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VAN WETENSCHAPPEN
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KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING
of Saturday December 28, 1912 and January 25, 1913.

President: Prof. H. A. Lorentz.
Secretary: Prof. P. Zeeman.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 28 December 1912 en 25 Januari 1913, Dl. XXI).

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Physiology. — *"Influence of the seasons on respiratory exchange during rest and during muscular exercise"*. By Dr. C. J. C. van Hoogenhuyze and Dr. J. Nieuwenhuyse.

(Communicated by Prof. C. Eijkman in the meeting of October 26, 1912).

The primary object of our inquiry has been to find out, whether muscular exercise increases the metabolism in man as much in the cold as in the warm season.

We have taken the consumption of oxygen as the index of the metabolism.

Since it is still a matter of controversy, whether the seasons influence metabolism even during rest, we have thought fit to determine also the absorption of oxygen during rest in the same two persons, who were subjected to the muscular test. Besides, the gas-exchange has also been examined with two other subjects only during rest.

A. *Respiratory Gas-exchange during rest.*

In 1859 E. Smith [1]) presented to the Royal Society of London a series of observations upon the influence of different factors (i. a. the seasons) on the gas-exchange in man during rest. The amount of oxygen consumed was not determined, only that of carbon dioxide given off. If we are to take the latter as a quantitative index of the metabolism, Smith's experiments would prove that it is more intense in the cold months and less so in the warm season.

Eijkman [2]) made similar experiments in 1897 with improved means, and moreover measured the quantities of oxygen. As known, the latter afford a more reliable index of the intensity of the metabolism. He found no difference for the different seasons.

His opinion that the metabolism is the same in warm and in cold seasons is also corroborated by his previous investigations [3]) made in the East-Indies, from which it appeared that the amount of metabolism of man in the tropics agrees with that of people in our parts.

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[1]) Philosophical Transactions of the Royal Society of London 1859 p. 681.

[2]) C. Eijkman. Over den invloed van het jaargetijde op de menschelijke stofwisseling. Verslagen van de Koninklijke Akademie van Wetenschappen te A'dam, 8 Dec. 1897.

[3]) C. Eijkman. Beitrag zur Kenntniss des Stoffwechsels der Tropenbewohner. Virchow's Archiv. Band 133. 1893, p. 105.

Idem. Ueber den Gaswechsel der Tropenbewohner, Pflüger's Archiv. Band 64, 1896, p. 57.

Shortly before we had brought our experiments to a close, LINDHARD [1]) published an article, in which he reports the fluctuations of respiratory exchange in the different seasons, which according to him run parallel to the intensity of the sunlight.

It seems to us however, that his values of the oxygen intake do not differ sufficiently and are too inconstant to warrant such a conclusion.

For our determinations we used ZUNTZ and GEPPERT'S [2]) method. The subject, whose nose is shut off by a spring-clip, breathes through a mouth-piece, corresponding by means of a T-shaped tube with two very mobile gut-valves, one of which transmits only the air taken in, the other only the air which is exhaled. The latter passes, without encountering any resistance worth mentioning, through a slightly aspirating gasometer, a constant fraction of the expired air being continually separated for gas-analysis by means of a special apparatus. Furthermore a supple pig's bladder had been inserted between the valves and the gasometer. This highly facilitated expiration, as was apparent from the working-experiments to be discussed later on.

Outside air was supplied through a short and wide india-rubber tube, connected with the valves. The room which faced the North, was constantly well ventilated through the open windows.

We experimented every time under similar circumstances, i. e. the experiments were made in the morning, always at the same hour, and with the same interval after breakfast.

The breakfast varied for the several subjects, but for each individually it was the same. For a quarter of an hour before and during the experiment, the subject reclined in an easy chair, resting quietly. The temperature of the room was taken, the readings of the barometer and the sort of weather (misty, sunny, frosty etc.) were noted down.

Likewise the respiration, the number of liters of air exhaled, and the time (in seconds) were recorded on a kymographion (Fig. 1).

The time the experiment took us, was also registered by a timekeeper. Furtheron the relative moisture in the room was measured too as well as the temperature and the degree of moisture under the clothes.

Our subjects were four adults, all of them employed every day

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[1]) J. LINDHARD. Seasonal periodicity in respiration.
Skandinav. Archiv. f. Physiologie XXVI p. 221.

[2]) MAGNUS-LEVY. Ueber die Grösze des respiratorischen Gaswechsels u. s. w.
Pflüger's Archiv. f. die ges. Physiologie. Bd 55. 1894, p. 9.

at the hygienic laboratory at Utrecht. Their body-weights were widely different and did not change much with the same individual.

