol. percent of $AgNO_3$ or from 52 to 100 mol. percent of $AgNO_3$: either the pure salts are deposited or else their mixed crystals.

The fact that mixtures with a high percentage of either $AgNO_3$ or $TlNO_3$ are not quite solidified until close upon 80° proves that there can be only a very slight mixing in the solid phases.

It is however, impossible to separate the crystals from the melt sufficiently completely to make it possible to decide, by means of an analysis of the separated crystals, whether a small intermixture occurs or not.

This may be more accurately found out by determining the transition points of the separated crystals.

At the $AgNO_3$ — side, the rhombohedric crystals (whether consisting of pure $AgNO_3$ or mixed crystals) which are deposited from the melt at a high temperature, will change into the rhombic form when they are left in contact with the melt at a lower temperature; this change is accompanied by a retardation in the fall of the temperature. When the melt deposits pure $AgNO_3$ th change takes place at 159°, but in the case of mixed crystals the temperature must be either higher or lower than 159°.

The same is true of the crystals which deposite on the $TlNO_3$ — side. On observing the course of the solidification the retardation always occurred at 152° in the case of mixtures at the $AgNO_3$ side, which solidified about 160° and consequently contained from 100 to about 80 percent at $AgNO_3$.

At the $TlNO_3$ side it always occurred at 142°.

From this it follows that mixed crystals are not deposited on either side, or, at most, mixed crystals containing a very small admixture.

4. The solidified mixtures of different concentrations are, therefore, conglomerates of the doublesalt with $AgNO_3$ or $TlNO_3$.

These, on a further decrease in temperature, undergo another change. When the mixtures are allowed to solidify on a glass slide and then exposed to a low temperature they gradually become opaque as may be noticed with the naked eye. The temperature at which the transformation takes place cannot be determined by optical or thermometric methode as the change proceeds too slowly, and therefore, the dilatometric process was applied.

First of all, a comparative experiment was made to demonstrate that the change in the conglomerates is a change in the double salt and not of $AgNO_3$ or $TlNO_3$ alone.

Temperature	Dilatometer $Tl NO_3$	Dilatometer $Ag NO_3$	Dilatometer 51 mol. pCt. $Ag NO_3$
36°.6	24.1	22.5	57.8
33°.7	31.9	28.3	52.3
31°	35.9	31.4	49.5
28°.6	40.8	35	46.1

These dilatometers were now cooled down to about 10°, left at that temperature for about 20 hours and then again heated to the original temperatures to see whether any change in volume had taken place.

In this way the following numbers were obtained:

31°	35.9	31.4	34.4

$Tl NO_3$ and $Ag NO_3$ have, therefore, undergone no alteration whilst the volume of the mixture has greatly diminished.

The transition temperature of different mixtures was determined next.

Temperature.	Time in hours.	Rise of level with mixtures of 40 pCt. $Ag NO_3$	50 pCt. $Ag NO_3$	60 pCt. $Ag NO_3$	70 pCt. $Ag NO_3$
34°.4	4	+ 6.4	+ 6.9	+ 7.2	+ 7.2
30°.9	4	+ 1.4	+ 1.9	+ 1.3	+ 1.5
27°	6	+ 0.5	+ 0.8	+ 0.4	+ 0.5
26°	6	— 0.35	— 0.4	— 0.2	— 0.3
24°	3	— 1.4	— 1.4	— 1.2	— 1.5
19°	1	— 1.4	— 2.0	— 1.8	— 1.6

With mixtures of 20 percent and of 80 percent of $Ag NO_3$ it was possible to determine that the transition temperature lies between 24° and 29°.

It, therefore, appears that all the mixtures have the transition temperature at 26°—27°. It will have to be proved by solubility experiments whether at this temperature, the double salt changes into another modification or breaks up into the components.

The following groups of phases exist in the different regions indicated in the figure:

I. $Tl NO_3\ \alpha$ + Melt. II. $Ag NO_3\ \alpha$ + Melt.
III. $Tl NO_3\ \beta$ + Melt. IV. $Ag NO_3\ \beta$ + Melt.
V. $Tl NO_3\ \beta$ + Double salt. VI. $Ag NO_3\ \beta$ + Double salt.

Region VII will contain the group $Tl NO_3\ \beta + Ag NO_3\ \beta$, or will have to be divided into two parts representing the conditions of existence of each of these salts with the new modification of the double salt.

Mathematics. — “*On Orthogonal Comitants*”. By Prof. JAN DE VRIES.

If we regard x_1 and x_2 as the coordinates of any point P with respect to the rectangular axes OX_1 and OX_2, the binary form

$$a_x^n \equiv (a_1 x_1 + a_2 x_2)^{(n)} \equiv a_{n,0}\, x_1^n + n\, a_{n-1,1}\, x_1^{n-1} x_2 + \binom{n}{2} a_{n-2,2}\, x_1^{n-2} x_2^2 + \\ \ldots\ldots + a_{0,n}\, x_2^n$$

is represented by n lines through O, containing the points for which the form a_x^n disappears.

If ξ_1 and ξ_2 are the coordinates of P with respect to the rectangular axes $O\Xi_1$ and $O\Xi_2$, between the quantities x_1, x_2 and ξ_1, ξ_2 exist relations of the form

$$x_1 = \lambda_{11}\,\xi_1 + \lambda_{12}\,\xi_2, \qquad \xi_1 = \lambda_{11}\,x_1 + \lambda_{21}\,x_2,$$

$$x_2 = \lambda_{21}\,\xi_1 + \lambda_{22}\,\xi_2, \qquad \xi_2 = \lambda_{12}\,x_1 + \lambda_{22}\,x_2.$$

If by these substitutions the form a_x^n is transformed into α_ξ^n, we have

$$a_x = a_1 x_1 + a_2 x_2 = (a_1 \lambda_{11} + a_2 \lambda_{21})\,\xi_1 + (a_1 \lambda_{12} + a_2 \lambda_{22})\,\xi_2,$$

so

$$\alpha_1 = \lambda_{11}\, a_1 + \lambda_{21}\, a_2,$$

$$\alpha_2 = \lambda_{12}\, a_1 + \lambda_{22}\, a_2.$$

This proves that the symbolical coefficients a_1, a_2 and α_1, α_2 are transformed into each other by the same substitution as the variables x_1, x_2 and ξ_1, ξ_2.

2. In order to obtain *comitants*, i. e. functions of a_1, a_2, x_1, x_2 that are invariant with respect to the indicated orthogonal transformations, we can start from the covariants

$$x_1^2 + x_2^2 \quad \text{and} \quad (x_1 - y_1)^2 + (x_2 - y_2)^2,$$

representing the square respectively of OP and of the mutual distance of two points P and Q, being therefore *absolute comitants.*

The second covariant can be replaced by

$$(x_1^2 + x_2^2) - 2(x_1 y_1 + x_2 y_2) + (y_1^2 + y_2^2) \equiv x_x - 2 x_y + y_y ,$$

whilst from the relation

$$(x_1 y_2 - x_2 y_1)^2 = (x_1^2 + x_2^2)(y_1^2 + y_2^2) - (x_1 y_1 + x_2 y_2)^2 ,$$

or

$$(xy)^2 = x_x y_y - x_y y_x$$

ensues that the covariant (xy) is related to the covariants x_x and $x_y \equiv y_x$.

Now from these three absolute comitants follows immediately the invariant character of the symbols

$$a_a , \qquad a_b \qquad \text{and} \qquad (ab) .$$

According to the above these absolute invariant symbols are connected by the relation

$$(ab)^2 = a_a b_b - a_b^2 .$$

So for the construction of orthogonal comitants we can dispose of the symbols

$$a_a , \quad a_b , \quad (ab) , \quad a_x , \quad (ax) , \quad x_x , \quad x_y , \quad (xy) .$$

Evidently *linear* invariants can be generated only by the symbol a_a and present themselves only in the study of forms of *even* degree. Consequently the form a_x^{2n} possesses the linear absolute invariant 1)

$$a_a^n \equiv a_{2n,0} + n\, a_{2n-2,2} + \binom{n}{2} a_{2n-4,4} + \dots + a_{0,2n} .$$

3. The quadratic form

$$a_x^2 \equiv a_{20} x_1^2 + 2 a_{11} x_1 x_2 + a_{02} x_2^2$$

furnishes the invariants

$$a_a \equiv a_{20} + a_{02} ,$$

$$a_b^2 \equiv a_{20}^2 + 2 a_{11}^2 + a_{02}^2 ,$$

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1) The existence of this invariant was proved by Mr. W. MANTEL by means of an infinitesimal transformation (Wiskundige Opgaven, Dl. VII, p. 148).

$$(ab)^2 \equiv 2\,(a_{20}\,a_{02} - a_{11}^2)\,,$$

united by the relation found above.

Whilst $(ab)^2 = 0$ points to the coinciding of the two lines indicated by $a_x^2 = 0$, a_a disappears when those lines are at right angles.

If c is the tangent of the angle formed by the two lines, their angular coefficients satisfy the relation

$$\left(\frac{m_1 - m_2}{1 + m_1\,m_2}\right)^2 = c^2\,,$$

or

$$4\,(a_{20}\,a_{02} - a_{11}^2) + c^2\,(a_{20} + a_{02})^2 = 0\,,$$

or

$$2\,(ab)^2 + c^2\,a_a\,b_b = 0\,,$$

or at last

$$(c^2 + 2)\;(ab)^2 + c^2\,a_b^2 = 0\,.$$

So the invariant a_b disappears when $c^2 = -2$.

4. By the interpretation of the substitution $x_y = 0$ or

$$y_1 : y_2 = x_2 : -x_1$$

follows immediately that the covariant

$$(ax)^2$$

disappears for two lines which are at right angles to the lines representing a_x^2.

The covariant

$$(ax)\,a_x$$

changes only its sign by the substitution $x_y = 0$.

So $(ax)\,a_x = 0$ represents two orthogonal lines.

Indeed the sum of the coefficients of x_1^2 and x_2^2 is equal to zero.

If $a_{11} = 0$, so that the lines of a_x^2 lie symmetrically with respect to the axes of coordinates, we have

$$(ax)\,a_x \equiv (a_{20} - a_{02})\,x_1\,x_2\,.$$

This proves that the covariant $(ax)\,a_x$ furnishes the bisectors of the angles of the lines $a_x^2 = 0$.

This result is confirmed by the following consideration:
By the equations

$$a_x a_y = 0 \qquad \text{and} \qquad x_y = 0$$

the pairs of lines are indicated lying respectively harmonically with the lines $a^2_x = 0$ and with the isotropical lines $x_x = 0$.

And now these two involutions have the pair of rays in common of which the equation is obtained by eliminating y between

$$a_1 a_x y_1 + a_2 a_x y_2 = 0 \qquad \text{and} \qquad x_1 y_1 + x_2 y_2 = 0 .$$

So the equation

$$(ax)\, a_x = 0$$

represents the orthogonal lines separating $a^2_x = 0$ harmonically.

5. If we put

$$a_b\, a_x b_x \equiv g^2_x ,$$

then with a view to the equivalence of the symbols a and b, we have

$$g_x g_y = a_b\, a_x b_y ,$$

and

$$g_x (gx) = a_b\, a_x (bx) .$$

But from the identical relation

$$a_a b_x - b_a a_x = (ab)(ax)$$

follows

$$(gx)\, g_x = a_a (bx)\, b_x - (ab)(ax)(bx) .$$

The second term of the right member disappearing identically and $(bx)\, b_x = 0$ representing the bisectors of the angles of the lines $b^2_x = 0$, the covariant

$$a_b\; a_x\; b_x$$

furnishes two lines having in common with the lines of a^2_x the axes of symmetry.

At the same time it is evident that the form $a_b\, a_x (bx)$ does not give a new covariant.

It is clear that $a_b\,(ax)\,(bx)$ represents the lines at right angles to $a_b\, a_x\, b_x = 0$.

6. To two quadratic forms a_x^2 and f_x^2 belong the simultaneous invariants

$$(af)^2\,, \qquad a_f^2 \equiv f_a^2\,, \qquad (af)\,a_f\,.$$

As is known the first disappears when the two pairs of lines separate each other harmonically.

Under the condition $(af)\,a_f = 0$ the lines determined by $(af)\,a_x\,f_x = 0$ are perpendicular to one another.

These right lines being the double rays of the involution $a_x^2 + \lambda f_x^2 = 0$, the equation $(af)\,a_f = 0$ indicates that the pair of lines $a_x^2 = 0$ and $f_x^2 = 0$ have common axes of symmetry.

This is confirmed by the following consideration. We have

$$(af)\,a_f = (a_{20} - a_{02})\,f_{11} - a_{11}\,(f_{20} - f_{02})\,.$$

If $f_{11} = 0$, the invariant disappears when at the same time $a_{11} = 0$ or $f_{20} = f_{02}$, i. e. when the two pairs of rays have common bisectors or when one pair of rays consists of the isotropical lines.

From the expression found above for the tangent of the angles of a pair of lines follows readily that the invariant

$$(ab)^2\,f_f\,g_g - (fg)^2\,a_a\,b_b$$

disappears, when these pairs of lines can be brought to coincidence by the rotation of one of them.

7. When the equations

$$a_x^2 \equiv a_{20}\,x_1^2 + 2\,a_{11}\,x_1\,x_2 + a_{02}\,x_2^2 = 0\,,$$

$$(fx)^2 \equiv f_{02}\,x_1^2 - 2\,f_{11}\,x_1\,x_2 + f_{20}\,x_2^2 = 0$$

have a root $x_1 : x_2$ in common, one of the lines $a_x^2 = 0$ is at right angles to a line of $f_x^2 = 0$. So the resultant of these equations must furnish a simultaneous invariant.

By elimination of $x_1 : x_2$ we find

$$(a_{20}\, f_{20} - a_{02}\, f_{02})^2 + 4\, (a_{20}\, f_{11} + a_{11}\, f_{02})\, (a_{02}\, f_{11} + a_{11}\, f_{20}) = 0\,.$$

By a simple computation this expression is reduced to the symbolic form

$$a_f^2\, b_g^2 - 2\, (ab)\, (fg)\, a_f\, b_g = 0\,,$$

where $a_x^2 \equiv b_x^2$ and $f_x^2 \equiv g_x^2$.

If in the preceding equations we put $a_{20} = 0$, then we have $f_{02} = 0$ or $a_{02}^2\, f_{02} + 4\, a_{02}\, a_{11}\, f_{11} + 4\, a_{11}^2\, f_{20} = 0$. In the former case a line of a_x^2 is at right angles to a line of f_x^2. In the latter case the substitution $a_{02} = 2\, i\, a_{11}$ furnishes the condition

$$-f_{02} + 2\, i\, f_{11} + f_{20} = 0\,,$$

from which ensues that one of the two isotropical lines belongs to each of the pairs; then again a line of a_x^2 is at right angles to a line of f_x^2.

The consideration of the orthogonal pair of rays of the involution

$$a_x^2 + \lambda\, f_x^2 = 0$$

leads to a simultaneous covariant.

This pair is indicated by

$$(a_1^2 + \lambda\, f_1^2) + (a_2^2 + \lambda\, f_2^2) = 0\,,$$

or by

$$a_a + \lambda\, f_f = 0\,,$$

so by

$$f_f\, a_x^2 - a_a\, f_x^2 = 0\,.$$

8. It is a matter of course, that to the cubic form

$$a_x^3 \equiv a_{30}\, x_1^3 + 3\, a_{21}\, x_1^2\, x_2 + 3\, a_{12}\, x_1\, x_2^2 + a_{03}\, x_2^3$$

belong only invariants with an even number of symbols, i. e. of even degree in the coefficients.

Setting aside the forms $(ab)\,a_b^2$ and $(ab)^3$ which disappear identically, we have the invariants

$$(ab)^2\,a_b = 2\,(a_{30}\,a_{12} - a_{21}^2 - a_{12}^2 + a_{03}\,a_{21})\,,$$

$$a_b^3 = a_{30}^2 + 3\,a_{21}^2 + 3\,a_{12}^2 + a_{03}^2\,.$$

From the identity $(ab)^2 + a_b^2 = a_a\,b_b$ evidently follows

$$a_a\,a_b\,b_b \equiv (ab)^2\,a_b + a_b^3\,.$$

For $a_{30} = 0$ and $a_{03} = 0$ we have

$$a_b^3 = 3\,(a_{21}^2 + a_{12}^2) \text{ and } (ab)^2\,a_b = -\,2\,(a_{21}^2 + a_{12}^2)\,,$$

so

$$2\,a_b^3 + 3\,(a\,b)^2\,a_b \equiv 2\,(a_{30}^2 + 3\,a_{30}\,a_{12} + 3\,a_{03}\,a_{21} + a_{03}^2) = 0.$$

Reciprocally the disappearing of this invariant indicates that two lines of $a_x^3 = 0$ are at right angles to each other. For, if by a rotation of the axes of coordinates a_x^3 is transformed into

$$3\,\alpha_{21}\,\xi_1^2\,\xi_2 + 3\,\alpha_{12}\,\xi_1\,\xi_2^2 + \xi_2^3\,,$$

which implies that one of the lines is represented by $\xi_2 = 0$, then the angular coefficients of the remaining lines are connected by the relation $m_2\,m_3 = 3\,\alpha_{21}$. The above named invariant being transformed into $3\,\alpha_{21} + 1$, its disappearing produces the relation $m_2\,m_3 + 1 = 0$, by which two perpendicular lines are indicated.

9. The comitant

$$a_y\,a_x^2 = 0$$

determines the polar of a_x^3 with respect to the line $y_1 : y_2 = x_1 : x_2$, or, what comes to the same thing, the double lines of the cubic involution of which $(x\,y) = 0$ is a threefold ray and $a_x^3 = 0$ forms a group.

For the double rays of the involution

$$(x\,y)^3 + \lambda\, a_x^3 = 0$$

are determined by

$$\begin{vmatrix} (x\,y)^2\, y_2 & , & a_x^2\, a_1 \\ -\,(x\,y)^2\, y_1 & , & a_x^2\, a_2 \end{vmatrix} = 0,$$

or by $a_y\, a_x^2 = 0$.

In connection with this consideration the covariant of HESSE

$$(a\,b)^2\, a_x\, b_x$$

furnishes two lines forming the threefold elements of a cubic involution of which $a_x^3 = 0$ is a group.

The lines of HESSE are orthogonal, when the invariant $(a\,b)^2\, a_b$ is equal to zero.

The lines $a_y\, a_x^2 = 0$ are orthogonal when the covariant $a_a\, a_y$ disappears, i. e. when we have

$$y_1 : y_2 = a_2\, a_a : -\, a_1\, a_a.$$

By substitution into $b_y\, b_x^2 = 0$ we find that the pair of rays in question is indicated by

$$(a\,b)\, a_a\, b_x^2 = 0.$$

The lines of HESSE are the double elements of the involution

$$(a\,b)^2\, a_x\, b_y = 0.$$

If $y_1 : y_2$ is replaced by $c_2\, c_c : -\, c_1\, c_c$, it is evident that the covariant

$$(a\,b)^2\, (b\,c)\, c_c\, a_x$$

determines the ray conjugate in this involution to the ray $a_a\, a_y = 0$.

Evidently the orthogonal pair of rays of this involution is indicated by

$$(a\,b)^2\, a_x\, (b\,x) = 0.$$

So this must correspond with $(a\,b)\,a_a\,b_x^2 = 0$, which indicates according to the above the same pair of rays. By applying the identity $(a\,b)\,(a\,x) = a_a\,b_x - b_a\,a_x$, we find $(a\,b)^2 b_x\,(a\,x) = (a\,b)\,a_a b_x^2 - (a\,b)\,b_a\,a_x\,b_x$, where the third covariant disappears identically.

10. The biquadratic form

$$a_x^4 \equiv a_{40}\,x_1^4 + 4\,a_{31}\,x_1^3\,x_2 + 6\,a_{22}\,x_1^2\,x_2^2 + 4\,a_{13}\,x_1\,x_2^3 + a_{04}\,x_2^4$$

has, beside the above mentioned invariant

$$h \equiv a_a^2 \equiv a_{40} + 2\,a_{22} + a_{04}$$

and the well known invariants

$$i \equiv (a\,b)^4 \quad \text{and} \quad j \equiv (a\,b)^2\,(a\,c)^2\,(b\,c)^2,$$

the quadratic invariants

$$m \equiv a_b^4 \equiv a_{40}^2 + 4\,a_{31}^2 + 6\,a_{22}^2 + 4\,a_{13}^2 + a_{04}^2,$$

$$l \equiv (a\,b)^2\,a_b^2 \equiv 2\,a_{22}\,(a_{40} - 2\,a_{22} + a_{04}) - 2\,(a_{31} - a_{13})^2 \,.$$

In consequence of the identity $(a\,b)^2 + a_b^2 = a_a\,b_b$ we have

$$(a\,b)^4 + 2\,(a\,b)^2\,a_b^2 + a_b^4 = a_a^2\,b_b^2\,,$$

so that we have also

$$i + 2\,l + m = h^2.$$

If we put $a_{40} = 0$ and $a_{04} = 0$, then

$$h = 2\,a_{22},$$

$$i = 2\,(3\,a_{22}^2 - 4\,a_{31}\,a_{13}),$$

$$j = 6\,(2\,a_{31}\,a_{22}\,a_{13} - a_{22}^3),$$

so

$$3\,h^3 = 6\,i\,h + 8\,j.$$

Consequently the invariant

$$8\,(ab)^2\,(ac)^2\,(bc)^2 + 6\,(ab)^4\,c_c^2 - 3\,a_a^2\;b_b^2\;c_c^2$$

disappears when the four lines $a_x^4 = 0$ contain two pairs at right angles.

11. Ternary forms can be represented by cones the top of which is situated in the origin of three axes of coordinates perpendicular to one another.

Here too it is evident that by a rotation of the axes of coordinates the symbolical coefficients a_k of the form

$$a_x^n \equiv (a_1\,x_1 + a_2\,x_2 + a_3\,x_3)^{(n)}$$

undergo the same substitution as the coordinates.

So the comitants

$$x_1^2 + x_2^2 + x_3^2\,, \qquad x_1\,y_1 + x_2\,y_2 + x_3\,y_3\,,$$

$$(x_1\,y_2 - x_2\,y_1)^2 + (x_2\,y_3 - x_3\,y_2)^2 + (x_3\,y_1 - x_1\,y_3)^2,$$

$$\begin{vmatrix} x_1 & x_2 & x_3 \\ y_1 & y_2 & y_3 \\ z_1 & z_2 & z_3 \end{vmatrix}$$

furnish the invariant symbols

$$a_a\,, \qquad a_b\,, \qquad (a_1\,b_2)^2 + (a_2\,b_3)^2 + (a_3\,b_1)^2$$

and

$$(abc)\,.$$

For quadratic cones we immediately find the orthogonal invariants

$$a_a \equiv a_{11} + a_{22} + a_{33}\,, \quad \Sigma\,(a_{11}\,a_{22} - a_{12}^2) \text{ and } (abc)^2 = \Sigma \pm a_{11}\,a_{22}\,a_{33}\,.$$

Bacteriology. — *"On Indigo-fermentation"*. By Prof. M. W. BEIJERINCK [1]).

At a former occasion it was demonstrated [2]) that the indigo-plants may be brought to two physiologically different groups, viz. indoxyl-plants, to which the woad (*Isatis tinctoria*) belongs and indican-plants. Of the latter, which seem the most numerously represented, were examined *Indigofera leptostachya*, *Polygonum tinctorium* and *Phajus grandiflorus* [3]). The result was that they contain specific enzymes differing from one another, which split the indican into indoxyl and glucose, while in woad there is no such enzyme. Indican can moreover be decomposed by katabolism [4]), i. e. by the direct action of the living protoplasm, which has been observed in some indicanplants, beside enzyme-action. Various microbes, too, can decompose indican and here the decomposition is generally effected by katabolism only; some species, however, contain specific indigo-enzymes. Hence the word "indigo-fermentation" means two quite different processes: a katabolic and an enzymatic process, and the enzymes are of twofold origin, products of higher plants and products of microbes. It is clear that in the formation of indigo from woad, in which no glucoside but free indoxyl occurs, there can be no question of „indigo-fermentation".

1. *Preparation of the Indican as used for the Experiments* [5]).

For the preparation of indican-solutions from indican-plants, a method was described (l. c. p. 122) the principle of which is so quickly to destroy the enzyme that the glucoside can be dissolved without decomposition [6]). This is best done for *Indigofera* and *Polygonum* by immersion in boiling water, by which an extract is obtained of 0.5 to 1 pCt. indican, which as such, or after mixing

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[1]) I am indebted to Mr. J. F. B. VAN HASSELT and Mr. A. VAN DELDEN for assistance in the following study.

[2]) "On Indigo-formation from the Woad (*Isatis tinctoria*)". Proc. Royal Acad. of Sciences. Amsterdam, Sept. 30, 1899, p. 120.

[3]) Received under this name from a horticultural institution.

[4]) For this expression see: Centralbl. f. Bacteriologie 2e Abt. Bd. 6. p. 5, 1900.

[5]) Further informations about the indican and the enzyme of *Indigofera* are found in the recently published interesting paper of Mr. J J. HAZEWINKEL, Maandelijksch Bulletin van het Proefstation voor Indigo, Klaten (Java). Aflevering I, Januari 1900, Samarang.

[6]) For the production of many other glucosides the same method can be applied.

with gelatine or agar is fit for bacteriologic or enzyme experiments.

The leaves of *Phajus grandiflorus* decompose the indican at high temperatures with so much energy, that the extraction by boiling does not produce indican but indoxyl, so that I first took *Phajus* for an indoxyl-plant. In this case, in order to perform the experiment at low temperature without indican decomposition, the preparation should be effected in presence of an enzyme poison which does not act on indican. To this effect the leaves are rubbed down in caustic lime or baryta, then filtered and carbonic acid passed through; after filtering again a very pure indican-solution is obtained [1]). The leaves can also be boiled in diluted ammoniac and the superfluous ammoniac be removed by evaporation. Another method is to crush the leaves under alcohol by which the enzyme, though not destroyed, precipitates in the cells, while the indican dissolves in the alcohol and after evaporation of the latter can be taken up in water.

By evaporating the solutions to dryness, the impure indican results as a brown mass, resembling sealing-wax, which can be powdered and, in dry condition, be kept unchanged an unlimited length of time. The crude, neutralized or feebly alkaline-solutions, when sterilized and preserved from the access of microbes, also remain unchanged for many months [2]).

A purified indican-preparation is obtained from the decoctions by evaporating them to dryness with caustic lime or baryta, dissolving in little water, filtering, passing through carbonic acid or precipitating the baryta with aluminium sulphate, then again filtering and evaporating to dryness. The thus formed preparation contains fewer pigments and fewer proteids than the crude solutions.

The impure or thus purified indican is fit for mixing with a solid medium destined for microbe-cultures. On such "indican agar" or "indican gelatine" poured out to plates, colonies or streaks of microbes produce or do not produce indigo, according to the species. Of this later more.

For our experiments we used the decoction or the crude indican prepared from it, either or not purified with lime, of *Polygonum tinctorium* and *Indigofera leptostachya*, cultivated partly in the garden of the Bacteriological Laboratory at Delft, partly at Wage-

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[1]) The extraction with caustic lime has also been applied by Mr. HAZEWINKEL for *Indigofera*.

[2]) But after a very long time the amount of indican diminishes when air finds access. When air was excluded I could note no change in the solutions.

ningen, and kindly procured by Mr. VAN LOOKEREN CAMPAGNE. I also received from Mr. HAZEWINKEL of Klaten, Java, perfectly well preserved extracts of *Indigofera* in tins, together with crude enzyme prepared from this plant.

2. *Preparation of the Enzymes.*

For this preparation I followed the method pointed out before (l. c. pag. 124). The plants are rubbed fine in a mortar under alcohol and during the rubbing the alcohol is a few times renewed. In the beginning alcohol of 96 pCt. is taken, which is sufficiently diluted by the juice of the plant, but afterwards some water is added as otherwise the chlorophyll-pigment cannot be completely extracted from the granules. I suppose this must be explained by the strong water-attracting power of the alcohol, which produces from the protoplasm a proteid, impervious to the chlorophyll pigment and possibly to the alcohol itself, but which, by water, becomes again permeable. In this operation the indigo-enzyme is precipitated in the cells and this occurs so quickly that the indican, which is soluble in alcohol has disappeared before its decomposition can set in. As by this method the chlorophyll is completely extracted by alcohol, a colourless product is obtained, which, after drying, first at 37° C. and then at 55° C., is a snow-white powder, directly, or after further pulverising, fit for enzyme experiments. In stoppered bottles I have kept such preparations for months without observing any decrease of activity [1]).

As, in the preparation of the indigo-enzyme from *Polygonum tinctorium* decomposition of the indican occurs much more easily than with *Indigofera*, it is necessary, in order to get colourless preparations from this plant, to proceed with greater precaution and to kill the protoplasm more quickly. This is done by taking only a small quantity of leaf substance at a time for the rubbing in the mortar so that the alcohol can penetrate in a few seconds. With *Indigofera* much larger quantities of leaves may be taken, without fear of obtaining preparations coloured by indigo.

As I could not point out by the ammoniac-experiment, the presence of free indoxyl in *Polygonum* leaves, I thought at first that the

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[1]) The loss of activity in enzyme preparations may be compared to the loss of germinating power in plant-seeds. If they are kept in complete absence of water, both, the activity of enzymes and the germinating power of seeds, will last an unlimited length of time.

difference was to be explained by admitting that the enzyme of *Polygonum* is more soluble in water than that of *Indigofera* and so, during the extraction could perhaps in higher concentration act on the indican. But the experiment showed that this is not the case. Neither can the acid reaction of the juice of *Polygonum*, caused by kalium bioxalate, account for this difference, as the addition of this salt, kalium biphosphate, or of a little acid, to the materials used for the preparing of the enzyme from *Indigofera*, produces no change in the course of the phenomena. The addition of asparagine is likewise without effect. Nor is the explanation to be found in the relation of both enzymes to the temperature. I have so come to the conclusion that in *Polygonum* part of the indican is decomposed by the direct action of the living protoplasm itself. This part is however small, and by quickly immersing in boiling water the protoplasm is killed before it causes decomposition.

In the preparation of indigo-enzyme from *Phajus grandiflorus* nothing particular is observed. But we saw before that the decoction method produces no indican but indoxyl from this plant.

As the figure below shows that the enzyme of *Phajus* becomes inactive already at a lower temperature (67° C.) than that of *Indigofera* (75° C.), I must admit that also in the leaves of *Phajus* katabolism exists together with enzyme action and that, at the immersion in boiling water, simultaneously with the dying of the protoplasm, this katabolism causes a vigorous indican decomposition [1]). Hence *Polygonum* and *Phajus* agree in so far as in both indigo-fermentation is caused by katabolism and by enzymes; but they differ in the fact that in *Phajus* the katabolism is quickened by high, in *Polygonum* by low temperature. In *Indigofera* katabolism seems not to occur at all and the decomposition of indican appears exclusively effected by the enzyme.

From the preparations obtained in the way described, the enzyme itself can but be imperfectly extracted. In water it proves almost quite insoluble, somewhat better in glycerine and best of all in a 10 pCt. solution of common salt, as was already indicated by Mr. Hazewinkel, and in a 10 pCt. solution of calcium chloride. In these solutions only a small quantity of enzyme is soluble, for the remaining substance is nearly as strongly active as before the extraction. In the solutions themselves alcohol produces hardly any precipitate, so that more active preparations cannot be procured in

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[1]) In § 3 p. 513, will be demonstrated that all the indican is localised in the rotoplasm.

this way. Accordingly the best results in the enzyme experiments are obtained by crude enzyme finely powdered.

3. *On the Distribution of Indican and the Indigo-enzymes in the Plants.*

By the examination of the different parts of indigo- and other plants in the two ways described, the distribution of the indican and the indigo-enzymes was established. It was thus made evident that both commonly occur or lack together.

They are accumulated in the leafy organs, especially in the green leaves; in flowers and flower-buds they are in smaller quantity. In the seeds and germs they fail entirely. The roots and stems of *Polygonum tinctorium* and of *Indigofera leptostachya* are also quite or nearly quite devoid of indican and indigo-enzyme. Only in transverse sections of branches of the latter, kept for some days in strongly diluted indican solution, I could detect traces of indigo-blue particularly in the medulla and the medullary rays and in the bark, which shows that these parts contain some, but very little indigo-enzyme. The absence of enzyme and indican in the stem and roots of *Polygonum tinctorium* can be easily shown as the stems of this plant have a great disposition to form radiculae which are, as the stems, by their herbaceous nature and broad-celled structure, quite fit for such experiments. If the roots are allowed to die off in a chloroform-atmosphere they remain colourless; this is likewise the case when the dying is occasioned by immersion in mercury followed by treatment with ammoniac vapour. But from this follows only that indican and enzyme do not occur together; if but either of them is present it is not detected by this experiment [1]), but may be demonstrated as follows.

If indigo-enzyme is added to a decoction made from the stems or roots of *Polygonum tinctorium*, or if this decoction is boiled with hydrochloric acid and a little ferrichlorid to decompose the indican and oxidise the indoxyl, then no indigo appears; so, indican is absent.

That in the said parts indigo-enzyme, too, is wanting follows from the fact that parts of stems and roots finely crushed in alcohol, after filtering off and drying, produce a powder quite inactive on indican-solution. Even the growing point and the region of growth of the

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[1]) This should be kept in view with regard to the "alcohol-experiment" of Mr. MOLISCH.

roots contain no enzyme [1]), as thin slices killed in alcohol, remain quite colourless in indican-solution at 45°. The same is the case with entire roots which, after killing in alcohol, are put in indican-solution.

From these facts seems to follow that the growth and development of indican-plants is not in inseparable relation to the presence of indican and enzyme.

To this result we are also led concerning the relation between the development and the presence of indoxyl in the woad, though its distribution in this plant is somewhat different from that of the indican. In woad the indoxyl occurs, besides in the young leaves, and buds, also in the young rootperidermis, in the root-buds and in the growing root-ends [2]). The distribution of the indican agrees with that of the indoxyl in the fact that they are both completely wanting within the thicker stems and all the thicker roots. So there is in woad no indoxyl in the inner part of the stem organs of the leaf-rosettes in spring, when they are ready to elongate and push out the inflorescence which is then in the very period of the most intensive cell-partition and cell-elongation. Likewise, there is no indoxyl in the cambium and the secondary tissues of the woad-roots. Even the flower-buds are in an early period, and when still growing vigorously, free from indoxyl; likewise the embryos, seeds and fruits. First at the germination indoxyl can be pointed out in the seeds and other parts of the germinating plant. So it is very probable that neither indican nor indoxyl are necessarily related to the growth or development of the indigo-plants. But the possibility remains that in certain cases these substances originate as quickly as they disappear. So, in the young leaves of *Indigofera leptostachya*, when kept some days in the dark, a little indoxyl may be detected by means of the ammoniac-experiment, while the normal plant is in all its parts quite free from indoxyl, whence it seems possible, that in normal conditions, there is a continual splitting of indican, which is not observable only because the freed indoxyl directly forms indican again with freshly supplied sugar. For the rest, the woad, of which all full-grown parts are devoid of indoxyl, proves that this substance can relatively quickly disappear.

The appearance of indican, particularly in the peripheric parts of the aerial organs, and the bitter taste it gives them, might suggest

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[1]) While in the stem these parts are extremely rich as well in indican as enzyme.

[2]) Which shows that the formation and accumulation of indoxyl is possible in the dark as well as in the light.

the idea that, like tannin, it serves as a defensive against insects and snails. But this supposition would explain only the function of the indican but not that of the splitting products and the indigo-enzyme. If a beneficient influence on the growth in general could be ascribed to indoxyl, then a useful action of this substance on the curing of hurt parts would become probable. And this would also spread more light on the function of the indican and the enzyme, for then it would be clear that the enzyme-action, which operates at the very dying off of the hurt cells, would promote the curing, not only by the formation of indoxyl but also by the production of glucose.

As to the localisation in the cell, I found the leaves of *Phajus grandiflorus* by their broad-celled structure fit for demonstrating microchemically indican as well as indigo-enzyme.

The indican can be precipitated as indigo-blue or indigo-red, and both ways point out that it is present in the protoplasm and wanting in the cell-walls, cell-nuclei, and cell-sap. To demonstrate this a not too thin microscopic transverse section of a leaf is put in living condition in a boiling mixture of strong hydrochloric acid and ferri-chloride. The indican is suddenly decomposed and the freed indoxyl as quickly oxidized into indigo-blue, which is easily detected under the microscope as a precipitate in the shape of small blue granules in the colourless protoplasm of the green parenchyma and the epidermis. I could not trace it with certainty in the chlorophyll-granules.

If the sections, in living condition, are put in a boiling mixture of hydrochloric acid and isatine, the indican passes into indigo-red, which sets off in the protoplasm as very characteristic red crystal needles [1]).

The enzyme, on the contrary, is exclusively accumulated in the chlorophyll-granules as is proved by the following.

If living microscopic sections of leaves of *Phajus* are put in an indican-solution (e. g. in a decoct of *Indigofera* or *Polygonum*) they become blackish blue in a short time, which colour is exclusively caused by indigo-blue precipitated in the chlorophyll-granules. In the epidermis much indigo is precipitated only in

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[1]) The presense of indoxyl in urine may be shown with much more certainty and exactness in the form of indigo-red than of indigo-blue. To this end the urine is boiled with hydrochloric acid and isatine by which the colour grows red. At cooling the indigo-red crystallises in characteristic microscopic needles. These are easily filtered and dissolve beautifully red in alcohol (best is to boil out the whole filter with alcohol).

the cells of the stomata, elsewhere none at all. If the microscopic sections are beforehand killed and extracted with alcohol, the enzyme spreads in the cell but remains confined within the cell-walls, so that, by putting them into an indican solution they become of a uniform intense blue, in which only the bast bundles remain colourless.

The accumulation of enzyme in the chlorophyll-granules is perhaps connected with the formation of starch from the glucose of the indican.

As to the localisation of indoxyl in the leaves of woad I have acquired no certainty, but I suppose that, like indican, it occurs only in the protoplasm.

The hypothesis of Mr. MOLISCH [1]) according to which indoxyl and indican should be in close relation to the decomposition of carbonic acid in the chlorophyll, appears contrary to the great accumulation of indoxyl in the root-peridermis, which is completely free from chlorophyll, and in the colourless root-buds of the woad, which seems unnoticed by Mr. MOLISCH. Nor do I think his arguments and figures convincing for the occurrence of indoxyl and indican in the chlorophyll-granules; moreover was Mr. MOLISCH unacquainted with the existence of indigo-enzymes and their localisation.

Elsewhere than in the indigo-plants indigo-enzymes seem but seldom to occur. Like Dr. VAN ROMBURGH [2]) I observed that emulsine of almonds decomposes indican, and in § 6 the intensity of this action is graphically represented in connection with temperature.

The said fact may serve to demonstrate in a simple way the localisation of emulsine in almonds. If thin sections of the seed-lobes are put in an indican-solution at 50° C., the vascular bundles will first take a deep blue colour, which shows that there the emulsine is the most accumulated. Then the parenchyma around them grows blue, and finally the more peripheric parenchyma. This points out that the emulsine is nowhere wholly absent but is accumulated about the confines of the central-cylinder, which becomes distinctly visible by this experiment [3]).

A rather great number of other plants examined for indigo-enzymes have all given negative results [4]).

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[1]) Berichte der deutschen Bot. Gesellschaft, Bd. 17, p. 230, 1899.

[2]) Communicated by Mr. HAZEWINKEL, Maandelijksch Bulletin N⁰. 1, pag. 8.

[3]) Nearly the same has been found by JOHANNSEN, who examined the decomposition of amygdaline with separate parts of the seedlobes. (Ann. Sci. Nat. Botan. Série 7, T. 6, p. 118, 1887).

[4]) So I could not find indigo-enzymes in: *Indigofera dosua*, *Polygonum persicaria*,

Neither is indican decomposed by sections of branches or leaves of apricots, pears, apples, peaches, while in the kernels of the fruits of these species a feebly decomposing emulsine is found.

Malt, malt-diastase, pancreas, papayotine, pepsine and saliva are inactive; likewise mustard-seed and myrosine prepared from *Tropaeolum majus.*

Glucase, from maize does not decompose indican, which is the more noteworthy as amygdaline is decomposed by it.

4. *Decomposition of Indican by Microbes in general.*

Mr. Molisch has drawn attention to the fact, that various species of microbes give rise to indigo-formation from indican and that others do not, which may be rendered useful for differential diagnosis. He experimented with the decoct of *Polygonum tinctorium* or *Indigofera* mixed with agar or gelatine, pouring it out to plates and using these as a solid nutrient. Aerobics and temporary anaerobics from the soil or from canal water sown out on it will develop, and in and around the colonies which split the indican, indigo-blue will separate out in microscopic lumps or globules which often show crystal structure. The „indican microbes" are in this way elegantly distinguished as pigment-microbes among the non-decomposers. [1])

The indican, as a powder, may be added in a percentage of 0.5 to 1 pCt. to solid or liquid nutrients, adapted for the examination of specific mikrobe groups.

P. aviculare, P. fagopyrum, P. bistorta, P. sacchalinense, Trifolium repens, ***T.*** *pratense, Medicago sativa, Lotus corniculata, Pisum sativum, Vicia faba, Robinia pseudoacacia, Baptisia australis, Melilotus caeruleus, Spiraea filipendula, S. ulmaria, Rubia tinctorium, Asperula odorata, Solanum tuberosum, Amsonia salicifolia, Asclepias cornuti, Scorzonera hispanica, Linaria vulgaris, Stellaria holostea, Cochlearia armoracia, Brassicca oleracea, Isatis tinctoria, Iris germanica.*

[1]) Sitz.ber. der Akad. d. Wiss. zu Wien. Math. Naturw.Classe, Bd. 107, p. 758, 1898. Mr. Molisch enumerates the following species as decomposing indican: *Bacillus anthracis, B. prodigiosus, Streptothrix odorifera, S. dichotoma, Sarcine lutea, Penicillium sp.* and *Mucor mucedo*; as non-decomposing: *Streptococcus pyogenes, Staphylococcus pyogenes aureus, Bacillus subtilis, B. coli communis, B. fluorescens liquefaciens, B. megatherium* and pressed yeast. Mr. van Hasselt and I saw no decomposition with *Acetobacter aceti, A. rancens, Bacillus cyaneus, B. cyanogenus, B. pyocyaneus, B. diastaticus, B. prodigiosus, B. pseudotuberculosis.* Many spore-forming bacteria, such as *B. subtilis, B. megatherium, B. pulcher, B. mesentericus* and others sometimes decompose and sometimes do not. Further there is no indican splitting by beer-yeast (*Saccharomyces cerevisiae*), wine-yeast (*S. ellipsoideus*), pressed-yeast (*S. panis*), *S. mycoderma, S. passularum, S. uvarum, Schizosaccharomyes octosporus, S. pombe* and by the following moulds; *Aspergillus niger, A. oryzae, Amylomyces rouxii, Mucor oryzae, Oidium lactis, Endomyces magnusii.*

I found that some species decompose indican with extraordinary facility. Especially the common ferment-bacteria of plant infusions, which of late I united in the genus *Aërobacter* [1]), decompose with so much intensity, that they may with some reason claim the name of „indigobacteria"; they will later be discussed in particular. For the species which split with more difficulty this power depends on circumstances not yet quite clear to me. It may occur that in pure cultures colonies of one and the same origin, and separated from the common stock by a few generations only, behave quite differently, so that species, which for a long time I considered as non-decomposing, later proved vigorous indigo-producers. This I observed for instance in the photogenic bacteria of the Northsea. I suppose this fact to be connected with the influence of the sugar freed at the splitting of the indican, as other experiences prove that this influence is not constantly the same for all individuals of a species. That especially glucose acts vigorously on the life of some bacteria, and, even in small quantities, e.g. 0.05 pCt. to 0.1 pCt. may be a violent poison for some photogenic bacteria, I proved before, and this is noteworthy as still smaller quantities are favourable to the same species.