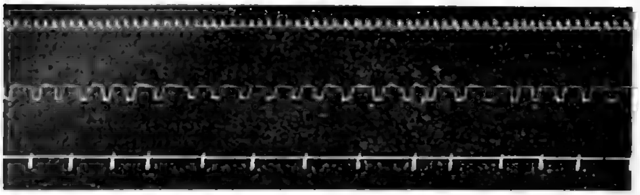

Fig. 1.

The lowest temperature, at which we worked was 3°, the highest 30°.

The experiments were made in May, June, July, September, October, November 1911 and in January, February, and July 1912.

There was only a small difference in the summer- and the winter-attire. No overcoat was ever put on in cold weather nor was any article of attire taken off in the summer. As serious errors would originate in case the subject should shiver, this was a point of careful observation.

In looking over our results, in the first place with regard to the amount of oxygen, we notice rather considerable fluctuations with the same subject under apparently similar circumstances, which is in accordance with the experience of other workers.

Benedict [1]), for instance, found in experiments with the same subject under equal circumstances the following oxygen-consumption: 194—213—169, showing as great a difference as 26°/₀.

We also found with N. on 15—7—'12, at 30°, 765,5 mm. barometric pressure, relative moisture of 52°/₀, the value 256,8, and on 16—7—'12, at 30° and 765,5 mm. barometric pressure, relative moisture of 50°/₀, the value 292. This yields a difference of rather more than 13°/₀.

It is obvious, therefore, that if we wish to demonstrate seasonal influence, an extended series of experiments is required, and furthermore, that only striking differences should be attended to. If we take the average of the results at a temperature below 13° (the months of Nov. Dec. Jan. Feb.) and of those above 13° (the other months) we note:

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[1]) Benedict. The metabolism and energy transformation of healthy man during rest. (Carnegie Institution of Washington. Publication no. 126, 1910, p. 107.)

	below 13°			above 13°	
with *v.H.*	(5 exp.	281.8	c. c. per min.	(18 exp.	269.2
„ *N.*	8 „	252.4	„ „ „	21 „	256
„ *E.*	6 „	290.8	„ „ „	9 „	297.4
„ *K.*	4 „	207.7	„ „ „	12 „	197.7

The average of
4 subjects (23 exp.) 1032.7 : 4 =258.2 and (60 exp.) 1020.3 : 4=255.1.

In considering the results obtained with each individual separately we notice differences in one way or another, comparatively small though they may be.

In connection with what has been said above we believe that no great value should be set upon these differences.

Taking the averages of all the subjects, we find fairly corresponding values, viz. 258.2 in the cold and 255.1 in the warm season, so that we may conclude, that the season has no influence upon the metabolism in a state of repose.

It appears then, that our results agree with those of EIJKMAN [1]) who got his averages in like manner, finding 253.8 in the winter and 253.3 in the summer.

Without tabulating our results at large we subjoin a somewhat more detailed report about them:

I *V. H.* Body-weight 87½ Kilos (without clothing) Height 1.84 m.
Averages of results of all experiments (23): Amount of O_2-consumption and CO_2-production per minute expressed in c.c. reduced to 0° and 760 mm. barometric pressure.

CO_2	O_2	CO_2 O_2
225,2	271,1	0,830
minimum 185	min. 239,5 = 11 % below the average.	
maximum 264,6	max. 322,5 = 19 % above „ „	

The average O_2-consumption in 5 experiments at 4½—12½° C. amounted to
281,8
min. 259,9
max. 322,5

The O_2-consumption in 18 experiments at temperatures of from 14½—30° C. averaged
269,2
min. 239,5
max. 294,2

At the lowest temperature (4½° C.) we found 274,1, at 7½° C. 322,5.
„ „ highest temperatures (30 ° C.) „ „ 291,7 and 294,2.

II. *N.* Body-weight 70½ Kilos (without clothing) Height 1,80 m.
Averages of results of all experiments (29):

CO_2	O_2	CO_2 O_2
230	255	0,900
min. 191,7	min. 222,2 = 13 % below the average.	
max. 267	max. 292 = 14 % above „ „	

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[1]) C. EIJKMAN. Koninkl. Akademie v. Wetenschappen 8 Dec. 1897.

The average O_2-consumption in 8 experiments at temperatures of 4—13° C. amounted to

252,4
min. 230,5
max. 285,1

The O_2-consumption in 21 experiments at temperatures of 14—30° C. averaged

256
min. 222,2
max. 292

At the lowest temperatures (4 °) we found 260,7 and 285,1.
„ „ highest „ (30°) „ „ 256,8 292 and 277,7.

III *E.* Body-weight 83,3 Kilos (without clothing) Height 1,82 m.
Averages of results of all experiments (15)

CO_2	O_2	$O_2.O_2$
258,6	294,7	,801
min. 219,6	min. 250,8 = 15 °/₀ below the average	
max. 309,7	max. 330,1 = 12 °/₀ above „ „	

The average O_2-consumption in 6 experiments at temperatures of 8—13° C. amounted to

290,8
min. 272,6
max. 330,1

The average O_2-consumption in 9 experiments at temperatures of 14—26° C. amounted to

297,4
min. 279,9
max. 328.4

IV. *K.* Body-weight 58 Kilos (without clothing) Height 1.75 m.
Averages of results of all experiments (16)

CO_2	O_2	CO_2/O_2
175,1	200,2	0,874
min. 152	min. 172 = 14 °/₀ below the average	
max. 205,9	max. 238,6 = 19 °/₀ above „ „	

The average O_2-consumption in 4 experiments at temperatures of 3—12½° C. amounted to

207,7
min. 177,7
max. 228,6

The O_2-consumption in 12 experiments at temperatures of 14—30° C. averaged:

197,7
min. 172,0
max. 238,6

Our endeavours to detect any influence of the seasons on the carbon-dioxide elimination, the tidal air, and the number of respirations per minute proved as fruitless as they had been in ascertaining such influence on the oxygen-consumption.

B. *Respiratory Gas-exchange during muscular exercise.*

Little has been written as yet about the influence of muscular work on the respiratory exchange in the several seasons.

E. Smith reported in his publication, of which mention has already been made, that equal muscular work has a greater influence on the respiratory exchange in winter than in summer; his experimentation, however, does not, in our opinion, vouch for this conclusion.

Our experiments were made in the months of March, April, May, June, and July 1912.

We proceeded as follows. The experimentation took place in the afternoon, at the same hour, shortly before dinner, in order to give scope to the presumable influence of close heat. We were sitting on a bicycle without wheels, placed on a stand. A rotatory disk had been fixed at the place of the large chain-wheel. Round it a steel brake-band could be tightened or slackened to render the work more severe or lighter (Fig. 2).

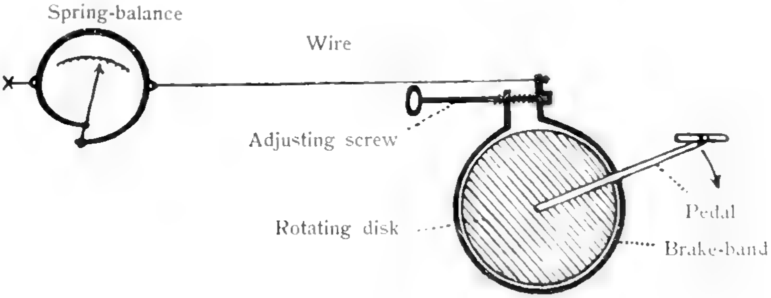

Fig. 2.

The upper part of the band was connected with a spring-balance by means of a long wire. When the adjusting screw was tightened the friction increased and the band was taken along by the disk, while the pedalling continued, which caused the springbalance to register a higher figure. The increase, however, was not such as to alter the static moment materially. Both the bracket-spindle of the bicycle and the rim of the disk were continually being oiled during the experiment.

The pedalling rate was regulated by a metronome, ticking 133 times per minute.

Before the subjects, both skilled cyclists, started pedalling, a determination was made, while they were quietly seated on the bicycle; which involved only a very light static muscular activity. In the subsequent period of the experiment the subject was pedalling for a quarter of an hour, while breathing freely and after this for five minutes, while breathing through the valves. Only then the estimation was performed, while the subject went on pedalling; we then could reasonably presume that a condition of equilibrium between internal and external gas-exchange had been established.

The breathing through the valves for the space of five minutes previous to the estimation, served to prevent a somewhat irregular respiration that might possibly arise in the transition from free breathing to respiring through the valves. In the interval the temperature in the gasometer attained its new equilibrium.

Throughout the whole experiment an assistant had to watch the springbalance, which was to point to the same mark. In case of a deviation, the band was at once slackened or tightened during the pedalling, which did not cause any disturbance.

The work done was calculated by multiplying the circumference of the disk, i. e. the distance covered after one rotation, by the weight indicated on the springbalance, by the number of rotations per time-unit and by a correcting factor [1]. This showed an amount of labour of 22800 K.G.M. per hour.

The exertion required for the work, was not such as to exhaust the subjects. Still, at the finish of the experiment they felt tired as if they had been cycling a long distance.