That the different conditions of the bacteria may be of influence on their power for decomposition, follows for instance from the fact that *Bacillus radicicola*, from the tubercles of *Pisum sativum* and *Trifolium*, decomposes the indican, while this is not done by the bacteroids of the tubercles of these plants. Closely allied species may also behave differently; thus, *Bacillus ornithopodis*, from the root-tubercles of *Ornithopus sativus*, does not decompose at all and, among lactic-acid ferments, I observed vigorous decomposition by the rod-shaped ferments used in the yeast-industry (*Lactobacter longus*), and no decomposition by the diplococci and streptococci (*L. lactis*) of the dairy industry. The ease with which this reaction is effected and its clear result recommend it for further research.

The splitting of the indican by microbes is operated in the same way as in indigo-plants, either by katabolism, i. e. by direct ferment-action of the living protoplasm on the indican, or by specific indigo-enzymes. Consequently the forms belonging to the former group decompose the indican in living condition only [2]), those of the latter both living and dead. The experiment, demonstrating this, may be performed as follows.

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[1]) Centralbl. f. Bacteriologie, 2e Abth. Bd. 6, N^{o}. 7, pag. 193, 1900.

[2]) The optimum temperature of the decompositon by katabolism agrees, for the examined species, with that of the growth.

Of a culture, grown on a solid nutrient substratum with copious access of air, some material is put on a glass-slide and killed in such a way that eventually present enzyme remains unhurt. This may be done by immersing the material in strong alcohol, in which it should remain at least 24 hours to be quite sure that the microbes are killed, or by exposition to ether-, alcohol- or chloroform-vapour [1]). In the latter case the microbe-material is placed in a glass-box beside a vessel with chloroform, where ferments moulds, and most bacteria die after $^1/_2$ to 1 hour already, while the enzymes in the cells remain unhurt.

If a small lump of killed microbes is put in an indican-solution, poured out to a thin layer in a white porcelain vessel floating on water of circa 45° C., then only those microbes will become blue, which contain indigo-enzyme, while those, acting by katabolism, don't cause decomposition. If in the latter case not all but only most of the microbes have been killed, there will at first be no manifest decomposition, but it will set in as soon as the living individuals have sufficiently multiplied, which is at the same time a good control of the experiment.

The microbes containing enzymes can be dried and powdered after killing and such "crude enzymes", when kept dry, preserve their activity very long. By the little dissolubility of the indigo-enzymes in water, glycerine and salt-solutions, it was not possible by extracting the crude enzymes and precipitating with alcohol, to obtain more active preparations from them.

It has been proved that all examined bacteria, blastomycetes [2]) and moulds, which decompose indican, do not effect this by enzymes but by katabolism, while among alcohol-ferments both cases occur. So indican is decomposed katabolically by *Saccharomyces ludwigi* and *Monilia candida*, while *Saccharomyces sphaericus* [3]), *S. apiculatus*, *S. muciparus* [4]), *S. tyrocola* [5]) contain indigo-enzymes. One of

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[1]) In alcohol vapour many microbes die sooner than in strong alcohol, this having a water absorbing power and thus acting protectingly.

[2]) Blastomycetes have the shape of yeast-cells but produce no alcohol. To these belong e. g. the red "yeasts" *Blastomyces glutinis*, *B. roseus*, *B. granulosus* (of which the last colours deep blue with jodine), and which all decompose indican vigorously.

[3]) Under this name, given by NÄGELI, I united the various forms of aethyl-acetate yeast. (Verhandelingen 5e Natuur- en Geneeskundig Congres te Amsterdam, 1895, p. 301).

[4]) This name I give to a saccharose-yeast, very common in pressed yeast and which does not ferment maltose.

[5]) *S. tyrocola* is a lactose-yeast, not rare in Edam cheese. Its cultures on wort-gelatine are sometimes rose-coloured.

these enzymes, that of *S. sphaericus*, which acts the most strongly of all, will be treated in § 6.

Here I wish to remark that indigo-enzymes originate in the yeast-cells only then, when cultured on a solid medium e. g. on wort-gelatine, with abundant access of air. When cultured in nutrient liquids, even with a current of air passing through, they produce no or only very little enzyme.

The indigo-blue, formed by most moulds and yeast-species in the decomposition of indican, is for the greater part confined within the protoplasm, as was already described and figured by Mr. MOLISCH (l. c.); but in those cases when decomposition is very strong, as with many bacteria, the indoxyl streams out and also precipitates outside of the cell in granules of indigo-blue.

5. *Indigo-fermentation by Aërobacter.*

When a decoction of *Indigofera* or *Polygonum* is infected with garden-soil, canal-water or mud, and placed at 28° C., there originates, during a copious formation of indigo, a rich bacteria-flora in which the common gas-producing ferments, which I recently united [1]) in the genus *Aërobacter*, perform the chief part. The first who drew attention to this fact was ALVAREZ, but he went too far by admitting the existence of specific bacteria for indigo-fermentation [2]). By bringing a drop of the first crude fermentation into a second quantity of a decoction and so on, an accumulation, sometimes a pure culture of *Aërobacter* is obtained [3]).

By sowing out an *Aërobacter*-fermentation on indican-gelatine, not only the *Aërobacter*-colonies, but also those of various other bacteria colour deeply blue by indigo. Commonly, however, the *Aërobacter*-species are recognised by their number. But the chief characteristic of *Aërobacter* is its fermenting power and its temporary anaerobiosis, by which the splitting of indican goes on even at temporary exclusion of air, which is not the case with the aerobics. On this characteristic is based the supplanting of the aerobics by *Aërobacter* in liquid cultures and the prevailing part which these bacteria have in the splitting

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[1]) Centralblatt für Bacteriologie. 2e Abt. Bd. 6 N°. 7, 1900.

[2]) Comptes rendus, T. 105, pag. 287, 1887.

[3]) In several other plant-infusions, not from indigo-plants, quite the same is observed. The strongest *Aërobacter*-fermentations are obtained by mixing rye-flour with water to a thick pap and placing it at 28° C. After a few hours the development sets in of carbonic acid and hydrogen, caused by the *Aërobacter*-species, never wanting in flour, which in the beginning supplant all other bacteria.

of the indican in the spontaneous indigo-fermentations. In pure cultures this splitting can of course be as well effected by various common aerobics, albeit more slowly.

The decomposition of indican by *Aërobacter* is operated katabolically, as in all other examined bacteria also, so that killed bacteria are inactive and indigo-enzyme cannot be separated out. The optimum temperature for the decomposition agrees with that of the growth and is, for instance, 28° C. for a variety of *A. aërogones* isolated from milk.

The number of *Aërobacter*-forms obtained by sowing out from the decoctions is very great but may be reduced to three chief species, described by me elsewhere (l.c. pag. 200). They are *Aërobacter aërogenes*, *A. coli* and *A. liquefaciens*, all represented by many varieties and allied by intermediate forms. Not all varieties are equally active. So, among the forms of *A. coli*, which for the greater part decompose most vigorously, the variety *A. coli* var. *commune*, isolated from the intestines or from faeces, is but feebly active or not active at all and recognisable by this feature.

The products of the decomposition of indican by *Aërobacter* (and by bacteria in general) are the same as by enzyme action, i. e. indoxyl and glucose. If a nutrient liquid containing indican, e. g. decoct of indigo-plants, broth, or yeast-water, is passed into a fermentation tube and infected with *Aërobacter*, indigo-blue is formed in the open end, while in the closed one carbonic acid and hydrogen originate from the glucose of the indican [1]), and indoxyl which remains a long time unchanged.

In proportion as the oxidation of the indoxyl proceeds more slowly, more indigo-red is produced, similarly to the splitting of indican by enzymes and acids. Now the splitting of the indican, and consequently the oxidation of the indoxyl can proceed with much rapidity by the action of enzymes and still more rapidly by acids in presence of ferrichloride, while it is impossible to make the process go on as quickly by bacteria. So it is inevitable that the formation of indigo-red is very great in the case of the bacterial fermentation of the indican, while it is possible to reduce its amount practically to zero in the case of chemical decomposition. As it is besides hardly possible to separate the indigo-blue from the substance of the bacteria,

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[1]) That the development of gas is due to the sugar of the indican, and not to the free sugar already present in the decoctions or the indican preparations, is proved by the fact that the gas-development is the same when beforehand all free sugar has been removed from the liquid by means of pure beer-yeast, which acts not on indican.

only an impure indigo can be obtained by means of their action.

In consequence of the growth of *Aërobacter* the reaction of plant extractions, particularly of the indigo-plants, first becomes feebly acid, later feebly alkaline by the formation of free alkali. This is also prejudicial to the production of indigo, as in acid solutions the indoxyl oxidises very slowly, by which again much indigo-red is formed, while at the same time part of the indoxyl gets lost in another way.

Worthy of note is the influence of varions sugars on the indican decomposition by *Aërobacter*. Mr. VAN HASSELT found that already $^1/_2$ pCt. glucose, as well in liquid cultures as in gelatine experiments, prevents decomposition, while much larger quantities, even to 10 pCt. of cane-sugar, maltose and lactose have no effect at all and levulose but very little. Evidently the very sugar produced by the splitting counteracts this splitting, while other sugars have not this effect, or in less degree. To this rule mannose makes an exception, as indican decomposition is in the same way counteracted by it as by glucose. This opposing influence gives consequently only partly and not completely the answer to the question after the nature of the sugar separated out of the glucoside by bacteria [1]).

There are however forms of *Aërobacter* which, in ferment-experiments, produce unequal quantities of carbonic acid und hydrogen from glucose and mannose, and by their help it is proved that the sugar formed from indican can only be glucose.

Nitrates, also, have a remarkably opposing influence on the production of indigo by *Aërobacter*. Common saltpetre is active already at $^1/_{20}$ pCt., which is in perfect accordance with the antifermenting action of this salt in general, on which reposes its use in the dairy industry, to prevent one of the most important defects of cheese, in Holland called "rijzers".

6. *Indican-decomposition by the Indigo-enzymes.*

The indigo-enzymes prepared from *Indigofera leptostachya*, *Polygonum tinctorium*, *Phajus grandiflorus*, aethyl-acetate-yeast (*Saccharomyces sphaericus*) and emulsine of sweet almonds, have been

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[1]) Mr. VAN HASSELT prepared the osazon from the indican-sugar and found, after recrystallisation from alcohol, the melting point to be at 195° to 199° C., that is nearly the same as that of glucosazon, which is 204° to 205° C. But the melting point of mannosazon is about as high.

compared as to their intensity of action on indican at different temperatures, for which notable differences have been found. No other group of enzymes is known to lead with equal ease and certainty to the determination of these relations as this group of the indigo-enzymes.

The experiments were conducted as follows. Of solutions of about 0.5 pCt. indican [1]) 10 cc. were passed into equal test-tubes selected for the purpose. After heating them to the required temperature in a large beakerglass, arranged as waterbath, with thermoregulator and thermometer, the enzyme was added and the temperature kept constant.

After a few hours the tubes were taken out, alcalised and the indoxyl oxidised by strong shaking, then acidified, by which a very fine, equally divided, purely blue precipitate of indigo-blue is obtained, which allows colorimetrically to establish the intensity of action with sufficient exactness.

It proved wholly indifferent whether in these experiments use was made of the indican of *Indigofera* or of *Polygonum*. Evidently it is the same in both plants.

Great attention should however be paid to the degree of acidity of the indican solutions. The most favourable enzyme action was observed at the rate of about 0.5 cc. normal acid per 100 cc. liquid. An increase of the acid to 2 cc. slackens the reaction notably; likewise the addition of alkali to feebly alkaline. Acid salts, as kaliumbioxalate and kaliumbiphosphate, act in the same way as free acids.

The quantities of the enzymes employed for the experiments amounted to 2—60 milligrams of finely powdered crude enzyme per 10 cc. of the $^1/_2$ pCt. indican-solution.

First of all was now established the maximum temperature at which the action of the enzymes ceases entirely, that is, where the enzymes are nearly suddenly destroyed. For *Indigofera* this maximum is at 75° C., but when using a great deal more enzyme a feeble action could still be observed at 78° C. which however quite ceased at 80° C. For *Polygonum* the maximum temperature is at 55° C., and in large quantities a feeble action was still observable at 60° C. For this determination the tubes were placed, for *Indigofera*, at 72°.5, 75°, 78° and 80° C.; for *Polygonum*, at 52°.5, 55°, 58° and 60° C. For both enzymes the action at the rising of the temperature diminishes very quickly near the maximum. In a similar way were

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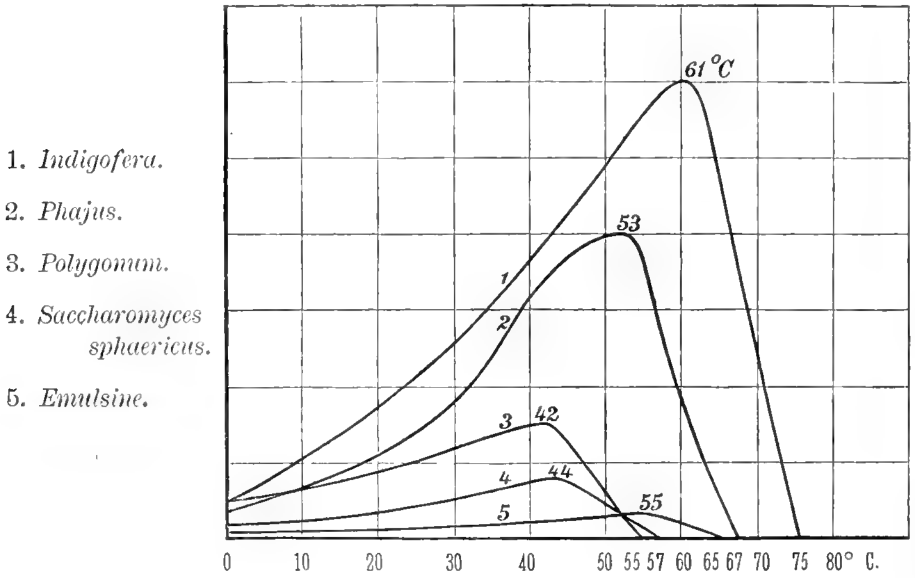
[1]) Stronger solutions give no more exact results.

found as maximum temperatures for *Saccharomyces sphaericus* about 60° C., for *Phajus grandiflorus* 67°, and for emulsine 70° C.

After this the optimum temperatures for the enzyme action were fixed, for *Indigofera* by searching between 55° and 65° the maximum intensity of indigo-formation, testing all temperatures from 55°, 57°, 59° C. and so on. The strongest inversion was found at 61° C. both for powdered crude enzyme and for enzyme-solution in 10 pCt. common salt and 10 pCt. calcium chloride. Changes in the degree of alkalinity or acidity within the narrow confines between which enzyme action is at all possible, deplace the optimum temperature but little[1]. A difference in temperature of 1° C. was only to be observed between 61° and 62°; at 62° C. the decomposition was certainly a little feebler, but between 60° and 61° C. there existed some doubt. At lower temperatures distinct differences in the intensity of the decomposition could only be noted at intervals of 2° C.

The enzyme of *Polygonum*, examined in the same way between 35° and 45° C., gives the most copious production of indigo at 42° C., with a rapid decrease in action above, a slow one below that point.



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[1] Mr. van Delden found upon addition of acid both for *Indigofera* and *Polygonum* a rising of 1° in optimum, which however disappeared when the employed solutions of crude indican were diluted with an equal volume of water and then, before the addition of enzyme, were brought to the same acidity.

For aethyl-acetate-yeast the optimum lies at 44°, for *Phajus* at 53° C., and for emulsine at 55° C.[1]).

Particularly for emulsine the intensity of action is feeble, and the feebler it is, the more troublesome exactly to fix the temperature-optimum, as is clearly shown by the course of the curved line in the graphic representation.

For the exact determination of the shape of the curved line which indicates the general relation between decomposition and temperature, temperatures above and below the optimum were sought, at which the quantities of indigo, formed after an hour's action, were quite the same. In a system of coordinates with the temperatures as abscisses and the intensity of decomposition as ordinates, these points have then equal ordinates and by determining some such couples the whole course of the curve becomes known. When looking at the curves found in this way we see that the decrease of action above the optimum is much more rapid than the rising below and that the last rising is not proportioned to the temperature.

At the same temperature the indican-decomposition by the various enzymes is operated with very unequal intensity. Proportionate ciphers between them were fixed as follows. In the experiments described before, so much of the enzymes to be compared was added to 10 cc. of indican-solution that at the optimum temperatures effects of equal intensity were observed. This proved to be the case when use was made of the following quantities of crude enzyme in milligrams: *Indigofera* 5, *Polygonum* 20, *Saccharomyces sphaericus* 40, emulsine 100, which numbers stand to one another as 1 : 4 : 8 : 20. When all these quantities were doubled or reduced to the half, the proportions underwent no change. Consequently from these numbers follows that the intensity of decomposition for the different enzymes is expressed thus: *Indigofera* 20, *Polygonum* 5, aethyl-acetate-yeast 2.5, emulsine 1. In the graphic figure the length of the ordinates is taken proportionately with these numbers.

So we find that the curve of the *Polygonum*-enzyme is about uniform with that of the much stronger enzyme of *Indigofera*, but at 0° C. they cross each other, so that at a still lower temperature the action becomes an inverse one.

The great difference in intensity of action is also proved by the fact, that, for the manifest appearance of indigo in 10 cc. of the

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[1]) As is seen, the difference between the optimum and maximum temperature is for all enzymes about 14° C.

indican-solution, there is at least required of the different crude enzymes 2 milligrams of *Indigofera*, 20 of *Polygonum* and *Saccharomyces sphaericus*, and 60 of emulsine.

CONCLUSIONS.

The splitting of the indican by the cell can occur in two ways: by ferment-action of the living protoplasm itself (katabolism), and by enzymes.

All examined bacteria, which act on indican, split by katabolism and hence are in dead condition inactive. The most important among them are the common ferment-bacteria (*Aërobacter*) of sugar-containing plant infusions.

All indican-plants and some species of alcohol-ferments contain indigo-enzymes and consequently can decompose the indican in dead condition too. Indigo-enzymes originate only at abundant access of air. Five of these enzymes proved specifically different, with temperature optima of 61° (*Indigofera*), 55° (emulsine), 53° (*Phajus*), 44° (*Saccharomyces sphaericus*) and 42° (*Polygonum*). For all of them the action is favoured by free acid to an amount of 0.5 cc. normal per 100 cc. of the employed indican-solution; more acid, like alkali, opposes the action.

Indigofera decomposes the indican only by enzyme-action; in the case of *Polygonum tinctorium* and *Phajus grandiflorus* the indican is decomposed partly by katabolism, partly by enzyme-action.

In the leaves of *Phajus grandiflorus* indican is localized in the colourless protoplasm of mesophyll and epidermis, the indigo-enzyme exclusively in the chlorophyll-granules.

Chemistry. — "*Indican — its hydrolysis and the enzyme causing the same.*" By J. J. Hazewinkel, Director of the experimental station for Indigo at Klaten (Java). (Communicated by Prof. S. Hoogewerff).

The following investigations were done by me in November 1898. After the investigation was closed, I received by the mail the treatise of Marchlewski and I then went to Buitenzorg to consult Dr. van Romburgh about these researches.

I first thought it would be better, in the interest of the Javanese indigo growers to keep the results of my work a secret, but having been informed by Prof. Beijerinck that he also had taken up the study of indican and had in many respects come to the same conclusions as myself, I decided to publish my results, as it would be impossible to keep the matter a secret.

It so happened that VAN ROMBURGH had also occupied himself with researches on indican and, without being acquainted with my work, had obtained results confirming my own. His results will, of course, be communicated in this paper.

If the juice from the leaves of Indigofera leptostachya is collected in such a manner that there cannot be any question of enzyme-actions, for instance by treatment with boiling water or by using enzyme poisons (lime-water, solution of mercuric chloride), a liquid is obtained which, if not too acid, is perfectly stable, and contains a substance which is capable of yielding indigo.

This may be demonstrated in four ways.

1. By acidifying and carefully adding ferric chloride or any other suitable oxidizing agents.
2. By the action of an enzyme contained in the indigo plant.
3. By the action of enzymes not derived from the indigo plant.
4. By the action of different bacteries.

Enzyme 2 was prepared by repeatedly rubbing fresh indigo leaves with strong alcohol and removing the alcohol by squeezing the mass with the hands. The residue was then pressed between blotting paper in a copying press and allowed to dry in the sun. The dry product was then finely powdered and passed through a sieve. By keeping this powder under alcohol for a long time, it may be obtained perfectly white.

The active principle is somewhat soluble in water, but much more so in a 10 per cent solution of common salt [1]).

When I now allowed the powder or the solution prepared from it, to act on the liquid obtained by treating indigo leaves with boiling water, or on the solution obtained by crushing the leaves with milk of lime or lime water and neutralising the filtrate, I noticed the following effect:

1. After a few minutes the liquid discoloured and yielded a little indigo.

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[1]) Dr. VAN ROMBURGH paid me a visit at my laboratory when I was engaged with these experiments and then informed me that he had also prepared active leaf powder in a slightly different manner. This when in contact with sterilized infusion of indigo leaves caused the same effect as the usual fermentation principles. We, therefore, have come to the same result independently of each other.

2. The formation of indigo was much stronger when a current of air was passed through the liquid in the presence of an alkali.

3. The copper-reducing power of the liquid obtained by the action of the air and subsequent filtration was much larger than that of the original liquid which had not been treated with the extracted leaf-powder.

4. After a short action the liquid began to show fluorescence. This phenomenon was observed more readily if a current of carbon dioxide was passed through the liquid; no indigo is then deposited.

5. The indigo-yielding substance could be removed by agitating the liquid with ether and chloroform. [1])

6. This substance was identical with the one present in the liquor after the so-called technical fermentation had ceased.

7. The action was destroyed by a number of enzyme poisons.

8. Addition of alcohol up to a certain concentration stopped all action, but on diluting with water action recommenced.

9. Heating above a certain temperature definitely destroyed the action.

10. Cooling below a definite temperature retarded the action as long as that temperature was maintained.

The observations recorded in 3, 7, 8, 9 and 10 together with the solubility of the active principle in brine and glycerol put it beyond doubt that we are dealing here with an enzyme.

In agreement with this I found that emulsin acts on the liquid in precisely the same manner. This experiment was made on the advice of Dr. VAN ROMBURGH.

As the enzyme may differ from emulsin I will, provisionally, call it „indimulsin". This indimulsin does not act below 5°. In a dry condition it gradually becomes inactive at higher temperatures, but its power is completely destroyed after being heated for half an hour to 125°. Its solution in brine becomes totally inactive at 88—92°.

No great change of action is observed in liquids containing 10 per cent of alcohol by volume, but in the presence of 25 per cent all action ceases. Several other enzyme poisons such as mercuric chloride, copper sulphate, lead acetate, alkalis, acids, sulpher dioxide temporarily or definitely retard the complete or partial action of the enzyme according to their nature and quantity.

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[1]) Dr. VAN ROMBURGH was the first to prove that the indigo-yielding substance contained in the so-called fermentation liquor could be extracted with chloroform or ether.

The solution of the enzyme in salt was prepared by shaking 1 part of the prepared leaf-powder with 20 parts of a 10 per cent solution of salt, for 20 minutes.

There remains, therefore, no doubt that the action described is due to an enzyme and such a one whose action is analogous or identical with that of emulsin.

The substance which is decomposed under the influence of the enzyme must, therefore, be a glucoside. Then:

1. It is decomposed (hydrolysed) by enzymes.
2. One of those enzymes is emulsin which, as is perfectly well known, is an enzyme capable of decomposing glucosides.
3. This hydrolysis is accompanied by a large increase in copper-reducing power.
4. By the action of acids, dextrose is formed. [1])

Although the said glucoside possesses properties which differ from those usually ascribed in the literature to indican, I think it is as well to retain that name for the glucoside.

Although I had no time to attempt the isolation of indican, some of its properties may be described here.

1. Acid oxidating agents convert it into indigo which, in turn, is oxidized by an excess of the reagent.
2. It is soluble in alcohol but not in ether and cannot be removed by means of ether from neutral or acid solutions.
3. It may be preserved for an indefinite period if kept sterilized.
4. It is stable at the boiling heat.
5. It is very stable in the presence of strong alkaline solutions at not too high a temperature.
6. With concentrated acids it forms red products, particularly on warming, if excess of acid be avoided. A knowledge of these products will be of the greatest importance for the study of the so-called indigo-red which occurs in samples of natural indigo.
7. An excess of ferric chloride gradually decomposes indican completely, without formation of indigo.
8. Indican reduces an ammoniacal solution of silver nitrate in the cold with separation of metallic silver.

The first property suggests many means of determining the yield of indigo from a given solution of indican.

My first decisive experiment was made by oxidizing equal parts of indican solution with different quantities of an oxidizer (5 KBr +

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[1]) VAN LOOKEREN CAMPAGNE, Landwirtschaftliche Versuchstationen, Bnd. 45 pg. 195 a.n.

$KBrO_3$); a graphic representation was then made to show the results. These showed that the leaf (foliage without stems) may yield about 0.60 per cent of indigo-blue which amounts to about 0.30 per cent in a plant containing 50 per cent of leaves.

I must, provisionally, keep secret some other analytical processes of a more simple description.

A closer study of the product which is formed during the fermentation on the large scale and also by the action of the enzyme on a solution of indican and which on oxidation yields indigo, taught me that this product consists of indoxyl. [1])

Then I found that the substance which on oxidation yields indigo, whether during the technical fermentation or by the action of the enzyme:

1. is soluble in acids.
2. is soluble in water, chloroform and ether.
3. has a strong fluorescence.
4. slowly forms indigo when exposed to the air in acid solutions, but rapidly in solutions having an alkaline reaction.
5. changes into a red substance and emits a pungent odour when boiled with an acid.
6. yields indigo more readily when to the faintly acid solution a small quantity of ferric chloride is added.
7. may get lost or modified to such a degree as to be incapable of yielding indigo, by the action of other constituents of the plant. This requires some further explanation.

I prepared an alcoholic solution which one might call solution of crude chlorophyll in the following manner:

Indigo leaves were crushed or rubbed with (20 pCt.) alcohol. By working quickly there was scarcely any danger of enzyme-action taking place. The turbid juice was filtered, the residue on the filter was taken up with water, again filtered and now extracted with alcohol.

This alcoholic solution had the power to stop the formation of indigo in the fermentation liquid. This may be elegantly demonstrated in the following manner:

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1) It is an interesting fact that BAUMANN and TIEMANN have suspected this to some extent. They wrote already in 1879 Ber. d. D. Chem. Gesell. **12** 1103: „Bezüglich des Pflanzenindicans, wird es nicht uninteressant sein zu ermitteln ob in demselben als Paarling Indoxyl oder Indigweiss, welche beide leicht in Indigo übergehen, vorkommt und ob des im rohen Indigo enthaltene Indigroth in naher Beziehung zu dem Indoxylcondensationsproducte steht oder gar damit identisch ist."

If 5 c.c. of fermentation liquid, or 5 c.c. of a liquid obtained by the action of indimulsin on solution of indican are placed in a stoppered cylinder mixed with 50 c.c. of the crude chlorophyll [1]) and a little ammonia and then well shaken, it will be found that not a trace of indigo-blue is formed. By agitating with ether the chlorophyll may be separeted from the aqueous layer, both portions may then be filtered and the filter examined for indigo. If, however, the experiment is made by first adding the ammonia and thoroughly shaking to promote oxidation, the addition of the chlorophyll solution will not prevent the formation of indigo-blue.

8. I also found that both in acid and alkaline solutions the substance yields red resinous products unless the air is excluded.

All these reactions are typical indoxyl-reactions. To make more sure, I prepared indoxyl according to the easy and elegant process of HEUMANN and BACHOFEN. [2])

It was then shown that the solution of this indoxyl gave all the reactions mentioned in 1—8 particularly the chlorophyll test. A fairly pure aqueous solution of indoxyl may, of course, be made by agitating the acid solution with ether, evaporating the same in a current of cold air and dissolving the residue in water.

What struck me during the preparation is the difficulty of obtaining a solution of indoxyl which does not yield indigo when exposed to the air unless it had an alkaline reaction. Even when starting from indigo purified by sublimation this seemed impossible. I could not ascertain for certain whether indoxyl has the property of gradually forming indigo in acid solutions, or whether this formation is due to any impurities. But even if it should not be a property of indoxyl itself, the formation of indigo in the fermentation fluid need not cause any surprise, as this is a very impure solution of indoxyl and, as will be seen, its reaction is much altered during the oxidation. [3])

From the foregoing it may be concluded with certainty that in

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[1]) When using this expression, I do not, of course, mean to say that chlorophyll itself exercises the said action.

[2]) Ber. d. D. Chem. Gesell. 26. p. 225.

[3]) The following interesting phenomenon may be mentioned to show the influence of the dissolved substances. If sulphuric acid is added to a solution of indoxyl until the liquid turns red, scarcely any indigo will be formed on shaking. If however, an excess of Na_2HPO_4 is added indigo will be formed. Still, the amount of Na_2HPO_4 may be easily regulated so as to leave the liquid acid. It is also interesting to know that the liquid containing Na_2HPO_4 does not immediately give the isatinsoda reaction.

the fermentation liquid and in the liquid prepared with enzyme and indican solution, the indigo is formed from indoxyl. This is confirmed by me, being successful in obtaining from those liquids three typical reaction-products of indoxyl, namely the indigonides of isatin, benzaldehyde and pyro-uvic acid.

I applied these reactions in the following manner: To 25 c.c. of indican solution was added 1 gram of the leaf powder (This is preferable to using the solution, as during the action of the enzyme red resinous products are formed which are not retained by paper filters. These products, however, adhere to the leaves, otherwise they might cause wrong conclusions to be drawn from the reactions particularly as we will see later on that indoxyl under some circumstances does not yield indirubin). After sufficient action 20 c.c. of or saturated solution of isatin in 50 pCt. alcohol and 50 c.c. of a saturated solution of sodium carbonate were added, or a little benzaldehyde or pyro-uvic acid and then for every 100 parts of liquid 40 parts of hydrochloric acid of 1.13 sp. gr.

The substances which were formed all had the qualitative properties which are ascribed in the literature to the three indigonides.

As one of the components is known and the other exhibits all the properties of indoxyl and *no other ones*, whilst the formed products agree, qualitatively, completely with the substances which the said reagents form from indoxyl, it is proved that indoxyl is the other component.

I have not made any ultimate analyses of the substances as it was extremely difficult to purify them. Moreover, I think that their identity has been sufficiently established.

The fact that the fermentation product is indoxyl, explains the formation of large quantities of indigo-red in some processes of indigo manufacture.

I may call attention to the fact that during the so-called fermentation no indican ever passes into the surrounding liquid. This was, of course, easily proved by rendering the liquid so strongly alkaline that no enzyme-action could take place, then passing a current of air to oxidize my indoxyl and testing the filtrate after neutralisation with enzyme powder or solution of the same.

I noticed some phenomena which must not be lost sight of when testing for indoxyl.

If to a solution of indican is added a little phenol-phtalein, then so much lime-water that the solution has a decided alkaline reaction and then some enzyme powder, the red colour gradually vanishes. This may be caused by the presence of some acid contained in the eaves which has not been completely extracted by alcohol.[1] If now lime-water is added cautiously so as not to interfere with the action of the enzyme, but just sufficient to keep the reaction alkaline, a filtrate is obtained which does not give the isatin-soda reaction unless the liquid is previously acidified. As already stated, this reaction also fails when an excess of Na_2HPO_4 is added to the acid indoxyl solution.

Whether on adding isatin to an acid solution of indoxyl a condensation product may be formed (on account of the acidity) which yields indirubin in the presence of alkalis, of whether isatin acts on a possibly existing lime-indoxyl compound in a different manner is still an open question.

If we like to make ourselves independent of this phenomenon in a simple and practical manner, this may be done by adding a decent quantity of ferrous sulphate, which causes the end reaction to be acid without affecting the action of the enzyme. On filtering and extracting the residue with alcohol, the indican is obtained in solution. The $FeSO_4$ should be allowed to act upon the indican for 20 minutes. If in this experiment the leaf powder is used and if the same has not been extracted too much with alcohol, the liquid yields afterwards a filtrate which is quite free from iron provided a sufficiency of the powder has been used; this is capable of absorbing 10—20 per cent of its weight of $FeSO_4$. That the $FeSO_4$ has not caused any reduction may be seen from the fact that on shaking with milk of lime, filtering and neutralizing, a solution of indican is obtained which is perfectly identical with the one to which $FeSO_4$ has not been added.

The variations in the reactions of the fermentation liquid before and after oxidation are also very interesting. VAN ROMBURGH pretended it to be acid, VAN LOOKEREN and VAN DER VEEN pretented it to be alkaline. But as the first named tested the liquid immediately after the fermentation and the others did so after the oxidation, the difference in opinion is easily explained.

I also found that in the first case the liquid was acid. This liquid is now, however, treated with air and in consequence one of the dissolved substances (indoxyl) is oxidated to indigo, a substance which is quite indifferent to litmus. Now, a good deal depends on the question: how does a solution of pure indoxyl behave towards bases and acids.

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[1] 20 grams of the enzyme powder treated at the ordinary temperature with 2000 cc. of water and a little chloroform yielded a liquid requiring 20 cc. of lime-water for neutralization.

It is known that indoxyl possesses both week acid and basic properties. This has been recorded by A. v. BAYER who noticed the week acid and basic properties of indoxyl prepared from indoxylic acid, therefore, presumably a very pure product. If now the indoxyl should be partly combined with lime, the oxidation must cause a loss of acidity.

The acidity is also bound to become less by the gradual disappearance of the free CO_2 which is always formed during the technical fermentation and in the laboratory experiment. This fully explains the reason why the liquid gradually changes from the acid to an alkaline condition. Finally, I wish to call attention to the following point: If a solution of indican is prepared by crushing the leaves with lime-water and filtering the neutralized liquid, and when to this is added a perfectly neutral solution of enzyme, a solution of indican is finally obtained which yields no indirubin with isatin and sodium hydroxide. If the solution is oxidated in a current of air free from CO_2, the filtrate is distinctly alkaline. It is, therefore, plain that indican forms a neutral saline compound, which is decomposed like free indican by indimulsin (somewhat analogous to myronic acid and its potassium salt).

Klaten (Java), Jan. 1900.

Chemistry. — Prof. S. HOOGEWERFF presents a communication, also on behalf of Mr. H. TER MEULEN, entitled: "*Contribution to the knowledge of indican*".

Observations made lately by BEIJERINCK [1]) and HAZEWINKEL [2]) on indican have shown that this substance is not so readily decomposed as was formerly believed [3]). It is not decomposed by evaporating its aqueous solution, but on the contrary, if free acids and enzymes are absent, it possesses a fair degree of stability and a solid mass of "crude indican" may be obtained by evaporating the decoctions of Indigofera leptostachya and Polygonum tinctorium [4]).

It was only natural that these important observations should lead to an effort to obtain the indican on a pure condition and to determine its composition. The formula $C_{26}H_{31}NO_{17}$ proposed by SCHUNCK [3]) as the result of investigations which are in many respects

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[1]) Proc. Royal Acad. of Sc. Amsterdam, Sept. 1899 p. 91.

[2]) See preceding article.

[3]) SCHUNCK Phil. Mag. [4] X p. 73 and [4] XV p. 29, 117, 183.

[4]) BEYERINCK l. c. p. 95.

very meritorious, is not based on the analysis of free indican, but on the analysis of lead compounds obtained from extract of woad and has been accepted with a certain amount of reservation [1]). Moreover, the important observations of BEYERINCK communicated at the September meeting on the chromogen of the woad have shaken the foundation of the formula. SCHUNCK's coadjutor MARCHLEWSKI [2]) had, however, already proposed another formula for indican in 1898, starting the hypothesis that it should be looked upon as indoxyl-glucoside; he even gave a structural formula illustrating the connection between the glucose residu and the indoxyl-group. MARCHLEWSKI has apparently not had material at his disposal to prove experimentally the correctness of his hypothetical indican formula $C_{14}H_{17}NO_6$, although in the meantime indican has been proved to be a real indoxyl-glucoside [3]).

The following circumstances enabled us to carry on the investigation. Prof. BEIJERINCK had the kindness to present us with 17 kilos of his own grown Polygonum tinctorium for the extraction of the indican and also with an extract prepared by himself from the leaves of Indigofera leptostachya. From Mr. HAZEWINKEL we received tins containing somewhat purified solutions of indican prepared by himself from indigo-leaves at Klaten. We beg to offer them our best thanks for this co-operation.

The leaves were immersed by us in boiling water, boiled for a few minutes and further systematically exhausted; 2.5 liters of water were used for 1 kilo of the leaves. Without any sensible decomposition the decoctions could be evaporated in vacuo if care was taken to keep the reaction alkaline. The dry residue was extracted with methyl alcohol and to the solution was added ether as long as a precipitate was formed; these precipitates were rich in ash but very poor in nitrogen and were practically free from indican. From the solution, the alcohol and ether were distilled off, the residue was completely dried in vacuo and then dissolved in water. The filtered and concentrated solution deposited on cooling well defined crystals of indican almost colorless and ash free. A large proportion of the impurities may be removed by heating the decoction of the leaves before concentration with baryta-water, filtering and removing the excess of barium by a current of carbon dioxide; the filtrate is then treated as described. If the treatment with baryta

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[1]) Compare BEILSTEIN Org. chem. 3 Aufl. Bd. III p. 595.

[2]) MARCHLEWSKI and RADCLIFFE Journal Soc. chem. Industry 1898 p. 430.

[3]) Compare HAZEWINKEL and BEYERINCK l.c.

is omitted the leaves of Indigofera leptostachya yield a gelatinous body which greatly impedes the purification of the indican. 17 kilos of the leaves of Polygonum tinctoria yielded 5 grams of pure indican.

Indican crystallized from aqueous solutions consists of spear-shaped crystals which Prof. SCHROEDER VAN DER KOLK, as the result of a preliminary nomination, declares to belong to the rhombic system. The crystals contain 3 mols. of water of crystallisation, melt at 51° and losing some of the water are transformed into a gummy-like mass which is gradually decomposed on heating above 100°. Dried in vacuo over sulphuric acid indican loses its water of crystalisation, but when the anhydrous mass is exposed to the air, it reabsorbs moisture and practically regains its original weight. Dried indican melts at 100°—102°, is tolerably soluble in water, methyl- or ethyl-alcohol and acetone, but only slightly soluble in benzene, carbondisulphide and ether.

Heated on a platinum foil or in a test-tube purple-coloured fumes are given off which condense on the sides of the tube: this does not take place in a current of carbon dioxide. When an aqueous solution of indican is decomposed by the galvanic current, indigotin is formed at the anode.

Indican has a bitter taste. It is optically active, a 2 per cent solution gives a polarization of — 2° when examined in a 20 c.m. tube at 15°. After acting on the solution with hydrochloric acid and oxidizing the resulting indoxyl the liquid shows a right-handed polarisation [1]). As soon as we shall have again at our disposal larger quantities of indican, we wil make further experiments with a view to determine its specific rotary power and we will also try to isolate the sugar formed in the hydrolysis of the indican.

As will be seen from the subjoined analyses and the determination of the molecular weight, the molecular formula of the vacuum-dried indican is $C_{11}H_{17}NO_6$ this confirming MARCHLEWSKI's hypothesis. The crystallized compound contains 3 mols. of water of crystallization; it may be observed here that amygdaline also contains 3 mols. of water of crystallization and also polarises to the left [2]).

By passing a current of air through a hot solution of indican in dilute hydrochloric acid, containing a little ferric chloride as oxygen carrier, 91 per cent of indican was converted into indigotin according to the equation:

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[1]) Compare C. J. VAN LOOKEREN CAMPAGNE. Landw. Versuch. XLV, 195.

[2]) Indican is, therefore isomeric with FISCHER's amygdonitril. Ber. D. Chem. Ges. XXVIII, 1508.

$$2\,C_{14}\,H_{17}\,NO_6 + O_2 = C_{16}\,H_{10}\,N_2\,O_2 + 2\,C_6\,H_{12}\,O_6$$

or rather:

$$C_{14}\,H_{17}\,NO_6 + H_2\,O = C_6\,H_{12}\,O_6 + C_8\,H_7\,NO$$
$$2\,C_8\,H_7\,NO + O_2 = 2\,H_2\,O + C_{16}\,H_{10}\,N_2\,O_2$$

but the experiment will have to be repeated on a larger scale so as to be able to judge of the purity of the indigo-blue and ascertain its percentage of indigo-red which also seems to be formed.

We also wish to state that during this investigation not the least difference was noticed between the indican prepared from Indigofera leptostachya and that obtained from Polygonum tinctorium and we, therefore incline to the belief that both plants contain the same indican. As soon as larger quantities of indican are again at our disposal, we hope to continue and extend the investigation of this important compound.

The following results were obtained when subjecting indican to ultimate analysis. The sample was dried in vacuo over sulphuric acid.

I. 0.2416 gram of indican (Indigofera) yielded on combustion with copperoxide in a current of oxygen 0.4960 gram of carbon dioxide and 0.1257 gram of water.

II. 0.2397 gram yielded 0.4928 gram of carbon dioxide and 0.1244 gram of water.

III. 0.1539 gram of the indican treated by the KJELDAHL-GUNNING process yielded 5.12 cc. of $N/_{10}$ ammonia.

IV. 0.6310 gram similarly treated yielded 20.60 cc. of $N/_{10}$ ammonia.

On comparing the percentages of carbon-hydrogen and nitrogen with those calculated from MARCHLEWSKI's formula:

	I.	II.	III.	IV.	Calculated for $C^{14}\,H^{17}\,NO^6$.
C	56.0 pCt.	56.1 pCt.	—	—	56.95 pCt.
H	5.8 pCt.	5.8 pCt.	—	—	5.76 pCt.
N	—	—	4.7 pCt.	4.7 pCt.	4.75 pCt.

it is apparent that while the figures for the hydrogen and nitrogen practically agree, those of the carbon are somewhat too low. We, therefore, repeated the determination of carbon by means of the

MESSINGER-FRITSCH[1]) moist combustion process so as to make more sure about the true percentage of carbon. We first tested the accuracy of the process by some blank experiments and some combustions of salicylamide.