Our results are the following:

I. *V. H.* } sitting quietly (*a*):
pedalling (*b*):

Averages of all the experiments (12) made in March, April, May, June, July 1912, lowest temperature 12°, highest temperature 30°:

	CO_2 per min.	O_2	$\frac{CO_2}{O_2}$
a	280,8	min. 299 max. 386,8 330,4	0.850
b	868,4	1001,5 min. 781,2 max. 1448	0,8671

The average of 8 experiments below 21½°:

	CO_2	O_2	$\frac{CO_2}{O_2}$
a	273,3	min. 299 max. 358,8 323,5	0,8448
b	746,2	863,4 min. 781,2 max. 988,5	0,8643

The average of 4 experiments above 21½°:

	CO_2	O_2	$\frac{CO_2}{O_2}$
a	295,9	min. 322.1 max. 386.8 344,5	0,8589
b	1113,1	1277,7 min. 1052 max. 1448	0,8712

Increase set in after 11—6—'12 (above 21½°).

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[1] The correcting factor is the quotient of the lever on which the wire of the springbalance is fixed and the radius of the disk.

II. *N.* {sitting quietly *a*: {pedalling *b*:

Averages of all the experiments (14) made in the same months; lowest temperature 12°, highest 31°:

	CO_2	O_2	$\frac{CO_2}{O_2}$
a	212,5	min. 229 max 314,9 265,4	0,8346
b	819,6	895,6 min. 652,1 max. 1091	0,9152

The average of 8 experiments below 20½°:

	CO_2	O_2	$\frac{CO_2}{O_2}$
a	214,6	min. 229,6 max. 314,9 268,8	0,7984
b	717,9	791 min. 652,1 max. 922,7	0,9076

The average of 6 experiments above 20½°:

	CO_2	O_2	$\frac{CO_2}{O_2}$
a	209,6	min. 229 max. 288,9 260,8	0,8037
b	955,2	1034,9 min. 977,2 max. 1091	0,923

Increase set in above 20½°, after 13–5–'12.

Also in this series of investigations the individual fluctuations were rather considerable.

We see that for either subject the average oxygen-intake is higher when sitting quietly on the bicycle than when lying in a chair, viz.

V. H.	(lying)	average Oxygen-intake	271.1 cc.
	(sitting)	.. ..	330.4 ..
N.	(lying)	.. ..	255 ..
	(sitting)	.. ..	265.4 ,,

We also observe that the average value of the sitting-experiments at more than 21½° with *V. H.* is a little higher than that of the experiments below 21½° viz.

the first value: 344.5, the second 322.5.

Again, that for *N* there is no such difference between the two periods. On the contrary with him rather the reverse takes place, the first value being 260.8, the second 268.8. However, this difference is too small to be taken into account.

While pedalling *V. H.* shows an essential increase of oxygen-intake, when the temperature rises beyond 21°, at the beginning of June. With *N* the increase is not so great, but it starts a month earlier, when the temperature rises beyond 20° viz.

with *V. N.* from average 863.4 to 1277.7, nearly 48 %
.. *N.* .. .. 791 .. 1034.2. .. 31 %

The lowest value of the warm period in *H*'s experiments (1052) is distinctly higher than the highest of the cold period (988.5).

Likewise with *N* viz. the one 977.2, the other 922.7.

On the days of the higher values either subject felt, as if the muscular work required a greater physical exertion than on other days, though they were both in good health and followed their daily routine.

In noting the average increase of the absorption of oxygen, resulting from the pedalling, we find:

with *V. H.* below 20½° 863—323.5 = 441.5
above 21½° 1277—244.5 = 933.2,

a difference of 491.7 (nearly 112 $^0/_0$).

With *N* below 21½° 791 —268.8 = 522.2
above 20½° 1034.9—260.8 = 774.1,

a difference of 251.9 (rather more than 48 $^0/_0$).

The numbers expressing the carbon-dioxide output are running parallel to those indicating the oxygen-intake. This tallies with the approximate accordance of the respiratory quotients of the experiments made at a temperature higher than $20^1/_2$° and $21^1/_2$°, with those of the other experiments.

In the case of *N* the temperature under the clothes, on the cessation of the pedalling was 35—$35^1/_2$° C., the relative moisture 65—90 $^0/_0$, throughout the whole period above 20½°. In the period below 20½° the former varied from 30° — 34°, the latter from 30$^0/_0$—47$^0/_0$.

With *V. H.* those values were:

in the period above 21½° : 34— $35^1/_2$°
90—100$^0/_0$
„ „ „ below 21½° : 30— $34^1/_2$
40— 75$^0/_0$

As regards the respirations per minute and the tidal air at the end of the pedalling experiments we find:

		number of respir. per min.	Tidal air
average with *V. H.*	below 21½°	17.2	1009.6
	above 21½°	16.2	1444
with *N.*	below 20½°	20.1	840.7
	above 20½°	21.7	1003.5

We see, therefore, that the number of respirations per minute remains fairly constant, whereas in the warm season the tidal air is considerably augmented, viz.

with *V. H.* an increase of more than 34 %
„ *N.* „ „ „ „ „ 19 %.

We have previously remarked, that the increased respiratory exchange at a higher temperature cannot be attributed to this, seeing that the determination had not been made, until an equilibrium had presumably been established between internal and external gas-exchange. Indeed, the O_2-consumption and the CO_2-elimination increased more considerably than the tidal air.

Our experimental evidence seems to show that muscular work at a high temperature is less economical than at a low temperature, and also that this difference is more marked with one subject than with another.

The increase of gas-exchange parallel to the rise of temperature was not gradual, but sudden at 21°—22°.

Physiology. — "*The influence of the reaction upon the action of ptyalin*". By Dr. W. E. Ringer and H. v. Trigt.

(Communicated by Prof. C. A. Pekelharing in the meeting of November 30, 1912).

One of us (v. Tr.) has for some time been studying the effect of diet on the action of the diastatic enzyme of the saliva, to which the name ptyalin has been applied. The results of other researchers into this subject are to some extent conflicting with each other[1]. Nor do van Trigt's experiments positively demonstrate an influence of diet. Though, taking one with another, they seemed to point to an influence, occasionally there appeared striking deviations without our being able to fix upon the cause, so that we did not know what to make of the results.

This experimentation was conducted as follows: saliva was added to amylum solutions and after some time the reducing power of the solutions was determined. This method involves the risk of fluctuations in the reaction of the fluids, e.g. such as are brought about by the flask-wall or by carbon dioxide from the air, since in approximately neutral fluids without regulating-mixtures the reaction may be considerably shifted by a trifling disturbance. This would account for the striking deviations mentioned just now, recent researches having shown that slight modifications of the reaction markedly affect the activity of enzymes.

Now if, in prosecuting our experiments, due care being taken all

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[1] Cf. Hammarsten's Lehrbuch der physiologischen Chemie.

the time to obviate any noxious influence of the flask-wall or of the carbon-dioxide upon the reaction, we should detect unmistakable influence of the diet, this might be owing to various causative factors. First of all the concentration of the enzyme might have been altered by the diet. In the second place the organism might efficiently alter the concentrations of the ions, which are so material to the action of the enzyme, especially the H- and OH-ions, as well as the Cl-ions and others.

We thought proper, therefore, to cautiously watch the influence of the H- and OH-ions in order to ascertain by subsequent experiments, whether variations in the activity of the enzyme are to be attributed to changes in the concentrations of the said ions. Moreover, an accurate knowledge of the influence of these ions may lead to a clearer insight into the action of the enzyme.

Previous inquiries into the effect of acids and alkalis on the action of ptyalin yielded rather contradictory results [1], from which it was supposed that either acids or alkalis acted favourably.

As a rule we used in our investigations the methods employed by SÖRENSEN [2] in his remarkable experiments on enzymic actions. We adopted the following course:

filtered saliva, designated "enzyme" in the following tables, was made to act at 37° upon $1^{\circ}/_{0}$ amylum solutions. After the action of the enzyme had been arrested by heating it was estimated by the determination of the reducing power of the digestion-fluid, of the rotatory power and by reaction with iodine. Various reactions were given to amylum solutions. To obtain them and to maintain them constant three buffing- or regulating-mixtures were applied, viz.

1. phosphate-mixtures,
2. citrate-mixtures,
3. acetate-mixtures.

The process of digesting lasted 20 minutes for all series of experiments but one.

1. *Experiments with phosphate mixtures.*

(all the glass vessels had been exposed to steam for 15 minutes.)

Into ERLENMEIJER-flasks (Jena-glass), capable of holding 300 c.c. were placed:

10 c.c. of a phosphoric acid solution 1.485 n., varying amounts of sodium hydrate 0,5670 n., and water up to 50 c.c. To this 200

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[1] Cf. HAMMARSTEN's Lehrbuch der physiologischen Chemie.

[2] Comptes rendus des travaux du Laboratoire de Carlsberg. 8me Vol. 1r. Livraison 1909.

c.c. of the amylum solution was added by means of a pipette. As a matter of course, all the tests of the same series were made with the same freshly prepared solution, which was obtained by mixing 25 gr. of dried amylum with one liter of water and heating it to the boiling point, while stirring the fluid and maintaining this temperature for about a minute. After cooling the mixture was made up to 2 liters [1]) and filtered through glass-wool or muslin.

The flasks holding the phosphate-mixtures and the amylum, were first heated to 37° and then maintained at this temperature in the thermostat for at least 20 minutes previous to the addition of the enzyme. After the enzyme had been working on for 20 minutes, the flask was dipped into a boiling waterbath and was constantly and regularly moved, always in the same manner, till a temperature of 90° was reached, so that every time the action of the enzyme was arrested in the same way.