V. 0.1371 gram of indican (Indigofera) heated with sulphuric acid and potasium dichromate yielded 0.2341 gram of carbon dioxide = 56.5 percent of carbon.

VI. 0.2169 gram of indican (Polygonum) yielded 0.4517 gram of carbon dioxide = 56.8 percent of carbon.

If we now take take the mean of these two determinations the composition of indican is:

56.7 pCt. C
5.8 pCt. H
4.7 pCt. N

which satisfactorily agrees with that calculated from MARCHLEWSKI's formula.

For the determination of the molecular weight the cryoscopic method was used, as indican is too little soluble in the liquids generally used in the process based on the increase of the boiling point.

Two determinations were made:

I. 0.1935 gram of indican (Polygonum) dissolved in 24.89 gram of water lowered the freezing point to the extent of 0.058°.

II. 0.8301 gram of indican dissolved in 24.89 gram of water lowered the freezing point to the extent of 0.208°.

From these determinations the following figures are calculated for the molecular weight:

I 248 en II 297

which shows that it is not a multiple of 295. $C_{14}H_{17}NO_6$ must be accepted as the molecular formula of indican.

The determinations of the water of crystallization were done with indican from Polygonum.

I. 0.4149 gram of indican lost on drying in vacuo 0.0594 gram of water.

II. 3.2262 gram lost 0.4943 gram.

III. 0.2291 gram of the dried indican when exposed to the air until the weight was constant, absorbed 0.0393 gram of water[2]).

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[1]) Lieb. Ann. 294. p. 79.

[2]) The amount of water which is reabsorbed depends on the state of humidity of the air.

The percentage of water contained in crystallized indican is, therefore:

I 14.3 pCt.

II 15.4 pCt.

III 17.2 pCt.

the formula $C_{14}H_{17}NO_6 + 3H_2O$ requires 15.5 pCt.

Chemical Laboratory of the Polytechnical School.

Mathematics. — "*A special case of the differential equation of* MONGE." by Prof. W. KAPTEYN.

To the communications inserted in the Proceedings of Nov. 25th and Dec. 30th 1899 we here add the results of our investigation of a case where the equation of MONGE consists of three terms.

If the equation of MONGE has the form

$$s + \lambda t + \mu = 0$$

this equation will admit of two intermediate integrals, only when

$$\lambda = \frac{1}{\varrho}\frac{\partial}{\partial q}(p\varrho + v) \quad , \quad \mu = \frac{1}{\varrho} H(p\varrho + v),$$

where ϱ represents any function of x, y, z, q, and the function v satisfies the differential equation

$$\frac{1}{\varrho}\frac{\partial \varrho}{\partial q}\frac{\partial v}{\partial y} + \left(1 + \frac{q}{\varrho}\frac{\partial \varrho}{\partial q}\right)\frac{\partial v}{\partial z} - \frac{1}{\varrho} H(\varrho)\frac{\partial v}{\partial q} = \frac{\partial \varrho}{\partial x}$$

and H denotes the operation $\frac{\partial}{\partial y} + q\frac{\partial}{\partial z}$.

Then one of the intermediate integrals is

$$p\varrho + v = f(x),$$

where f denotes an arbitrary function, the second being found by connecting the two integrals of the complete system

$$H(\varrho)\frac{\partial V}{\partial q} - \frac{\partial \varrho}{\partial q}\frac{\partial V}{\partial y} - \left(\varrho + q\frac{\partial \varrho}{\partial q}\right)\frac{\partial V}{\partial z} = 0,$$

$$H(v)\frac{\partial V}{\partial q} - \frac{\partial v}{\partial q}\frac{\partial V}{\partial y} - \varrho\frac{\partial V}{\partial x} - q\frac{\partial v}{\partial q}\frac{\partial V}{\partial z} = 0.$$

Special cases:

I. $s + \lambda t = 0$

Here $\mu = \frac{1}{\varrho} H(p\varrho + v) = 0$; therefore

$$H(\varrho) = 0 \quad \text{and} \quad H(v) = 0,$$

whilst the differential equation for v reduces to

$$\frac{\partial v}{\partial z} = \frac{\partial \varrho}{\partial x}.$$

Let σ be any function of x, q, $u = z - qy$. We then find here

$$\lambda = \frac{1}{\frac{\partial \sigma}{\partial u}}\left[p\left(\frac{\partial^2 \sigma}{\partial u\,\partial q} - y\frac{\partial^2 \sigma}{\partial u^2}\right) + \frac{\partial^2 \sigma}{\partial x\,\partial q} - y\frac{\partial^2 \sigma}{\partial x\,\partial u}\right].$$

The differential equation $s + \lambda t = 0$ now possesses the two intermediate integrals

$$p\frac{\partial \sigma}{\partial u} + \frac{\partial \sigma}{\partial x} = f(x) \quad \text{and} \quad y\frac{\partial \sigma}{\partial u} - \frac{\partial \sigma}{\partial q} = f(q),$$

where f represents an arbitrary function.

These results are more general than those formerly communicated sub IV; we find these back by putting

$$\varrho = e^{-\int \Phi(q)\,dq}, \qquad v = -\int e^{-\int \Phi(q)\,dq}\,\psi(x, q)\,dq.$$

II. $s + \mu = 0$.

Here $\lambda = \frac{1}{\varrho}\frac{\partial}{\partial q}(p\varrho + v) = 0$; therefore

$$\frac{\partial \varrho}{\partial q} = 0 \quad \text{and} \quad \frac{\partial v}{\partial q} = 0,$$

whilst the differential equation for v reduces to

$$\frac{\partial v}{\partial z} = \frac{\partial \varrho}{\partial x}.$$

Let σ be an arbitrary function of x, y, z. We shall now find

$$\mu = \frac{1}{\frac{\partial \sigma}{\partial z}} \left[p \left(\frac{\partial^2 \sigma}{\partial y\, \partial z} + q\, \frac{\partial^2 \sigma}{\partial z^2} \right) + \frac{\partial^2 \sigma}{\partial x\, \partial y} + q\, \frac{\partial^2 \sigma}{\partial x\, \partial z} \right].$$

The differential equation $s + \mu = 0$, for which may be written

$$\frac{d^2 \sigma}{dx\, dy} = 0,$$

possesses as intermediate integrals

$$\frac{d\sigma}{dx} = \frac{\partial \sigma}{\partial x} + p\, \frac{\partial \sigma}{\partial z} = f(x),$$

$$\frac{d\sigma}{dy} = \frac{\partial \sigma}{\partial y} + q\, \frac{\partial \sigma}{\partial z} = f(y),$$

where f denotes an arbitrary function.

These results differ in form only from those formerly communicated sub V.

Mathematics. — *"On the locus of the centre of hyperspherical curvature for the normal curve of n-dimensional space"*. By Prof. P. H. Schoute.

At the close of the preceding paper we have pointed out that the characteristic numbers of the locus of the centre of hyperspherical curvature are lowered if some of the points of the given rational curve lying at infinity coincide. At present we wish to trace for a special case the amount of those lower numbers, viz. for the case where the given curve is the "normal curve" N_n^n of the n-dimensional space S_n, in which it is situated. It is known that this curve is represented on rectangular coordinates by the equations

$$x_i = t^i, \quad (i = 1, 2, \ldots n) \quad , \quad \ldots \ldots \quad (1)$$

where t is again the parametervalue of the "point t" of the curve.

The quintic ν of the preceding paper being unity here, $\nu = 0$ considered as an equation of degree n has here n infinite roots, from which ensues that the n points at infinity of the curve coincide in a single point, the point at infinity of the x_n-axis. As an introduction to the general case of an arbitrary n, let us first however consider the case $n = 3$ of the skew parabola.

1. If to avoid indices we write for the rectangular coordinates of a point of S_3 as is customary x, y, z instead of x_1, x_2, x_3, the skew parabola is represented by

$$x = t, \quad y = t^2, \quad z = t^3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

The equation of the normal plane in the point t is

$$x - t + 2\,t\,(y - t^2) + 3\,t^2\,(z - t^3) = 0,$$

or classified according to t

$$3\,t^5 + 2\,t^3 - 3\,z\,t^2 + (1 - 2\,y)\,t - x = 0 \quad . \quad . \quad . \qquad (3)$$

This equation being of degree 5 in t, five normal planes of the skew parabola pass through any given point and so the locus R_s is of order five, as was formerly found.

The equation of the developable enveloped by the series of normal planes is found by eliminating t out of (3) and its differential coefficient according to t. This is immediately reduced to the elimination of t between the two cubic equations

$$\left.\begin{array}{l} 4\,t^3 \qquad\qquad - 9\,z\,t^2 + 4\,(1 - 2\,y)\,t \qquad\quad - 5\,x = 0 \\ 135\,z\,t^3 + 12\,(10\,y - 7)\,t^2 + 3\,(25\,x - 8)\,t + 4\,(1 - 2\,y) = 0 \end{array}\right\} ,$$

by which is found by means of the wellknown method of elimination

$$\begin{vmatrix} 4\,, & -9\,z\,, & 4 - 8\,y\,, & -5\,x\,, & 0\,, & 0 \\ 0\,, & 4\,, & -9\,z\,, & 4 - 8\,y\,, & -5\,x\,, & 0 \\ 0\,, & 0\,, & 4\,, & -9\,z\,, & 4 - 8\,y\,, & -5\,x \\ 135\,z\,, & 120\,y - 84\,, & 75\,x - 24\,, & 4 - 8\,y\,, & 0\,, & 0 \\ 0\,, & 135\,z\,, & 120\,y - 84\,, & 75\,x - 24\,, & 4 - 8\,y\,, & 0 \\ 0\,, & 0\,, & 135\,z\,, & 120\,y - 84\,, & 75\,x - 24\,, & 4 - 8\,y \end{vmatrix} = 0.$$

So the developable referred to is of degree six; so six is the rank of R_s.

By solving x, y, z out of (3) and its first and second differential coefficients according to t we find

$$\left.\begin{aligned} x &= 2t^3(9t^2+1) \\ 1-2y &= 3t^2(15t^2+2) \\ z &= 2t(5t^2+1) \end{aligned}\right\} , \quad \ldots \ldots \quad (4)$$

from which ensues that the curve R_s is of degree five. So, instead of 5, $2(5-1)$, $3(5-2)$ or 5, 8, 9, the characteristic numbers of R_s are 5, 6, 5.

In passing we can remark here, that the normal plane

$$2(3t^2x-3ty+z)=108t^7+147t^5+38t^3+t \quad \ldots \quad (5)$$

of the curve R_s in the point t is parallel, as it should be, to the plane of curvature

$$t^3-3t^2x+3ty-z=0$$

of the skew parabola in the point t. The equation (5) being of degree seven in t, the locus R'_s, belonging to R_s as original curve, is of class seven. This agrees with the general result obtained in the preceding paper. For the number $3n-2$, here 13, must be diminished by four on account of the particularity sub ^{a}) and by two on account of the particularity sub ^{b}). For, ν being a constant, the quintic equation $\nu=0$ has five equal infinite roots; moreover the three equations $\alpha'_1=0$, $\alpha'_2=0$, $\alpha'_3=0$ have the factor $15t^2+1$ in common, in connection with which the curve R'_s proves to contain two conjugate complex cusps.

2. The method followed here for $n=3$ not being so easy to apply to the space S_n, we shall try to find another way, where that drawback does not present itself. To do so we must recall in mind the proof of the theorem formerly used, according to which the envelope of a space with $n-1$ dimensions, of which the equation, linear in the coordinates x_i $(i=1, 2, \ldots n)$, contains a parameter t to degree k, has the characteristic numbers

$$k, \quad 2(k-1), \quad 3(k-2), \ldots \ldots (n-1)(k-n+2),$$

where it is taken for granted that $k > n-2$, as otherwise the last envelope contains *either* a morefold infinite number of points and is then not a curve, *or* — in case it really consists of a singly infinite number of points — it is situated in a space S_{n-1}. Here k is always $2n-1$.

The indicated proof can be given by means of the two following considerations:

a). The system of $s+1$ equations consisting of the equation of degree k

$$f(t) \equiv a_0\, t^k + a_1\, t^{k-1} + \ldots .\ a_{k-1}\, t + a_k = 0$$

and its first, second.... s^{th} differential coefficients according to t may be replaced by a system of $s+1$ equations of degree $k-s$ in t, all admitting coefficients that are linear forms of the coefficients of $f(t)=0$.

b). The degree of the locus represented by $s+1$ equations of degree $k-s$ in t, of which the coefficients are linear forms in the coordinates $x_i\ (i=1,2,\ldots n)$, is obtained by adding to the system $n-s$ entirely arbitrary equations linear in the coordinates and by eliminating the n coordinates between the so formed system of $n+1$ equations of which $n-s$ do not contain t. The degree of the resulting equation in t is the order of the locus we were in search of.

The proof of these two lemmae is very simple. The first is but an extension of a wellknown theorem of EULER. If we transform the equation $f(t)=0$ by the substitution $t=\dfrac{u}{v}$ into the homogeneous form $\varphi(u,v)=0$, the $s+1$ indicated equations are

$$\frac{\partial^s\varphi}{\partial u^s}=0,\quad \frac{\partial^s\varphi}{\partial u^{s-1}\,\partial v}=0\ \ldots,\ \frac{\partial^s\varphi}{\partial v^s}.$$

And by following the method pointed out in the second lemma we find the number of points common to the locus of $n-s$ dimensions, determined by the $s+1$ equations of degree $k-s$ and the space S_s, being the intersection of any system of $n-s$ spaces S_{n-1}.

If the condition is written down, that the eliminant of the system of $n+1$ equations, linear in the n coordinates, disappears, we obtain an equation of degree $(s+1)(k-s)$ in t, which proves the theorem.

3. It goes without saying that the lowering, which the characteristic numbers of the locus R_s belonging to the skew parabola undergo, is closely connected with the particular structure of the equation. First, this equation is not complete, for t^4 is lacking; secondly, not all existing terms contain the three coordinates x, y, z

in their coefficients. We shall first point out, that the latter peculiarity explains the lowering appearing here even then, if we neglect to avail ourselves of the simplification indicated in the lemma a); we shall then show that the first particularity has no effect here.

By substituting in the eliminant of the system for each element the number indicating its degree in t and by representing the places made vacant by differentiation by the symbol $\dagger$, then in the three cases $s=0,\ 1,\ 2$, appearing in the skew parabola, we have — independent of the lacking of t^4 in (3) — to deal with the three symbolic equations

$$\begin{vmatrix} 0 & 1 & 2 & 5 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{vmatrix} = 0, \quad \begin{vmatrix} 0 & 1 & 2 & 5 \\ \dagger & 0 & 1 & 4 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{vmatrix} = 0, \quad \begin{vmatrix} 0 & 1 & 2 & 5 \\ \dagger & 0 & 1 & 4 \\ \dagger & \dagger & 0 & 3 \\ 0 & 0 & 0 & 0 \end{vmatrix} = 0,$$

which really show that the corresponding equations in t are respectively of degree $5,\ 6,\ 5$.

By substituting furthermore in the eliminant for each element the term of the highest degree in t, we then find omitting the first case, clear enough in itself,

$$\begin{vmatrix} 1 & t & t^2 & t^5 \\ \dagger & 1 & 2t & 5t^4 \\ a_1 & a_2 & a_3 & a_4 \\ b_1 & b_2 & b_3 & b_4 \end{vmatrix} = 0, \quad \begin{vmatrix} 1 & t & t^2 & t^5 \\ \dagger & 1 & 2t & 5t^4 \\ \dagger & \dagger & 2 & 20t^3 \\ a_1 & a_2 & a_3 & a_4 \end{vmatrix} = 0$$

and now, taking the arbitrariness of the coefficients a, b of the equations of the planes S_2 into consideration, it is clear that the terms of the highest degree

$$\begin{vmatrix} a_1 & a_2 \\ b_1 & b_2 \end{vmatrix} \cdot \begin{vmatrix} t^2 & t^5 \\ 2t & 5t^4 \end{vmatrix} = 3\,(a_1\,b_2)\,t^6, \quad - a_1 \begin{vmatrix} t & t^2 & t^5 \\ 1 & 2t & 5t^4 \\ \dagger & 2 & 20t^3 \end{vmatrix} = -\,12\,a_1\,t^5$$

and the constant terms

$$(a_3\,b_4), \quad 2\,a_4$$

of these equations cannot be expelled by applying the method of the first lemma or by making use of the lacking of t^k in (3), by which equations $f(t)=0$ etc. of still lower degree are obtained. For, these operations correspond with the diminishing of the elements of a row of the determinant indicated above by the corresponding elements of another now multiplied by a form in t, and by this method of transformation, much in use with determinants, the degree of the determinant in t cannot be lowered. So it is only apparently that by applying the first lemma the degree of the general eliminant is lowered from

$$k+(k-1)+\ldots+(k-s)=\frac{(2k-s)(s+1)}{2} \text{ to } \frac{(2k-2s)(s+1)}{2};$$

in reality the eliminant of the equations

$$f(t)=0, \quad \frac{\partial f}{\partial t}=0, \ldots \quad \frac{\partial^s f}{\partial t^s}=0$$

is already of degree $(s+1)(k-s)$, although judging by the form it seems to be of a higher degree. On the other hand in the case of the skew parabola

$$\begin{vmatrix} 0 & 1 & 2 & 5 \\ \dagger & 0 & 1 & 4 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{vmatrix} = 0 \text{ passes into } \begin{vmatrix} 0 & 1 & 2 & 3 \\ \dagger & 0 & 1 & 4 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{vmatrix} = 0 \quad \text{and} \quad \begin{vmatrix} 0 & 1 & 2 & 3 \\ 1 & 2 & 3 & 2 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{vmatrix} = 0,$$

if in succession we make use of the method of the first lemma or of the two cubic equations used in the direct solution; so the determinant remains of degree six in t.

4. We are now able to treat the general case completely, where n and $s<n$ are arbitrary and k is equal to $2n-1$. If as is customary we represent the analytical faculty

$$p(p+r)(p+2r)\ldots\{p+(q-1)r\}$$

by $p^{q|r}$ the equation under investigation appears in the form

$$\begin{vmatrix}
1 & t & t^2 & \dots & t^{n-s-1} & t^{n-s} & \dots & t^{n-1} & t^{2n-1} \\
\dagger & 1 & 2t & \dots & (n-s-1)t^{n-s-2} & (n-s)\,t^{n-s-1} & \dots & (n-1)\,t^{n-2} & (2n-1)\,t^{2n-2} \\
\dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots \\
\dots & \dots & \dots & \dots & \dots & \dots & \dots & (n-s)^{s|1}t^{n-s-1} & (2n-s)^{s|1}t^{2n-s-1} \\
a_{1,1} & a_{1,2} & a_{1,3} & \dots & a_{1,n-s} & a_{1,n-s+1} & \dots & a_{1,n} & a_{1,n+1} \\
a_{2,1} & a_{2,2} & a_{2,3} & \dots & a_{2,n-s} & a_{2,n-s+1} & \dots & a_{2,n} & a_{2,n+1} \\
\dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots \\
a_{n-s,1} & a_{n-s,2} & a_{n-s,3} & \dots & a_{n-s,n-s} & a_{n-s,n-s+1} & \dots & a_{n-s,n} & a_{n-s,n+1}
\end{vmatrix} = 0.$$

By multiplying the second row by t, the third by t^2 etc. and the $s+1^{\text{st}}$ by t^s, the first $s+1$ elements of each column assume the same power of t. From this ensues that

$$(n-s) + (n-s+1) + \dots + (n-1) + 2n-1$$

diminished by

$$1 + 2 + \dots \qquad + s$$

or $2n-1+s(n-s-1)$ indicates the degree of the equation, if the terms of the highest degree and the constant term do not disappear. The constant term is the product of the numbers $1, 2, 6, 24, \dots$, and a determinant of coefficients $a_{i,k}$; so this does not disappear. And taken together the terms of the highest degree $2n-1+s(n-s-1)$ have as coefficient the product of a determinant of quantities $a_{i,k}$ and

$$\begin{vmatrix}
1 & 1 & \dots & 1 & 1 \\
n-s & n-s+1 & \dots & n-1 & 2n-1 \\
\dots & \dots & \dots & \dots & \dots \\
\dots & \dots & \dots & \dots & \dots \\
\dots & \dots & \dots & (n-s)^{s|} & (2n-s)^{s|1}
\end{vmatrix},$$

which is reducible to

$$\begin{vmatrix} 1 & 1 & \ldots\ldots & 1 & 1 \\ n-s & n-s+1 & \ldots\ldots & n-1 & 2n-1 \\ (n-s)^2 & (n-s+1)^2 & \ldots\ldots & (n-1)^2 & (2n-1)^2 \\ \ldots & \ldots & \ldots & \ldots & \ldots \\ (n-s)^s & (n-s+1)^s & & (n-1)^s & (2n-1)^s \end{vmatrix}$$

and this differs from zero, it being the product of all possible differences of the $s+1$ numbers $n-s,\ n-s+1, \ldots .\ n-1,\ 2n-1$ and no equal ones appearing among them.

According to the final result obtained in this way the characteristic numbers of the locus of the centre of hyperspherical curvature R_h for the normal curve N_n^n are respectively

$$2n-1,\quad 3n-3,\quad 4n-7.\quad 5n-13,\quad 6n-21, \ldots .\ 2n-1,$$

from which ensues that they do not change if taken in reversed order. In particular we find for

$n = 2 \ldots .\ 3,\ 3$
$n = 3 \ldots .\ 5,\ 6,\ 5$
$n = 4 \ldots .\ 7,\ 9,\ 9,\ 7$
$n = 5 \ldots .\ 9,\ 12,\ 13,\ 12,\ 9$
$n = 6 \ldots .\ 11,\ 15,\ 17,\ 17,\ 15,\ 11$
$n = 7 \ldots .\ 13,\ 18,\ 21,\ 22,\ 21,\ 18,\ 13$
$n = 8 \ldots .\ 15,\ 21,\ 25,\ 27,\ 27,\ 25,\ 21,\ 15$
$n = 9 \ldots .\ 17,\ 24,\ 29,\ 32,\ 33,\ 32,\ 29,\ 24,\ 17$
$n = 10 \ldots .\ 19,\ 27,\ 33,\ 37,\ 39,\ 39,\ 37,\ 33,\ 27,\ 19.$

With this the table inserted in the preceding paper referring to the general rational skew curve of minimum degree can be compared.

Physics. — "*Equations in which functions occur for different values of the independent variable*". By J. D. VAN DER WAALS JR. (Communicated by Prof. J. D. VAN DER WAALS.)

§ 1. Let us imagine an electric vibrator at a distance r from a reflecting plane. If we wish to construe the equation of motion of that vibrator at the moment t we shall have to take into consideration that forces act on the vibrator, which it has given out itself and which have then been reflected by the plane. These forces are determined by the condition of the vibrator at the moment t' at which the vibrations were given out, i. e. at the moment which precedes with an interval of $2\,\frac{r}{V}$ the moment, at which we want to know the way of motion. The equation of motion, which determines the motion of the vibrator, will therefore besides the electric moment of the vibrator and its fluctions at the moment t, contain the same quantities at the moment $t' = t - 2\,\frac{r}{V}$.

Similar problems of a more intricate kind may occur in great numbers. First we may want to examine the influence which different vibrators exercise on each other, in which case a set of simultaneous differential equations is to be solved which show the peculiarity which we are discussing.

Further the different bodies in question may move, which makes r and therefore the difference of time between t and t' variable. If we have e.g. a vibrator, which moves normally towards a reflecting plane, it will have been at the moment t' at a distance from the wall which we call r', so that:

$$t' = t - \frac{r + r'}{V}.$$

Now it may be that we want to examine the ponderomotoric actions, so that the quantity r, which occurs in t' is at the same time the quantity, which is not given as function of t, but which we want to determine as function of t by means of the differential equation.

Similar problems are of course also found in the theory of sound.

Though these problems are possibly not of so much importance, that it is worth while drawing up a complete theory of the equations in consideration, I will point out some particulars of the solutions, as they have never been discussed as far as I know.

§ 2. In the physical problems there occur always differential equations. I will however begin with the simpler case in which the equation to be solved does not contain any differential quotients. In general such an equation may be represented by:

$$F(y', y, x', x) = 0.$$

Here y' represents the value of y which is obtained by substituting x by x' in $y=f(x)$. Now we must also know in what connection x' is with the other quantities. In general this is done by giving:

$$F_1(y', y, x', x) = 0.$$

The problem is therefore reduced to the solution of:

$$F(y', y, x', x) = 0 \quad \text{and} \quad F_1(y', y, x', x) = 0$$

where we must take into account, that the dependence of y' on x' and that of y on x is expressed by the same function.

From these two equations we may think y' and x' as being solved:

$$x' = \chi_1(x, y) \qquad y' = \chi_2(x, y).$$

Let us now assume an arbitrary value $x = x_1$ and a perfectly arbitrary function $y = \psi_1(x)$. Let us now calculate $y_1 = \psi_1(x_1)$ and $x_2 = \chi_1(x_1 y_1)$. Then we can represent the quantity y between the limits x_1 and x_2 by the perfectly arbitrary function. If we substitute in $\chi_1(x y)$ and $\chi_2(x y)$ the value $\psi_1(x)$ for y, we get x' and y' both expressed in x:

$$x' = \chi'_1(x) \qquad y' = \chi'_2(x).$$

By eliminating x from these two equations we get $y' = \psi_2(x')$.

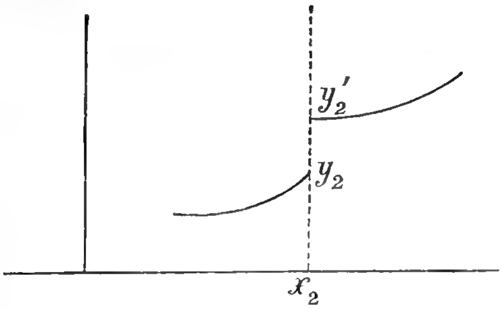
If we then determine:

$$y_2 = \psi_2(x_2) \qquad \text{and} \qquad x_3 = \chi_1(x_2 y_2)$$

we may represent the value y by $\psi_2(x)$, when x ranges between the limits x_2 and x_3. In exactly the same way we may determine functions $\psi_3(x)$, $\psi_4(x)$ etc., which will respectively be a solution for x between x_3 and x_4, x_4 and x_5 etc. With the aid of the integrals of Fourier we may write the solution as follows:

$$y = \int_{x_1}^{x_2} \int_0^{\infty} sin\,(ux)\, sin\,(vu)\, \psi_1(v)\, dv\, du +$$

$$+ \int_{x_2}^{x_3} \int_0^{\infty} sin\,(ux)\, sin\,(vu)\, \psi_2(v)\, dv\, du + \text{ etc.}$$



In this way however we do not get a continuous curve as solution. In general the function will have two values at x_1, x_2, x_3 etc., and it will then consist of two branches, which have no connection with each other. We have viz. not taken care, that the value $y_2 = \psi_1(x_2)$ with which the portion of the curve between x_1 and x_2 ends, is the same as $y'_2 = \psi_2(x_2)$ with which the portion between x_2 and x_3 begins. It is this last value for y_2 which we have to substitute for y' in $F(y', y, x', x) = 0$ and $F_1(y', y, x', x) = 0$, if we want to find out whether the data are fulfilled by taking the points (x_1, y_1) and (x_2, y_2) as points (x, y) and (x', y').

By putting:

$$y = \psi_1(x, c_1, c_2, \ldots\ldots c_{n-1})$$

in which $c_1, c_2, \ldots\ldots c_{n-1}$ represent constants, which are still at our disposal, we find for ψ_2, ψ_3 etc. also functions, which contain these same constants.

If we put

$$y_2 = y'_2, \quad y_3 = y'_3 \ldots y_n = y'_n$$

we may solve the c's by means of these $n-1$ equations. By substituting the values of these c's obtained in this way in $y = \psi_1(x, c_1 \ldots c_{n-1})$ we get between x_1 and x_{n+1} a curve as solution, whose coordinates do no longer show any discontinuity. In general however the quantity $\frac{dy}{dx}$ will vary discontinuously at the points $x_2 \ldots x_n$.

We must state here, that it is not necessary that

$$x_1 < x_2 < x_3 < x_4 \text{ etc.}$$

If this inequality is not satisfied, y will show several values at a given value of x, even if ψ_1 is a one-valued function. Complications which may present themselves, e.g. that x' becomes imaginary for certain values of x, or that $x' = x$ or similar cases, are left out of account here.

§ 3. Besides these general solutions, others are also possible, in which y may be represented by a continuous function of x. I shall call such solutions function-solutions.

I shall demonstrate the existence of such a function-solution by means of a very simple example.

Let us take as being given:

$$x' = P_1\, y + Q_1\, x \qquad \text{and} \qquad y' = P_2\, y + Q_2\, x\,.$$

If we represent the function-solution of y by $\psi(x)$, we, have:

$$y' = \psi(x') \quad \text{or} \quad \psi\,[P_1\, \psi(x) + Q_1\, x] = P_2\, \psi(x) + Q_2\, x\,.$$

This equation must be fulfilled identically. It is clear that we may do so by putting:

$$\psi(x) = a\, x\,.$$

Then:

$$P_1\, a^2 + Q_1\, a = P_2\, a + Q_2$$

or

$$P_1\, a^2 + (Q_1 - P_2)\, a - Q_2 = 0$$

$$a = \frac{P_2 - Q_1}{2\, P_1} \pm \frac{1}{2\, P_1} \sqrt{(P_2 - Q_1)^2 + 4\, P_1\, Q_2}\,.$$

§ 4. We shall now pass to the discussion of differential equations. As example we shall take a single differential equation (and not a set of simultaneous differential equations) of the first order; while no differential coefficients occur in the equation, which indicates in what way the value of x' is found.

The equation to be solved is then:

$$F\left(\frac{dy'}{dx'},\, \frac{dy}{dx},\, y',\, y,\, x',\, x\right) = 0\,,$$

while:

$$x' = \varphi\,(y',\, y,\, x)\,.$$

is also given.

If we take an arbitrary value x_1 and put as a solution which only holds for a part:

$$y = \psi_1\,(x)\,,$$

we may calculate again:

$$y_1 = \psi_1(x_1)$$

and with the aid of this equation:

$$x_2 = \varphi\,[\psi_1(x_2)\,,\; y_1\,,\; x_1]$$

from which x_2 may be solved. Here x_1 and x_2 are again the limits between which y may be represented by $\psi_1(x)$.

From the two equations:

$$x' = \varphi\,(y',\, y,\, x) \qquad \text{and} \qquad y = \psi_1(x)$$

we may eliminate y and then solve x as function of y' and x'.

Let us represent this by:

$$x = \chi_1(x',\, y') \qquad \text{then} \qquad y = \psi_1\,[\chi_1(x', y')]$$

and

$$\frac{dy}{dx} = \frac{d\,\psi_1\,[\chi_1(x', y')]}{d\,\chi_1(x', y')}$$

By substituting these values of x, y and $\frac{dy}{dx}$ in the given equation:

$$F\left(\frac{dy'}{dx'}\,,\; \frac{dy}{dx}\,,\; y',\; y,\; x',\; x\right) = 0$$

we get a differential equation:

$$F_1\left(\frac{dy'}{dx'}\,,\; y',\; x'\right) = 0$$

in which only $\frac{dy'}{dx'}$, y' and x' occur. If the solution of this equation is:

$$y' = \psi_2(x',\, c),$$

we may represent y by $\psi_2(x)$ between the limits x_2 and x_3, which x_3 may be again calculated from x_2 by means of the formulae:

$$x_3 = \varphi\,(y_3\,,\; y_2\,,\; x_2)$$

$$y_2 = \psi_2(x_2) \qquad \text{and} \qquad y_3 = \psi_2(x_3)$$

ψ_2 contains a constant c, of which we may still dispose. We determine it in such a way that:

$$y_2 = \psi_1(x_2) = y'_2 = \psi_2(x_2\,,\; c)\,.$$

By treating ψ_2 in the same way as ψ_1, we may deduce another differential equation:

$$F_2\left(\frac{dy'}{dx'}, y', x'\right) = 0$$

Its solution:

$$y = \psi_3(x, c)$$

will represent the required function between the limits x_3 and x_4.

In this way we may represent y again as the sum of integrals of FOURIER, provided we can solve the differential equations $F_1 = 0$, $F_2 = 0$ etc. The ordinates of the curve construed in this way will show no discontinuities, but the differential coefficient $\frac{dy}{dx}$ will be in general discontinuous in the points $x_2 \ldots x_n$. By taking in ψ_1 again an arbitrary number of constants, we shall be able to make the $\frac{dy}{dx}$ continuous in an arbitrary number of these points.

If we had solved a differential equation of the second order, ψ_2 would contain two constants, of which we may dispose in such a way, that both the y_2 and the $\frac{dy}{dx}$ are continuous in x_2, without our being obliged to introduce artificially constants in ψ_1. As in mechanical problems always differential equations of at least the second order occur, it follows that this solution fulfils the condition, that both the coordinates and their fluctions change continuously. The change of the second fluctions can be discontinuous in some points, but this is not in contradiction with the requirements of mechanics.

Indeed in some problems the case may present itself that second fluctions, which were 0, get suddenly a finite value, even without our having to assume infinite forces, e. g. when the fibre, on which the apparatus is suspended, breaks or when a circuit is closed. Let us for instance imagine a condenser with a difference of potential V and a charge Q. The condenser is nearly closed by means of a wire. Before the circuit is closed the current $i = \frac{dQ}{dt}$ and also the $\frac{di}{dt} = \frac{d^2Q}{d\,t^2}$ will be zero. If we then close the circuit, i will remain zero at the first moment; but $\frac{di}{dt}$ will suddenly assume the value V.

These differential equations too have function-solutions.

§ 5. As an example of an application of this kind of differential equations I shall take the problem which Galitzin [1]) has solved, without taking into account the difference between t and t'. In order to get a simpler representation, I shall modify his suppositions slightly, without changing the essential properties of the problem.

I take, namely, two Hertz's vibrators, which are at rest in the points P_1 and P_2. Both vibrate in the same direction, normal to the line which joins them. I shall take the line passing through the vibrators as axis of x, and the direction in which they vibrate as axis of z. If we call the distance between them $x_0 = x_1 - x_2$, then we have

$$t' = t - \frac{x_0}{V}\,.$$

Let us represent the moments of the vibrators by a_1 and a_2 and their distances from an arbitrary point Q by r_1 and r_2, and let us put:

$$\chi_1 = -\frac{a_1}{r_1} \qquad \chi_2 = -\frac{a_2}{r_2}.$$

The electric force emitted by the vibrator in P_1 has a component in the direction of the z-axis, which in an arbitrary point Q amounts to:

$$Z = V^2 \left[\frac{\partial^2 \chi_1}{\partial x^2} + \frac{\partial^2 \chi_1}{\partial y^2}\right].$$

In the point P_2, where $y = 0$, this component has the value of:

$$Z = V^2 \left\{ \frac{1}{x_0 V^2} \frac{d^2 a_1}{dt^2} + \frac{1}{x_0^2 V} \frac{d a_1}{dt} + \frac{1}{x_0^3} a_1 \right\}.$$

Let us further assume that the vibration in each vibrator separately is determined by a force proportional to the deviation, and that moreover a damping exists proportional to $\frac{d^3 a}{dt^3}$, then the problem is reduced to the solution of two equations of the following form:

$$A_1 \frac{d^3 a_1}{dt^3} + A_2 \frac{d^2 a_1}{dt^2} + A_3\, a_1 + A_4 \left(\frac{d^2 a_2}{dt^2}\right)' + A_5 \left(\frac{d a_2}{dt}\right)' + A_6\, (a_2)' = 0. \quad (1)$$

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[1]) Wied. Ann. B. 56, H. 1. 1895. P. 89—94.

$$B_1 \frac{d^3 a_2}{dt^3} + B_2 \frac{d^2 a_2}{dt^2} + B_3 a_2 + A_4 \left(\frac{d^2 a_1}{dt^2}\right)' + A_5 \left(\frac{d a_1}{dt}\right)' + A_6 (a_1)' = 0. \quad (2)$$

where $(\ )'$ means that we have to take the quantity between brackets as it was at the moment $t - \frac{x_0}{V}$. The function-solution of these equations may be represented by

$$a_1 = C_1 e^{st} \qquad a_2 = C_2 e^{st} .$$

If we substitute these expressions in the equations (1) and (2) and if we divide by e^{st}, we get:

$$C_1 (s^3 A_1 + s^2 A_2 + A_3) + C_2 (s^2 A_4 + s A_5 + A_6) e^{-s\frac{x_0}{V}} = 0.$$

$$C_2 (s^3 B_1 + s^2 B_2 + B_3) + C_1 (s^2 A_4 + s A_5 + A_6) e^{-s\frac{x_0}{V}} = 0.$$

from which we deduce:

$$\frac{C_1}{C_2} = - \frac{s^2 A_4 + s A_5 + A_6}{s^3 A_1 + s^2 A_2 + A_3} e^{-s\frac{x_0}{V}} = - \frac{s^3 B_1 + s^2 B_2 + B_3}{s^2 A_4 + s A_5 + A_6} e^{s\frac{x_0}{V}}$$

$$(s^2 A_4 + s A_5 + A_6)^2 - (s^3 A_1 + s^2 A_2 + A_3)(s^3 B_1 + s^2 B_2 + B_3) e^{2s\frac{x_0}{V}} = 0. \quad (3)$$

As an exponential function is periodic, an infinite number of values of s will satisfy this equation, and the system will be able to vibrate with an infinite number of periods.

The equations of motion, which **Galitzin** used, instead of our equations (1) and (2) were:

$$i + C L \frac{d^2 i}{dt^2} + C M \frac{d^2 i'}{dt^2} = 0$$

$$i' + C' L' \frac{d^2 i'}{dt^2} + C' M \frac{d^2 i}{dt^2} = 0.$$

From these he deduces instead of our equation (3) an equation of the following form: [1])

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[1]) Equation 7 P. 93, Loc. cit. The quantity z, which occurs there, is the quantity s of this formula.

$$P s^4 + Q s^2 + 1 = 0.$$

To show the connection which exists between this equation and our equation (3) we make the following assumptions:

a. We neglect the damping. Then the terms with A_1 and B_1 do not occur.

b. We do not take HERTZ's vibrators, but condensers, the plates of which are so near each other, that $a_1 = a_2 = 0$, even if finite quantities of electricity have passed through the wire. Instead of $\frac{da}{dt}$ we write then $\frac{i}{l}$, as $i = l\,Q$, where Q represents the charge and l the distance of the plates of the condenser. The wire is to be considered as a nearly closed circuit and as long compared with l. Assuming this, the terms with A_6 are suppressed.

c. As the inductive action of a current does not depend on the intensity i, but only on its fluction $\frac{di}{dt}$, we assume, that the terms with A_5 do not occur.

d. Finally we only try to find a solution for the case, that the systems are so near each other, that x_0 may be considered as very small. Even if s is complex (in which case we represent it by $\alpha + \beta i$) $e^{s\frac{x_0}{V}}$ is approximately equal to unity, if α or β are not so great that $\alpha \frac{x_0}{V}$ or $\beta \frac{x_0}{V}$ noticeably differs from 0. If we put $e^{s\frac{x_0}{V}} = 1$ our equation becomes identical with that of GALITZIN.

The solution which GALITZIN has found is therefore indeed an approximated solution of the problem. But it is an incomplete solution. For however small a_0 may be, we may always take such high values for α and β, that $\alpha \frac{x_0}{V}$ or $\beta \frac{x_0}{V}$ noticeably differs from zero, and then we get solutions, which could not be found by the method of GALITZIN. Without making a fuller investigation of the interpretation of equation (3), we can say, that only three sets of roots may exist, namely.

1. The roots found by GALITZIN.

2. Roots for which the supposition that $\alpha \frac{x_0}{V}$ is small is not satisfied. Then β may still have an arbitrary value. The physical meaning of these roots is not clear to me.

3. Roots, for which $\beta \frac{x_0}{V}$ is not small and α may still have an arbitrary value.

β has then at least a value of the order $\frac{V}{x_0}$ and the period is of the order $\frac{x_0}{V}$. A priori we might have foreseen that such solutions must exist. If we imagine two plane reflecting plates instead of the vibrators, a vibration might exist between them with a time of oscillation $\frac{2\,x_0}{V}$. As the vibrators have another shape and as they emit vibrations in all directions, and not only towards each other, we shall have to apply a correction to this time of oscillation, just as is the case with the open ends of an organ tube. This correction is perhaps very considerable. But a vibration with a time of oscillation of the order $\frac{x_0}{V}$ must exist. Moreover we shall find a series of overtones, as equation (3) has an infinite number of roots.

Thus far we have occupied ourselves only with the function-solution. It is however easy to find also the general solution.

If we represent between the moments t_1 and $t_1 + \frac{x_0}{V}$ the electric moment a_1 by $\varphi_1(t)$ and a_2 by $\psi_1(t)$, the equations (1) and (2) take the following forms:

$$A_1 \frac{d^3 a_1}{dt^3} + A_2 \frac{d^2 a_1}{dt^2} + A_3\, a_1 + A_4 \frac{d^2\, \psi_1\left(t - \frac{x_0}{V}\right)}{d\left(t - \frac{x_0}{V}\right)^2} + A_5 \frac{d\,\psi_1\left(t - \frac{x_0}{V}\right)}{d\left(t - \frac{x_0}{V}\right)} +$$

$$+ A_6\, \psi_1\left(t - \frac{x_0}{V}\right) = 0$$

$$B_1 \frac{d^3 a_2}{dt^3} + B_2 \frac{d^2 a_2}{dt^2} + B_3\, a_2 + A_4 \frac{d^2\, \varphi_1\left(t - \frac{x_0}{V}\right)}{d\left(t - \frac{x_0}{V}\right)} + A_5 \frac{d\,\varphi_1\left(t - \frac{x_0}{V}\right)}{d\left(t - \frac{x_0}{V}\right)} +$$

$$+ A_6\, \varphi_1\left(t - \frac{x_0}{V}\right) = 0$$

These equations can certainly be solved.

Let us represent the solution by:

$$a_1 = \varphi_2 (t) \qquad \text{and} \qquad a_2 = \psi_2 (t)$$

then φ_2 and ψ_2 are the solution of the problem between the moments

$$t_1 + \frac{x_0}{V} \qquad \text{and} \qquad t_1 + \frac{2\,x_0}{V} .$$

§ 6. From a mathematical point of view perhaps the function-solutions only may be considered as genuine solutions of the problem. We seek namely a quantity y as function of x, which is in a certain relation to a quantity y', which represents the same function of x, but for a different value of x. If in the general solution y is equated to $\psi_1 (x)$, y' is represented by another function of x, namely $\psi_2 (x)$. It is not essential that we take ψ_1 only between the limits x_1 and x_2, ψ_2 between the limits x_2 and x_3: we might also have taken as a solution:

$$y = \psi_1 (x) + \psi_2 (x) + \psi_3 (x) + \text{etc.}$$

We must take care, however, that if for a given value of x we take y on a branch belonging to the curve $y = \psi_n (x)$, we take y' on a branch of the curve $y = \psi_{n+1} (x)$.