The reducing power of the cooled fluid was determined after BERTRAND and was expressed in m. Gr. copper per 100 c.c. of the fluid.

The determination of the reaction was performed electrometrically. The hydrogen-electrodes were treated after HASSELBACH's [2]) shaking method, and measured by means of mercury-calomel-electrodes with normal and $^1/_{10}$ n potassium chloride The reaction is expressed in p_H : the negative logarithm of the hydrogen-ions-concentration.

The following tables show the results of the most important series of experiments.

1st Series of experiments. Enzyme v. *T.*

Nr.	Phosphoric acid solution c.c.	NaOH c.c.	H_2O c.c.	Amylum c.c.	Enzyme c.c.	Reduction m.Gr. Cu	Rotation minutes	Iodine reaction	p_H
1	10	13.4	26.6	200	2	71.10	—	—	5.186
2	10	13.7	26.3	200	2	182.15	—	—	5.69
3	10	14	26	200	2	212.30	—	—	5.80
4	10	15	25	200	2	**218.95**	—	—	**6.22**
5	10	16	24	200	2	214.85	—		6.40
6	10	18	22	200	2	176.50	—	—	6.78

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[1]) Occasionally 4 liters had to be made.

[2]) Biochemische Zeitschrift, Bd. 30, p. 317.

2d Series of experiments. Enzyme *R* diluted with 3 vol. of water.

Nr.	Phosphoric acid solution c.c.	NaOH c.c.	H_2O c.c.	Amylum c.c.	Enzyme c.c.	Reduction m.Gr. Cu	Rotation minutes	Iodine reaction	p_H
1	10	13	27	200	2	Reduction not perceptible	+192	blue	4.53
2	10	13.5	26.5	200	2	180.10	188	blue, shade of violet	5.33
3	10	14	26	200	2	234.80	186	violet, shade of blue	5.86
4	10	14.5	25.5	200	2	**244.55**	185	violet	**6.05**
5	10	15	25	200	2	235.70	186.5	violet, shade of blue	6.24
6	10	15.5	24.5	200	2	223.60	188	violet-blue	6.30
7	10	17	23	200	2	179.10	191.6	blue, shade of violet	6.61
8	10	20	20	200	2	105.40	195	blue	7.01

3d Series of experiments. Enzyme *D.*

Nr.	Phosphoric acid solution c.c.	NaOH c.c.	H_2O c.c.	Amylum c.c.	Enzyme c.c.	Reduction m.Gr. Cu	Rotation minutes	Iodine reaction	p_H
1	10	13.2	26.8	200	2	106.45	194	blue	4.90
2	10	13.5	26.5	200	2	194.50	190.3	blue, shade of violet	5.52
3	10	14	26	200	2	251.25	190	violet-blue	5.83
4	10	14.5	25.5	200	2	270.10	189.7	violet, shade of blue	6.08
5	10	15	25	200	2	**271.20**	188	violet	**6.19**
6	10	15.5	24.5	200	2	265.55	191	violet, shade of blue	6.37
7	10	17	23	200	2	220.55	192	violet-blue	6.61
8	10	20	20	200	2	156.60	195	blue	7.03

From these experiments it appears, that the concentration of the hydrogen-ions exerts a considerable influence upon the action of the enzyme; further that an increase of c_H, consequently a decrease of p_H accelerates its activity, until a certain optimum is reached, after which the action slackens again. We also observe the same behaviour with enzymes from different sources, however with a noticeable difference in their activity. From another series of experiments we gathered that the optimal reaction lies at about the same point in much more dilute phosphate solutions; we also learnt, that all over the series the action of the enzyme was more vivid. It follows then, that phosphate-mixtures are inhibitive to the action; less so in highly dilute than in the concentrated solutions.

2. *Experiments with citrate-mixtures.* A citrate solution was made from 275 gr. of pure citric acid (pro analysi), 105 gr. of NaOH (Merck's e natrio pro analysi) and water to 1 liter. 20 c.c. of this citrate solution diluted with water to 250 c.c. yielded $p_H = 4.915$.

4th Series of experiments. Enzyme *R*.

Nr.	Citrate solution c.c.	NaOH c.c.	H_2O c.c.	Amylum c.c.	Enzyme c.c.	Reduction in Gr. Cu	Rotation minutes	Iodine reaction	p_H
1	10	14.7	25.3	200	2	247.60	195	bluish-violet	5.99
2	10	19.57	20.43	200	2	357.15	189	reddish-violet	6.49
3	10	19.94	20.06	200	2	380.15	189	red, shade of violet	6.526
4	10	20.40	19.6	200	2	380.65	188	reddish-brown	6.62
5	10	21.3	18.7	200	2	**396.00**	187	reddish-brown	**6.73**
6	10	22.1	17.9	200	2	358.65	187	red, shade of violet	7.09
7	10	23	17.0	200	2	183.15	197	blue, shade of violet	7.425

5th Series of experiments. Enzyme *R* diluted with 1 vol. of water.