From a physical point of view, however, the general solution with FOURIER's integrals is in fact the genuine solution. For let us imagine that we have only one system with n degrees of freedom which is made to move after a certain method, and which after the moment t is suffered to move freely. The motion after the moment t will then be determined only by the n generalized coordinates and their n fluctions. On the other hand, if we have two systems which act on each other with forces which propagate with finite velocity through a medium, and if we suffer these after the moment t to move freely, the motion after the moment t will depend not only on the n coordinates and their fluctions, but also on the condition of the medium. The condition of the medium at the moment t gives an accurate image of what has happened with the systems during some time preceding the moment t, that is to say it gives an accurate idea of the way in which the systems are made to move.

Let us for instance take the problem of GALITZIN, and let us imagine that the molecules are set vibrating by the collisions, and that a collision lasts a very short time θ, so that $\theta < \frac{x_0}{V}$. Let us now imagine that at the moment t_1 the molecule I collides with the molecule III. Between t_1 and $t_1 + \theta$ the value $\frac{d^2 a_1}{dt^2}$ will then be very great. Afterwards that quantity will be reduced to an average value; but at the moment $t + \frac{x_0}{V}$ the wave emitted by molecule I will arrive at molecule II and will cause $\frac{d^2 a_2}{dt^2}$ to have an abnormally great value between $t_1 + \frac{x_0}{V}$ and $t_1 + \frac{x_0}{V} + \theta$. Between the moments $t_1 + 2\frac{x_0}{V}$ and $t_1 + 2\frac{x_0}{V} + \theta$ the value of $\frac{d^2 a_1}{dt^2}$ will be again abnormally great and so on. This solution is certainly not contained in the function-solution.

Therefore before we assume the theory of GALITZIN of the broadening of the lines of the spectrum as proved, we should have to make a separate examination, in order to investigate in how far we may assume that the motion of the molecules may be represented approximately by the function-solution, and in how far the roots which GALITZIN has not found, have influence on the phenomenon. In this investigation we should have to start from the hypothesis about the way in which the molecules are made to vibrate.

I shall however, not occupy myself further with this problem, but I shall try to solve the more intricate problem of vibrators which are in motion, in order to investigate, if a connection may be found between the ponderomotoric forces of radiation and the molecular forces. The solution of this problem I have had in view from the very beginning.

Astronomy. — "*The 14-monthly period of the motion of the pole of the earth from determinations of the azimuth of the meridian marks of the Leiden observatory from* 1882–1896". By J. WEEDER (Communicated by Prof. H. G. VAN DE SANDE BAKHUYZEN).

1. From the motion of the poles of the earth over the earth's surface results not only a variation of the geographical latitude of each place, but also a variation of the direction of the meridian; hence the azimuth of each direction varies accordingly.

If in seconds of arc x and y express the deviations of the north pole from its mean place in the direction of the meridian of Greenwich (x) and in the direction of 90° West of Greenwich (y), then we can represent the azimuthal deviation Δ of a meridian with regard to its mean direction for a place at geographical longitude λ (West of Greenwich) and latitude β, in seconds of time by the formula:

$$+ (x \sin \lambda - y \cos \lambda) \frac{\sec \beta}{15} = \Delta$$

This formula represents also the variable part of each azimuth when these azimuths are taken so as to increase from North to West.

2. Prof. TH. ALBRECHT [1]) has deduced from the variations of latitude of several places a continuous series of values for the co-ordinates x and y, beginning with 1890.0; these show that the path of the pole of the earth is geometrically rather intricate. In 1891 Dr. S. C. CHANDLER found a 14-monthly as well as a yearly period in the motion of the pole, but thought that two periodical terms of the periods mentioned would be insufficient to express the co-ordinates of this motion. Dr. E. F. v. D. SANDE BAKHUYZEN on the contrary has contented himself with using these two periodical terms [2]). According to his computation the results derived with regard to the motion of the pole from observations after 1858 can be brought to agree fairly well with the supposition that each of the co-ordinates x and y consists of 2 singly-periodical terms one having a period of about 14 months, the other of exactly a year. It appears then that the terms of the 14-monthly period may also be the components of a circular motion of the pole.

The most probable elements of this circular motion are according to Dr. E. F. v. D. SANDE BAKHUYZEN:

Period	430.66 days
Amplitude	0.″159
Epoch of the greatest latitude for Greenwich	Julian date 2408568 or 1882 May 2

and the components for the Julian date t corresponding to this:

$$x = + 0.''159 \cos. 2 \pi \frac{t - 2408568}{430.66}$$

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[1]) TH. ALBRECHT, Berichte über den Stand der Erforschung der Breitenvariation, in December 1897, 98, und 99.

[2]) E. F. VAN DE SANDE BAKHUYZEN, Sur le mouvement du pôle terrestre, d'après les observations des années 1890—97, et les résultats des observations antérieures. *Archiv. Néerl. Série 2. T. II.*

$$y = -0.''159\ sin.2\,\pi\ \frac{t - 2408568}{430.66}$$

From the terms of the yearly period follows a motion of the pole in an ellipse whose axes are 0."121 and 0."057; on September 28 the pole is in the major axis, in the meridian 19° East of Greenwich.

3. The following investigation intends to deduce the 14-monthly part of the motion of the pole from the results for the azimuth of the meridian marks of the Leiden observatory. The pier of the north mark was renewed in 1880, the pier of the south mark in 1882; the determinations of azimuth used for this research, were begun for the north mark only not until Juli 1882, for the mean azimuth of both marks in January 1884, and so in each case more than a year after the construction of the pier, when the masonry was for the greater part solidified.

The period of the observations used here ends July 1896, and so includes 14 years or 12 14-monthly periods so that the variations of azimuth of the latter period could be deduced independently of the yearly period. The material consists of transits of *α* Ursae minoris in both culminations and without using the artificial horizon. The observers were E. F. v. d. Sande Bakhuyzen and J. H. Wilterdink.

The following tables I and II show, for both observers and culminations separately, the number of the observations made and their distribution over the years and the months.

TABLE I.

	July 1882 July 1883	83 84	84 85	85 86	86 87	87 88	88 89	89 90	90 91	91 92	92 93	93 94	94 95	95 96
Observer: E. F. v. d. S. BAKHUYZEN.														
Upp. Culm.	30	28	26	23	22	13	18	13	16	25	21	12	6	3
Low. Culm.	31	32	39	27	21	9	24	10	12	25	22	14	2	5
Observer: J. H. WILTERDINK.														
Upp. Culm.	37	23	23	28	17	11	37	19	15	23	20	11	8	2
Low. Culm.	32	30	35	29	26	18	25	17	17	19	15	9	8	6

TABLE II.

Months.	J.	F.	M.	A.	M.	J.	J.	A.	S.	O.	N.	D.	Total.
Observer: E. F. v. d. S. BAKHUYZEN.													
Upp. Culm.	15	28	27	30	17	17	5	16	30	28	24	19	256
Low. Culm.	3	20	37	50	28	43	25	25	17	11	11	3	273
Observer: J. H. WILTERDINK.													
Upp. Culm.	16	36	32	42	33	10	9	13	22	27	20	14	274
Low. Culm.	9	9	20	28	29	40	34	31	41	14	25	6	286

4. The following remarks may help to form an opinion about the value of this material for the investigation of the motion of the pole:

1st. The mean value of the accidental error in the azimuth, deduced from one transit-observation, is two or three times greater than the amplitude of the 14-monthly motion.

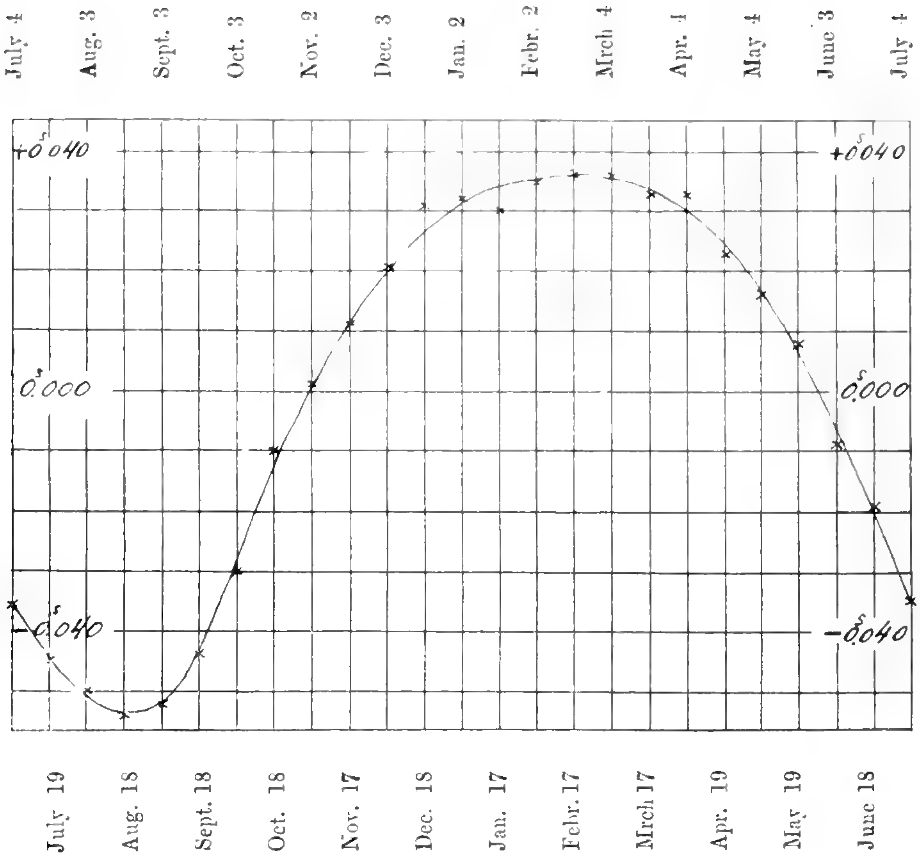
2nd. The directions of the marks in the horizontal plane are by no means absolutely stable, on the contrary their accidental variations throughout the whole period have been greater than the variation of the direction of the meridian resulting from the motion of the pole.

3rd. In spite of the remarks 1 and 2, the number of the observations and their distribution over a long period may lead us to expect a satisfactory determination of the periodical influences on the azimuth.

Yet for an independent determination of the length of the period, the time during which the observations were made was too short. Therefore I had to content myself with a determination of the amplitude and the epoch.

Besides the accidental variations the two directions of the marks are liable to systematic yearly-periodical motions in azimuth, as is clearly proved by the differences in azimuth of the two directions, which are of course independent of the motion of the pole. The graphical representation of this periodical variation (Fig. 1) has been deduced from the readings of the marks from 1883 Aug. 10—1898 Aug. 10.

Fig. 1.



One part of this periodical annual variation is caused by a motion of the direction of the north mark, another part by a similar motion in the direction of the south mark, and probably the mean azimuth of the two directions is also influenced by the same motion. As communicated in § 3 the determinations of azimuth from 1882 July to the end of 1883 concerned the north mark only; in order to be able to unite the azimuth of this period with those of the following years to a system as homogeneous as possible, the azimuths of the north mark before 1894 are diminished by half the difference in azimuth between the two directions from fig. 1; after having applied this correction, the remaining influence of the periodic motion on the azimuth of the north mark, is equal to that on the mean azimuth of both marks.

In the azimuths this influence is combined with that of the periodic motion of the meridian direction, resulting from the yearly-periodical part of the motion of the pole; as we cannot compute the two influences separately, we cannot compare these determinations of azimuth with the elements of the yearly motion of the pole.

As with regard to the 14-monthly motion of the pole there is no reason to expect changes of the same period in the directions of the marks, I have attributed the variation of azimuth to the meridian direction, and therefore to the motion of the pole only, and from the latter I have calculated, assuming a period of $430^2/_3$ days, the amplitude and epoch of the above-mentioned part of the motion of the pole.

5. About the reduction of the observations I will communicate as much as is required to understand the deduction of the numbers to be given below, and also their meaning with respect to the 14-monthly motion of the pole. The observed time of transit reduced to the middle thread, has been corrected for the inclination of the axis of rotation, the collimation constant, the clock-correction, and also partly for the azimuth of the telescope and the personal equation of the observer.

The azimuth constant of the transit instrument used for this reduction is deduced from approximate values of the azimuth of the north mark up to 1884, further for the mean azimuth of both marks, which approximate values are derived from the results of preliminary calculations and are taken so as to vary with the time as regularly as possible. A few corrections have been applied to these values:

1°. In agreement with the idea mentioned above, half the difference in azimuth of the north and south marks has been added to the azimuth of the north mark before 1884.

2°. periodical corrections have been applied to the azimuths over the whole period, which corrections result from a 14-monthly motion of the pole according to Dr. E. F. v. d. Sande Bakhuyzen, and are expressed by the formula:

$$\Delta = \frac{+\ 0.159\ sec\ \beta}{15}\ sin\left(2\pi\ \frac{t - 2408568}{430.66} + \lambda\right)$$

β and λ being the latitude and longitude (West of Greenwich) of the Leiden observatory. (Proc. Vol. I, p. 202).

By applying the correction 2 for the periodic motion of the pole to the approximate values of the azimuth constant, the corrections of that constant deduced from the discussion of the whole series of observations are freed from the greater part of the influence of the 14-monthly periodic motion as proved by the results. By means of the azimuth-differences between the telescope and the north mark (before 1884) or the mean of the two marks (after 1884) as deduced from the micrometer readings on the marks, we have deduced the approximate values of the azimuth of the transit circle from those of the azimuths of the marks.

The personal equations of the observers which have been applied here are the differences of the Right Ascension of Polaris according to their observations and the Right Ascension of this star according to the "Fundamental Catalog der Astronomische Gesellschaft." These approximate values are deduced from former observations of Polaris, in the supposition that the personal equation for both culminations and under all circumstances is the same.

6. After the reduction mentioned in § 5 each time of transit *o* should represent, if the elements of reduction were exact, the apparent Right Ascension of Polaris *c* as deduced for the moment of observation from the mean place of the Fundamental Catalog. The apparent Right Ascensions are borrowed from the "Berliner Jahrbuch"; only in the years 1882—85 the mean Right Ascension of the "Jahrbuch" differs from that of the "Katolog" and then the apparent Right Ascension of the Jahrbuch have been reduced to the later system. The differences $o-c$ of the observed and computed Right Ascensions further have served to determine the corrections of the personal equation and the instrumental errors and principally those of the assumed azimuths of the marks.

7. For the discussion of the quantities $o-c$ the following course has been taken. First the mean of the values $o-c$ for three successive months have been formed for each observer and for each culmination separately in order to determine that part of the values $o-c$ which, independently of the influence of the accidental and systematical errors of the instrument, is the same for the two culminations. For the determination of this part the observations of the two observers at first have been treated separately. In so far as the two culminations were both observed during the same periods of three months half the sums of their mean results are taken; as it appeared that these values showed periodical annual variations, the periodic part has first been deduced and afterwards the annual means of the residuals are computed. It then appeared that the results for the two observers agreed fairly well, both with regard to the annual means and to the co-efficients of the periodic part. Therefore I have combined the corresponding results of the two observers in one system; and have represented graphically the annual means obtained in this way by a smooth curve. The sum of the ordinates of this curve and of the deviations resulting from the periodical annual variation form the part of the quantities $o-c$, common to both the culminations;

this part has been subtracted from them. Finally a constant correction for personal equation, different for each observer has been applied to the $o—c$, in order to reduce the mean value of the corrected $o—c$ for each observer to 0.

8. The quantities $o—c$ corrected as explained in 7 consist of the accidental errors of observation and the influences of systematical errors in the adopted values for the inclination of the axis, the constant of collimation and the azimuth. The azimuth-corrections might have been determined with greater precision if the observations had been or could be made free from the influence of the first mentioned systematical errors. The observations at my disposal do not contain any data from which to determine the systematical corrections of the inclinations adopted; some reflection-observations of POLARIS from 1882–84, made for this purpose, have not been considered as their number was too small for the determination of a satisfactory correction of the inclination. Somewhat different from this is the opportunity for correcting the constants of collimation from the observations themselves as they have been made in the two positions of the instrument. During the period of the observations the transit circle has been reversed 24 times which divide the whole interval into 12 periods in which the clamp was east and 11 during which it was west.

The longest of these periods lasted 28 months, the shortest nearly 2 months.

The influence of an error in the assumed amount of the constant of collimation on the azimuth-correction, calculated from the value of $o—c$, changes in sign by the reversal of the instrument; it can therefore be found when we compare the azimuth-corrections from observations of Polaris, immediately before and after the reversal, or, if that error proves to be constant during a longer time, when we compare the mean azimuth-corrections deduced from observations during a longer period before and after the reversal.

It now appeared that the observations of Polaris immediately before and after the reversals were not numerous and that moreover one single observation is not accurate enough to betray a small systematic error. The graphical representation of the mean azimuth-corrections during long periods, on the contrary showed clearly the influence of a small error in the assumed constant of collimation. These mean values during the same position of the instrument showed generally a regular variation; if however we would combine the means of all the periods in a regular chronological order, then the curve obtained disagreed for the greater part of the time with the idea of a regular variation of the azimuths of the marks.

9. That a small correction of the assumed constant of collimation for Polaris, which might give a regular variation of the azimuth during the whole period, is not impossible may be seen from what follows. This constant consists of two parts: the constant of collimation determined in the nadir by the reflection of the vertical thread on the horizontal mercury-surface, and the small correction for the flexure of the rotation axis expressed by the formula $b\,(1 + \cos z)$. The first part, the constant of collimation in the nadir, is probably very exact (only in the period 1884—1885 the degree of precision may be a little less, the level being less reliable), but the value of the flexure found by determining from time to time the constant of collimation in the horizontal position of the telescope by pointing at the marks before and after a reversal is less trustworthy, especially as it appeared that it varies distinctly, when the position of the cell of the object glass was altered.

Therefore I thought myself justified in deducing from the Polaris-observations and the readings of the meridian marks small corrections to the constant of collimation, which rendered the variation of the azimuth-correction more regular, and which, with a few exceptions were constant in the periods during which the cell of the object glass was in the same position.

In order to be able to judge in how far the motion of the pole in the 14-monthly period deduced from the observations is dependent on this correction, I have computed this motion supposing: 1st that the constant of collimation is left unchanged, 2nd that the small correction mentioned has been applied to it.

10. The values of $o-c$, during 14 years (1882 July to 1896 July) corrected according to 7, for each observer separately, are divided according to the time of the observations into 12 groups, each enclosing 430 days (the assumed value of the period of the pole-motion) and each of these periods is subdivided into 43 periods of 10 days ¹). The mean values of $o-c$, during these 10 days for each culmination separately, were now formed and to each mean was given the weight 1, independent of the number of values. So we obtained a series of numbers (at a maximum of 24), representing the values of $o-c$ in both culminations belonging to one and the same

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¹) In this computation the period is actually reduced to $430^2/_{30}$ days, by causing a period of 430 days to succeed two periods of 431 days. In the periods of 431 days one of the subdivisions consists of 11 days instead of 10 days.

phase of the pole-motion; after this the means of these values belonging to a same phase were taken, after changing the sign of $o-c$ at lower culmination, because the influence of a variation of azimuth on $o-c$ in both culminations has a different sign. Finally for each observer the deviations of these 43 numbers from their mean has been formed, which deviations after the reduction from differences in time of transit to differences in azimuth, represent the still remaining influence of a periodical change of the pole on the azimuth of the marks.

A great part of that influence has been removed by applying to the azimuth, assumed in the reduction, the periodic corrections mentioned in § 5 sub 2^0, computed after the formula deduced for the 14-monthly motion of the pole by Dr. E. F. VAN DE SANDE BAKHUYZEN. In order to obtain the whole influence of this periodic motion, this correction of the azimuth has again been added to those 43 values for each observer.

Of these values U_B and U_W for the two observers the mean has been taken independently of the number of the observations and these numbers are given in Table III.

TABLE III.

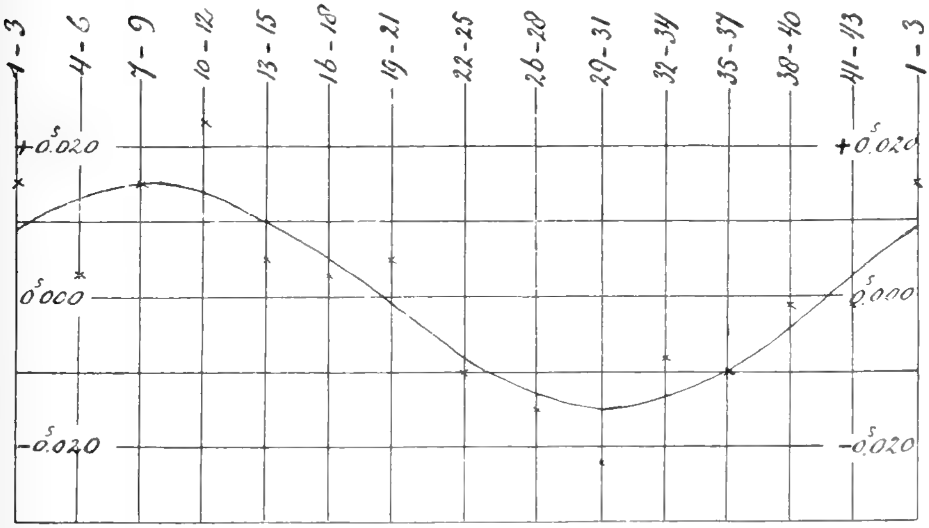
Ordinal number.	Before the correction of the constant of collimation.		After the correction of the constant of collimation.		
n	$^1/_2(U_B+U_W)$	$^1/_2(U_B-U_W)$	$^1/_2(U_B+U_W)$	$^1/_2(U_B-U_W)$	Obs.—Comp.
1	+ 0.017	+ 0.013	+ 0.010	+ 12	+ 0.003
2	+ 26	+ 01	+ 19	— 05	+ 10
3	+ 17	+ 07	+ 17	+ 06	+ 07
4	+ 12	+ 01	+ 14	— 08	+ 02
5	00	+ 04	+ 03	+ 04	— 10
6	— 12	+ 10	— 07	+ 07	— 21
7	— 02	— 02	+ 06	00	— 08
8	+ 18	— 03	+ 22	— 03	+ 07
9	+ 13	— 04	+ 16	00	+ 01
10	+ 25	+ 11	+ 29	+ 06	+ 15
11	+ 29	— 03	+ 32	+ 01	+ 18
12	— 05	+ 08	+ 07	+ 06	— 06
13	+ 16	+ 04	+ 11	+ 10	— 01

Ordinal number.	Before the correction of the constant of collimation.		After the correction of the constant of collimation.		
n	$^1/_2(U_B+U_W)$	$^1/_2(U_B-U_W)$	$^1/_2(U_B+U_W)$	$^1/_2(U_B-U_W)$	Obs.—Comp.
14	+ 02	— 03	— 06	— 01	— 16
15	+ 19	— 07	+ 11	— 07	+ 02
16	— 18	+ 16	— 23	+ 15	— 30
17	+ 21	+ 06	+ 20	+ 07	+ 15
18	+ 24	+ 05	+ 11	+ 06	+ 08
19	+ 20	— 14	+ 08	— 09	+ 07
20	+ 14	— 05	+ 09	— 07	+ 10
21	— 04	+ 01	— 02	+ 01	+ 02
22	+ 01	— 01	+ 03	00	+ 09
23	— 25	— 24	— 15	— 19	— 07
24	— 08	+ 08	— 07	+ 14	+ 02
25	— 24	+ 07	— 20	+ 05	— 09
26	— 20	+ 03	— 20	+ 05	— 08
27	— 11	— 01	— 07	— 02	+ 06
28	— 19	+ 02	— 17	+ 01	— 03
29	— 24	+ 21	— 30	+ 19	— 15
30	— 21	— 07	— 22	— 06	— 07
31	— 11	— 01	— 14	— 09	+ 01
32	— 20	— 12	— 20	— 12	— 06
33	— 05	— 08	+ 03	— 09	+ 16
34	— 10	+ 05	— 07	+ 07	+ 05
35	— 08	— 21	— 10	— 19	+ 01
36	— 16	— 21	— 07	— 15	+ 03
37	— 25	+ 07	— 14	+ 03	— 06
38	— 21	+ 05	— 18	+ 05	— 12
39	+ 10	— 06	+ 10	— 03	+ 14
40	+ 13	— 03	+ 04	— 03	+ 06
41	+ 10	— 05	+ 11	— 03	+ 10
42	— 03	+ 04	— 10	+ 02	— 13
43	00	+ 04	— 05	— 01	— 10

The first column contains the ordinal numbers of each period of 10 days, the second and fourth columns contain the half sums of U_B and U_W in the two suppositions: that the correction of the constant of collimation mentioned in §§ 8 and 9 has, or has not been applied. The degree of precision of these numbers can be derived from the values of half the differences $\frac{1}{2}(U_B - U_W)$ which, if the observations are correct, must be equal to 0.

I have formed the means from each set of three successive values of $^1/_2\,(U_B + U_W)$ and have represented them graphically in Fig. 2.

Fig. 2.



If we try to represent the numbers $^1/_2\,(U_B + U_W)$ of the 4th column by an ordinary sinusoid and, assuming that this formula is exact for the middle-epoch, we reckon the time t in days from May 19th 1888, we obtain the following formula for the influence of the motion of the pole on the azimuth of the meridian marks at Leiden:

$$U = 0^s.0148\ Sin\left(\frac{360}{430,66}\,t + 19^\circ.0\right)$$

Column 6 of table III gives the differences of the results according to this formula and the observed quantities in column 4. According to this formula the influence of the motion of the pole on the azimuth is 0 on April 26th 1888; at that moment the latitude of Leiden resulting from that periodic variation attained its maximum.

The amplitude a of the circular motion of the pole, is found from the amplitude of the variation of azimuth $0^s.0148$ by means of the formula

$$a = 15 \times 0.0148\ Cos\ \varphi = 0.''136$$

in which φ represents the latitude of Leiden.

If from this formula for the variation of latitude for Leyden we want to deduce that for the variation of latitude for Greenwich, we must only take for the date of the maximum latitude 5 days earlier i. e. April 21st 1888, so that the co-ordinates of the motion of the pole for Greenwich are:

$$x = +\,0''.136 \cos 2\pi \frac{t-2410749}{430.66}$$

$$y = -\,0''.136 \sin 2\pi \frac{t-2410749}{430.66}$$

in which t represents the Julian date.

11. If we compare this epoch for the maximum latitude of Greenwich with that deduced by Dr. E. F. v. d. S. Bakhuyzen, we see a difference of 2181 and after subtracting 5 periods or 2153 days, it appears that the epoch found by me occurs 28 days later than that according to Dr. E. F. v. d. S. Bakhuyzen.

In the Astronomische Nachrichten n⁰ 3207 A. Sokoloff has given the results of an investigation of the motion of the pole in a period of 430 days by means of the meridian marks of the transit-instrument in the observatory at Pulkowa. In order to compare his results with those found by me, I here give the results deduced by Sokoloff from the observations from 1880—1887 made by Wagner, Wittram and Harzer.

a. From 476 transits of α Ursae-Minoris
Amplitude = 0″.172
Epoch for Greenwich = 2410743
i. e. 22 days later than according to E. F. v. d. S. B.

b. From 288 transits of δ Ursae-Minoris:
Amplitude = 0″.195
Epoch for Greenwich = 2410771
i. e. 50 days later than according to E. F. v. d. S. B.

c. From 226 transits of 51 H. Cephei:
Amplitude = 0″.156
Epoch for Greenwich = 2410759
i. e. 38 days later than according to E. F. v. d. S. B.

In Sokoloff's computation the time of the period is assumed to be 429.7 days. The epoch of maximum latitude of Greenwich given above, has been reduced by me from the year 1884 to the year 1888 by using a period of 430.66 days.

Physics. — "*Considerations on Gravitation*". By Prof. H. A. LORENTZ.

§ 1. After all we have learned in the last twenty or thirty years about the mechanism of electric and magnetic phenomena, it is natural to examine in how far it is possible to account for the force of gravitation by ascribing it to a certain state of the aether. A theory of universal attraction, founded on such an assumption, would take the simplest form if new hypotheses about the aether could be avoided, i. e. if the two states which exist in an electric and a magnetic field, and whose mutual connection is expressed by the well known electromagnetic equations were found sufficient for the purpose.

If further it be taken for granted that only electrically *charged* particles or ions, are directly acted on by the aether, one is led to the idea that every particle of ponderable matter might consist of two ions with equal opposite charges — or at least might contain two such ions — and that gravitation might be the result of the forces experienced by these ions. Now that so many phenomena have been explained by a theory of ions, this idea seems to be more admissible than it was ever before.

As to the electromagnetic disturbances in the aether which migh possibly be the cause of gravitation, they must at all events be of such a nature, that they are capable of penetrating all ponderable bodies without appreciably diminishing in intensity. Now, electric vibrations of extremely small wave-length possess this property; hence the question arises what action there would be between two ions if the aether were traversed in all directions by trains of electric waves of small wave-length.

The above ideas are not new. Every physicist knows LE SAGE's theory in which innumerable small corpuscula are supposed to move with great velocities, producing gravitation by their impact against the coarser particles of ordinary ponderable matter. I shall not here discuss this theory which is not in harmony with modern physical views. But, when it had been found that a pressure against a body may be produced as well by trains of electric waves, by rays of light e. g., as by moving projectiles and when the RÖNTGEN-rays with their remarkable penetrating power had been discovered, it was natural to replace LE SAGE's corpuscula by vibratory motions. Why should there not exist radiations, far more penetrating than even the X-rays, and which might therefore serve to account for a force which as far as we know, is independent of all intervening ponderable matter?

I have deemed it worth while to put this idea to the test. In what follows, before passing to considerations of a different order (§ 5), I shall explain the reasons for which this theory of rapid vibrations as a cause of gravitation can *not* be accepted.

§ 2. Let an ion carrying a charge e, and having a certain mass, be situated at the point $P(x, y, z)$; it may be subject or not to an elastic force, proportional to the displacement and driving it back to P, as soon as it has left this position. Next, let the aether be traversed by electromagnetic vibrations, the dielectric displacement being denoted by $\mathfrak{d}$, and the magnetic force by $\mathfrak{H}$, then the ion will be acted on by a force

$$4 \pi V^2 e \mathfrak{d} ,$$

whose direction changes continually, and whose components are

$$\mathrm{X} = 4 \pi V^2 e \mathfrak{d}_x , \quad \mathrm{Y} = 4 \pi V^2 e \mathfrak{d}_y , \quad \mathrm{Z} = 4 \pi V^2 e \mathfrak{d}_z . \quad . \quad (1)$$

In these formulae V means the velocity of light.

By the action of the force (1) the ion will be made to vibrate about its original position P, the displacement (x, y, z) being determined by well known differential equations.

For the sake of simplicity we shall confine ourselves to simple harmonic vibrations with frequency n. All our formulae will then contain the factor $\cos nt$ or $\sin nt$, and the forced vibrations of the ion may be represented by expressions of the form

$$\left.\begin{aligned} \mathrm{x} &= a e \mathfrak{d}_x - b e \dot{\mathfrak{d}}_x , \\ \mathrm{y} &= a e \mathfrak{d}_y - b e \dot{\mathfrak{d}}_y , \\ \mathrm{z} &= a e \mathfrak{d}_z - b e \dot{\mathfrak{d}}_z , \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

with certain constant coefficients a and b. The terms with $\dot{\mathfrak{d}}_x$, $\dot{\mathfrak{d}}_y$ and $\dot{\mathfrak{d}}_z$ have been introduced in order to indicate that the phase of the forced vibration differs from that of the force (X, Y, Z); this will be the case as soon as there is a resistance, proportional to the velocity, and the coefficient b may then be shown to be positive. One cause of a resistance lies in the reaction of the aether, called forth by the radiation of which the vibrating ion itself becomes the centre, a reaction which determines at the same time an apparent increase of the mass of the particle. We shall suppose however that we have kept in view this reaction in establishing the equations of motion, and in assigning their values to the coefficients a and b.

Then, in what follows, we need only consider the forces due to the state of the aether, in so far as it not directly produced by the ion itself.

Since the formulae (2) contain e as a factor, the coefficients a and b will be independent of the charge; their sign will be the same for a negative ion and for a positive one.

Now, as soon as the ion has shifted from its position of equilibrium, new forces come into play. In the first place, the force $4\pi V^2 e\,\mathfrak{d}$ will have changed a little, because, for the new position, $\mathfrak{d}$ will be somewhat different from what it was at the point P. We may express this by saying that, in addition to the force (1), there will be a new one with the components

$$4\pi V^2 e\left(\mathrm{x}\frac{\partial \mathfrak{d}_x}{\partial x} + \mathrm{y}\frac{\partial \mathfrak{d}_x}{\partial y} + \mathrm{z}\frac{\partial \mathfrak{d}_x}{\partial z}\right), \text{ etc.} \quad . \quad . \quad . \qquad (3)$$

In the second place, in consequence of the velocity of vibration, there will be an electromagnetic force with the components

$$e\,(\dot{\mathrm{y}}\,\mathfrak{H}_z - \dot{\mathrm{z}}\,\mathfrak{H}_y)\,, \text{ etc.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

If, as we shall suppose, the displacement of the ion be very small, compared with the wave-length, the forces (3) and (4) are much smaller than the force (1); since they are periodic — with the frequency $2n$, — they will give rise to new vibrations of the particle. We shall however omit the consideration of these slight vibrations, and examine only the mean values of the forces (3) and (4), calculated for a rather long lapse of time, or, what amounts to the same thing, for a full period $\frac{2\pi}{n}$.

§ 3. It is immediately clear that this mean force will be 0 if the ion is *alone* in a field in which the propagation of waves takes place equally in all directions. It will be otherwise, as soon as a second ion Q has been placed in the neighbourhood of P; then, in consequence of the vibrations emitted by Q after it has been itself put in motion, there may be a force on P, of course in the direction of the line QP. In computing the value of this force, one finds a great number of terms, which depend in different ways on the distance r. We shall retain those which are inversely proportional to r or r^2, but we shall neglect all terms varying inversely as the higher powers of r; indeed, the influence of these, compared with that of the first mentioned terms will be of the order $\frac{\lambda}{r}$, if λ is the wave-length, and we shall suppose this to be a very small fraction. We shall also omit all terms containing such factors as $\cos 2\pi k \frac{r}{\lambda}$ or $\sin 2\pi k \frac{r}{\lambda}$ (k a moderate number). These reverse their signs by a very small change in r; they will therefore disappear from the resultant force, as soon as, instead of *single* particles P and Q, we come to consider systems of particles with dimensions many times greater than the wave-length.

From what has been said, we may deduce in the first place that, in applying the above formulae to the ion P, it is sufficient, to take for $\mathfrak{d}$ and $\mathfrak{H}$ the vectors that would exist if P were removed from the field. In each of these vectors two parts are to be distinguished. We shall denote by $\mathfrak{d}_1$ and $\mathfrak{H}_1$ the parts existing independently of Q, and by $\mathfrak{d}_2$ and $\mathfrak{H}_2$ the parts due to the vibrations of this ion.

Let Q be taken as origin of coordinates, QP as axis of x, and let us begin with the terms in (2) having the coefficient a.

To these corresponds a force on P, whose first component is

$$4\pi V^2 e^2 a \left(\mathfrak{d}_x \frac{\partial \mathfrak{d}_x}{\partial x} + \mathfrak{d}_y \frac{\partial \mathfrak{d}_x}{\partial y} + \mathfrak{d}_z \frac{\partial \mathfrak{d}_x}{\partial z}\right) + e^2 a (\dot{\mathfrak{d}}_y \mathfrak{H}_z - \dot{\mathfrak{d}}_z \mathfrak{H}_y) \quad . \quad . \quad (5)$$

Since we have only to deal with the mean values for a full period, we may write for the last term

$$-e^2 a (\mathfrak{d}_y \dot{\mathfrak{H}}_z - \mathfrak{d}_z \dot{\mathfrak{H}}_y),$$

and if, in this expression, $\dot{\mathfrak{H}}_y$ and $\dot{\mathfrak{H}}_z$ be replaced by

$$4\pi V^2 \left(\frac{\partial \mathfrak{d}_z}{\partial x} - \frac{\partial \mathfrak{d}_x}{\partial z}\right) \quad \text{and} \quad 4\pi V^2 \left(\frac{\partial \mathfrak{d}_x}{\partial y} - \frac{\partial \mathfrak{d}_y}{\partial x}\right),$$

(5) becomes

$$2\pi V^2 e^2 a \frac{\partial(\mathfrak{d}^2)}{\partial x}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where $\mathfrak{d}$ is the numerical value of the dielectric displacement.

Now, $\mathfrak{d}^2$ will consist of three parts, the first being $\mathfrak{d}_1^2$, the second $\mathfrak{d}_2^2$ and the third depending on the combination of $\mathfrak{d}_1$ and $\mathfrak{d}_2$.

Evidently, the value of (6), corresponding to the first part, will be 0.

As to the second part, it is to be remarked that the dielectric displacement, produced by Q, is a periodic function of the time. At distant points the amplitude takes the form $\frac{c}{r}$, where c is independent of r. The mean value of $\mathfrak{d}^2$ for a full period is $\frac{1}{2}\frac{c^2}{r^2}$ and by differentiating this with regard to x or to r, we should get r^3 in the denominator.

The terms in (6) which correspond to the part

$$2\left(\mathfrak{d}_{1x}\,\mathfrak{d}_{2x} + \mathfrak{d}_{1y}\,\mathfrak{d}_{2y} + \mathfrak{d}_{1z}\,\mathfrak{d}_{2z}\right)$$

in $\mathfrak{d}^2$, may likewise be neglected. Indeed, if these terms are to contain no factors such as $\cos 2\pi k\frac{r}{\lambda}$ or $\sin 2\pi k\frac{r}{\lambda}$, there must be between $\mathfrak{d}_1$ and $\mathfrak{d}_2$, either no phase-difference at all, or a difference which is independent of r. This condition can only be fulfilled, if a system of waves, proceeding in the direction of QP, is combined with the vibrations excited by Q, in so far as this ion is put in motion by that system itself. Then, the two vectors $\mathfrak{d}_1$ and $\mathfrak{d}_2$ will have a common direction perpendicular to QP, say that of the axis of y, and they will be of the form

$$\mathfrak{d}_{1y} = q\cos n\left(t - \frac{x}{V} + \varepsilon_1\right)$$

$$\mathfrak{d}_{2y} = \frac{c}{r}\cos n\left(t - \frac{x}{V} + \varepsilon_2\right).$$

The mean value of $\mathfrak{d}_{1y}\,\mathfrak{d}_{2y}$ is

$$\frac{1}{2}\frac{qc}{r}\cos n\left(\varepsilon_1 - \varepsilon_2\right),$$

and its differential coefficient with regard to x has r^2 in the denominator. It ought therefore to be retained, were it not for the extremely small intensity of the systems of waves which give rise to such a result. In fact, by the restriction imposed on them as to their direction, these waves form no more than a very minute part of the whole motion.

§ 4. So, it is only the terms in (2), with the coefficient b, with which we are concerned. The corresponding forces are

$$-4\pi V^2 e^2 b\left(\dot{\mathfrak{d}}_x\frac{\partial \mathfrak{d}_x}{\partial x} + \dot{\mathfrak{d}}_y\frac{\partial \mathfrak{d}_x}{\partial y} + \mathfrak{d}_z\frac{\partial \mathfrak{d}_x}{\partial z}\right) \quad . \quad . \quad . \quad (7)$$

and

$$-e^2 b\left(\ddot{\mathfrak{d}}_y\,\mathfrak{H}_z - \ddot{\mathfrak{d}}_z\,\mathfrak{H}_y\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

If Q were removed, these forces together would be 0, as has already been remarked. On the other hand, the force (8), taken by itself, would then likewise be 0. Indeed, its value is

$$n^2 e^2 b \, (\mathfrak{d}_y \, \mathfrak{H}_z - \mathfrak{d}_z \, \mathfrak{H}_y) \, , \quad . \; . \; . \; . \; . \; . \; . \; . \quad (9)$$

or, by POYNTING's theorem $\frac{n^2 e^2 b}{V^2} \, S_x$, if S_x be the flow of energy in a direction parallel to the axis of x. Now, it is clear that, in the absence of Q, any plane must be traversed in the two directions by equal amounts of energy.

In this way we come to the conclusion that the force (7), in so far as it depends on the part $(\mathfrak{d}_1)$, is 0, and from this it follows that the total value of (7) will vanish, because the part arising from the combination of $(\mathfrak{d}_1)$ and $(\mathfrak{d}_2)$, as well as that which is solely due to the vibrations of Q, are 0. As to the first part, this may be shown by a reasoning similar to that used at the end of the preceding §. For the second part, the proof is as follows.

The vibrations excited by Q in any point A of the surrounding aether are represented by expressions of the form

$$\frac{1}{r} \, \vartheta \cos n \left(t - \frac{r}{V} + \varepsilon \right),$$

where ϑ depends on the direction of the line QA, and r denotes the length of this line. If, in differentiating such expressions, we wish to avoid in the denominator powers of r, higher than the first — and this is necessary, in order that (7) may remain free from powers higher than the second — $\frac{1}{r}$ and ϑ have to be treated as constants. Moreover, the factors ϑ are such, that the vibrations are perpendicular to the line QA. If, now, A coincides with P, and QA with the axis of x, in the expression for $\mathfrak{d}_x$ we shall have $\vartheta = 0$, and since this factor is not to be differentiated, all terms in (7) will vanish.

Thus, the question reduces itself to (8) or (9). If, in this last expression, we take for $\mathfrak{d}$ and $\mathfrak{H}$ their real values, modified as they are by the motion of Q, we may again write for the force

$$\frac{n^2 e^2 b}{V^2} \, S_x \, ;$$

this time, however, we have to understand by S_x the flow of energy as it is in the actual case.

Now, it is clear that, by our assumptions, the flow of energy must be symmetrical all around Q; hence, if an amount E of energy traverses, in the outward direction, a spherical surface described around Q as centre with radius r, we shall have

$$S_x = \frac{E}{4 \pi r^2},$$

and the force on P will be

$$K = \frac{n^2 e^2 b E}{4 \pi V^2 r^2}.$$

It will have the direction of QP prolonged.

In the space surrounding Q the state of the aether will be stationary; hence, two spherical surfaces enclosing this particle must be traversed by equal quantities of energy. The quantity E will be independent of r, and the force K inversely proportional to the square of the distance.

If the vibrations of Q were opposed by no other resistance but that which results from radiation, the total amount of electro-magnetic energy enclosed by a surface surrounding Q would remain constant; E and K would then both be 0. If, on the contrary, in addition to the just mentioned resistance, there were a resistance of a different kind, the vibrations of Q would be accompanied by a continual loss of electro-magnetic energy; less energy would leave the space within one of the spherical surfaces than would enter that space. E would be negative, and, since b is positive, there would be attraction. It would be independent of the signs of the charges of P and Q.

The circumstance however, that this attraction could only exist, if in some way or other electromagnetic energy were continually disappearing, is so serious a difficulty, that what has been said cannot be considered as furnishing an explanation of gravitation. Nor is this the only objection that can be raised. If the mechanism of gravitation consisted in vibrations which cross the aether with the velocity of light, the attraction ought to be modified by the motion of the celestial bodies to a much larger extent than astronomical observations make it possible to admit.

§ 5. Though the states of the aether, the existence and the laws of which have been deduced from electromagnetic phenomena, are found insufficient to account for universal attraction, yet one may try to establish a theory which is not wholly different from that of electricity, but has some features in common with it. In order to obtain a theory of this kind, I shall start from an idea that has been suggested long ago by MOSSOTTI and has been afterwards accepted by WILHELM WEBER and ZÖLLNER.

According to these physicists, every particle of ponderable matter consists of two oppositely electrified particles. Thus, between two particles of matter, there will be four electric forces, two attractions between the charges of different, and two repulsions between those of equal signs. MOSSOTTI supposes the attractions to be somewhat greater than the repulsions, the difference between the two being precisely what we call gravitation. It is easily seen that such a difference might exist in cases where an action of a specific electric nature is not exerted.

Now, if the form of this theory is to be brought into harmony with the present state of electrical science, we must regard the four forces of MOSSOTTI as the effect of certain states in the aether which are called forth by the positive and negative ions.

A positive ion, as well as a negative one, is the centre of a dielectric displacement, and, in treating of electrical phenomena, these two displacements are considered as being of the same nature, so that, if in opposite directions and of equal magnitude, they wholly destroy each other.

If gravitation is to be included in the theory, this view must be modified. Indeed, if the actions exerted by positive and negative ions depended on vector-quantities of the same kind, in such a way that all phenomena in the neighbourhood of a pair of ions with opposite charges were determined by the resulting vector, then electric actions could only be absent, if this resulting vector were 0, but, if such were the case, no other actions could exist; a gravitation, i. e. a force in the absence of an electric field, would be impossible.

I shall therefore suppose that the two disturbances in the aether, produced by positive and negative ions, are of a somewhat different nature, so that, even if they are represented in a diagram by equal and opposite vectors, the state of the aether is not the natural one. This corresponds in a sense to MOSSOTTI's idea that positive and negative charges differ from each other to a larger extent, than may be expressed by the signs + and —.

After having attributed to each of the two states an independent and separate existence, we may assume that, though both able to act on positive and negative ions, the one has more power over the positive particles and the other over the negative ones. This difference will lead us to the same result that **Mossotti** attained by means of the supposed inequality of the attractive and the repulsive forces.

§ 6. I shall suppose that each of the two disturbances of the aether is propagated with the velocity of light, and, taken by itself, obeys the ordinary laws of the electromagnetic field. These laws are expressed in the simplest form if, besides the dielectric displacement $\mathfrak{d}$, we consider the magnetic force $\mathfrak{H}$, both together determining, as we shall now say, *one* state of the aether or one field. In accordance with this, I shall introduce two pairs of vectors, the one $\mathfrak{d}$, $\mathfrak{H}$ belonging to the field that is produced by the positive ions, whereas the other pair $\mathfrak{d}'$, $\mathfrak{H}'$ serve to indicate the state of the aether which is called into existence by the negative ions. I shall write down two sets of equations, one for $\mathfrak{d}$, $\mathfrak{H}$, the other for $\mathfrak{d}'$, $\mathfrak{H}'$, and having the form which I have used in former papers [1]) for the equations of the electromagnetic field, and which is founded on the assumption that the ions are perfectly permeable to the aether and that they can be displaced without dragging the aether along with them.

I shall immediately take this general case of moving particles.

Let us further suppose the charges to be distributed with finite volume-density, and let the units in which these are expressed be chosen in such a way that, in a body which exerts no electrical actions, the total amount of the positive charges has the same numerical value as that of the negative charges.

Let ϱ be the density of the positive, and ϱ' that of the negative charges, the first number being positive and the second negative.

Let $\mathfrak{v}$ (or $\mathfrak{v}'$) be the velocity of an ion.

Then the equations for the state ($\mathfrak{d}$, $\mathfrak{H}$) are [2])

$$\left.\begin{aligned} Div\ \mathfrak{d} &= \varrho \\ Div\ \mathfrak{H} &= 0 \\ Rot\ \mathfrak{H} &= 4\pi\varrho\mathfrak{v} + 4\pi\dot{\mathfrak{d}} \\ 4\pi V^2\ Rot\ \mathfrak{d} &= -\dot{\mathfrak{H}}\ ; \end{aligned}\right\} \quad \ldots\ldots \quad (I)$$

---

[1]) **Lorentz.** La théorie électromagnétique de **Maxwell** et son application aux corps mouvants, Arch. Néerl. XXV, p. 363; Versuch einer Theorie der electrischen und optischen Erscheinungen in bewegten Körpern.

[2]) $Div\ \mathfrak{d} = \frac{\partial \mathfrak{d}_x}{\partial x} + \frac{\partial \mathfrak{d}_y}{\partial y} + \frac{\partial \mathfrak{d}_z}{\partial z}$.

$Rot\ \mathfrak{d}$ is a vector, whose components are $\frac{\partial \mathfrak{d}_z}{\partial y} - \frac{\partial \mathfrak{d}_y}{\partial z}$, etc.

and those for the state $(\mathfrak{d}', \mathfrak{H}')$

$$\left.\begin{array}{c} Div\ \mathfrak{d}' = \varrho' \\ Div\ \mathfrak{H}' = 0 \\ Rot\ \mathfrak{H}' = 4\,\pi\,\varrho'\,\mathfrak{v}' + 4\,\pi\,\dot{\mathfrak{d}}' \\ 4\,\pi\,V^2\,Rot\ \mathfrak{d}' = -\,\dot{\mathfrak{H}}'. \end{array}\right\} \quad \ldots\ldots \quad (II)$$

In the ordinary theory of electromagnetism, the force acting on a particle, moving with velocity $\mathfrak{v}$, is

$$4\,\pi\,V^2\,\mathfrak{d} + [\mathfrak{v}\,.\,\mathfrak{H}]\,,$$

per unit charge [1]).

In the modified theory, we shall suppose that a positively electrified particle with charge e experiences a force

$$k_1 = \alpha\,\{4\,\pi\,V^2\,\mathfrak{d} + [\mathfrak{v}\,.\,\mathfrak{H}]\}\,e\,. \quad \ldots\ldots \quad (10)$$

on account of the field $(\mathfrak{d}, \mathfrak{H})$, and a force

$$k_2 = \beta\,\{4\,\pi\,V^2\,\mathfrak{d}' + [\mathfrak{v}\,.\,\mathfrak{H}']\}\,e \quad \ldots\ldots \quad (11)$$

on account of the field $(\mathfrak{d}'\ \mathfrak{H}')$, the positive coefficients α and β having slightly different values.

For the forces, exerted on a negatively charged particle I shall write

$$k_3 = \beta\,\{4\,\pi\,V^2\,\mathfrak{d} + [\,\mathfrak{v}'.\,\mathfrak{H}]\}\,e' \quad \ldots\ldots \quad (12)$$

and

$$k_4 = \alpha\,\{4\,\pi\,V^2\,\mathfrak{d}' + [\mathfrak{v}'\,.\,\mathfrak{H}']\}\,e', \quad \ldots\ldots \quad (13)$$

expressing by these formulae that e is acted on by $(\mathfrak{d}, \mathfrak{H})$ in the same way as e' by $(\mathfrak{d}', \mathfrak{H}')$, and vice versa.

§ 7. Let us next consider the actions exerted by a *pair* of oppositely charged ions, placed close to each other, and remaining so during their motion. For convenience of mathematical treatment, we may even reason as if the two charges penetrated each other, so that, if they are equal, $\varrho' = -\,\varrho$.

---

[1]) $[\mathfrak{v}\,.\,\mathfrak{H}]$ is the vector-product of $\mathfrak{v}$ and $\mathfrak{H}$.

On the other hand $\mathfrak{v}' = \mathfrak{v}$; hence, by (I) and (II),

$$\mathfrak{d}' = -\mathfrak{d} \quad \text{and} \quad \mathfrak{H}' = -\mathfrak{H}.$$

Now let us put in the field, produced by the pair of ions, a similar pair with charges e and $e' = -e$, and moving with the common velocity $\mathfrak{v}$. Then, by (10)—(13),

$$k_2 = -\frac{\beta}{\alpha} k_1 \quad , \quad k_3 = -\frac{\beta}{\alpha} k_1 \quad , \quad k_4 = k_1.$$

The total force on the positive particle will be

$$k_1 + k_2 = k_1 \left(1 - \frac{\beta}{\alpha}\right)$$

and that on the negative ion

$$k_3 + k_4 = k_1 \left(1 - \frac{\beta}{\alpha}\right).$$

These forces being equal and having the same direction, there is no force tending to *separate* the two ions, as would be the case in an *electric field.* Nevertheless, the pair is acted on by a resultant force

$$2\, k_1 \left(1 - \frac{\beta}{\alpha}\right).$$

If now β be somewhat larger than α, the factor $2\left(1 - \frac{\beta}{\alpha}\right)$ will have a certain negative value $-\varepsilon$, and our result may be expressed as follows:

If we wish to determine the action between two ponderable bodies, we may first consider the forces existing between the positive ions in the one and the positive ions in the other. We then have to reverse the direction of these forces, and to multiply them by the factor ε. Of course, we are led in this way to NEWTON's law of gravitation.

The assumption that all ponderable matter is composed of positive and negative ions is no essential part of the above theory. We might have confined ourselves to the supposition that the state of the aether which is the cause of gravitation is propagated in a similar way as that which exists in the electromagnetic field.

Instead of introducing two pairs of vectors ($\mathfrak{d}$, $\mathfrak{H}$) and ($\mathfrak{d}'$, $\mathfrak{H}'$), both of which come into play in the electromagnetic actions, as well as in the phenomenon of gravitation, we might have assumed one pair for the electromagnetic field and one for universal attraction.

For these latter vectors, say $\mathfrak{d}$, $\mathfrak{H}$, we should then have established the equations (I), ϱ being the density of ponderable matter, and for the force acting on unit mass, we should have put

$$-\eta\left\{4\pi V^2 \mathfrak{d} + [\mathfrak{v} \,.\, \mathfrak{H}]\right\},$$

where η is a certain positive coefficient.

§ 8. Every theory of gravitation has to deal with the problem of the influence, exerted on this force by the motion of the heavenly bodies. The solution is easily deduced from our equations; it takes the same form as the corresponding solution for the electromagnetic actions between charged particles [1]).

I shall only treat the case of a body A, revolving around a central body M, this latter having a given constant velocity p. Let r be the line MA, taken in the direction from M towards A, x, y, z the relative coordinates of A with respect to M, w the velocity of A's motion relatively to M, ϑ the angle between w and p, finally p_r the component of p in the direction of r.

Then, besides the attraction

$$\frac{k}{r^2}, \quad \ldots\ldots\ldots\ldots \quad (14)$$

which would exist if the bodies were both at rest, A will be subject to the following actions.

1st. A force

$$k \,.\, \frac{p^2}{2V^2} \,.\, \frac{1}{r^2} \quad \ldots\ldots\ldots\ldots \quad (15)$$

in the direction of r.

2nd. A force whose components are

$$-\frac{k}{2V^2}\frac{\partial}{\partial x}\left(\frac{p_r^2}{r}\right), \quad -\frac{k}{2V^2}\frac{\partial}{\partial y}\left(\frac{p_r^2}{r}\right), \quad -\frac{k}{2V^2}\frac{\partial}{\partial z}\left(\frac{p_r^2}{r}\right) \quad . \quad (16)$$

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[1]) See the second of the above cited papers.

3rd. A force

$$-\frac{k}{V^2}p \cdot \frac{1}{r^2}\frac{dr}{dt}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

parallel to the velocity p.

4th. A force

$$\frac{k}{V^2}\frac{1}{r^2}p\,w\cos\vartheta, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

in the direction of r.

Of these, (15) and (16) depend only on the common velocity p, (17) and (18) on the contrary, on p and w conjointly.

It is further to be remarked that the additional forces (15)—(18) are all of the second order with respect to the small quantities

$$\frac{p}{V} \text{ and } \frac{w}{V}.$$

In so far, the law expressed by the above formulae presents a certain analogy with the laws proposed by WEBER, RIEMANN and CLAUSIUS for the electromagnetic actions, and applied by some astronomers to the motions of the planets. Like the formulae of CLAUSIUS, our equations contain the absolute velocities, i. e. the velocities, relatively to the aether.

There is no doubt but that, in the present state of science, if we wish to try for gravitation a similar law as for electromagnetic forces, the law contained in (15)—(18) is to be preferred to the three other just mentioned laws.

§ 9. The forces (15)—(18) will give rise to small inequalities in the elements of a planetary orbit; in computing these, we have to take for p the velocity of the Sun's motion through space. I have calculated the *secular* variations, using the formulae communicated by TISSERAND in his Mécanique céleste.

Let a be the mean distance to the sun,

e the eccentricity,

φ the inclination to the ecliptic,

θ the longitude of the ascending node,

$\tilde{\omega}$ the longitude of perihelion,

$\varkappa'$ the mean anomaly at time $t = 0$, in this sense that, if n

be the mean motion, as determined by a, the mean anomaly at time t is given by

$$z' + \int_0^t n \, dt.$$

Further, let λ, μ and ν be the direction-cosines of the velocity p with respect to: 1st. the radius vector of the perihelion, 2nd. a direction which is got by giving to that radius vector a rotation of 90°, in the direction of the planet's revolution, 3rd. the normal to the plane of the orbit, drawn towards the side whence the planet is seen to revolve in the same direction as the hands of a watch.

Put $\omega = \bar{\omega} - \theta$, $\frac{p}{V} = \delta$ and $\frac{n\,a}{V} = \delta'$ ($n\,a$ is the velocity in a circular orbit of radius a).

Then I find for the variations *during one revolution*

$$\Delta\, a = 0$$

$$\Delta\, e = 2\,\pi \sqrt{(1-e^2)} \left\{ \lambda\, \mu\, \delta^2 \frac{(2-e^2) - 2\sqrt{(1-e^2)}}{e^3} - \lambda\, \delta \delta' \frac{1-\sqrt{(1-e^2)}}{e^2} \right\}$$

$$\Delta \varphi = \frac{2\pi}{\sqrt{(1-e^2)}}\, \nu \left\{ [-\lambda \delta^2 \cos\omega + \delta\,(e\delta' - \mu\delta) \sin\omega]\, \frac{1-\sqrt{(1-e^2)}}{e^2} + \mu \delta^2 \sin\omega \right\}$$

$$\Delta\, \theta = - \frac{2\,\pi}{\sqrt{(1-e^2)}\sin\varphi}\, \nu \left\{ [\lambda\, \delta^2 \sin\omega + \delta\,(e\,\delta' - \mu\,\delta) \cos\omega]\, \frac{1-\sqrt{(1-e^2)}}{e^2} + \right.$$

$$\left. + \mu\, \delta^2 \cos\omega \right\}$$

$$\Delta\, \bar{\omega} = \pi\,(\mu^2 - \lambda^2)\, \delta^2 \frac{(2-e^2) - 2\sqrt{(1-e^2)}}{e^4} + 2\,\pi\,\mu\,\delta\delta' \frac{\sqrt{(1-e^2)} - 1}{e^3} -$$

$$- \frac{2\,\pi\, tg\, \frac{1}{2}\varphi}{\sqrt{(1-e^2)}}\, \nu \left\{ [\lambda\, \delta^2 \sin\omega + \delta\,(e\,\delta' - \mu\,\delta) \cos\omega]\, \frac{1-\sqrt{(1-e^2)}}{e^2} + \mu\, \delta^2 \cos\omega \right\}$$

$$\Delta\, z' = \pi\,(\lambda^2 - \mu^2)\, \delta^2 \frac{(2+e^2)\sqrt{(1-e^2)} - 2}{e^4} - 2\,\pi\,\delta^2 - 2\,\pi\,\mu^2\,\delta^2 -$$

$$- 2\,\pi\,\mu\,\delta\,\delta' \frac{(1-e^2) - \sqrt{(1-e^2)}}{e^3}.$$

§ 10. I have worked out the case of the planet Mercury, taking 276° and + 34° for the right ascension and declination of the apex of the Sun's motion. I have got the following results :

$$\Delta a = 0$$

$$\Delta e = 0{,}018\,\delta^2 + 1{,}38\,\delta\,\delta'$$

$$\Delta \varphi = 0{,}95\,\delta^2 + 0{,}28\,\delta\,\delta'$$

$$\Delta \theta = 7{,}60\,\delta^2 - 4{,}26\,\delta\,\delta'$$

$$\Delta \bar{\omega} = -\,0{,}09\,\delta^2 + 1{,}95\,\delta\,\delta'$$

$$\Delta \varkappa' = -\,6{,}82\,\delta^2 - 1{,}93\,\delta\,\delta'$$

Now, $\delta' = 1{,}6 \times 10^{-4}$ and, if we put $\delta = 5{,}3 \times 10^{-5}$, we get

$$\Delta e = 117 \times 10^{-10} \quad , \quad \Delta\varphi = 51 \times 10^{-10},$$

$$\Delta\theta = -\,137 \times 10^{-10}, \quad \Delta\bar{\omega} = 162 \times 10^{-10}, \quad \Delta\varkappa' = -\,355 \times 10^{-10}.$$

The changes that take place in a century are found from these numbers, if we multiply them by 415, and, if the variations of φ, θ, $\bar{\omega}$ and $\varkappa'$ are to be expressed in seconds, we have to introduce the factor $2{,}06 \times 10^5$. The result is, that the changes in φ, θ, $\bar{\omega}$ and $\varkappa'$ amount to a few seconds, and that in e to 0,000005.

Hence we conclude that our modification of NEWTON's law cannot account for the observed inequality in the longitude of the perihelion — as WEBER's law can to some extent do — but that, if we do not pretend to explain this inequality by an alteration of the law of attraction, there is nothing against the proposed formulae. Of course it will be necessary to apply them to other heavenly bodies, though it seems scarcely probable that there will be found any case in which the additional terms have an appreciable influence.

The special form of these terms may perhaps be modified. Yet, what has been said is sufficient to show that gravitation may be attributed to actions which are propagated with no greater velocity than that of light.

As is well known, LAPLACE has been the first to discuss this question of the velocity of propagation of universal attraction, and later astronomers have often treated the same problem. Let a body B be attracted by a body A, moving with the velocity p. Then, if the action is propagated with a finite velocity V, the influence which reaches B at time t, will have been emitted by A at an anterior moment, say $t - \tau$. Let A_1 be the position of the acting body at this moment, A_2 that at time t. It is an easy matter to calculate the distance between these positions. Now, if the action at time

t is calculated, as if A had continued to occupy the position A_1, one is led to an influence on the astronomical motions of the order $\frac{p}{V}$; if V were equal to the velocity of light, this influence would be much greater than observations permit us to suppose. If, on the contrary, the terms with $\frac{p}{V}$ are to have admissible values, V ought to be many millions of times as great as the velocity of light.

From the considerations in this paper, it appears that this conclusion can be avoided. Changes of state in the aether, satisfying equations of the form (I), are propagated with the velocity V; yet, no quantities of the first order $\frac{p}{V}$ or $\frac{w}{V}$ (§ 8), but only terms containing $\frac{p^2}{V^2}$ and $\frac{pw}{V^2}$ appear in the results. This is brought about by the peculiar way — determined by the equations — in which moving matter changes the state of the aether; in the above mentioned case the condition of the aether will *not* be what it would have been, if the acting body were at rest in the position A_1.

Physiology. — "*On the power of resistance of the red blood corpuscles*". By Dr. H. J. HAMBURGER.

(Will be published in the Proceedings of the next meeting.)

Physics. — "*On the critical isotherm and the densities of saturated vapour and liquid in the case of isopentane and carbonic acid*". By Dr. J. E. VERSCHAFFELT (Communicated by Prof. H. KAMERLINGH ONNES).

(Will be published in the Proceedings of the next meeting).

(April 25, 1900.)

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday April 21, 1900.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 21 April 1900 Dl. VIII).

CONTENTS: „Solar Phenomena, considered in connection with Anomalous Dispersion of Light." By Prof. W. H. JULIUS, p. 575. — „On the critical Isothermal Line and the densities of Saturated vapour and Liquid in Isopentane and Carbon dioxide." By Dr. J. E. VERSCHAFFELT (Communicated by Prof. H. KAMERLINGH ONNES), p. 588 (With one plate). — „The theorem of JOACHIMSTHAL of the Normal curves." By Prof. P. H. SCHOUTE, p. 593. — „Approximation formulae concerning the prime numbers not exceeding a given limit." By Prof. J. C. KLUYVER, p. 599. — „Thermodynamics of Standard Cells (1st Part)." By Dr. ERNST COHEN (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM), p. 610. — „Studies on Inversion (1st Part)". By Dr. ERNST COHEN (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM), p. 618. — „Determinations of the diminution of Vapour-pressure and of the elevation of the Boiling-point of dilute Solutions." By Dr. A. SMITS (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM), p. 635. — „Some reflexes on the Respiration in connection with LABORDE's method to restore, by rhythmical traction of the Tongue, the respiration suppressed in Narcosis." By M. A. VAN MELLE (Communicated by Prof. C. WINKLER). (With one plate), p. 640. — „Echinopsine, a new crystalline vegetable base." By Dr. M. GRESHOFF (Communicated by Prof. A. P. N. FRANCHIMONT), p. 645. — „The constitution of the vapourphase in the system: Water-Phenol, with one or two liquidphases." By Dr. F. A. H. SCHREINEMAKERS (Communicated by Prof. J. M. VAN BEMMELEN), p. 645.

The following papers were read:

Physics. — "*Solar Phenomena, considered in connection with Anomalous Dispersion of Light*". By Prof. W. H. JULIUS.

(Read February 24, 1900.)

The rule that the propagation of light is, in all directions, rectilinear, holds only for quite homogeneous media. If various considerations lead us to assume that the solar rays on their course penetrate media of unequal density, or of different composition, the rays must be curved, and the supposition that the observed light is emitted by objects situated in the direction of vision becomes untenable.

Now, though no one doubts the unequal distribution of matter in and near the sun, yet in theories concerning this celestial body hardly any attention has been paid to refraction. The study of atmospheric refraction had, long since, made us acquainted with the laws of curved rays [1]), but the first important attempt to investigate the influence which refraction in the sun itself must have had on the course of the rays, which reach our eye, and consequently on the optical image we get of it, was made by Dr. A. SCHMIDT. His paper „Die Strahlenbrechung auf der Sonne; ein geometrischer Beitrag zur Sonnenphysik" [2]) leads to very remarkable results, and at any rate urges the necessity of submitting the existing theories of the sun to a severe criticism from this point of view.

If it is taken for granted that refraction in the solar atmosphere must be taken into account, we must also pay attention to those special cases in which extraordinary values — great or small — of the refractive index occur; in other words, the phenomenon of anomalous dispersion must be reckoned with.

It is my purpose to show that many peculiarities, which have been observed at the border of the sun and in the spots, may easily be considered as caused by anomalous dispersion.

It is not difficult to obtain the experimental evidence that the index of refraction of sodium vapour for light differing but slightly in wavelength from that for the *D*-lines, is very different from the index for the other rays of the spectrum.

H. BECQUEREL (C. R. 127, p. 399; and 128, p. 145) used for the study of the phenomenon KUNDT's method of crossed prisms, in a slightly modified manner. The image of the crater of an arc-light was projected on a horizontal slit, placed in the focus of a collimator-lens. The parallel beam next passed through a sodium flame, which BECQUEREL had succeeded in giving the form of a prism with horizontal refracting edge, and was then, through a telescope lens, focussed into an image of the horizontal slit, falling exactly on the vertical slit of a spectroscope of rather great dispersion. As long as the sodium flame was absent, a continuous spectrum was seen in the spectroscope, the height of which naturally depended on the width of the horizontal slit. When the flame was introduced in its proper place, and good care was taken to limit the parallel beam by means of an easily adjusted diaphragm, in such a manner that only such light could penetrate into the telescope lens as had passed a properly prismatical part of the flame, the spectrum clearly

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[1]) The litterature on this subject is to be found i. a. in a dissertation by O. WIENER, Wied. Ann. 49, p. 105-149, 1893.

[2]) Stuttgart, Verlag von J. B. METZLER 1891.

exhibited the anomalous dispersion. On either side of the two dark sodium lines the originally horizontal spectrum-band was boldly curved, so that for rays with wave-lengths, slightly larger than λ_{D_1} or λ_{D_2} the sodium vapour appeared to possess an index of refraction rapidly increasing in the neighbourhood of an absorption-line; whereas for rays of wave-lengths, slightly smaller than λ_{D_1} or λ_{D_2}, the index of refraction rapidly decreased when approaching the absorption-lines. The amount of the anomalous dispersion near D_2 exceeded that near D_1.

In repeating this experiment I obtained materially the same results. Moreover, I noticed a peculiarity in the phenomenon, not mentioned by BECQUEREL, and not exhibited in the diagrams accompanying his paper. BECQUEREL states, that when he introduced a flame, rich in sodium, the lines D_1 and D_2 appeared as broad, dark bands, and that on either side of both bands the spectrum was curved. According to his diagrams these displacements only refer to light, outside the bands; the rays inside this region, in the more immediate neighbourhood of the D-lines, are totally wanting. Fig. 1 refers to a prismatic part of the flame, edge upwards; fig. 2, to a prismatic part, edge downwards. Both cases represent the image as seen in a telescope, so, reversed.

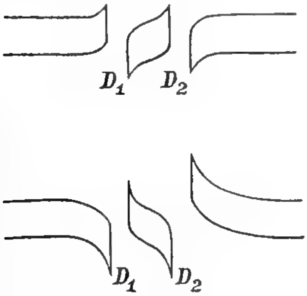

Fig. 1 and 2.

I myself, however, have observed the phenomenon in the form of fig. 3. The dotted lines indicate the places of D_1 and D_2. When the electric light is intercepted by means of a screen introduced between the flame and the horizontal slit, the D-lines appear in those places as two faintly luminous, sharply defined slit-images. The light is faint because the flame is placed at a distance of more than 70 cms. from the vertical slit, and its radiation is all but intercepted by the

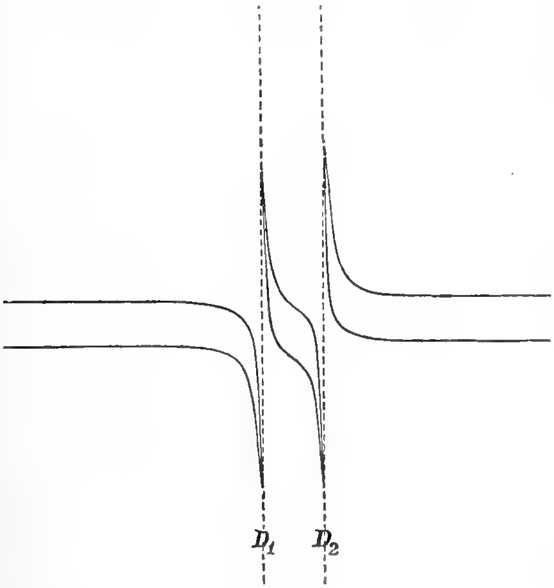

Fig. 3.

adjustable diaphragm, which allows only a beam of a cross-section of about 0.2 cm^2. to enter the telescope lens.

When next the arc light is allowed to cross the flame, the spectrum of fig. 3 appears with such intensity, that the bright sodium lines are undistinguishable in the centre of the dark bands. In the upper and lower parts of the field of vision however, they can yet be seen as continuations of the four bright arrows of light which are, as it were, flashed forth from the horizontal spectrum into the dark.

By repeatedly intercepting and re-admitting the light of the main source, I have actually convinced myself that the intense arrow-light, with the dispersion used, gradually passes into the faint light of the emission-lines, both with respect to intensity and place in the spectrum. A flat ROWLAND grating with 47000 lines was used in the spectroscope; one spectrum of the first order being extremely brilliant. The crosswires of a micrometer eye-piece (65 divisons of which corresponding to the distance of the *D*-lines in the first diffraction spectrum) were repeatedly adjusted as close as possible to the extreme part that was yet distinctly visible of such an arrow, the sodium lines of the flame being all but invisible. I next removed the diaphragm near the flame, intercepted the main light, so that the sodium lines now became clearly visible, and took a number of the readings of the emission line. The mean readings of two series of observations did not mutually differ by one division; the arrow, therefore, approached the *D*-line to within 0.01 $\mu\mu$.

From the data furnished by BECQUEREL (C. R. 128. p. 146) it can be inferred, that the distance between the *D*-lines and the most deflected parts of the arrows upon which, in his experiments, the cross-wires could still be adjusted, was on an average greater than 0.1 $\mu\mu$.

I am not quite sure how this difference in the results must be accounted for; perhaps BECQUEREL's flame contained more sodium than mine; anyhow so much sodium is not wanted to produce strong anomalous dispersion.

The following experiment convinced me how narrow was in reality the absorption-region of each of the sodium-lines. An additional lens of 20 cm focal distance was placed between the telescope lens and the vertical slit, in such a manner that on this slit was thrown the image of the prismatic part of the sodium flame, and not that of the horizontal slit, as before. In this image, therefore, all rays that had passed the flame and had been refracted in different directions, must be found re-united. The absorption-lines were now actually ery narro w, the emission-lines in some places all but covering them.

The additional lens being removed, the light-arrows forthwith re-appeared above and below the rather broad dark bands in the curved spectrum.

It appears therefore, from our observations that in spite of the considerable width of the dark bands in the main spectrum, the corresponding light is but very slightly absorbed by the sodium lines. The flame has allowed every kind of light to pass, even that of which the wavelength differed ever so little from that of the D-lines; but it has caused these rays to be deflected from the straight line much more forcibly than the other parts of the spectrum lying further removed from the absorption lines.

Here, then, we have a case where the absorption spectrum of a vapour exhibits broad bands not deserving the name of absorption bands. The special manner in which the experiment was made, enabled us to see what had become of the light that had disappeared around the sodium lines; but very likely the broad bands would have been attributed entirely to absorption if somehow this abnormally refracted light had fallen outside the field of vision of the spectroscope. In studying the absorption spectra of gases and vapours, we should be careful to see — which is not always done — that the absorbing layer shall have equal density in all its parts and shall not act anywhere as a prism. It would be worth while investigating in how far the anomalous dispersion can have influenced cases in which broadening or reversal of absorption-lines have been observed.

In my arrangement the absorption-lines were narrow, if the main light had passed through a pretty much homogeneous and *non*-prismatic part of the flame.

The experiment, as described above, offers no opportunity for obtaining reliable values of the refractive indices. A better method to arrive at more reliable results is now being investigated; for the present all we can say is that the deviation of rays whose wavelength is very near λ_{D_1} or λ_{D_2} is at least six or eight times greater than that which the remoter parts of the spectrum were subject to. BECQUEREL says that the index for waves greater than λ_{D_1} and λ_{D_2} may attain 1.0009; for waves on the other side of the absorption line the index falls considerably below unity. The line D_2 produces in a much higher degree than D_1 refractive indices smaller than unity [1]); the very high indices are represented in pretty much the same degree near D_1 and D_2.

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[1]) In the woodcut Fig. 3, pag. 577 the upper arrow near D_2 is spoiled and rather short compared with that near D_1.

From all this we infer:

1. Where light emitted by a source that yields a continuous spectrum, traverses a space in which sodium vapour is unequally distributed, the rays in the neighbourhood of the *D*-lines will be much further deflected from their course than any others. Of all things this holds good of those rays whose wavelength differs so little from λ_{D_1} and λ_{D_2} that they can hardly be distinguished from sodium light. A pretty strong light, therefore, misleadingly resembling sodium light, but in reality owing its existence to other sources, may seem to proceed from a faintly luminous sodium vapour, in a direction deviating from that of the incident light.

2. A spectroscopic examination of the light that has traversed, in a fairly rectilinear direction, the space filled with sodium vapour, shows, in the places where the *D*-lines are to be found, broad dark bands owing to the fact that the light of these places in the spectrum has deviated sideways from its course, and has not reached the slit of the spectroscope.

The former of these inferences we will now apply to certain phenomena in the neighbourhood of the disc of the sun; the latter to some peculiarities of the sun-spots.

Let the arc ZZ' represent a part of the disc of the sun, the observer being stationed far off in the direction of O. This ZZ' may be taken to be either the limit of the photosphere, or the critical sphere which in A. SCHMIDT's theory of the sun plays such an important part. In either case, a ray emitted from any point A on the surface at an angle of nearly 90° will reach the point O along a path the curvature of which diminishes regularly, if we assume that the density of the sun's atmosphere in a direction normal to the surface decreases continuously.

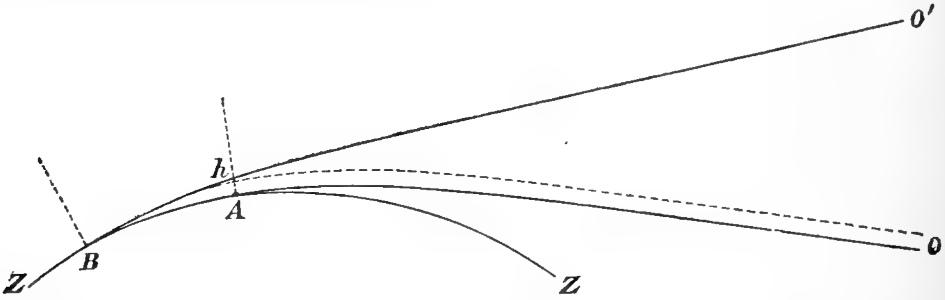

Fig. 4.

A ray emitted from B under the same circumstances will proceed along BO' and does not, therefore, reach O; the observer in O will see A lying just within the margin of the disc of the sun; light proceeding from *B* is invisible to his eye. Slight irregularities of density in the atmosphere on the path *AO* will indeed deflect the course of the rays, but only slightly if the gases have a normal index of refraction. The irregularities show themselves as shallow elevations and depressions in the edge of the sun's disc. In the same manner, rays like *BO'* do not materially deviate from the course which they would have to follow in a perfectly calm atmosphere of continuously decreasing density.

Let us now suppose unequally distributed sodium vapour to be present near *A* above the limit *ZZ'* (the photosphere). We suppose this vapour to be hardly luminous, if at all. The greater part of the shaft of white light *BO'* is only slightly irregularly refracted in it, just as in the other gases to be found there; but those rays whose wavelength differs but slightly from λ_{D_1} or λ_{D_2} are much more deflected, and they may even follow the course indicated by the dotted line *Bh O*. Then from *O* at a small distance *Ah* above *A*, light may be seen proceeding from *B* — a source of light with a continuous spectrum — closely resembling sodium light. A spectroscopic examination of this light, however, will show that it differs more or less from that of the *D*-lines.

It might be thought that only rays with an abnormally high refractive index, i. e. with wavelengths rather greater than λ_{D_1} or λ_{D_2} can reach the observer along the path *Bh O*. Such, however, is not the case; for if above *A*, there were a layer comparable to a prism with the refracting edge perpendicular on the plane of the woodcut and with base turned upwards, rays with an index smaller than unity must be able to traverse the path *Bh O*.

Accordingly in the spectrum of the light that appears outside the sun's disc we can expect to find rays which are situated on either side of the *D*-lines; perhaps the probability is a little greater for the light on the red side of the absorption-lines, because from *A* to *h* the density is more likely to decrease than otherwise.

It is further clear that very near the limb there is the greatest probability of also seeing light, that differs relatively much in wavelength from the sodium light; for there a less degree of abnormality of index suffices to deflect rays in the direction of *O*. On the other hand, far above *A*, we can, as a rule, discern only such light as is hardly to be distinguished from *D*-light.

These actually prove to be the principal characteristics of the chromosphere-lines. Mostly they have a broad base and are arrow-headed. Compare the description and the diagrams to be found in LOCKYER's Chemistry of the Sun pp. 109 and 111.

Their typical form appears very strikingly in the hydrogen lines of the chromosphere.

There is no reason to assume that the above considerations, with regard to sodium vapour, do not hold good as well for other gases and vapours. With some of these the anomalous dispersion has been proved already [1]; with others we have been less successful; but the dispersion theories point to its existence in a more or less degree in all substances.

The characteristic form of the chromosphere lines might, of course, also be accounted for, as is generally done, by the strongly radiating luminous gases and metallic vapours which are thought to be present in the chromosphere and of which the density near the photosphere must then be taken to be very considerable and to be rapidly decreasing at greater distances. The observed light would then be emitted by those glowing vapours.

Our view of the origin of the chromosphere light does not by any means preclude the possibility of this light owing its existence, partly at least, to self-radiation of incandescent gas; what we have shown is, that it may also be refracted photosphere light. Further investigation of the various phenomena of the sun must decide which explanation goes farthest in considering the whole subject.

Sometimes the chromosphere lines appear under very singular forms, with broadenings, ramifications, plumes, detached parts etc. (cf. LOCKYER, l. c. p. 120). Thus far this has been accounted for only on the principle of DOPPLER, viz. by assuming that the radiating gases move towards, or away from, us with tremendous velocity — even as much as 200 kilometers per second and more. Astronomers are all agreed that this explanation is open to many objections of which we need not remind the reader here.

Beside DOPPLER's principle, however, we find in the anomalous dispersion another, according to which a gas has the power to originate, under certain circumstances, light differing in wavelength from the characteristic rays of that substance.

Let us suppose, for example, that at some distance above the sun's limb there is a quantity of hydrogen, with great varieties of density in some of its parts. It will emit not only its own characteristic light, but will, here and there, also deflect earthwards the photosphere light of adjacent wavelengths. This will, of course, manifest itself in excrescences or ramifications of the hydrogen lines or as isolated light patches in their neighbourhood.

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[1] WINKELMANN, Wied. Ann., 32, p. 439.

This phenomenon may be expected especially, when the slit is adjusted for the examination of prominences, where violent disturbances take place and where, consequently, considerable differences of density occur.

Though the present explanation of these irregularities in the spectrum is based, like the other one, on the hypothesis that violent disturbances in the solar atmosphere go hand in hand with them, yet the tremendous velocities, required when applying DOPPLER's principle, do by no means follow from it.

A portion, therefore, of all the light that reaches us from chromosphere and prominences *may* be due to self luminosity of the gases to be found there; but another, and to all likelihood a very considerable, portion is refracted photosphere light, reaching us in a manner that reminds us of TÖPLER's well-known "Schlierenmethode". But there's this difference, that in the "Schlierenmethode" every kind of rays emitted by the source helps to bring out the same irregularities of the medium by ordinary refraction; as a rule no colour-phenomena are to be seen, the dispersion of most media being small compared with the average deviation of rays. The chromosphere gases, on the other hand, are to be seen in characteristic colours, because they have an exceptionally high or low refraction index for particular sorts of light. In this case the dispersion is great in comparison with the average deviation of the rays.

Momentarily disregarding the self-radiation of the gases in the solar atmosphere we shall — if the slit is radially adjusted — find those chromosphere-lines to be longest and brightest which show the greatest anomalous dispersion. We have seen that the two sodium-lines show considerable difference in their respective powers to call forth this phenomenon. Let us make the pretty safe supposition that also the different hydrogen-lines and the other chromosphere lines show analogous individual differences, and we have the explanation why in the chromosphere spectrum some lines of an element are long and others short, and why the relative intensity of the lines of an element is so different in this spectrum from that in the emission spectrum or in the FRAUNHOFER absorption spectrum. A careful examination of the anomalous dispersion of a great number of substances will, of course, have to be made before it can be made out in how far our view will account for the facts already known or yet to be revealed in the chromosphere spectrum. Amongst other things it must then appear whether those elements whose lines are most conspicuous in the chromosphere light, do actually cause uncommonly great anomalous dispersion — a wide field for experimental research which to explore the first steps have scarcely been taken as yet.

On the other hand, as regards the self-luminosity of gases, LOCKYER's ingenious experimental method of long and short lines affords us an invaluable help to investigate what is the influence of the temperature (and the density?) of the radiating substance on the emission spectrum. So it seems possible to make out by experiment whether it is radiation or refraction to which the different chromosphere lines are most probably due.

This decision ought, of course, to be founded on a most accurate knowledge of the character which each of the spectral lines of the solar atmosphere exhibits in different circumstances. The coming total solar eclipses offer a good opportunity to observe the chromosphere spectrum minutely, little disturbed by the dazzling light of the photosphere. Especially it is to be hoped that some good spectrograms will be obtained with high dispersion apparatus.

Let us now consider from the point of view of anomalous dispersion the well-known "reversing-layer", which in total eclipses causes the so-called "flash". We have seen before that the theory of dispersion assigns anomalous dispersion to all waves whose periods lie near each characteristic vibration-period of a substance; but the amount of the anomalous dispersion may be slight. In such a case the arrows, in an experiment similar so that described for sodium-light, would be short and narrow, but, for all that, of great intensity. If, therefore, such substances exist in the solar atmosphere even at great distances from the photosphere, with irregularities in density similar to those assumed for sodium, hydrogen etc., the anomalous refraction will betray the presence of those substances merely in the immediate vicinity of the edge of the sun's disc, and only during a few seconds at the beginning and the end of the totality of an eclipse.

This view of the subject makes it a matter of course that the lines of the flash should be very bright; for properly speaking, it is not chiefly the radiation, emitted by the vapours, that we observe, but photosphere light of pretty much the same wavelength. Nor is it necessary that the gases in those places should be of extraordinary great density, or that their presence should be restricted to a thin reversing layer — one of the most mysterious things the solar theory has led up to and which they have tried to escape in various ways.

The light of the chromosphere- and of the flash-lines may be symmetrically distributed on either side of the corresponding FRAUNHOFER-lines; if so, they seem to coincide with the latter; but in certain places of the limb the case must arise that the bright lines would appear to have shifted their position with regard to the absorption-lines. For in proportion to the distribution of the density of the vapours, it will be, in turns, especially the rays with very great refractive index (on the red side of the absorption lines) and those with very small refractive index (on the violet side of them) that are curved towards us.

As, upon the whole, the density of the gases of the solar atmosphere will decrease rather than otherwise in proportion as they are farther from the centre, it may be expected (according to what we observed with regard to Fig. 4) that the bright lines will oftener shift their position with respect to the FRAUNHOFER lines in the direction of greater wavelengths than in that of smaller.

These details will probably become clearly visible in the eclipse-photograms obtained with slit-spectrographs with great dispersion. It is not impossible that in many of the chromosphere-lines a dark core may be seen.

Summarising what we have said, we maintain the following position with respect to that part of the solar atmosphere situated outside what is called the photosphere.