Nr.	Citrate solution c.c.	NaOH c.c.	H_2O c.c.	Amylum c.c.	Enzyme c.c.	Reduction m.Gr. Cu	Rotation minutes	Iodine reaction	p_H
1	5	5.0	40	200	2	81.35	202.7	blue	5.80
2	5	8.20	36.8	200	2	139.70	200	blue	6.26
3	5	9.78	35.22	200	2	**158.10**	197	blue, shade of violet	**6.55**
4	5	10.20	34.80	200	2	147.85	199.3	blue, shade of violet	6.74
5	5	10.65	34.35	200	2	128.45	201	blue	6.85
6	5	10.90	34.10	200	2	107.95	202.7	blue	7.046
7	5	11.05	33.95	200	2	90.05	204	blue	7.11
8	5	11.30	33.70	200	2	60.90	204.5	blue	7.41
9	5	11.60	33.40	200	2	reduction not perceptible	205	blue	7.497

Here again an optimal reaction is educed, which, however, has slightly shifted towards the neutral point. A decrease of concentration diminishes this deviation.

3. *Experiments with acetate-mixtures.* A solution of sodium acetate 170 gr. per liter was mixed with different quantities of 1 °/₀ acetic acid. The following experiments were made:

6th Series of experiments. Enzyme R. diluted with 3 vol. of water

Nr	Acetate solution c.c.	Acetic acid solution c.c.	H_2O c.c.	Amylum c.c.	Enzyme c.c.	Reduction m.Gr. Cu	Rotation minutes	Iodine reaction	[1] p_H
1	20	0	30	200	2	47.60	turbid	blue	7.297
2	20	1	29	200	2	137.65	202	blue, shade of violet	6.65
3	20	2	28	200	2	182.65	199	bluish-violet	6.55
4	20	4	26	200	2	221.05	198	bluish-violet	6.21
5	20	5.6	24.4	200	2	**222.05**	195	violet-blue	**6.106**
6	20	7	23	200	2	221.55	197	violet-blue	5.98
7	20	12	18	200	2	200.05	199	bluish-violet	5.78
8	20	30	0	200	2	118.20	200	blue	5.37

Again an optimal reaction is evolved: it is equal to that of the phosphate solutions. On either side of it the action of the enzyme diminishes, first slowly, then rapidly. The optimal reaction lies in phosphate solutions at $p_H = 6.05$, as may be seen from a graphic representation of the reduction as function of the p_H. In acetate solutions we find $p_H = 6.08$, whereas in citrate-experiments values vary according to the concentration. In the 5th series we found an optimal reaction $p_H = 654$.

All values of p_H communicated thus far, were estimated at 18°. They are somewhat different at 37°, the temperature at which the experiments were made. The reactions of the fluids, that were optimal, have also been determined by us. We found:

in the phosphate solutions $p_H = 6.00$

in the citrate solutions (10 c. c. of citrate 4th series) $p_H = 6.86$

in the acetate solutions $p_H = 6.028$.

The neutral point lies at 37° at $p_H = 6.796$.

For purposes of comparing the action of the various regulating-mixtures we carried out the following experiment. (p. 805).

It is evident from this test that, the reaction being neutral, the influence of phosphate is inhibitory; when the reaction is slightly acid ($p_H = 6.5$; a neutral reaction is not easily obtained with citrate)

7th Series of experiments. Enzyme R diluted with 1 vol. of water.

	Regulating mixture	H_2O c.c.	Amylum c.c.	Enzyme c.c.	Reduction m.Gr. Cu.	Reaction (determined at 18°) p_H
a	none	50	200	2	318.20	electrometrical determination not practicable on account of the lack of electrolytes. Neutral behaviour to litmus, so $p_H \pm 7.07$
b	10 c.c. phosphoric acid 20.6 c.c. NaOH	19.4	200	2	245.05	7.07
c	10 c.c. phosphoric acid 16.25 c.c. NaOH	23.75	200	2	425.15	6.50
d	10 c.c. citrate, 19.55 c.c. NaOH	20.45	200	2	221.55	6.468

a comparison between citrate and phosphate shows that inhibition is much stronger with the former than with the latter.

From the removal of the optimal reaction towards the neutral point, as well as from the tests published in this paper, it is apparent, that citrate inhibits most strongly on the side of the minor p_H's, and that this impeding action weakens towards the neutral point.

The optimal reactions being identical in phosphate- and acetate-mixtures, it was likely, that either of them should slacken the action of the ptyalin in the same way. The following test illustrates the fact that, if the reactions are the same, both mixtures equally affect the enzymic action.