The various elements whose presence in that atmosphere has been inferred from spectral observations, are much more largely diffused in it than has generally been assumed from the shape of the light phenomena; they may be present everywhere, up to great distances outside the photosphere, and yet be visible in few places only; their self-radiation contributes relatively little to their visibility (with the possible exceptions of helium and coronium); the distances, at which the characteristic light of those substances is thought to be seen beyond the sun's limb, are mainly determined by their local differences of density and their power to call forth anomalous dispersion.

In conclusion I wish to say a few words concerning phenomena presented by the sun-spots. In the spectrum of these spots many of the FRAUNHOFER-lines appear considerably broadened (see e. g. the diagram in LOCKYER, Chemistry of the Sun p. 100). The cause for this has been sought in the presence of very dense absorbing gases, and the broad bands have been attributed exclusively to absorption. The question is whether the second conclusion that we have drawn from the phenomena of refraction in a sodium-flame (p. 580) is not applicable here.

We proceed from the opinion that in a sunspot are found great differences of density dependent on strong vertical currents or, according to Faye, on vortex movements in the atmosphere. The phenomenon is commonly localized in the level of the fotosphere, at all events, not far above or below it. Now if the total body situated within the photosphere, actually forms a sharp contrast with the outer atmosphere and if its surface radiates to every side an almost equally intense light with a continuous spectrum, the broadening of the Fraunhofer lines and the darkness of the spots cannot be accounted for by merely attributing the spots to differences of density. The phenomenon must then be set down to differences of temperature, smaller radiating power, condensation, stronger absorption, etc.

Matters are different, however, if A. Schmidt's view is taken to be the correct one, according to which the sun's limb is an optical illusion caused by regular refraction in a gradually dispersing, nowhere sharply bounded mass of gas. In this theory the apparent surface of the photosphere is merely a critical sphere, characterized by its radius being equal to the radius of curvature of rays of light travelling along its surface horizontally; there is not the least question of any discontinuity in the distribution of matter on either side of this spherical surface; inside as well as outside the critical sphere the average density of matter and its radiating power increase gradually towards the centre and it is only at great depths that the condition of matter need be such as to emit a continuous spectrum.

Let the circle ZZ' in the diagram be the section of the critical sphere with the ecliptic, and let the earth be in the direction MA. Suppose a spot visible in the centre of the sun's disc; it is seen projected on the critical sphere in P. Now let us suppose that the density increases all around from the centre P of the spot, locally producing there cylindrical, rather coaxial layers with the line of vision for basis. Rays pA and qA suffering normal refraction, may, as is easily seen, have traversed in the sun the paths rp, sq and may, there-

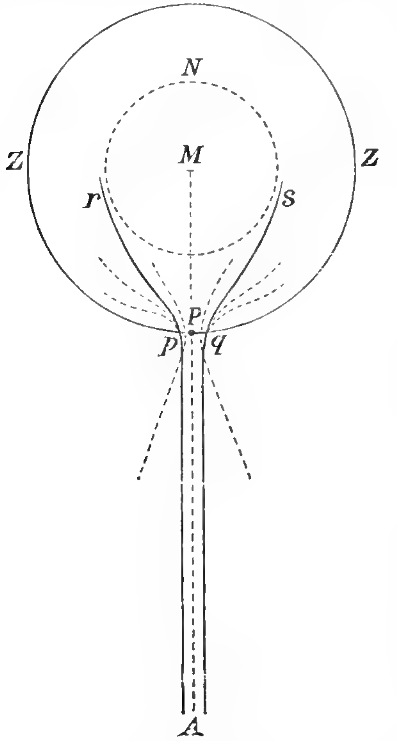

Fig. 5.

fore, originate not, it is true, from the most luminous centre, but yet from pretty intensely radiating parts of the sun. They yield the white light of the umbra and of the penumbra, which though standing out dark against the other parts of the sun, yet are relatively bright enough.

Slight irregularities in the distribution of density around *P* render it possible that parallel to *PA* there emerge rays that have followed other paths which, nevertheless, will essentially be included in the solid angle *rPs*.

But rays which have undergone anomalous dispersion and yet reach our eye in a direction parallel to *PA*, must have proceeded from a much greater diversity of directions and need not, therefore, have been emitted in such numbers by the intensely luminous central part of the sun.

We may also put the matter thus: Of all the light, coming from the intensely radiating nucleus of the sun (to which may be reckoned all that lies within the sphere *N*) and emerging from the vicinity of *P*, those rays, whose refractive index is abnormally high or low, will be more effectually dispersed in all directions, owing to the local differences of density, than rays with a normal index.

The consequence is that the observer looking in a given direction towards *P*, will see less of those abnormally refracted rays than of the other light. Those rays will, therefore, seem absent in the spectrum of the spot: the FRAUNHOFER line is seen broadened.

Whereas our considerations concerning the chromosphere light were made independent of any theory of the nature of the photosphere, the present broadly outlined explanation of the phenomenon of the sun-spots is to a certain extent based on the theory of SCHMIDT — with which, in fact, it stands or falls.

If subsequent investigations should prove the lines that mostly appear broadened in the spectra of the spots, and those which call forth strong anomalous dispersion, to be identical, this would support SCHMIDT's solar theory.

For the rest it is easy to see that henceforth the principle of anomalous refraction will have to be considered side by side with that of DOPPLER in every instance when an explanation is required of the many irregularities that have been observed in certain FRAUNHOFER lines both near the sun's limb and in faculae and spots; cf. the illustrations in LOCKYER's Chemistry of the Sun pp. 122 and 123. YOUNG, The Sun, pp. 157 and 210. SCHEINER "Die Spectralanalyse der Gestirne", p. 349.

Such phenomena *may* be caused by refraction, whereas hitherto the only possible explanation was sought in the assumption of tremendous velocities in the line of vision.

The foregoing considerations may suffice to show that anomalous dispersion naturally accounts for a great number of solar phenomena. At any rate no future theory of the sun can ignore the laws of refraction.

Physics. — "*On the critical isothermal line and the densities of saturated vapour and liquid in isopentane and carbon dioxide.*" By Dr. J. E. VERSCHAFFELT (Communication N⁰. 55 from the Physical Laboraty at Leiden by Prof. H. KAMERLINGH ONNES).

(Read March 31, 1900).

To be able to deduce from my researches on the capillary ascensions near the critical temperature [1]) the surface tension I laid down the empiric formula:

$$\varrho_l - \varrho_v = 0{,}243\,(1 - m)^{0{,}367}$$

which fairly well represents the densities of liquid ϱ_l and vapour ϱ_v of carbon dioxide at the absolute temperature T and the reduced temperature $m = \frac{T}{T_k}$ given by AMAGAT. This is not the case for the temperatures $\tau = 0^\circ{,}1$, $\tau = 0^\circ{,}35$, $\tau = 0^\circ{,}85$, (supposing $\tau = T_k - T$) in which

$$\frac{\Delta \log (\varrho_l - \varrho_v)}{\Delta \log \tau} = \begin{array}{lll} 0{,}521 & \text{between } \tau = 0^\circ{,}1 & \text{and } 0^\circ{,}35 \\ 0{,}468 & \quad \text{»} \quad \tau = 0^\circ{,}35 & \text{» } \ 0^\circ{,}85 \end{array}$$

(see Comm. N⁰. 28 p. 12). In order to represent the interpolation-curve given by AMAGAT by my formula, it would in this region be necessary to raise the exponent of $(1 - m)$ in this formula from 0.367 to for instance 0.5, the value occurring in the formula $\varrho_l - \varrho_v = A\sqrt{(1-m)}$, which has been deduced theoretically by VAN DER WAALS, and given empirically by CAILLETET and MATHIAS.

This deviation might as remarked in Communication N⁰. 28, be caused by the fact that AMAGAT, without giving a satisfactory experimental proof for it, has rounded off his interpolation-curve

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[1]) Comm. from the Phys. Lab. at Leiden N⁰. 28, Dr. J. E. VERSCHAFFELT. Measurements on the capillary ascension of liquefied carbon dioxide near the critical temperature.

towards the critical state with a parabola of the second degree. In the very accurate determinations of density by SYDNEY YOUNG, to which no corrections by interpolation have been applied and for which I have computed a formula of the same form as the one mentioned above viz.

$$\varrho_l - \varrho_v = 0{,}11058\ \tau^{0{,}3434}$$

the agreement between observation and calculation appears to exist even at the highest temperatures ($\tau = 0^\circ{,}4$).

$$\frac{\Delta\ log\ (\varrho_l - \varrho_v)}{\Delta\ log\ \tau} \text{ is } \quad \text{between} \begin{array}{l} \tau = 1^\circ{,}8 \text{ and } 0^\circ{,}8 \text{ still } 0{,}344 \\ \tau = 0^\circ{,}8 \text{ and } 0^\circ{,}4 \text{ still } 0{,}337 \end{array}$$

while, according to the law of the corresponding states we might predict already at $\tau = 1^\circ{,}5$ a distinct increase from the above-mentioned deviation in the case of the interpolation-curve of carbon dioxide.

Therefore for the time being no *experimental* proofs can be given for the supposition, that up to the immediate neighbourhood of the critical state $\varrho_l - \varrho_v = A\,(1 - m)^{0{,}3434}$ would not hold instead of the theoretical formula $\varrho_l - \varrho_v = A\,(1 - m)^{\frac{1}{2}}$.

The table given here shows that my formula gives precisely the difference in density till about $\tau = 60^\circ$. With lower temperatures the agreement diminishes.

TABLE I.

τ	$(\varrho_l - \varrho_v)$ observ.	$(\varrho_l - \varrho_v)$ calculat.
0,4	0,0810	0,0807
0,8	0,1023	0,1024
1,8	0,1351	0,1353
2,8	0,1567	0,1575
4,8	0,1889	0,1895
7,8	0,2240	0,2239
11,8	0,2591	0,2581
17,8	0,2982	0.2972
27,8	0,3477	0,3464
37,8	0,3862	0,3849
47,8	0,4169	0,4173
57,8	0,4443	0,4454
67,8	0,4680	0,4705

2. The relation deduced by VAN DER WAALS between the surface-tension σ and the reduced temperature m

$$\sigma = C(1-m)^{3/2}$$

is intimately connected with the form of the isothermals near the critical point, by means of which also the formula for the densities of liquid and vapour (with the aid of the MAXWELL–CLAUSIUS theorem) must be determined.

It now appears that in the place of the exponent $1/2$ in the difference of liquid and vapour density a less simple fraction must be substituted. Hence as according to VAN DER WAALS' simple supposition the isothermal is a curve of the third degree, I have investigated whether the critical isothermal could not be expressed in an analogous way by means of a fractional exponent. The result I arrived at, was that the observations of S. YOUNG on the form of the critical isothermal of isopentane are well expressed by the formulae:

$$p = p_c - p_c\left(1 - \frac{v_c - b}{v - b}\right)^n, \quad \text{for} \quad v > v_c$$

and

$$p = p_c + p_c\left(\frac{v_c - b}{v - b} - 1\right)^n, \quad \text{for} \quad v < v_c;$$

in which p_c=32,92 atm., v_c=4,266 c.c. (specific volume), b=0,518 c.c., and n = 4,259. The following table shows that these formulae are in good harmony with the observations:

TABLE II.

v	p (observ.)	p (calcul.)
19,41	19,99	20,06
16,91	21,95	21,99
14,40	24,13	24,27
11,91	26,84	26,86
9,440	29,69	29,65
4,505	32,92	32,92
3,160	33,70	33,73
3,050	34,39	34,35
2,939	35,49	35,56
2,829	37,49	37,32
2,718	40,51	40,37
2,608	45,49	45,27
2,497	53,51	53,58
2,431	60,59	60,42
2,394	65,24	65,60
2,361	70,63	70,87

From the formula given for $v > v_c$ it follows that for very great volumes $pv = 525,5$, from which $R = 1,140$, in good harmony with the value 1,138 found by applying AVOGRADO's law as holding for the limit [1]).

In order to know whether my formulae give also a sufficient approximation for very high pressures, I have calculated the critical isothermal from AMAGAT's system of isothermals for carbon dioxide. As critical temperature I found 31°,4 C., hence $p_c = 73,6$ atm.; for v_c I took the value 0.00424 (the normal volume being chosen as unit), computed from the critical density 0.464. The following table shows that if $n = 4$ and $b = 0,00045$, my formulae well represent the observations up to pressures of about 800 atm. The third column gives the pressures I have computed from the volumes observed, and the fourth column gives the volumes computed from the pressure observed.

TABLE III.

p	v	p (calcul.)	v (calcul.)
1000	0,001752	1055	0,001764
950	1767	989	1776
900	1782	927	1789
850	1799	864	1803
800	1815	808	1817
750	1832	752	1835
700	1847	709	1850
650	1864	659	1868
600	1887	603	1888
550	1909	552	1910
500	1934	504	1936
450	1965	448,5	1964
400	1998	397,3	1996
350	2037	346,7	2034
300	2087	294,3	2081
275	2115	268,5	2108
250	2148	242,9	2139
225	2182	220,3	2175
200	2220	198,6	2217

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[1]) Using the theoretical normal density for hydrogen
$$0,00008955 \times 1.00069 = 0,00008961$$
and the molecular weight of $C_5 H_{12} = 71.82$ (Comp. Comm. from the Leiden laboratory N°. 47 page 12.)

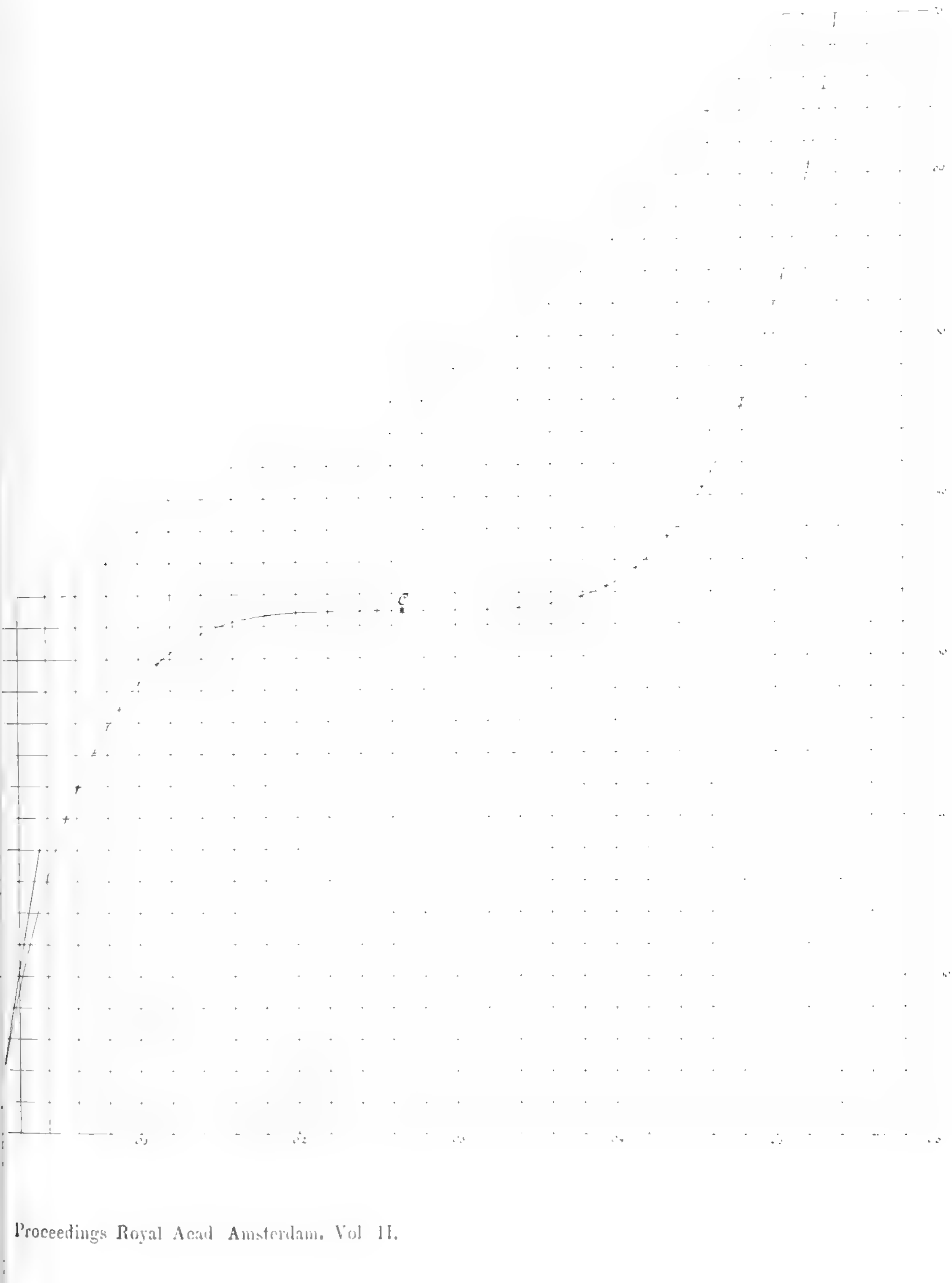
p	v	p (calcul.)	v (calcul.)
175	0,002263	177,6	0,002269
150	2333	151,0	2336
125	2432	124,6	2430
100	2600	98,7	2587
76,30	3090	76,25	3086
74,50	3283	74,57	3295
73,75	3573	73,76	3576
73,26	547	73,34	558
72,37	630	72,46	637
71,42	682	71,62	693
69,50	771	69,76	782
67,57	850	67,83	861
64,63	968	64,72	972
59,71	0,01156	59,74	0,01157
54,77	1356	54,83	1359
49,81	1584	49,88	1588
44,84	1856	44,85	1856
39,86	2187	39,86	2186

3. The formulae I have found for the critical isothermals are purely empirical. I was led to using formulae of the form given above by the remark that it was possible to find such a value of b that the critical isothermal, drawn in a diagram with p as axis of ordinates and $\frac{1}{v-b}$ as axis of abscissae showed a centre of symmetry in the critical point. In the annexed figure, representing the critical isothermals of isopentane, this symmetry is very conspicuous.

The marks represent the observations, the line drawn represents my formula.

It may be seen that only in a very forced way a division of the pressure into a thermodynamical and a cohesion pressure can be deduced from my formula, which division is the basis of van der Waals' theory. If therefore my formulae have a theoretical meaning, this seems to be based on a principle somewhat different from van der Waals' equation of state; I did however not succeed in deducing such a principle.

Dr. J. E. VERSCHAFFELT, „On the critical isothermal line and the densities of saturated vapour and liquid in isopentane and carbon dioxide."



Mathematics. — "*The theorem of* JOACHIMSTHAL *for the normal curves*", by Prof. P. H. SCHOUTE.

The circle through the feet of the three normals, which we can let fall from any point of the plane of a parabola on this curve, passes through the vertex of the curve. In other words:

"The circles of JOACHIMSTHAL presenting themselves for a parabola form a net with one basepoint, the vertex of the parabola".

And the relation between the point P through which the three normals pass, and the centre M of the corresponding circle of JOACHIMSTHAL can be expressed as follows:

"If P describes the point-field of which the plane of the parabola "is the bearer, M generates in the same plane a point-field affinely "related to this."

We shall now investigate how far these theorems can be extended to the normal curve N_n^n of the space S_n with n dimensions, and we shall commence this investigation with the simple case $n=3$ of the skew parabola.

1. *The spheres of* JOACHIMSTHAL *for the skew parabola.* If the skew parabola is represented by the equations

$$x=t, \qquad y=t^2, \qquad z=t^3,$$

then

$$3\,t^5+2\,t^3-3\,z\,t^2+(1-2\,y)\,t-x=0 \quad \ldots \ldots \quad (1)$$

is the equation of the normal plane in point t. This equation in t being of degree five, through any point P five normal planes pass; the feet of these normal planes we shall call "conormal points" of the curve. These conormal points form on the curve an involution of degree five with three dimensions, for, if three points of such a quintuple are taken arbitrarily, the point P in space through which the five normal planes must pass, and in this way likewise the supplementary pair of feet, is unequivocally determined. So there must exist two relations between the parametervalues t of five conormal points. If in general $\underset{k,l}{\Sigma} m$ represents the sum of the products l by l of k quantities m, we deduce immediately from (1)

$$\underset{5,1}{\Sigma}\, t=0, \qquad 3\underset{5,2}{\Sigma}\, t=2 \quad \ldots \ldots \quad (2)$$

On the other hand the six points of intersection of the given curve with the sphere

$$(x-p)^2+(y-q)^2+(z-r)^2-s^2=0$$

are determined by the equation

$$(t-p)^2+(t^2-q)^2+(t^3-r)^2-s^2=0,$$

or

$$t^6+t^4-2rt^3+(1-2q)t^2-2pt+p^2+q^2+r^2-s^2=0\ . \quad (3)$$

These "conspherical points" form on the skew parabola an involution of degree six with four dimensions; for, if four of the six points of intersection be chosen, the sphere is determined and together with it the supplementary pair of points of intersection. From (3) follows immediately that six conspherical points are connected by the two relations

$$\sum_{6,1} t=0, \qquad \sum_{6,2} t=1\ . \ . \ . \ . \ . \ . \ . \ . \quad (4)$$

between their parametervalues.

We now prove the following theorems:

"The spheres determined by the quadruples of points of the skew "parabola, conormal with a given point t_1, intersect this curve still "in two fixed points, determined by the equation

$$3t^2-3t_1t+1=0;$$

so they form a net of which these two points are the basepoints. And the point t_1 describing the curve, these basepoints generate on it a quadratic involution of one dimension, of which the two points $\pm\frac{1}{3}\sqrt{3}$ are the double points.

If $\tau_1, \tau_2, \tau_3, \tau_4$ are four points conormal with t_1, then according to (2) we have the relations

$$\sum_{4,1}\tau+t_1=0, \qquad \sum_{4,2}\tau+t_1\sum_{4,1}\tau=\frac{2}{3}\ . \ . \ . \ . \quad (5)$$

If $\tau_1, \tau_2, \tau_3, \tau_4$ are four points conspherical with t_2, t_3, then according to (4) we have

$$\sum_{4,1}\tau+t_2+t_3=0, \qquad \sum_{4,2}\tau+(t_2+t_3)\sum_{4,1}\tau+t_2t_3=1\ . \quad (6)$$

So from (5) and (6) follows immediately:

$$t_2+t_3=t_1, \qquad t_2t_3=\frac{1}{3}\ , \ . \ . \ . \ . \ . \ . \quad (7)$$

with which is proved what was asserted. For the spheres belonging in the indicated way to the point t_1, which we name the spheres of JOACHIMSTHAL of this point, pass through two fixed points t_2, t_3 and their number is twofold infinite, it being possible to assume arbitrarily besides t_1 still two of the other four points τ.

2. *The affinely-related point-fields (P) and (M).* If the point P, through which the five normal planes pass, describes the normal plane of point t_1, and t_1, as was assumed above, is always one of the five conormal points, the centre M of the sphere of JOACHIMSTHAL passing through the four other points moves in the plane that bisects orthogonally the distance of the points t_2, t_3 belonging to t_1. Indicating the first plane by π and the second plane by μ, we have the theorem:

"The point-fields (P) and (M) in the planes π and μ corresponding "with each other are affinely related."

From (3) ensues

$$2\,x_m = \sum_{6,5} t, \qquad 1-2\,y_m = \sum_{6,4} t, \qquad 2\,z_m = \sum_{6,3} t,$$

where the sums refer to six conspherical points.

If t_2, t_3 appear among these and if we call the others again τ_1, τ_2, τ_3, τ_4, we find

$$\left.\begin{aligned} 2\,x_m &= t_2\,t_3 \sum_{4,3}\tau + (t_2+t_3)\sum_{4,4}\tau \\ 1-2\,y_m &= t_2\,t_3 \sum_{4,2}\tau + (t_2+t_3)\sum_{4,3}\tau + \sum_{4,4}\tau \\ 2\,z_m &= t_2\,t_3 \sum_{4,1}\tau + (t_2+t_3)\sum_{4,2}\tau + \sum_{4,3}\tau \end{aligned}\right\} \quad . \; . \; . \; . \quad (8)$$

Moreover, if t_1 is conormal with τ_1, τ_2, τ_3, τ_4, we obtain according to (1)

$$\left.\begin{aligned} t_1 + \sum_{4,1}\tau &= 0\;. \\ t_1 \sum_{4,1}\tau + \sum_{4,2}\tau &= \frac{2}{3} \\ t_1 \sum_{4,2}\tau + \sum_{4,3}\tau &= z_p \\ t_1 \sum_{4,3}\tau + \sum_{4,4}\tau &= \frac{1}{3}(1-2\,y_p) \\ t_1 \sum_{4,4}\tau \qquad\quad &= \frac{1}{3}\,x_p \end{aligned}\right\} \quad . \; . \; . \; . \; . \; . \quad (9)$$

So in connection with (7) we find by elimination of the quantities Σr the relations

$$\left.\begin{aligned} 18\, x_m &= 3\,(x_p + z_p) - 3\,t_1^2 - 2\,t_1 \\ 18\, y_m &= 6\, y_p + 3\,t_1^2 + 4 \\ 6\, z_m &= 3\, z_p - t_1 \end{aligned}\right\} , \quad . \quad . \quad . \quad . \quad (10)$$

proving what was asserted.

However the two point-fields (P) and (M) are not in perspective. For on the line of intersection of the planes π and μ not a single point corresponds to itself. For the conditions $x_p = x_m$, $y_p = y_m$, $z_p = z_m$ involve

$$x = -\frac{t_1\,(3\,t_1^2 + 1)}{15}, \quad y = \frac{3\,t_1^2 + 4}{12}, \quad z = \frac{t_1}{3}$$

and this point is not situated in the normal plane of t_1. So the connecting lines PM of the corresponding points P and M of π and μ form a system of rays (3, 1).

3. *Relation between the spacial systems* (P) *and* (M). To a point P taken arbitrarily five points M correspond. For, if P is given, the five conormal points, the normal planes of which intersect in P, are given and any point of this quintuple may be regarded as the above given point t_1.

To investigate how many points P correspond to any point M, we deduce the equation of the plane μ belonging to the normal plane π of the point t_1. The plane μ bisecting the distance of the points t_2, t_3 orthogonally, it is represented by the equation

$$(x - t_2)^2 + (y - t_2^2)^2 + (z - t_2^3)^2 = (x - t_3)^2 + (y - t_3^2)^2 + (z - t_3^3)^2,$$

which reduces itself in connection with (7) to

$$3t_1^5 - t_1^3 - 6\,z\,t_1^2 + 2\,(1 - 3\,y)\,t_1 + 2\,(z - 3\,x) = 0 \quad . \quad (11)$$

As t_1 presents itself to degree five in this equation, any given point M is centre of five spheres of JOACHIMSTHAL and so a quintuple of points P corresponds to this point M. So we find :

"The relation of the spacial systems (P) and (M) is a correspondence (5,5)".

Although it would not be difficult to trace by means of the equations (10) the complex of the connecting lines PM, we shall avoid this for brevity's sake.

4. *Cyclographic representation of the spheres of* JOACHIMSTHAL. If we wish to extend FIEDLER's cyclographic representation of circles lying in a plane to spheres in space, we must suppose that the three-dimensional space containing the spheres forms part of a space S_4 with four dimensions. We represent in S_4 a sphere lying in S_3 and having M as centre and ϱ as radius by the two points M_1, M_2 of the normal in M on S_3 at a distance $MM_1 = MM_2 = \varrho$ from M.

We shall now first investigate what is the representation of the net of the spheres of JOACHIMSTHAL passing through the points t_2, t_3 of the skew parabola. If the ordinate in the direction perpendicular on S_3 is indicated by w, the equations

$$\left.\begin{aligned}(x - t_2)^2 + (y - t_2^2)^2 + (z - t_2^3)^2 = w^2 \\ (x - t_3)^2 + (y - t_3^2) + (z - t_3^3)^2 = w^2\end{aligned}\right\} \quad . \quad . \quad . \quad (12)$$

will indicate the two quadratic hypercones forming successively the representation of all the spheres through t_2 and all the spheres through t_3. By subtracting these equations from each other we find that the section of the two hypercones lies in a three-dimensional space perpendicular to S_3 along the plane (11). So the locus of pairs of points M_1, M_2 corresponding to this net of spheres of JOACHIMSTHAL is, as the section of a hypercone of revolution with a three-dimensional space parallel to the axis of the hypercone, a hyperboloid of revolution with two sheets, and the orthogonal one.

Passing on to the investigation of the curved space containing the pairs of images of all the spheres of JOACHIMSTHAL, we have to deal with a simple infinite number of orthogonal hyperboloids of revolution with two sheets. To find the degree of that curved space we have but to observe that the point common to all the normals on S_3 does not belong to the locus and that the number of points of that curved space situated on a definite one of those normals is double the number of planes (11) passing through the point (M) where that normal meets S_3. This number being five, the curved space must be of order ten. It is not difficult to deduce the equation of the locus; we have but to eliminate t_2 and t_3 between the two equations (12) and $t_2 t_3 = \frac{1}{3}$. To this end we give the equations (12) the form

$$\left.\begin{aligned} T_2 \equiv t_2^6 + t_2^4 - 2\,x\,t_2^3 + (1 - 2\,y)\,t_2^2 - 2\,z\,t_2 + v^2 = 0 \\ T_3 \equiv t_3^6 + t_3^4 - 2\,x\,t_3^3 + (1 - 2\,y)\,t_3^2 - 2\,z\,t_3 + v^2 = 0 \end{aligned}\right\},$$

where v^2 stands for $x^2 + y^2 + z^2 - w^2$. Reducing $t_3^3\,T_2 - t_2^3\,T_3 = 0$ and $t_3^2\,T_2 - t_2^2\,T_3 = 0$ by means of the relation $3\,t_2\,t_3 = 1$, we find in t_1 as variable

$$\left.\begin{aligned} 3\,(1 - 27\,v^2)\,t_1^2 + 51\,z\,t_1 + 27\,v^2 + 18\,y - 7 = 0 \\ 3\,t_1^3 + (1 - 27\,v^2)\,t_1 + 6\,(3\,z - x) = 0 \end{aligned}\right\},$$

and so after elimination of t_1 we obtain the equation

$$\begin{vmatrix} 3(1-27\,v^2), & 54\,z\;\;, & 27\,v^2+18\,y-7, & 0\;\;, & 0 \\ 0\;\;, & 3(1-27\,v^2), & 54\,z\;\;, & 27\,v^2+18\,y-7, & 0 \\ 0\;\;, & 0\;\;, & 3\,(1-27\,v^2)\;, & 54\,z\;\;, & 27\,v^2+18\,y-7 \\ 3\;\;, & 0\;\;, & 1-27\,v^2\;, & 6\,(3\,z-x)\;, & 0 \\ 0\;\;, & 3\;\;, & 0\;\;, & 1-27v^2\;, & 6\,(3\,z-x) \end{vmatrix} = 0,$$

which is really of degree ten. For by developing we find

$$3^{15}\,v^{10} + \;\cdot\;\;\cdot\;\;\cdot\;\;\cdot\;\;\cdot\;\; - 2^6.7 = 0.$$

Of this curved space the sphere, according to which the hypercone $v_2 \equiv x_2 + y_2 + z_2 - w_2 = 0$ intersects the space at infinity, is a fivefold surface, etc.

In passing we remark that the plane (11) envelops the developable of which the rational skew curve of degree five represented by the equations

$$\left.\begin{aligned} 6\,x = t\,(18\,t^4 + 9\,t^2 - 1) \\ 2\,(1 - 34) = 3\,t^2\,(15\,t^2 - 1) \\ 2\,z = t\,(10\,t^2 - 1) \end{aligned}\right\}$$

is the cuspidal edge; as follows from the common factor $30\,t^2 - 1$ of the derivatives of x, y, z according to t this curve has two real cusps, etc.

5. *The normal curve N_n^n of S^n.* If we represent the curve by the equations

$$x_i = t^i, \quad (i = 1, 2, \ldots \ldots n),$$

the following theorems are proved in an entirely similar way:

"The hyperspheres H_{n-1} with $n-1$ dimensions determined by "groups of $n+1$ points of the curve N_n^n conormal with $n-2$ given "points $t_1, t_2, \ldots \, t_{n-2}$ of that curve, intersect the curve still in "$n-1$ fixed points $s_1, s_2, \ldots s_{n-1}$ and form therefore a net, of "which the hypersphere H_{n-3} determined by those $n-1$ points s is "the base. And if the system of the $n-2$ given points describes "the curve N_n^n, the groups of $n-1$ points s determine on N_n^n an invo"lution of degree $n-1$ with $n-2$ dimensions."

"If the point P describes the plane π common to the normal "spaces of $n-2$ given points $t_1, t_2, \ldots \, t_{n-2}$, the centre M of the "corresponding hypersphere of JOACHIMSTHAL describes the plane μ, "which is the locus of the points at equal distance from the "$n-1$ points s depending in the indicated way on the $n-2$ given "points t; then P and M describe in the planes π and μ affinely "related point-fields (P) and (M)."

"Between the spacial systems (P) and (M) with n dimensions "exists a correspondence $(2n-1, 2n-1)$."

"The cyclographic representation of all the hyperspheres of "JOACHIMSTHAL demands the given space S_n to be supposed to be "part of a S_{n+1}; it leads to a curved space of order $2\,(2n-1)$ with "n dimensions in this S_{n+1} as locus of the pairs of images, etc."

We believe we can suffice with these general indications; we only wish still to observe that the coefficients of the equation determining the $n-1$ fixed points are connected in a simple way with the symmetrical functions $\sum\limits_{n-2,\,k} t$ of the $n-2$ points t taken arbitrarily.

Mathematics. — "*Approximation formulae concerning the prime numbers not exceeding a given limit*". By Prof. J. C. KLUYVER.

RIEMANN's method for determining the total number of the prime numbers p less than a given number c is equally serviceable, when it is required to evaluate other arithmetic expressions involving these prime numbers, for example the sum $\sum\limits_{p<c} p^{-s}$ of their $(-s)^{\text{th}}$ powers, or the least common multiple $M(c)$ of all integers less than c. The different results, thus deduced, constantly contain a set of terms depending on the complex zeros μ of the RIEMANN ζ-function. The most important of these terms is always one and the same disconti-

nuous functions of c; the remaining ones are continuous and of less consequence.

A direct evaluation of the discontinuous term is not to be thought of; if however we suppose given beforehand the number of the prime numbers less than c, we can eliminate the discontinuous term and we are enabled, as will be shown subsequently, to arrive at rather close approximations of other more or less symmetric functions of these prime numbers.

In order to obtain the formulae we have in view, we must apply **Riemann**'s method to the discontinuous integral

$$G_s(c) = \frac{1}{2\pi i}\int_{a-i\infty}^{a+i\infty} \frac{c^z}{z}\, log\, \zeta(z+s)\, dz\,,$$

the path of integration being a straight line parallel to the imaginary axis and on the positive side of it.

By **Euler**'s equation we have, supposing $z+s>1$,

$$log\, \zeta(z+s) = \sum_{n=1}^{n=\infty} \frac{1}{n} \sum p^{-z-s}$$

and by inserting this value in the integral we find

$$G_s(c) = \sum_{n=1}^{n=\infty} \frac{1}{n} \sum_{p^n<c} p^{-ns}\,.$$

On the other hand we may express $\zeta(z+s)$ as an infinite product, that is we may write

$$log\, \zeta(z+s) = -\,log\, 2 - log\,(z+s-1) + \frac{z+s}{2}(C + log\, \pi) +$$

$$+ \sum_{\mu} log\left(1 - \frac{z+s}{\mu}\right) + \sum_{n=1}^{n=\infty} \left\{ log\left(1 + \frac{z+s}{2n}\right) - \frac{z+s}{2n} \right\},$$

or by subtracting at both sides $log\, \zeta(s)$,

$$log\, \zeta(z+s) = log\, \zeta(s) - log\left(1 - \frac{z}{1-s}\right) + \frac{z}{2}(C + log\, \pi) +$$

$$+ \sum_{\mu} log\left(1 - \frac{z}{\mu - s}\right) + \sum_{n=1}^{n=\infty} \left\{ log\left(1 + \frac{z}{2n+s}\right) - \frac{z}{2n} \right\},$$

where in the series

$$\sum_{\mu} log\left(1 - \frac{z}{\mu - s}\right)$$

the terms should be arranged according to the ascending moduli of the μ's. Using this expansion of $log\,\zeta\,(z+s)$ in the integral $G_s\,(c)$ and adhering strictly to the reasoning adopted by RIEMANN for the integral $G_0\,(c)$, we obtain

$$G_s\,(c) = log\,|\,\zeta\,(s)| + Li\,(c^{-s+1}) + \int_{c}^{\infty} \frac{dt}{t^{1+s}\,(t^2-1)\,log\,t} - \sum_{\mu} Li\,(c^{\mu-s})\ .$$

It is desirable to give a somewhat different form to the series of integrallogarithms arising here. Let us assume the zeros μ to be of the form $\frac{1}{2} \pm i\,\beta$, then, by pairing off conjugate complexes, we have

$$\sum_{\mu} Li\,(c^{\mu-s}) = \sum_{\mu} \left[Li\,(c^{\frac{1}{2}-s+i\beta}) + Li\,(c^{\frac{1}{2}-s-i\beta})\right] =$$

$$= \sum_{\beta} \left[\int_{-\infty+i\beta}^{\frac{1}{2}-s+i\beta} \frac{c^x}{x}\,dx + \int_{-\infty-i\beta}^{\frac{1}{2}-s-i\beta} \frac{c^x}{x}\,dx\right] =$$

$$= 2\sum_{\beta} \left[cos\,(\beta\,log\,c) \int_{-\infty}^{\frac{1}{2}-s} \frac{c^x\,x\,dx}{x^2+\beta^2} + \beta\,sin\,(\beta\,log\,c) \int_{-\infty}^{\frac{1}{2}-s} \frac{c^x\,dx}{x^2+\beta^2}\right] =$$

$$= 2\sum_{\beta} \left[\frac{sin\,(\beta\,log\,c)}{\beta} \int_{-\infty}^{\frac{1}{2}-s} c^x\,dx + \frac{cos\,(\beta\,log\,c)}{\beta^2} \int_{-\infty}^{\frac{1}{2}-s} c^x\,x\,dx \,- \right.$$

$$\left. - \frac{1}{\beta^2} \int_{-\infty}^{\frac{1}{2}-s} \frac{c^x\,x^2\,dx}{\sqrt{x^2+\beta^2}} \cdot sin\left(\beta\,log\,c + sin^{-1}\frac{x}{\sqrt{x^2+\beta^2}}\right)\right] =$$

$$= \frac{2\,c^{\frac{1}{2}-s}}{log\,c} \left[\sum_{\beta} \frac{sin\,(\beta\,log\,c)}{\beta} + \left(\tfrac{1}{2} - s - \frac{1}{log\,c}\right) \sum_{\beta} \frac{cos\,(\beta\,log\,c)}{\beta^2} + \varrho \sum_{\beta} \frac{1}{\beta^3}\right],$$

ϱ denoting a quantity the absolute value of which is less than

$$\left|\ (\tfrac{1}{2} - s)^2 - \frac{2}{log\,c}\,(\tfrac{1}{2} - s) + \frac{2}{(log\,c)^2}\ \right|\ .$$

Dealing similarly with the integral

$$\int_c^\infty \frac{dt}{t^{1+s}\,(t^2-1)\,\log t}\,,$$

it appears that we may replace it by

$$\frac{\theta}{(2+s)\,(c^2-1)^{1+\frac{1}{2}s}\,\log c}\,,$$

where θ is positive and less than unity.

Hence the preceding equation for $G_s(c)$ can be written

$$G_s(c) = \log \mid \zeta(s) \mid + Li(c^{-s+1}) + \frac{\theta}{(2+s)\,(c^2-1)^{1+\frac{1}{2}s}\,\log c} -$$

$$-\frac{2\,c^{\frac{1}{2}-s}}{\log c}\left[\sum_\beta \frac{\sin(\beta \log c)}{\beta} + \left(\frac{1}{2} - s - \frac{1}{\log c}\right)\sum_\beta \frac{\cos(\beta \log c)}{\beta^2} + \varrho \sum_\beta \frac{1}{\beta^3}\right]$$

and in particular we have for $s = 0$

$$G_0(c) = -\log 2 + Li(c) + \frac{\theta'}{2\,(c^2-1)\,\log c} -$$

$$-\frac{2\,c^{\frac{1}{2}}}{\log c}\left[\sum_\beta \frac{\sin(\beta \log c)}{\beta} + \left(\frac{1}{2} - \frac{1}{\log c}\right)\sum_\beta \frac{\cos(\beta \log c)}{\beta^2} + \varrho' \sum_\beta \frac{1}{\beta^3}\right]$$

In these equations we have got expressed as trigonometrical series the terms the occurrence of which makes it nearly impossible to arrive at a direct and complete determination of either $G_s(c)$ or $G_0(c)$. All we know about these series, is that

$$\sum_\beta \frac{\cos(\beta \log c)}{\beta^2} \quad \text{and} \quad \sum_\beta \frac{1}{\beta^3}$$

converge unconditionally and that their values are rather small, because we have

$$\sum_\beta \frac{1}{\beta^2} = 0.023105, \quad \sum_\beta \frac{1}{\beta^3} < 0.002.$$

Further, that

$$\sum_\beta \frac{\sin(\beta \log c)}{\beta}$$

is a discontinous function of c suddenly changing its value, each time its argument becomes equal to the first, second, third,... power of a prime number.

This suggests that we eliminate the discontinuous function between the two equations and merely retain the relation

$$\left[G_s(c) - log \mid \zeta(s) \mid - Li\,(c^{-s+1})\right] - c^{-s}\left[G_0(c) + log\,2 - Li\,(c)\right] =$$

$$= \frac{2\,s\,c^{\frac{1}{2}-s}}{log\,c}\left[\sum_\beta \frac{cos\,(\beta\,log\,c)}{\beta^2} + A \sum_\beta \frac{1}{\beta^3}\right] + \frac{B}{c^{2+s}\,log\,c}\,.$$

Whatever may be here the values of the coefficients A and B, from what precedes we may infer that they are finite and rather small, so that for $s > \frac{1}{2}$ and for tolerably large values of c the right-hand side tends rapidly to zero.

Regarding it as a vanishing quantity we are led to conclude that the relation

$$\left[G_s(c) - log \mid \zeta(s) \mid - Li\,(c^{-s+1})\right] = c^{-s}\left[G_0(c) + log\,2 - Li\,(c)\right]$$

furnishes approximatively the value of $G_s(c)$ as soon as $G_0(c)$ be given, that is, as soon as we know how many prime numbers and powers of prime numbers are to be found among the integers not exceeding c.

The last equation necessarily takes a slightly altered form when s is tending to unity. In that case we must make use of the expansions

$$log \mid \zeta(s) \mid = - log\,(s-1) + (s-1)\,P_1(s-1),$$

$$Li\,(c^{-s+1}) = C + log\,log\,c^{s-1} + (s-1)\,P_2(s-1),$$

from which we have ultimately

$$\lim_{s=1}\left[log \mid \zeta(s) \mid + Li\,(c^{-s+1})\right] = C + log\,log\,c.$$

Hence the value of $G_1(c)$ may be derived approximately from

$$\left[G_1(c) - C - log\,log\,c\right] = c^{-1}\left[G_0(c) + log\,2 - Li\,(c)\right].$$

Moreover it is evident that a relation similar to that between

$G_s(c)$ and $G_0(c)$ exists between two integrals $G_s(c)$ and $G_t(c)$, and that for $s > t$ and $s > \frac{1}{2}$ we may write

$$\left[G_s(c) - \log \mid \zeta(s) \mid - Li(c^{-s+1})\right] =$$

$$= c^{-s+t} \left[G_t(c) - \log \mid \zeta(t) \mid - Li(c^{-t+1})\right].$$

Lastly, we may remark that it is perfectly admissible to differentiate with respect to s the equation connecting $G_s(c)$ and $G_0(c)$.

Remembering that

$$-\left[\frac{d}{ds} G_s(c)\right]_{s=0}$$

is equal to the logarithm of the least common multiple $M(c)$ of all integers less than c, and that $\zeta'(0) : \zeta(0) = \log 2\pi$, we find, by putting s equal to zero after the performance of the differentiation,

$$\left[\log M(c) + \log 2\pi - c\right] - \log c \left[G_0(c) + \log 2 - Li(c)\right] =$$

$$= -\frac{2c^{\frac{1}{2}}}{\log c}\left[\sum_\beta \frac{\cos(\beta \log c)}{\beta^2} + A \sum_\beta \frac{1}{\beta^3}\right] + \frac{B'}{c^3 \log c}.$$

Now although the second member increases as c increases, it remains relatively small with respect to c and $\log M(c)$; therefore we may expect the relation

$$\left[\log M(c) + \log 2\pi - c\right] = \log c \left[G_0(c) + \log 2 - Li(c)\right]$$

to furnish approximately the value of $\log M(c)$.

The following test-cases abundantly show, that already for a c of moderate magnitude the approximation is very close.

I. $c = e^2 = 7.389, \quad G_2(c) = 0.45277, \quad G_3(c) = 0.18077.$

$$[G_3(c) - \log \zeta(3) - Li(e^{-4})] = 0.00052,$$
$$e^{-2}[G_2(c) - \log \zeta(2) - Li(e^{-2})] = 000054.$$

II. $c = e^3 = 20.086, \quad G_1(c) = 1.69330, \quad G_2(c) = 0.48456.$

$$[G_2(c) - \log \zeta(2) - Li(e^{-3})] = 0.00089,$$
$$e^{-3}[G_1(c) - C - \log 3] = 0.00088.$$

III. $c = e^5 = 148.413$, $G_0(c) = 38.50953$, $G_1(c) = 2{,}18005$,
$\log M(c) = 141.66097$.

$$[G_1(c) - C - \log 5] = -0.00661,$$
$$e^{-5}[G_0(c) + \log 2 - Li(e^5)] = -0.00662.$$

$$[\log M(c) + \log 2\pi - e^5] = -4.914,$$
$$\log e^5 [G_0(c) + \log 2 - Li(e^5)] = -4.913.$$

IV. $c = e^7 = 1096.633$, $G_0(c) = 191.79563$, $G_1(c) = 2.52401$.

$$[G_1(c) - C - \log 7] = 0.00088,$$
$$e^{-7}[G_0(c) + \log 2 - Li(e^7)] = 0.00090.$$

If we have $s > 1$, it is fairly evident that for large values of c already the expression

$$[G_s(c) - \log \zeta(s) - Li(c^{-s+1})]$$

itself may be considered as evanescent, and that by equating it to zero we are sure to obtain, quite independent of the value of $G_0(c)$, a result for $G_s(c)$ that involves only a very small error.

But if we had $s = 1$, or even $\frac{1}{2} < s < 1$, this result would become unreliable, so that for $s \leqq 1$ a previous knowledge of the value of $G_0(c)$ remains indispensable.

This is connected with the fact that in the latter case $G_s(c)$ diverges as c becomes infinite.

Indeed we have for $s = 1$

$$G_1(c) = \sum_{p<c} p^{-1} + \sum_{n=2}^{n=\infty} \frac{1}{n} \sum_{p^n<c} p^{-n},$$

and it is the first term $\sum\limits_{p<c} p^{-1}$ that increases beyond all limits for $c = \infty$ [1]).

We will examine more clocely the behaviour of $\sum\limits_{p<c} p^{-1}$.

As s still surpasses $\frac{1}{2}$, we may write.

$$\lim_{c=\infty} [G_1(c) - C - \log\log c] = 0,$$

or

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[1]) This was already stated by EULER ("Introductio in Analysin infinitorum," I, § 279).

$$\lim_{c=\infty}\left[\sum_{p<c} p^{-1} - \log\log c\right] = C - \sum_{n=2}^{n=\infty}\frac{1}{n}\sum p^{-n}.$$

The numerical constant at the right-hand side is evaluated as follows. We suppose $s > 1$ and consider again the relation

$$\log\zeta(s) = \sum_{1}^{\infty}\frac{1}{n}\sum p^{-ns}.$$

From it we have conversely

$$\sum p^{-s} = \sum_{h=1}^{h=\infty}\frac{(-1)^{\mu_h}}{h}\log\zeta(hs)\ ^{1)},$$

where h denotes the successive terms of the infinite sequence

$$1,\quad 2,\quad 3,\quad 5,\quad 6,\quad 7,\ \ldots\ldots,$$

formed by writing in ascending order the integers not admitting multiple factors, and μ_h stands for the number of prime factors of h (this number h itself, if prime, included).

Thus making s tend to unity we have simultaneously

$$\lim_{s=1}\left[\sum p^{-s} - \log\zeta(s)\right] = -\sum_{n=2}^{n=\infty}\frac{1}{n}p^{-n},$$

$$\lim_{s=1}\left[\sum p^{-s} - \log\zeta(s)\right] = \sum_{h=2}^{h=\infty}\frac{(-1)^{\mu_h}}{h}\log\zeta(h) = -0.31572,$$

and at once find

$$\sum_{n=2}^{n=\infty}\frac{1}{n}\sum p^{-n} = 0.31572,$$

so that finally

$$\lim_{c=\infty}\left[\sum_{p<c} p^{-1} - \log\log c\right] = C - 0.31572 = 0.26150.$$

We mentioned this result in order to compare it with a similar

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[1] From this formula it is readily seen: 1st that Σp^{-s} is an analytic function $f(s)$ of s, we may affirm to exist in the right half-plane; 2nd that the band between the parallels $s = \frac{1}{2} + i\kappa$ and $s = 0 + i\kappa$ is dotted with an infinity of logarithmic discontinuities of $f(s)$; 3rd that these discontinuities grow more and more dense as we approach the axis of imaginaries, so as to prevent $f(s)$ effectually from being continued into the left half-plane.

though wholly empirical formula communicated by LEGENDRE[1]). According to LEGENDRE we shall have

$$\sum_{p<c} p^{-1} = \log\,(\log c - 0.08366) - 0.22150\,,$$

but LEGENDRE not taking 2 for a prime number, as we did, 0,5 should be added to his result, so that we must read

$$\sum_{p<c} p^{-1} = \log\,(\log c - 0.08366) + 0.27850\,,$$

or ultimately for $c = \infty$

$$\underset{c=\infty}{Lim}\left[\sum_{p<c} p^{-1} - \log\log c\right] = 0.27850\,.$$

Thus it appears that the error in LEGENDRE's formula for $c = \infty$ amounts to 0.017, this error diminishing somewhat, when the formula is used for large though finite values of c.

In the preceding we have considered almost exclusively the integrals $G_s(c)$; we now proceed to show that we may deal similarly with the sum $\sum\limits_{p<c} p^{-s}$, though by so doing the formulae lose in simplicity.

From

$$\Sigma\, p^{-(z+s)} = \sum_{h=1}^{h=\infty} \frac{(-1)^{\mu_h}}{h} \log \zeta\,(hz + hs)$$

we derive

$$\sum_{p<c} p^{-s} = \sum_{h=1}^{h=\infty} \frac{(-1)^{\mu_h}}{h} \cdot \frac{1}{2\pi i}\int_{a-i\infty}^{a+i\infty} \frac{c^z}{z} \log\zeta(hz+hs)dz = \sum_{h=1}^{h=\infty} \frac{(-1)^{\mu_h}}{h}\, G_{hs}\,(c^{\frac{1}{h}}).$$

But since

$$G_t\,(b) = 0\,,$$

if the limit b be less than 2, the foregoing infinite series actually contains only a finite number of terms and the summation letter h throughout satisfies the inequality

$$h < \frac{\log c}{\log 2}\,.$$

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[1]) "Essai sur la théorie des nombres," 1808, p. 394. D'une loi remarquable observée dans l'énumération des nombres premiers.

Suppose that h successively becomes equal to

$$1, \quad 2, \quad 3, \quad \ldots . \quad h', \quad h'', \quad \ldots . \quad h''',$$

where h' and h'' denote any pair of consecutive values of h, and consider the expression

$$H_s(c) = \sum_{p<c} p^{-s} - \sum_{h=1}^{h=h'} \frac{(-1)^{\mu h}}{h} \left[\log |\zeta(s)| + Li\,(c^{-s+\frac{1}{h}}) \right] -$$

$$- \sum_{h=h''}^{h=h'''} \frac{(-1)^{\mu h}}{h} G_{hs}(c^{\frac{1}{h}}) \,.$$

Obviously we may write also

$$H_s(c) = \sum_{h=1}^{h=h'} \frac{(-1)^{\mu h}}{h} \left[G_{hs}\,(c^{\frac{1}{h}}) - \log |\zeta(s)| - Li(c^{-s+\frac{1}{h}}) \right] ,$$

and, from what has been proved before, we infer that $H_s(c)$ approximately obeys the relation

$$H_s(c) = c^{-s} H_0(c) \,.$$

It is by means of this equation that we are able to find $\sum\limits_{p<c} p^{-s}$ as soon as $\sum\limits_{p<c} p^0$ be given.

The choice of h' and h'' is quite arbitrary. If desired we may take $h' = h'''$; in general it will be advisable to determine h'' by the condition that $c^{\frac{1}{h''}}$ is just a little less than 5, in order to avoid the application of the approximation formula for $G_{hs}(c^{\frac{1}{h}})$ in cases where $c^{\frac{1}{h}}$ is too small a number.

It will be seen from the following examples that the formula may be relied on, if a not too close approximation is required.

I. $\quad c = e^5 = 148.413, \quad \sum\limits_{p<c} p^o = 34, \quad \sum\limits_{p<c} p^{-1} = 1.87980.$

$$h' = 3, \qquad h'' = 5, \qquad h''' = 7.$$

$$H_0(c) = 34 - [-\log 2 + Li\,(e^5)] + \frac{1}{2} [-\log 2 + Li\,(e^{\frac{5}{2}})] +$$

$$+ \frac{1}{3} [-\log 2 + Li\,(e^{\frac{5}{3}})] + \frac{1}{5} [1] + \frac{1}{6} [1] + \frac{1}{7} [1] = -1.08524.$$

$$H_1(c) = \sum_{p<c} p^{-1} - \left[C + \log 5\right] + \frac{1}{2}\left[\log \zeta(2) + Li\left(e^{-\frac{5}{2}}\right)\right] +$$

$$+ \frac{1}{3}\left[\log\zeta(3) + Li\left(e^{-\frac{10}{3}}\right)\right] + \frac{1}{5}\left[\frac{1}{2^5}\right] - \frac{1}{6}\left[\frac{1}{2^6}\right] + \frac{1}{7}\left[\frac{1}{2^7}\right] = \sum_{p<c} p^{-1} - 1.88701.$$

The relation

$$H_1(c) = e^{-5} H_0(c)$$

gives

$$\sum_{p<c} p^{-1} = 1.87970, \qquad \Delta = 0.00010.$$

II. $c = e^7 = 1096.633, \quad \sum\limits_{p<c} p^0 = 183, \quad \sum\limits_{p<c} p^{-1} = 2.21239.$

$$h' = 3, \quad h'' = 5, \quad h''' = 10.$$

$$H_0(c) = 183 - \left[-\log 2 + Li(e^7)\right] + \frac{1}{2}\left[-\log 2 + Li\left(e^{\frac{7}{2}}\right)\right] +$$

$$+ \frac{1}{3}\left[-\log 2 + Li\left(e^{\frac{7}{3}}\right)\right] + \frac{1}{5}\left[2 + \frac{1}{2}\right] - \frac{1}{6}\left[2\right] + \frac{1}{7}\left[1\right] - \frac{1}{10}\left[1\right] = 0.88308.$$

$$H_1(c) = \sum_{p<c} p^{-1} - \left[C + \log 7\right] + \frac{1}{2}\left[\log \zeta(2) + Li\left(e^{-\frac{7}{2}}\right)\right] +$$

$$+ \frac{1}{3}\left[\log \zeta(3) + Li\left(e^{-\frac{14}{3}}\right)\right] + \frac{1}{5}\left[\frac{1}{2^5} + \frac{1}{3^5} + \frac{1}{2} \cdot \frac{1}{2^{10}}\right] - \frac{1}{6}\left[\frac{1}{2^6} + \frac{1}{3^6}\right] +$$

$$+ \frac{1}{7}\left[\frac{1}{2^7}\right] - \frac{1}{10}\left[\frac{1}{2^{10}}\right] = \sum_{p<c} p^{-1} - 2.21162.$$

The relation

$$H_1(c) = e^{-7} H_0(c)$$

gives

$$\sum_{p<c} p^{-1} = 2.21243, \quad \Delta = 0.00004.$$

III. $c = e^4 = 54.598, \quad \sum\limits_{p<c} p^0 = 16, \quad \sum\limits_{p<c} p^{-3} = 0.17472.$

$$h' = 2, \quad h'' = 3, \quad h''' = 5.$$

$$H_0(c) = 16 - \left[-\log 2 + Li(e^4)\right] + \frac{1}{2}\left[-\log 2 + Li(e^2)\right] +$$

$$+ \frac{1}{3}\left[2\right] + \frac{1}{5}\left[1\right] = 0.05949.$$

$$H_3(c) = \sum_{p<c} p^{-3} - \left[\log \zeta(3) + Li(e^{-8})\right] + \frac{1}{2}\left[\log \zeta(6) + Li(e^{-10})\right] +$$

$$+ \frac{1}{3}\left[\frac{1}{2^9} + \frac{1}{3^9}\right] + \frac{1}{5}\left[\frac{1}{2^{15}}\right] = \sum_{p<c} p^{-3} - 0.17472.$$

The relation

$$H_3(c) = e^{-12} H_0(c)$$

gives

$$\sum_{p<c} p^{-3} = 0.17472, \quad \Delta = 0.00000.$$

Chemistry. — "*Thermodynamics of Standard Cells*" (First Part).

By Dr. ERNST COHEN (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

1. As the elegant researches on the CLARK and WESTON cells performed by KAHLE, JAEGER and WACHSMUTH [1]) in the Physikalisch-Technische Reichsanstalt have now been brought to a close and their measurements have been verified by the highly accurate determinations of CALLENDAR and BARNES [2]), it appeared to me worth while to check these experimental results by thermodynamics.

Not only is the E. M. F. of the CLARK-cell used as the unit of E. M. F., but the value of the exact knowledge of that standard is much increased since by the measurements of CALLENDAR and BARNES [3]), the value of the heat-unit is based on it.

During the research which I shall communicate in the following lines, it has appeared to me that the accepted views regarding the mechanism of the action of the normal cells are incorrect because the old mistake has again been made of ignoring the actual phases of the substances which take part in the changes within the cell. This neglect has already given rise to erroneous calculations and conclusions.

These erroneous views will first be discussed and then a complete theory of the action of the normal cells will be given. We will

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[1]) KAHLE, Zeitschrift für Instrumentenkunde, **12**, S. 117 (1892); ibid. **13**, S. 191 S. 293 (1893). WIEDEMANN's Annalen **51**, S. 174 und 203 (1894), ibid **64**. S. 92 (1898); JAEGER und WACHSMUTH, Elektrotechn. Zeitschrift **15**. S. 507 (1894); WIEDEMANN's Annalen **59**. S. 575 (1896); W. JAEGER. Elektrotechn. Zeitschrift **18**. S. 647 (1897): WIEDEMANN's Ann. **63**. S. 354 (1897); JAEGER und KAHLE, Zeitschrift für Instrumentenkunde (1898) 161.

[2]) Proc. Roy. Society **62**. 117.

[3]) Rep. Brit. Association 1899. Section A. Physical Review, Vol. X No. 4, p. 202. April 1900.

then apply those considerations to the CLARK-cell for which the necessary date are in existence. It will be seen that there is a very satisfactory agreement between theory and practice.

2. By the investigations of JAHN [1]), the accuracy of the celebrated equation of GIBBS and v. HELMHOLTZ, which gives the relation between the electrical energy, the chemical energy and the temperature-coefficient of a reversible galvanic cell in qualitative as well as in a quantative direction, has been confirmed. We will take that equation as starting point,

$$E = \frac{E_c}{n\varepsilon_o} + T\frac{dE}{dT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which E represents the E. M. F. of the reversible cell at the temperature T, E_c the chemical energy of the chemical, or rather chemico-physical process which takes place in the cell (at T^o) when $n\varepsilon_o$ Coulombs pass through it; n is the valency of the moving ion and $\frac{dE}{dT}$ the temperature-coefficient of the E.M.F. at T^o.

3. Both the E.M.F. and the temperature coefficient of the CLARK- and WESTON-cell have been determined by the above mentioned with such a high degree of accuracy that they provide an excellent material from which E_c may be calculated by means of equation (1). We will give those calculations provisionally for the CLARK-cell only, as some data for the WESTON-cell are still wanting and will have to be determined experimentally. In order that E_c may also be calculated from the caloric figures, so as to compare the value thus found with that found by the electric method, one must first understand what happens in the cell when ε_o Coulombs pass through it. The mechanism of the change has so far, as for instance by NERNST in his "Theoretische Chemie" (2e Aufl. 1898), S. 657-658, been represented by the equation:

$$\mathrm{Zn} + \mathrm{Hg_2\,SO_4} \rightleftarrows 2\,\mathrm{Hg} + \mathrm{Zn\,SO_4} \quad . \quad . \quad . \quad . \quad . \quad . \quad (A)$$

If this representation were correct, then when 2 × 95640 Coulombs have passed through the cell and consequently 1 gram-atom of zinc has passed into solution, the heat-effect E_c would be repre-

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[1]) WIED. Ann. 28, S. 21 en 491 (1886); ibid 63, S. 44 (1897).

sented by the difference of the heats of formation of $Zn\,SO_4$ and $Hg_2\,SO_4$.

It must be at once pointed out that under the ordinary conditions in which the cell is used, namely below 39°, the $ZnSO_4$ generated by the current will take up 7 H_2O, which action is accompanied by evolution of heat.

One would thus be inclined to replace the equation *A* by:

$$Zn + Hg_2\,SO_4 + aq. = 2\,Hg + Zn\,SO_4 . 7\,H_2O \quad . \; . \; . \quad (A')$$

But even this representation of the matter is incomplete and gives totally wrong results if a calculation is based on it. I, here, refer to the article of Mac-Intosh in the Journal of Physical Chemistry, Vol. 2. p. 185 (1898), in which this erroneous view forms the starting point.

He investigated a cell of the Clark-type in which the Zn and $Zn\,SO_4 . 7\,H_2O$ had been replaced by Cu and $Cu\,SO_4 . 5\,H_2O$. The difference of the heats of formation of $Cu\,SO_4 . 5\,H_2\,O$ and $Hg_2\,SO_4$ in accordance with the equation:

$$Cu + Hg_2\,SO_4 + aq. = 2\,Hg + Cu\,SO_4 . 5\,H_2O \quad . \; . \; . \quad (B)$$

is regarded as the heat evolved by the reaction taking place in the cell.

From the measured E.M.F., 0,3613 volts, of this cell at $T = 290°$, and the temperature-coefficient $\frac{dE}{dT} = -\,0{,}0006$ volts at that temperature, he calculates (taking the heat of formation of $Cu\,SO_4 . 5\,H_2O$ as 201000 calories) the heat of formation of Hg_2SO_4 to be 175000 calories. With the aid of this figure and the heat of formation of $Zn\,SO_4 . 7\,H_2O$ (253000 calories) he calculates, starting from the equation *A'* the E.M.F. of the Clark-cell at 17°,0 to be 1.427 volts, whilst Kahle has found it to be 1.4304 at 17°,0.

We will see later on that the difference of 2,6 millivolts is due to the wrong principle on which the calculation is based.

4. I will now in the first place calculate E_c for the Clark-cell with the aid of the data given by the electrical measurements of Kahle, Jaeger, Wachsmuth, Callendar and Barnes. The calculations will all be worked out for $T = 291°$, as the calorimetric determinations of Thomsen, which we shall use later on are made at that temperature.

The E. M. F. of the CLARK-cell at t^o may, according to KAHLE, be represented by:

$$E_t = E_{15} - 0{,}00119\ (t-15) - 0{,}000007\ (t-15)^2 \quad . \ . \quad (2)$$

CALLENDAR and BARNES give as the result of their measurements:

$$E_t = E_{15} - 0{,}001200\ (t-15) - 0.0000062\ (t-15)^2 \ . \ . \quad (3)$$

From (2) follows:

$$\frac{dE}{dt} = -\ 0{,}00119 - 0{,}0000140\ (t-15) \quad . \ . \ . \ . \quad (2a)$$

From (3):

$$\frac{dE}{dt} = -\ 0{,}00120 - 0{,}0000124\ (t-15). \quad . \ . \ . \ . \quad (3a)$$

According to JAEGER and KAHLE, the E.MF. of the CLARK-cell at 15°,0 C. is 1,4328 volt.

If we now calculate the temperature-coefficient at 18° C. ($T=291$) we find:

According to (2a)

$$\left(\frac{dE}{dt}\right)_{T=291.} = -\ 0{,}001232 \text{ Volt.}$$

According to (3a)

$$\left(\frac{dE}{dt}\right)_{T=291.} = -\ 0{,}001237 \text{ Volt.}$$

For the E.M.F. of the CLARK-cell at 18° C. ($T = 291$) we find:

$$E_{291} = 1.4291 \text{ Volt.}$$

If these values are introduced into equation (1) p. 611 and everything expressed in caloric measure, 1 volt-coulomb being taken, in accordance with the measurements of JAHN [1]) as being equal to 0,2362 cal. we obtain:

$$E_c = 2 \times 40745 = \mathbf{81490} \text{ calories.}$$

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[1]). WIED. Ann. 25, S. 49 (1885), Zeitschr. für phys. Chemie 26.385 (1898).

5. If we now calculate this heating effect, by means of the incorrect equation A on pag. 611 we find:

$$E_c = \text{Heat of formation } Zn\,SO_4 - \text{Heat of formation } Hg_2\,SO_4.$$

The heat of formation of $Zn\,SO_4$ has been determined by THOMSEN[1]) as 230090 calories, that of $Hg_2\,SO_4$ determined by VARET[2]) some years ago in two totally different ways as 175000 calories.

By the calorimetric way we therefore find:

$$E_c = 230090 - 175000 = 55090 \text{ calories}$$

a value differing no less than 26000 calories from that obtained by the electrical method.

If with MAC-INTOSH, we take into consideration the fact that $Zn\,SO_4 . 7\,H_2\,O$ is formed, and allow, according to THOMSEN, 22690 calories for the heat of hydration of $Zn\,SO_4$ to $Zn\,SO_4 . 7\,H_2\,O$ we find:

$$E_c = 252780 - 175000 = 77780 \text{ calories}$$

a figure which still differs considerably from that calculated (81490 cal.).

6. Having now demonstrated that the prevailing ideas as to the reactions taking place in the CLARK-cell lead to great differences, we may investigate what really occurs in the cell when the current is closed.

Suppose 2 × 96540 Coulombs have passed; 1 gram-atom of zinc will have dissolved and this will have combined with an equivalent quantity of SO_4 from the $Hg_2\,SO_4$ to form $Zn\,SO_4$.

This $Zn\,SO_4$ will now immediately abstract water from the saturated solution of $Zn\,SO_4 . 7\,H_2O$ contained in the cell in order to form $Zn\,SO_4 . 7\,H_2O$. This abstraction of water will take place according to the equation:

$$Zn\,SO_4 + \frac{7}{A-7}\,(Zn\,SO_4\ A\ H_2O) = \frac{A}{A-7}\,Zn\,SO_4 . 7\,H_2O \quad . \; . \; . \; (C)$$

where A represents the number of mols. of water which are present in the saturated solution along with 1 mol. of $Zn\,SO_4$ at the temperature T of the cell.

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[1]) Thermochem. Untersuchungen III, S. 275 en II S. 245.

[2]). Ann. de chimie et physique, VIII (7) (1896). See also BERTHELOT, Thermochimie II p. 360 (1897).

The $ZnSO_4 . 7 H_2O$ formed will be deposited from the saturated solution contained in the cell and be added to the crystals already present.

The heating effect E_c in the cell is now equal to the difference of the heats of formation of $ZnSO_4$ and Hg_2SO_4 plus the heat effect W of the change represented by equation (C) which may be calculated from thermochemical data.

The value of A may be calculated from the solubility determinations made by CALLENDAR and BARNES[1]) and COHEN[2]). Their results, which agree perfectly, lead to the equation:

$$L = 41.80 + 0.522\, t + 0.00496\, t^2$$

where L represents the number of grams of $ZnSO_4$ which are soluble in 100 grams of water at t^0.

From this equation it is found that at 18° C. $A = 16.81$ so that at that temperature the equation (C) assumes the following form:

$$ZnSO_4 + 0.713\,(ZnSO_4 . 16.81\, H_2O) = 1.713\, ZnSO_4 . 7\, H_2O \ldots (C^1)$$

The heat effect accompanying this change may be found by supposing the systems on the left and on the right hand side of the equation to be dissolved in water so that both shall have the final-concentration $ZnSO_4 . 400\, H_2O$.

We then find:

Heat of solution $ZnSO_4 — ZnSO_4 . 400\, H_2O = + 18430$ calories THOMSEN, Thermochem. Untersuchungen III, S. 275.

The heat of dilution of ($ZnSO_4 . 16{,}81\, H_2O — ZnSO_4 . 400\, H_2O$) is calculated as follows:

The heat of dilution $ZnSO_4 . 20\, H_2O — ZnSO_4 . 50\, H_2O =$ + 318 calories THOMSEN l. c. p. 90.

therefore, heat of dilution $ZnSO_4 . 16{,}81\, H_2O — ZnSO_4 . 20\, H_2O$

$$= \frac{318}{30}\,(20 — 16.81) = + 33.8 \text{ calories.}$$

Since now, the heat of dilution $ZnSO_4 . 20\, H_2O — ZnSO_4 . 200\, H_2O$ = + 390 calories THOMSEN l. c. p. 37

and the heat of dilution $ZnSO_4 . 200\, H_2O — ZnSO_4 . 400\, H_2O =$ + 10 calories THOMSEN l. c. p. 91.

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[1]) Proc. Roy. Soc. 62. 117.

[2]) Proc. Roy. Acad. Amsterdam. Vol. II 1900, p. 337.

the heat of dilution required, $Zn\,SO_4 \,.\, 16{,}81\, H_2O - Zn\,SO_4 \,.\, 400\, H_2O = 33.8 + 390 + 10 = 433.8$ calories.
The heat of solution of $Zn\,SO_4 \,.\, 7\, H_2O - Zn\,SO_4 \,.\, 400\, H_2O = -4260$ calories THOMSEN, l. c. p. 275
Equation (C^1) now gives:

$$W = 18430 + 0.713 \times 433.8 + 1.713 \times 4260 = +26037 \text{ calories.}$$

The total heat-effect in the cell now becomes:

$$E_c = (230090 + 26037) - 175000 = \mathbf{81127} \text{ calories}$$

while the calculation based on the electrical measurements gave us **81490** which is a very satisfactory agreement.

We can, of course, express this result in a different manner and calculate the temperature-coefficient at 18° C. from the thermochemical data and compare it with that found experimentally.

The calculation gives:

$$\left(\frac{dE}{dt}\right)_{18^\circ} = -\frac{8006}{291 \times 22782} = -\mathbf{0{,}001207} \text{ Volt,}$$

whilst **0,001235** Volt. was found experimentally.

7. Thus far we have only considered cells such as are used in practice, that is to say cells which contain a large excess of undissolved $Zn\,SO_4 \,.\, 7\, H_2O$.

If the cell has a higher temperature than 39°, which is the transition point of the salt with 7 mols. of water of crystallisation, or when it has come down to a lower temperature after the complete change of the solid salt, the cell will contain undissolved $ZnSO_4.6H_2O$ [1]).

Similar considerations then lead to the following equation for the change which occurs during the passage of the current:

$$Zn\,SO_4 + \frac{6}{a-6}\, Zn\,SO_4\;\; a\; H_2\,O = \frac{a}{a-6}\, Zn\,SO_4 .\, 6\, H_2O \;.\;\;.\;\; (D)$$

For this cell we can also calculate E_c from JAEGER's electrical measurements and compare it with the value found by the calorimetric method.

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[1]) See CALLENDAR and BARNES, Proc. Roy. Soc. 62, 117. JAEGER, WIED. Ann. 63, 354. COHEN, Zeitschrift für phys. Chemie 25, 300 (1898). BARNES, Journal of physical Chemistry 4, 1 (1900).

We will, for instance, make the calculation for 15° C.; a is [1]) than 15,67 and the equation (D) becomes:

$$Zn\,SO_4 + 0{,}620\;Zn\,SO_4 . 15.67\;H_2O = 1{,}620\;Zn\,SO_4 .\;6\;H_2O \quad . \quad (D')$$

Calculating as before and using THOMSEN's figures we find:

$$W = 18430 + 0{,}620 \times 441 + 1{,}620 \times 843 = +\;20069 \text{ calories}$$

and for the total heat evolved in the cell:

$$E_c = (23090 + 20069) - 175000 = \mathbf{75159} \text{ calories} .$$

According to JAEGER's measurements, for a cell containing undissolved $Zn\,SO_4 .\;6\;H_2O$:

$$E_t = 1{,}400 - 0{,}00102\,(t-39) - 0{,}000004\,(t-39)^2 \quad . \quad . \quad (4)$$

therefore

$$E_{15} = 1{,}4225 \text{ Volts.}$$

It further follows from (4) that

$$\left(\frac{dE}{dt}\right)_{15^0} = -\;0{,}00102 + 48 \times 0{,}000004 = -\;0{,}000828 \text{ Volt}$$

therefore

$$E_c = 2\;(\,1{,}4225 + 288 \times 0{,}000828)\;22782 = \mathbf{75677} \text{ calories}$$

whilst caloric determinations gave $E_c = \mathbf{75159}$ calories an almost perfect agreement.

Results of the research.

1. The accepted views respecting the mechanism of the action of standard cells are incorrect, because insufficient attention has been paid to the actual phases of the substances which take part in the reactions going on in the cells.

2. The representation of the reaction in the CLARK-normal cell by the equation:

$$Zn + Hg_2\,SO_4 \rightleftarrows 2\;Hg + Zn\,SO_4$$

as given for instance by NERNST, must be replaced by the equations:

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[1]) Proceedings Royal Acad. Amsterdam. Vol. II, p. 338.

$$Zn + \underset{\text{liquid}}{\frac{7}{A-7}\,(ZnSO_4,\, A H_2O)} + Hg_2SO_4 \rightleftarrows 2\,Hg + \underset{\text{solid}}{\frac{A}{A-7}\,ZnSO_4 .\, 7\, H_2O.}$$

and

$$Zn + \underset{\text{liquid}}{\frac{6}{a-6}\,(ZnSO_4 .\, a\, H_2O)} + Hg_2SO_4 \rightleftarrows 2\,Hg + \underset{\text{solid}}{\frac{a}{a-6}\,ZnSO_4 .\, 6\, H_2O}$$

in which A, or a, represents the number of mols. of water which accompany one molecule of $ZnSO_4$ in the saturated solution at the temperature of the cell.

3. It has been demonstrated that calculations based on the old view lead to utterly faulty results.

4. The value of E_c in the equation of GIBBS and v. HELMHOLTZ is calculated by means of the new equation. For the CLARK-normal-cell in which undissolved $ZnSO_4 .\, 7\, H_2O$ is present the calculation gave:

at 18° C. $E_c =$ **81127** calories

whilst experimentally the value $E_c =$ **81490** calories was found or, the calculation gives as temperature-coefficient at 18° C.

— **0,001207** Volt.

whilst experimentally — **0,001235** »

was found.

For the CLARK-cell containing undissolved $ZnSO_4 .\, 6\, H_2O$, the calculation at 15° C. gives $E_c =$ **75159** calories,

whilst experiment gives $E_c =$ **75677** „

Amsterdam, University Chemical Laboratory,
April 1900.

Chemistry. — "*Studies on Inversion*" (First Part). By Dr. ERNST COHEN (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

1. A few years ago (1896) it was stated by RAÝMAN and ŠULC in a paper on catalytic hydration by metals [1]), that when cane-sugar is dissolved in very pure water (conductivity 0.7×10^{-6}) and exposed in platinum vessels to temperatures over 80° C. a decided inversion takes place which proceeds with a steadily increasing velocity.

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[1]) Zeitschrift für phys. Chemie 21. 481 (1896).

From their rather extensive material I have taken the following table:

TABLE I.

Temperature 80°.

Time (in hours).	Rotation of the solution.	k.
0	11°.56	—·——
8	11 .49	0.00025
14	11 .42	0.00029
26	10 .89	0.00076
36	9 .23	0.00203
48	4 .95	0.00523
58	0 .31	0.01032

I have calculated the velocity-constant k in the third column from the equation:

$$k = \frac{1}{t} l. \frac{A}{A - x}$$

in which A represents the initial concentration of the inverted sugar solution and x the concentration at the time t.

I have taken it for granted in that calculation that Raýman and Šulc have polarized their solutions at 25° C. Although they do not actually say so, I conclude such to be the case from a remark on p. 488 of their paper.

For the calculation of the end-rotation I have made use of the equation of Herzfeld [1]) who states that every degree of right-handed polarisation of the original solution gives (0.4266—0.005 t) degrees of left handed polarisation at the temperature t°.

I have now made a further investigation of the peculiar phenomenon described by Raýman and Šulc, in the laboratory of Prof. Svante Arrhenius at Stockholm to whom I wish here to express my hearty thanks for the great hospitality extended to me during my stay in Stockholm.

In the first place this article will deal with the method of working and the facts thus collected whilst in a future communication this material will be subjected to a closer calculation.

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[1]) See E. O. von Lippmann, die Chemie der Zuckerarten (1895) S. 516.

2. If it be supposed that both cane-sugar and the products obtained by inversion *d*-glucose and *d*-fructose are of an acidic nature, then the qualitative action in the experiments of RAÝMAN and ŠULC may be explained by assuming that the produced invert-sugar is a stronger acid than the originally present saccharose.

It was now my object to experimentally prove in the first place the correctness of that assumption. If it is correct then it must be assumed that by the action of pure water on saccharose two (stronger) acids are formed which as their amounts increase will accelerate the inversion.

That cane-sugar behaves like an acid is shown by the researches of C. KULLGREN in ARRHENIUS' laboratory. He determined the influence exercised by different non-electrolytes on the saponification-velocity of ethyl acetate by sodium hydroxide at 20°.7 C.

His results are represented graphically in fig. 1. The abscissae

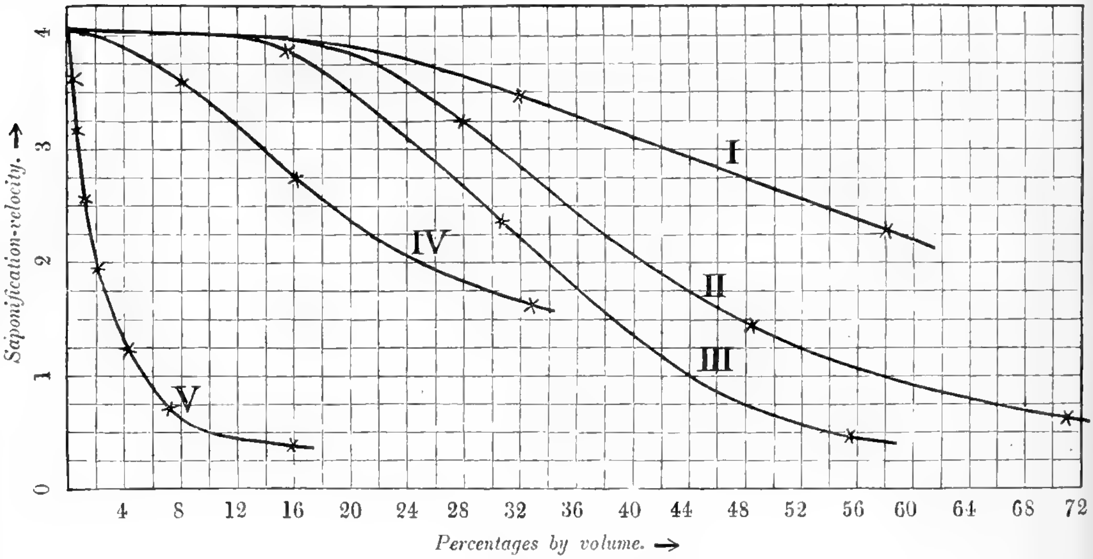

Fig. 1.

represent the concentrations of the added non-electrolytes (in percentage by volume).

Curve I relates to the experiments with acetone.
„ II „ „ „ „ „ ethyl alcohol.
„ III „ „ „ „ „ methyl alcohol.
„ IV „ „ „ „ „ glycerol.
„ V „ „ „ „ „ saccharose.

the ordinates the saponification-velocities at 20°.7 C.

From this representation we see at once that glycerol and particularly saccharose enormously diminish the saponification velocity. Now, these are just the substances which form salts with Na OH according to the scheme:

$$C_{12}H_{22}O_{11} + Na\,OH = C_{12}H_{21}O_{11}Na + H_2O.$$

Kullgren attributes the influence exercised by glycerol and saccharose to a chemical change in the above sense, showing plainly the acidic nature of cane-sugar.

If, on the strength of this view, the influence exercised by the addition of saccharose on the electrical conductive power of N./$_{40}$ NaOH solutions is calculated, a satisfactory agreement appears to exist between the calculation and the experiment as shown by the following table taken from **Kullgren**.

TABLE II.

Percentage by volume saccharose.	Relative Conductivity (at 20°.7 C.) found.	calculated.
0	4.04	—
0.533	3.06	3.32
1.058	2.79	2.36
2.11	2.12	2.33
4.20	1.63	1.78
7.00	1.26	1.31
15.87	0.78	0.73

3. I have now studied the influence which cane-sugar invert-sugar, d-glucose, d-fructose and finally mannitol exercise on the saponification-velocity of N./$_{40}$ ethylacetate by N./$_{40}$ Na OH. 25° was chosen as the temperature of the experiments.

Mannitol was also investigated in order to show once more that substances which do not yield salts exercise an influence of a quite different kind than those who do form such compounds.

The different solutions were mixed together in the well-known manner in 100 cc. flasks made of Jena-glass which were previously steamed. In every case the concentration of the ethyl acetate and of the lye was N./$_{40}$.

The flasks were suspended in a thermostat the temperature of which was constant within 0,03° (toluene-regulator and powerful stirring by means of **Heinrici** hot air-motor). From time to time (the chronometer showed a fifth of a second) 10 cc. were pipetted from the flasks and added to 10 cc. of standardised acid; the excess of acid was then titrated with $N./_{40}$ NaOH using phenolphthalein as indicator.

The standard liquids were kept in large bottles and duly protected from the carbon dioxide of the air [1]).

The preparation of lye free from CO_2 is generally done by allowing metallic sodium to liquefy under a jar in which a basin of water is placed. By following this method [2]) the preparation of, say, 1 litre of N. soda takes many days. I have, therefore, constructed a simple little apparatus which enables us to dissolve in a few hours 50 grams of sodium out of contact with the air. The apparatus may be put together by means of materials which are found in every laboratory [3]). (Fig. 2).

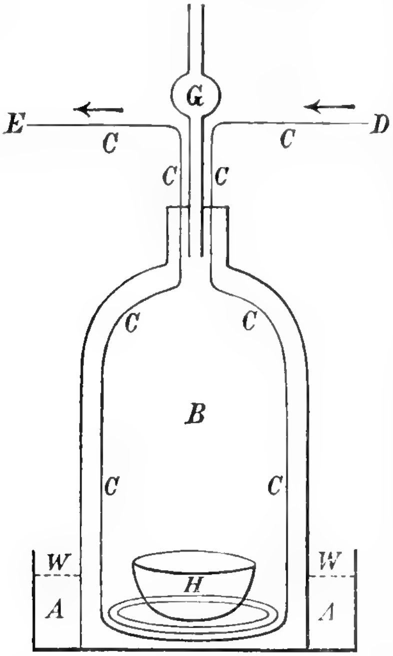

Fig. 2.

B is a jar (bottomless bottle) closed by a trebly-perforated cork. Through the hole in the centre passes a soda-lime tube *G*. Through both the other holes a thin copper tube enters (or leaves) the jar, which runs alongside the walls and is rolled circularly at the bottom (3 windings). Within the circle is placed a silver dish filled with metallic sodium cut up into small pieces. The jar with the dish is then placed into a crystallizing basin containing a little water so that the lower edge of the jar dips a few c.m. into the water. From a boiling-flask with a safety tube steam is passed through the copper tube the other end of which is connected with a water-airpump to remove condensed water.

Soon the jar gets filled with water vapour, hydrogen escapes through the soda-line tube and after a few hours, the sodium is completely liquefied and dissolved. Traces of carbon dioxide which may be present in the solution were removed by boiling the solution with a little $Ba(OH)_2$.

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[1] Compare **Spohr**, Zeitschrift für phys. Chemie 2, S. 194 (1888).

[2] **Ostwald**, Hand- und Hülfsbuch zur Ausführung physiko-chemischer Messungen, S. 281.

[3] Compare **Rosenfeld**, Journ. für pract. Chemie N. F. 48 (1893) 599.

A. *Experiments with saccharose.*

4. Pure sugar candy was dissolved in water [1]), precipitated with alcohol (96 vol. proc.), washed with ether and then dried in vacuo [2]). The ethyl acetate used in these and subsequent experiments was thrice redistilled and afterwards a $N./_{10}$ solution was made of it. I investigated the influence of $N./_5$, $N./_{10}$, $N./_{20}$, $N./_{40}$ and $N./_{80}$ sugar solutions on the saponification-velocity. These were prepared by means of $N./2^1/_2$ stock solution which was preserved with camphor to prevent fungoid growth. In these as in all subsequent experiments the solutions were always prepared quite independently of each other whilst for each solution the velocity-constant was determined 5 (or more) times. The mean of the two series thus obtained will be taken as the end-figure.

When calculating the constant (k), the concentration at the first observation was considered as the initial concentration, so that the influence of the first errors becomes trifling. The constant follows from the equation [3]):

$$k = \frac{C_1 - C_n}{C_1\, C_n\, (t_n - t_1)}\,.$$

Before giving the results obtained on saponifying solutions to which saccharose had been added, I will first give some determinations made with purely aqueous solutions.

In all the following tables, t represents the time required for saponification in minutes, C_n the concentration of the lye (expressed in $N./_{40}$ NaOH); the third column contains the value $k\,C_1$.

TABLE III.

$N./_{40}$ ethyl acetate + $N./_{40}$ NaOH.

First series.				Second series			
t	Cn	k C_1		t	Cn	k C_1	
2	7.29	———		2	7.20	———	
4	5.82	0.126		4	5.75	0.126	
6	4.90	0.122	k = **6,85**	6	4.81	0.124	
8	4.18	0.124		9	3.90	0.121	k = **6,88**
10	3.63	0.126		12	3.18	0.126	
12	3.23	0.125		15	2.73	0.123	
	average	0.125			average	0.124	

---

[1]) The water used in the experiments was distilled with particular care and freed from carbon dioxide by passing a current of air (free from CO_2) for 6 hours.

[2]) See E. O. VON LIPPMANN, die Chemie der Zuckerarten (1895), S. 59.

[3]) See VAN 'T HOFF–COHEN, Studien zur chemischen Dynamik (1896), S. 13; ARRHENIUS, Zeitschrift für phys. Chemie I. 112 (1887).

As the average of both series we, therefore, find k = 6,86 at 25°.

By way of comparison we may put the figures of **Arrhenius** and Spohr side by side:

Arrhenius [1])	found at 24°.7 ($N./_{40}$ ethyl acetate + $N/_{40}$ NaOH) 6.45 and 6.59 aver.	6.52
Spohr [2])	found at 25°.0 ($N./_{40}$ ethyl acetate + $N./_{40}$ NaOH)	6.51

The found figure 6.86 at 25°.0 agrees very well with **Arrhenius'** figure 6.52 at 24°.7, if we consider that a difference in temperature of 0°.3 already influences the velocity of the reaction to the extent of about 6 pCt. [3]).

TABLE IV.

$N./_{40}$ ethyl acetate + $N/_{10}$ Na OH + $N./_{5}$ saccharose.

First serie.				Second series.			
t	Cu	kC_1		t	Cu	kC_1	
10	6.43	—		10	6.45	—	
15	5.51	0.0333		15	5.55	0.0324	
20	4.85	326	k = **2,03**	20	4.90	316	k = **1,99**
25	4.30	330		25	4.38	315	
35	3.58	318		35	3.53	330	
	average	0.0327			average	0.0321	

TABLE V.

$N./_{40}$ ethyl acetate + $N./_{40}$ Na OH + $N./_{10}$ saccharose.

First series.				Second series.			
t	Cu	kC_1		t	Cu	kC_1	
5	6.91	—		5	6.81	—	
10	5.45	0.0535		10	5.40	0.0525	
15	4.47	545	k = **3,14**	15	4.45	530	k = **3,10**
20	3.81	542		20	3.78	534	
25	3.30	547		25	3.33	522	
	average	0.0542			average	0.0528	

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[1]) Arrhenius, Zeitschrift für phys. Chemie 1. 112 (1887).

[2]) Spohr, ibid 2. 194 (1888).

[3]) Studien zur chemischen Dynamik S. 129.

TABLE VI.

N./$_{40}$ ethyl acetate + N./$_{40}$ Na OH + N./$_{20}$ saccharose.

First Series.				Second series.			
t	Cn	kC$_1$		t	Cn	kC$_1$	
3	7.20	—		6	5.81	—	
7	5.52	0.076		9	4.90	0.0619	
9	4.91			13	4.02	635	k = **4,32**
13	4.08	764	k = **4,26**	17	3.43	630	
17	3.48	763					
		average 0.0766				average 0.0628	

TABLE VII.

N./$_{40}$ ethyl acetate + N./$_{40}$ Na OH + N./$_{40}$ saccharose.

First series.				Second series.			
t	Cn	kC$_1$		t	Cn	kC$_1$	
3	6.91	—		3	6.93	—	
6	5.43	0.0908		6	5.48	0.0882	
9	4.48	903	k = **5,22**	9	4.50	900	k = **5,15**
12	3.82	901		12	3.85	888	
15	3.33	896		15	3.37	880	
		average 0.0902				average 0.0887	

TABLE VIII.

N./$_{40}$ ethyl acetate + N./$_{40}$ Na OH + N./$_{80}$ saccharose.

First series.				Second series.			
t	Cn	kC$_1$		t	Cn	kC$_1$	
2	7.40	—		2	7.30	—	
4	6.08	0.108	k = **5,84**	4	6.00	108	k = **5,92**
6	5.12	106		6	5.05	111	
9	4.21	108		12	3.52	107	
12	3.55	108					
		average 0.108				average 0.108	

B. *Experiments with invert-sugar.*

A N.2½ solution of invert-sugar was prepared by inverting a N.2½ solution of cane-sugar by means of a little acid at 60° C.

A weighed quantity of saccharose was dissolved in a little water contained in a measuring flask, 20 cc. of $N./_{20}$ HNO_3 were added and the whole kept for 24 hours at 60°. The acid was then neutralized with lye and the liquid was diluted to the mark. I made sure about the completeness of the inversion by a polariscopic test.

Operating in this manner, the liquid contains but little $NaNO_3$; the presence of salts should be avoided as, according to **Spohr**'s experiments they exercise a great influence on the saponification-velocity of ethyl acetate by $NaOH$.

To be more sure, I inverted a second solution with a trace of oxalic acid: the figures which I obtained afterwards on saponification were identical with those given by the solution inverted with HNO_3. Both the solutions were, therefore, used in the further saponification experiments. I have studied closer an additional phenomenon which might have been of influence on the experiments where invert-sugar or d-glucose and d-fructose were used.

Lobry de Bruyn and Alberda van Ekenstein [1]) when studying the action of dilute alkalis on carbohydrates have found that d-glucose and d-fructose undergo decomposition even by dilute solutions of $NaOH$. A portion of the added $NaOH$ disappears as it gets neutralized by the organic acids which are formed. The decomposition was very plainly observable at 63° after a short time, when $N./_{50}$ $NaOH$ was used.

It, therefore, became necessary to ascertain in how far a similar secondary reaction may interfere here at 25° C. during the time my observations lasted.

For that purpose, I mixed in a flask: 50 cc. $N.2^1/_2$ invert-sugar, 25 cc. of water and 25 cc. of $N./_{10}$ $NaOH$ and kept the mixture in a thermostat at 25° C. From time to time, the alkalinity was determined by titrating 10 cc. with $N./_{40}$ acid.

After	80	minutes	0.2 cc.	of	$N./_{40}$	$NaOH$	were	assumed.
„	250	„	0.3 cc.	„	$N./_{40}$	$NaOH$	„	„
„	1320	„	1.1 cc.	„	$N./_{40}$	$NaOH$	„	„

As in our case the experiments are finished within 150 minutes, the secondary action is not likely to influence the general result.

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[1]) Rec. des Trav. chim. des Pays-Bas. **14**, 156, 203 (1895).

TABLE IX.

$N./_{40}$ ethyl acetate + $N./_{40}$ Na OH + $N./_{5}$ invert-sugar.

t	C_n	kC_1	
30	7.52	—	
50	6.59	0.00705	
80	5.51	729	k = **0.379**
110	4.79	712	
	average	0.00715	

TABLE X.

$N./_{40}$ ethyl acetate + $N./_{40}$ Na OH + $N./_{10}$ invert-sugar.

First series.

t	C_n	kC_1	
15	7.78	—	
30	6.50	0.0131	
50	5.35	129	k = **0.68**
73	4.35	131	
105	3.59	142	
	average	0,0133	

Second series.

t	C_n	kC_1	
15	7.78	—	
30	6.50	0.0131	
50	5.38	127	k = **0.66**
75	4.39	128	
105	3 55	132	
	average	0.0139	

TABLE XI.

$N./_{40}$ ethyl acetate + $N./_{40}$ Na OH + $N./_{20}$ invert-sugar.

First series.

t	C_n	kC_1	
10	7.44	—	
20	6.10	0.0219	
30	5.20	215	k = **1.15**
45	4.28	211	
65	3.40	216	
	average	0.0215	

Second series.

t	C_n	kC_1	
10	7.40	—	
20	6.05	0.0223	
30	5.13	221	k = **1.18**
45	4.21	216	
65	3.42	212	
	average	0.0218	

TABLE XII.

$N./_{40}$ ethyl acetate + $N./_{40}$ Na OH + $N./_{40}$ invert-sugar.

First series.

t	C_n	kC_1	
5	7.51	—	
10	6.32	0.0376	
15	5.41	388	k = **2.01**
20	4.80	376	
30	3.90	370	
	average	0.0377	

Second series.

t	C_n	kC_1	
5	7.50	—	
15	5.42	0.0383	
20	4.78	379	k = **2.04**
30	3.81	387	
	average	0.0383	

TABLE XIII.

$N./_{40}$ ethyl acetate + $N./_{40}$ NaOH + $N./_{80}$ invert-sugar.

First series.				Second series.			
t	C_n	kC_1		t	C_n	kC_1	
3	7.60	—		3	7.52	—	
6	6.36	0.0650	k = **3.39**	6	6.32	0.0633	
9	5.48	644		9	5.42	645	k = **3.36**
12	4.82	641		12	4.80	629	
				17	4.01	625	
	average	0.0644			average	0.0633	

C. *Experiments with d-glucose.*

For these experiments I made use of a preparation sold by MERCK as "Traubenzucker purissimum, wasserfrei". By polarisation and a water determination, the article, however, appeared to contain about 6 pCt. of water.

A second preparation in beautiful crystals was kindly offered to me by Prof. RINDELL of Helsingfors. Both specimens gave the same figures in the saponification experiments and were used side by side.

TABLE XIV.

$N./_{40}$ ethyl acetate + $N./_{40}$ NaOH + $N./_{5}$ d-glucose

First series.				Second series.			
t	C_n	kC_1		t	C_n	kC_1	
15	7.32	—		15	7.32	—	
30	6.07	0.0137		30	6.02	0.0143	
45	5.13	142		45	5.14	142	
60	4.41	146	k = **0.79**	60	4.41	146	k = **0.79**
80	3.72	148		80	3.72	148	
110	3.05	147		110	3.05	147	
	average	0.0144			average	0.0145	

TABLE XV.

$N./_{40}$ ethyl acetate + $N./_{40}$ NaOH + $N./_{10}$ d-glucose.

First series.				Second series.			
t	C_n	kC_1		t	C_n	kC_1	
10	7.04	—		10	7.04	—	
20	5.68	0.0239		20	5.68	0.0239	
30	4.70	248	k = **1.36**	30	4.70	248	
45	3.83	239		45	3.83	239	k = **1.38**
60	3.20	240		60	3.18	242	
75	2.80	233		75	2.70	247	
	average	0.0240			average	0.0243	

TABLE XVI.

N./$_{40}$ ethyl acetate + N./$_{40}$ Na OH + N./$_{20}$ d-glucose.

First series.				Second series.			
t	C_n	kC_1		t	C_n	kC_1	
5	7.39	—		5	7.32	—	
10	6.08	0.0430	**k = 2,31**	10	6.03	0.0427	
15	5.18	426		15	5.11	432	**k = 2,32**
20	4.50	428		20	4.48	422	
				25	3.98	419	
				30	3.55	424	
	average 0.0428				average 0.0425		

TABLE XVII.

N./$_{40}$ ethyl acetate + N./$_{40}$ Na OH + N./$_{40}$ d-glucose.

First series.				Second series.			
t	C_n	kC_1		t	C_n	kC_1	
4	6.96	—		4	6.89	—	
7	5.81	0.0659		7	5.80	0.0626	
10	5.02	644	**k = 3,72**	10	4.99	634	**k = 3,66**
13	4.40	646		13	4.40	628	
17	3.80	639		17	3.78	633	
	average 0.0647				average 0,0630		

TABLE XVIII.

N./$_{40}$ ethyl acetate + N./$_{40}$ Na OH + N./$_{80}$ d-glucose.

First series.				Second series.			
	C_n	kC_1		t	C_n	kC_1	
	7.02	—		3	6.92	—	
6	5.60	0.0845		6	5.52	0.0845	
9	4.61	871	**k = 4.79**	12	3.98	818	**k = 4.79**
12	4.50	839		15	3.47	828	
15	3.53	824		18	3.10	821	
18	3.13	828					
	average 0.0841				average 0.0828		

D. *Experiments with d-Fructose.*

Two specimens of this substance were in my possession. A small quantity of crystallised d-fructose from **Merck** of Darmstadt and a larger quantity which Mr. **Alberda van Ekenstein**, director of the Government sugar laboratory of Amsterdam, had been kind enough to prepare and recrystallize for me. I will not neglect to express here my particular thanks for the great kindness with which Mr. **Alberda** has obliged me with this expensive preparation as this alone has rendered it possible for me to do the experiments with d-fructose on a somewhat larger scale.

Both preparations gave the same figures as will be noticed from the tables.

TABLE XIX.

$N./_{40}$ ethyl acetate + $N./_{40}$ Na OH + $N./_{5}$ d-fructose.

First series (Alberda's preparation.)				Second series (Merck's preparation.)			
t	C_n	kC_1		t	C_n	kC_1	
30	6.73	—		30	6.60	—	
45	5.82	0.0104		45	5.80	0.0092	
60	5.21	097	k = **0,59**	60	5.10	98	k = **0,59**
80	4.52	098		80	4.40	100	
111	3.73	099		110	3.63	102	
145	3.07	104		145	3.03	102	
	average	0.0100			average	0.00988	

TABLE XX.

$N./_{40}$ ethyl acetate + $N./_{40}$ Na OH + $N./_{10}$ d-fructose.

First series.				Second series.			
t	C_n	kC_1		t	C_n	kC_1	
11	7.48	—		10	7.53	—	
20	6.38	0.0191		20	6.38	0.0180	
30	5.49	190	k = **1,03**	33	5.44	192	k = **1,01**
45	4.51	193		45	4.50	192	
60	3.85	192		60	3.82	194	
80	3.22	191		80	3.15	198	
				100	2.76	192	
	average	0.0192			average	0.0191	

TABLE XXI.

N./$_{40}$ ethyl acetate + N./$_{40}$ Na OH + N./$_{20}$ d-fructose.

First series.				Second series.			
t	C_n	kC_1		t	C_n	kC_1	
5	7.68	—		5	7.60	—	
10	6.50	0.0363		10	6.39	0.0378	
15	5.64	363	k = 1.89	15	5.60	357	
20	4.92	373		20	4.90	367	k = 1.87
	average	0.0363 [1]		30	4.10	341	
				40	3.42	349	
				50	3.00	340	
					average	0.0355	

TABLE XXII.

N./$_{40}$ ethyl acetate + N./$_{40}$ Na OH + N./$_{40}$ d-fructose.

First series.				Second series.			
	C_n	kC_1		t	C_n	kC_1	
4	7.21	—		4	7.20	—	
8	5.90	0.0555		8	5.90	0.0550	
12	5.00	552		12	4.99	553	
16	4.38	538	k = 3.02	16	4.33	552	k = 3.05
20	3.87	539		20	3.82	553	
24	3.46	541			average	0.0552	
28	3.13	544					
	average	0.0545					

TABLE XXIII.

N./$_{40}$ ethyl acetate + N./$_{40}$ Na OH + N./$_{80}$ d-fructose.

First series.				Second series.			
t	C_n	kC_1		t	C_n	kC_1	
3	7.12	—		3	7.12	—	
9	4.87	0.0770		9	4.87	0.0770	
12	4.22	763	k = 4,29	12	4.25	750	k = 4,24
15	3.71	766		15	3.71	766	
20	3.11	758		20	3.11	758	
25	2.65	766		25	2.71	739	
	average	0.0764			average	0.0756	

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[1] As I find in my notes that the figure 4.92 is decidedly too low I have disregarded the value 0.0373 when calculating the average.

E. *Experiments with Mannitol.*

The preparation obtained from Kahlbaum was sharply dried and then used for making the solutions.

TABLE XXIV.

N./$_{40}$ ethyl acetate + N./$_{40}$ Na OH + N./$_5$ mannitol.

First series.

t	C_n	kC_1	
3	7.23	—	
9	4.68	0.0907	**k = 5,13**
12	3.92	938	
17	3.12	910	
		average 0.0928	

Second series.

t	C_n	kC_1	
3	7.19	—	
6	5.61	0.0938	
9	4.60	938	**k = 5,20**
12	3.90	937	
17	3.11	937	
		average 0.0938	

TABLE XXV.

N./$_{40}$ ethyl acetate + N./$_{40}$ Na OH + N./$_{10}$ mannitol.

First series.

t	C_n	kC_1	
2	7.53	—	
4	6.19	0.109	
6	5.21	111	**k = 5,83**
8	4.50	112	
11	3.80	109	
		average 0.110	

Second series.

t	C_n	kC_1	
2	7.49	—	
4	6.17	0.107	
6	5.20	110	**k = 5,87**
8	4.52	109	
11	3.70	113	
		average 0.110	

TABLE XXVI.

N./$_{40}$ ethyl acetate + N./$_{40}$ Na OH + N./$_{20}$ mannitol.

First series.

t	C_n	kC_1	
2	7 32	—	
4	6.01	0.109	
6	5.01	115	**k = 6,17**
8	4.33	115	
10	3.80	115	
		average 0.113	

Second series.

t	C_n	kC_1	
2	7.30	—	
4	5.97	0.111	
6	4.99	115	**k = 6,19**
8	4.31	115	
10	3.81	111	
		average 0.113	

TABLE XXVII.

$N./_{40}$ ethyl acetate + $N./_{40}$ Na OH + $N./_{40}$ mannitol.

First series.				Second series.			
t	C_n	kC_t		t	C_n	kC_t	
2	7.20	—		2	7.23	—	
4	5.84	0.116		4	5.84	0.119	
6	4.98	111	k = **6,33**	6	4.98	112	k = **6,47**
8	4.22	117		8	4.23	118	
10	3.76	114		10	3.71	118	
	average	0.114			average	0.117	

TABLE XXVIII.

$N./_{40}$ ethyl acetate + $N./_{40}$ Na OH + $N./_{80}$ mannitol.

First series.				Second series.			
t	C_n	kC_t		t	C_n	kC_t	
2	7.20	—		2	7.12	—	
4	5.79	0.121		4	5.75	0.119	
6	4.80	124	k = **6.88**	6	4.80	120	k = **6.74**
8	4.10	126		10	3.60	122	
10	3.62	124					
	average	0.124			average	0.120	

Summary of results obtained.

If we now take the mean of the figures obtained in the above tables as end-figure we get the following summary:

TABLE XXIX.

Saponification-velocity of $N./_{40}$ ethyl acetate + $N./_{40}$ Na OH at 25°.0 C.

In:	$N./_{5}$	$N./_{10}$	$N./_{20}$	$N./_{40}$	$N./_{80}$	
Water						6.86
Saccharose	2.01	3.12	4.29	5.19	5.88	
Invert-sugar	0.38	0.67	1.17	2.03	3.38	
d-Glucose	0.79	1.37	2.32	3.69	4.79	
d-Fructose	0.59	1.02	1.88	3.04	4.27	
Mannitol	5.17	5.85	6.18	6.40	6.81	

Fig. 3 gives a graphic representation of the results; the abscissae representent the concentrations and the ordinates, the velocities[1]).

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[1]) It must be observed that in fig. 1 which gives KULLGREN's results the abscissae represent percentages by volume, whilst here normalities have been used for calculation. In KULLGREN's case, this representation would have caused difficulties in connection with the great concentrations of several of the non-electrolytes used by him, in view of the scale to be used.

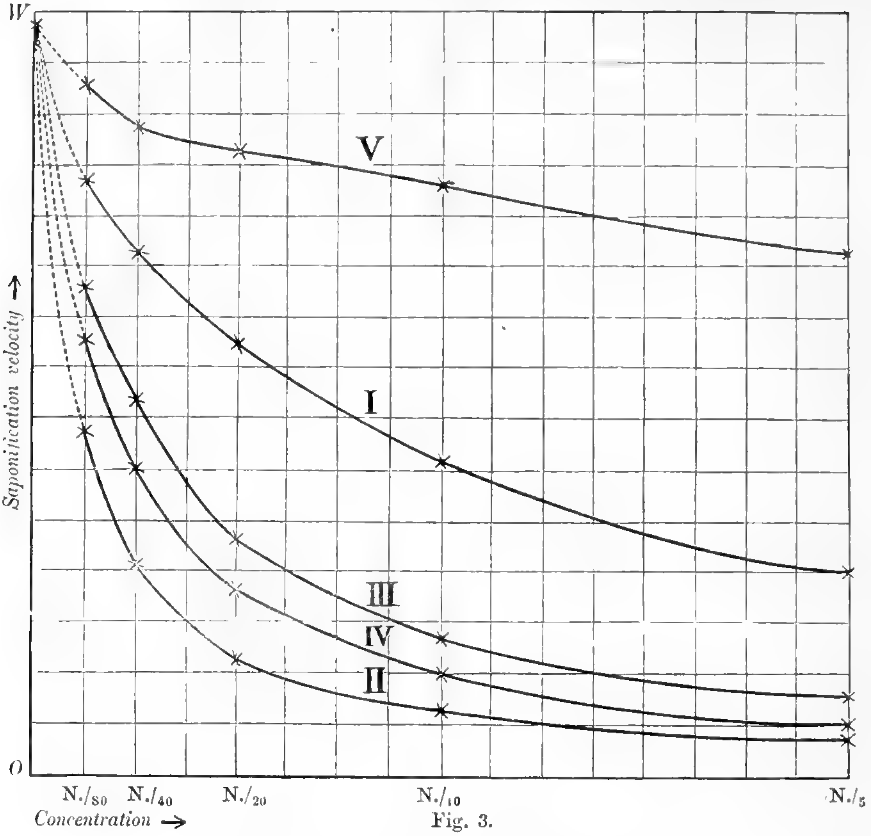

Fig. 3.

Curve I relates to saccharose.
Curve II " " invert-sugar.
Curve III " " d-glucose
Curve IV " " d-fructose.
Curve V " " mannitol.

These curves must, of course, intersect in one point (W).

A glance at the figure shows at once that the saponification-velocity is considerably retarted by saccharose; still more so by invert-sugar. The result showing that the influence exercised by d-glucose and d-fructose is different, is of importance as d-fructose retards the saponification to a much larger extent than d-glucose.

Mannitol, however, exercises but little influence even in the strongest solutions and thus behaves like ethyl and methyl alcohol.

In connection with what has been said at the commencement about Kullgrens researches, we see that saccharose, d-glucose, d-fructose and invert-sugar behave like acids. Invert-sugar is stronger than cane-sugar, d-fructose stronger than d-glucose. The remarkable behaviour of cane sugar solutions observed by Raýman and Šulc may be easily explained after these results.

In a following communication the results obtained will be subjected to calculation.

Stockholm, University physical Laboratory. Aug. 1899.

Chemistry. — "*Determinations of the diminution of vapourpressure and of the elevation of the boiling point of dilute solutions*", by Dr. A. SMITS (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

Introduction.

In a former article [1]) the apparatus has been described, which has enabled me to ascertain the decrease of the vapourpressure and the elevation of the boiling point of dilute solutions.

The method of experimenting when determining the diminution of vapourpressure is already described there, so that it is only necessary to say here that in determining the elevation of the boiling point, the manostat is always set at the same pressure; the thermometer, which remains continuously in the boiling water, controls the action of the manostat, since a small change of pressure in the apparatus is immediately betrayed by a change of temperature.

Regarding the accuracy of the two methods, the preference must be given to the determination of the increase in the boiling point. If, in the method for determining the diminution of vapourpressure, the decrease in the vapourpressure of the solution is to be calculated from the observed fall in the boiling point of pure water, it is necessary to use the table constructed by REGNAULT [2]) for the maximum pressure of watervapour, which gives the differences for each 0.1°. It is plain that errors are committed here; in the first place because the table is not quite correct and secondly because interpolation must be resorted to. The value of i obtained from the value of the decrease in the vapourpressure thus calculated can, therefore, not be very accurate. In the determination of i from the elevation of the boiling point, it is only necessary to divide by a constant factor; in this method the values of i can only be affected by a constant error.

I have, therefore, applied the two methods to the same solutions of $NaCl$, but in the case of the other salts, the elevation of the boiling points only has been determined. The results, which I have obtained with solutions of $NaCl$, KCl and KNO_3 are included in the following tables. Between each of the different series of observations of the $NaCl$-solutions, the manostat was set at a different pressure.

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[1]) Proceeding Royal Acad. Jan. 27, 1900, p. 471.

[2]) Mémoires de l'Acad. T. XXI, p. 632.

Results:

NaCl.

Concentration in gr. mols. per 1000 grs. of H_2O.	Observed decrease of the boiling point of the pure water.	Calculated diminution of the vapour pressure at 99,424° in m.m. of Hg.	*i*
0.0500	0.048	1.27	1.89
0.0750	0.073	1.94	1.93
0.1001	0.093	2.47	1.84
0.5001	0.468	12.41	1.85
1.0000	0.965	25.37	1.89

NaCl.

Boiling point of the pure water = 99.424° $t = 5.18$[1]).

Concentration in gr. mols. per 1000 grs. of H_2O.	Elevation of the boiling point of the solution.	Molecular elevation of the boiling point.	*i*
0.0500	0.050	10.00	1.93
0.0750	0.075	9.99	1.93
0.1001	0.096	9.60	1.85
0.5001	0.471	9.42	1.82
1.0000	0.968	9.68	1.869
2.0798	2.120	10.20	1.969

NaCl.

Boiling point of the pure water = 99.793° $t = 5.19$.

Concentration in gr. mols. per 1000 cc. of H_2O.	Elevation in the boiling point of the solution.	Molecular elevation of the boiling point.	*i*
0.0500	0.049	9.81	1.89
0.1000	0.095	9.50	1.83
0.5000	0.472	9.44	1 82
0.7497	0.717	9.56	1.84
1.0000	0.970	9.70	1.869

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[1]) t = molecular elevation of the boiling point calculated from VAN 'T HOFF's formulae $t = \frac{0,02\, T^2}{w}$. N.B. Although very few of the solutions are weak enough to warrant the calculation of i; this has been done for all concentrations to facilitate the comparison with previous results.

NaCl.

Boiling point of the pure water = 99.61° $t = 5.19°$.

Concentration in gr. mols. per 1000 grs. of H_2O.	Elevation of the boiling point of the solution.	Molecular elevation of the boiling point.	i
0.0560	0.049	9.68	1.87
0.10115	0.096	9.48	1.83
0.50566	0.479	9.47	1.82
1.0112	0.979	9.68	1.865

KCl.

Boiling point of the pure water = 99.695° $t = 5.19$.

Concentration in gr. mols per 1000 grs. of H_2O.	Elevation of the boiling point of the solution.	Moleculor elevation of the boiling point.	i
0.0504	0.050	9.93	1.91
0.1008	0.091	9.03	1.74
0.5037	0.455	9.03	1.74
1.0074	0.926	9.19	1.771

KNO_3.

Boiling point of the pure water = 99.691° $t = 5.19$.

Concentration in gr. mols. per 1000 grs. of H_2O.	Elevation of the boiling point of the solution.	Molecular elevation of the boiling point.	i
0.0499	0.051	10.21	1.97
0.0998	0.095	9.52	1.83
0.4991	0.450	9.02	1.74
0.7486	0.648	8.65	1.67
0.9981	0.858	8.57	1.651

From these tables it is apparent, that in the case of NaCl i reaches a minimum value at about 0.1 gr. mol. per 1000 grs. of water when the diminution of the vapourpressure is determined, and at about 0.5 gr. mol., when the elevation of the boiling point is determined. In the case of KCl, i also reaches a minimum between the concentrations 0.1 and 0.5 gr. mol. From 0.5 gr. mol. upwards a rise of i is observed as the concentration increases. Above 0.5 gr. mol. the results are therefore, qualitatively, the same as with the micromanometer. Below this concentration i seems to increase again with the dilution. In the case of KNO_3 i increases proportionally with the dilution just as I have observed with the micromanometer. Both at 100° and at 0° a solution of KNO_3 seems to behave differently to solutions of K Cl and Na Cl.

As regards the accuracy of the results, I may say that the greatest error of each thermometer was 0,002°. If these errors of the two thermometers have opposite signs, the error of observation amounts to 0,004°. As, however, each determination lasted 15 minutes, a reading being taken every 5 minutes, the average error must have been really less than 0,004° which is confirmed by the thorough agreement of the results obtained in the three series of observations on the Na Cl solutions.

Earlier observations.

W. LANDSBERGER 1) has already found in 1898 that more concentrated solutions of Na Cl show a rise in the molecular increase of the boiling point when the concentration increases. From his molecular weight determinations, I have calculated the following values for the molecular increase of the boiling point and for i.

N a C l.

$t = 5.12$.

Concentration in gr. mols per 1000 grs. of H_2O.	Elevation of the boiling point.	Molecular weight found.	Mol. elevation of the boiling point.	i
0.7145	0.676	32.2	9.46	1.82
1.0581	1.026	31.4	9.70	1.87
1.0872	1.080	30.7	9.93	1.91
1.1077	1.067	31.6	9.63	1.85
1.2427	1.235	30.6	9.94	1.91
2.0735	2.177	29.0	10.50	2,02
2.0855	2.186	29.0	10.50	2.20

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1) Zeitschr. f. Anorg. Chem. XVII 452. (1898).

Excepting the value of i for the concentration 1.1077 gr. mol., which is very probably too small on account of an experimental error, we also notice here a perciptible increase of i with increasing concentration.

LANDSBERGER says regarding the results:

„Die angeführten Zahlen für Natriumchlorid lehren, das die Dissoziation in wässeriger Lösung mit steigender Konzentration fortschreitet."

Although this conclusion seems to me to be erroneous I have quoted it in order to show that LANDSBERGER regards the observed changes as essential.

For concentrated solutions of Na Cl and K Cl, LEGRAND [1]) has already noticed the same phenomenon as I have now done for the more diluted ones.

From the following table this progressive change is plainly visible.

Number of grams of Na Cl per 100 grs. of H_2O.	Number of grams of K Cl per 100 grs. of H_2O.	Number of grams of KNO_3 per 100 grs. of H_2O.	Increase in the boiling point.
7.7	9.0	12.2	1°
13.4	17.1	26.4	2°
18.3	24.5	42.2	3°
23.1	31.4	59.6	4°
27.1	37.8	78.3	5°

We see from this table that with Na Cl and K Cl the elevation of the boiling point increases more rapidly than the concentration, whilst with KNO_3 the reverse is the case. At greater concentrations the molecular elevation of the boiling point of solutions of Na Cl and K Cl seems to increase with the concentration, whilst for solution of KNO_3 it steadily declines.

Summary of the results.

The result is, therefore, that the progressive change observed with concentrated solutions of KNO_3 also occurs with dilute solutions, whilst with concentrated solutions of Na Cl and K Cl it ends at a concentration of 0.5 gr. mol. where it takes another direction.

In my determinations of vapourpressure with the micromano-

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[1]) Ann. de Chim. et de Phys. T. LIII. Poggend. Ann. Bd. XXXVII.

meter, I did not notice a minimum of the molecular diminution of vapourpressure; it is possible that the cause of this is as follows:

At about 100°, I observed a minimum at the concentration of 0.5 gr. mol.; should the position of this minimum alter with the temperature which is quite possible, it may occur that at lower temperatures it is displaced in the direction of still more dilute solutions and that at 0° it may fall below the concentrations with which I was able to make sufficiently accurate observations.

To decide whether there really is a minimum which changes its position with the temperature, I propose to make further measurements of the diminution of vapourpressure of solutions at temperatures between 0° and 100°.

Amsterdam, University Chem. Laboratory.
April 1900.

Physiology. — "*Some reflexes on the respiration in connection with* LABORDE'S *method to restore, by rhythmical traction of the tongue, the respiration suppressed in narcosis*". By M. A. VAN MELLE (Communicated by Prof. C. WINKLER).

In the *Weekblad van het Nederlandsch Tijdschrift voor Geneeskunde*, March 31, 1900. Dr. WENCKEBACH inserts a note on LABORDE'S communications in the Académie de Médecine, which are published in the *Bulletins de l'Académie de Médecine*, N°. 45 1899 en N°. 2, 4, 5, 6. 1900 and with slight modifications in the *Comptes Rendus de la Societé de Biologie:* 1899. N°. 39 and N°. 2, 4, 5. 1900.

In this communication LABORDE gives fuller details about a method in which rhythmical traction of the tongue is used to restore the paralyzed respiration. An explanation is to be found for this phenomenon, as it cannot be considered as anything but a reflectory action, originating from the sensible nerves of the first air-passages on the so-called centres of respiration. LABORDE thinks, that according to his experiments the reflectory action depends on the Nn. laryngei superiores, the electrical and mechanical excitation of which brings about an "arrest" during the active respiration, whereas it restores the respiration when the latter was suppressed.

In the laboratory of Prof. WINKLER, under whose guidance important investigations on the mechanism of the respiration have been made [1]), I have tried to find further data about the effect on the respiration of the excitation of some periferic nerves. I have to return thanks to Mr. VAN CALCAR and Mr. H. JAGER for their valuable assistance. Since the impulse to this investigation which MARSHALL HALL's "Treatise of the Nervous System" gave in 1840, many experiments have been made on this subject, but on the whole the results do not agree very well. The difference of animals experimented on, of the conditions under which the experiment was made, of the nature of the excitation used, is so difficult to bring under simple points of view, that I thought it desirable to make a new attempt under conditions as much the same as possible.

For want of time I could make only a beginning with this very interesting study of the automatism of respiration, the knowledge of which is of the highest importance both from a physiological and a clinical point of view. Nevertheless it seems to me, specially with a view to LABORDE's opinion, that I am justified in communicating some of the obtained results.

The animals experimented on were dogs, almost all of the same species. The experiments were made in narcosis of pure chloroform. In the beginning this gave difficulties as it is a well-known fact, that dogs which are not morphinized, react very violently on the inhalation of chloroformvapours and therefore often succumb of the narcosis.

On purpose I did not make use of the mixed morphia-chloroform narcosis, because morphia introduces a factor, by no means to be neglected in the mechanism of respiration (as proved by the well-known morphia-sigh) which indicates over-irritability of inspiration-centres.

The chloroform also introduces an unknown factor, but this seemed to me a peremptory demand of humanity. Moreover if dogs are not narcotized there is also an unknown factor acting, because pain makes the respiration strongly irregular. When the narcosis with pure chloroform has become complete, it gives a fine regular respiration, which changes as long as active stimulation lasts, but generally returns immediately to the normal condition.

The explanation of the violent reaction, which takes place in the beginning of narcosis, is not found, as we should be inclined to assume, in the disagreeable irritating action of the chloroform on

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[1]) Proc. Roy. Acad. Amsterdam Oct. 29, 1898 and March 25, 1899. Dr. WIARDI BECKMAN. Diss. Inaug. 1899. Amsterdam. De invloed van de schors der voorhoofdshersenen op de ademhaling.

the olfactory mucous membrane, for I found the same reaction with one of the dogs, narcotized through the trachea after tracheotomy. This occurred, when I wanted to stimulate the fila olfactoria by means of electricity and therefore would not paralyze them beforehand by chloroformvapours. This violent reaction, when found with dogs which had been first tied, may cause the dogs to succumb; if however, we leave a possibility of free movement, which is best done by tying the dogs in a bag leaving only the head and the legs free, and the bag with the dog suspended in the air, the asphyxia is generally not found, and the further narcosis remains very calm and regular. The chloroform was administered by means of CURSCHMANN's inhalator.

The narcosis being deep enough, tracheotomy was performed and the chloroform was administered through the tracheal canula.

The registration took place with the pneumograph of MAREY. The sensible nerves were stimulated with a moderately strong induction current. Generally, differences in the strength of the current had little influence, except that a certain minimum had to be exceeded.

Under these circumstances, i which the results show much uniformity and constancy, it appeared that the stimulation of those periferic nerves, which are exclusively composed of sympathic nerve-fibres or contain many of them, brought about an arrest of the respiration and generally, as has been found already by HARLEY and HAMBURGER, in its expiratory position. So do the N. splanchnicus and the N. vago-sympathicus. I succeeded sometimes by mechanic stimulation of the N. splanchnicus (by traction of the entrails) in arresting the respiration for 65 seconds, as long as the stimulation lasted, while before and after the stimulation the respiration was perfectly regular. By electrical stimulation of the N. splanchnicus the same result was obtained. This proves that no centre has been disturbed by shock. The same thing is seen when the N. vago-sympathicus is stimulated (see fig. I—IV).

The excitation of the *N. laryngeus superior* gives also an arrest in the expiratory position, but has generally, in the same way as the sensible branches of the N. trigeminus, an after-effect of long duration. Some time passes before the dog breathes again calmly, and there is a tendency to get out of the narcosis. If the narcosis is very deep the effect is simple retardation (see fig. V).

That of the *N. glossopharyngeus* always gives a deep inspiratory position, as is never reached in simple breathing, but only with deep sighs. Strong currents bring about a forced deep inspiration lasting as long as the current lasts, weak currents at the same time acceleration (see fig. VII—XI).

That of the *N. lingualis N. trigemini* always gives, just as the N. laryng. sup. an arrest in expiratory position, but with accelerated superficial breathings and long continued after-effects (see fig. XIII—XV).

The stimulation of the *N. hypoglossus*, the *N. accessorius* and the *N. facialis* proved to have no influence on the respiration.

The stimulation of the *fila olfactoria* appeared to be exceedingly dangerous as there was a great chance of sudden death, but, gave in some cases a curve analogous to that of the stimulation of the N. sympathicus (see fig. VI and fig. XII).

Under the given circumstances, i.e. chloroformnarcosis and moderately strong induction current (we cannot lay too much stress on this), all sensible nerves of the tractus intestinalis and of the airpassages proved to have a retarding influence, with the exception of *N. trigeminus*, which may be considered as being in secondary connection with the deeper organs, being primarily a sensible nerve of the outward cover of the body. The arrest is a position of rest when the N. Splanchnicus, N. Vagus and the N. olfactorius are stimulated and the arrest is a forced inspiratory position when the N. Glossopharyngeus is stimulated. This result agrees on the whole with what others, under different circumstances, have found. Yet there are important deviations in some points. PHILIP KNOLL states in the „*Sitzungsberichte der Wiener Akademie*" Bd. 86. p. 483 and Bd. 92. p. 315, that the ramus lingualis N. trigemini belongs to the nerves, the excitation of which always gives inspiratory effects, whereas experimenting on five dogs with numerous stimulations, I have never found an inspiratory effect, but constantly an expiratory effect with acceleration of respiration. This is of importance because the statement of the author that there is no real difference in the working of the sensible stimulation for narcotized, not narcotized or brainless animals, proves not to be exact in all cases.

But these results are also of importance with a view to the theoretical considerations of LABORDE and this is in fact what gave rise to this communication.

LABORDE passes the N. glossopharyngeus over in a few words, which prove, that he does not pay sufficient attention to what is known about this nerve. He says about it:

„Grace à un des résultats nouveaux de mes recherches personnelles ce nerf (c. a. s. N. Laryngé supérieur) n'est pas le seul qui puisse intervenir efficacement dans la réalisation fonctionelle dont il s'agit.

Le nerf glossopharyngien considéré jusqu'à présent dans sa fonction essentielle comme un agent de sensibilité spéciale (sensibilité gustative), prend aussi une part réelle et active à titre de nerf sensitif de départ réflexe au fonctionnement respiratoire."

In 1883 Knoll considered the N. Glossopharyngeus as belonging to those nerves which have always an inspiratory reflex-action on the respiration and several physiologists deny the gustative signification of the N. glossopharyngeus altogether or consider it at least of little importance.

For the action of the rhythmical tongue-tractions we have to think of three sensible nerves, viz.:

1. N. laryngeus superior.
2. N. glossopharyngeus.
3. Ram. lingualis N. trigemini.

The first is of little importance to our purpose because on account of the distribution of its branches, it has the smallest chance of being really stimulated in Laborde's method. Moreover it gives regularly a suspension of expiration under my experiment-conditions, and the results arrived at by means of pure chloroformnarcosis have some more value in this case, because the method will find its most important application in the chloroform-asphyxia.

Yet it is not impossible that the N. laryng. sup. under certain conditions may restore the arrested respiration.

Laborde brought about suffocation of his animals, by closing the air passages completely. The respiration curve changes its character completely, it begins to resemble a normal curve, held upside down. Instead of expiratory we get inspiratory positions of rest (see curve XVII). It is not easy to explain this phenomenon, as it would be more likely that the air-resorption in lungs where the air cannot enter, would give mechanically an expiratory position. The craving for air (comp. the subjoined curve XVI) does not explain it satisfactorily either, as a double pneumothorax gives long positions of rest in expiration, interrupted by energetical inspirations. The stimulation of the N. laryngeus superior gives an arrest, generally in a strongly pronounced expiratory position.

The fact is that the electric excitation of the N. laryngeus superior has an opposite effect, which favours expiratory positions and in connection with the forced inspirations may bring about rhythmical in- and expiration.

Therefore it does not seem probable to me, that on account of the experiment of Laborde, about which no sufficient information is to be had, we may hold the N. laryng. sup. answerable for the usual action of the method, as it will most likely never be applied except for experiments on animals, when complete closure of the air passages has brought about cessation of respiraton. For it is exactly the experimental closure which modifies the usual type of respiration greatly, and which introduces unknown factors in the mechanism of respiration.

It is quite a different thing for the N. glossopharyngeus and the ram. ling. N. V. They must necessarily be stimulated by every traction of the tongue. The N. glossopharyngeus appears to have an exceedingly strong effect on the inspiration, an arrest with strong stimulations, an acceleration with weaker stimulations. As well according to the investigations of KNOLL of 1883, as to my investigations in Prof. WINKLER's laboratory, and to LABORDE's vague allusion, the 9th nerve of the brain has this strong reflex-action. It is therefore not very rational, not to look first of all to this nerve, in trying to find the explanation of the respiratory mechanism in LABORDE's method.

The excitation of the N. trigeminus may also produce inspiratory effects under the experimental conditions introduced by KNOLL (unknown to me); a pure chloroformnarcosis however, cannot have any or but a very small effect.

Chemistry. — "*Echinopsine, a new crystalline vegetable base*". By Dr. M. GRESHOFF (Communicated by Prof. A. P. N. FRANCHIMONT).

(Will be published in the Proceedings of the next meeting).

Chemics. — „*The constitution of the Vapour-phase in the System Water-Phenol, with one or two Liquid-phases.*" By Dr. F. A. H. SCHREINEMAKERS (Communicated by Prof. J. M. VAN BEMMELEN.

(Will be published in the Proceedings of the next meeting.)

(June 20, 1900.)

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