8th Series of experiments. Enzyme *R* diluted with one vol. water.

	Regulator	H_2O c.c.	Amylum c.c.	Enzyme c.c.	Reduction mGr. Cu	p_H
a	10 c.c. of acetate 5 c.c. of acetic acid	35	200	2	489.2	5.886
b	10 c.c. of phosphoric acid 14 c.c. NaOH	26	200	2	483.5	5.886

We now passed on to inquire how this influence of the reaction upon the action of ptyalin is to be accounted for. It may indeed be imagined, that H-ions favour the enzymic action, but how is it then that beyond the optimal c_H they largely impede the activity. Is it perhaps to be attributed to an injury to the enzyme? In order to find this out we made the following experiments:

9th *Series of experiments.*

a. 10 c. c. of phosphoric acid, 13 c. c. of sodium hydrate and 27 c. c. of water were mixed at room-temperature with a mixture of 25 c. c. of enzyme R + 25 c. c. of water. We examined directly the activity of this mixture, in which the enzyme had been diluted four times. It was subsequently warmed to and maintained at 37°, while at various intervals the action was noted, every time by allowing 2 c. c. to act upon mixtures of phosphate and amylum of the optimal. reaction.

Nr.	Time (minutes) during which the enzyme-mixture was maintained const. at 37°	Reduction m.Gr. Cu.	Rotation minutes	p_H (if determined).
1	0	177.55	194.3	6.06
2	8.75	179.10	—	—
3	16.75	179.10	193.0	6.00
4	41.75	179.10	—	—
5	88.75	179.10	193.0	6.075
6	178.75	181.60	—	—
7	268.75	179.10	193.0	5.975

The p_H of the enzyme-mixture was 5.502.

b. 10 c. c. of phosphoric acid, 12 c. c. of sodium hydrate, 28 c. c. of water. Addition: 25 c. c. of enzyme R + 25 c. c. of water, amylum solutions as in the preceding test; p_H of the enzyme-mixture 4.095.

Nr.	Time (minutes) during which the enzyme-mixture was maintained const. at 37	Reduction m.gr. Cu.	Rotation minutes	p_H
1	0	155.00	201.0	5.98
2	18	147.85	201.7	6.04
3	47.5	139.70	199.0	6.02
	fresh enzyme-mixture made of the same Enzyme *R* and the same p_H.			
4	0	162.25	199.3	6.03
5	138	113.10	201.5	6.08
6	373	56.30	203.0	6.03

Our results show that the enzyme is not yet injured at $p_H = 5.5$, but is gradually injured at $p_H = 4.095$. However, in view of the relatively short duration (20 min.) of the digestion-experiments described above, the injury is, even in the case of $p_H = 4.095$ only of small account. We conclude, therefore, that the inhibitory influence of the H-ions in concentrations beyond the optimal is not attributable to injury to the enzyme.

In addition we have also tried to ascertain, whether the enzymic activity is weakened in fluids made slightly alkaline.

c 10 c.c. of phosphoric acid, 27 c.c. of sodium hydrate, 13 c.c. of water. Addition: 25 c.c. of enzyme R + 15 c.c. of water, all the amylum solutions as in the preceding test, p_H of the enzyme-mixture 8.718.

Nr.	Time (minutes) during which the enzyme-mixture was maintained const. at 37°	Reduction m.Gr. Cu.	Rotation minutes	p_H
1	0	142.20	—	—
2	29.5	147.35	—	6.02
3	55.5	147.35	—	—
4	103.5	147.35	—	—
5	255.0	140.70	—	—
6	380.5	134.55	—	—

Consequently no injury in two hours' time with a faintly alkaline reaction, $p_H = 8.718$.

It is obvious, therefore, that in our experiments injury to the enzyme cannot have had any influence worth mentioning; on this account we could not expect the optimal reaction to shift in a prolonged digestion-test. Researches, each lasting 100 minutes, 5 times longer than the other experiments, confirmed our supposition.

Further experimentation will have to reveal the relation between the electric charge of ptyalin to its action, for which the iso-electric point has to be determined [1].

Summary.

For the action of ptyalin the concentration of the hydrogen-ions is highly important. In fluids in which the reaction has been deter-

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[1] Cf. MICHAELIS Bioch. Zeitschr. Bd. 35, S. 386, Bd. 36. S. 280.

mined by phosphate- and acetate-mixtures, we found at $p_H = 6.00$ an optimal reaction to the action of the enzyme. On either side the action decreases, first slowly, afterwards rapidly. Even at $p_H = 4.5$ and 7.5 it is stopped almost completely. At these p_H's injury to the enzyme is out of the question during the whole time of the test. The place of the optimal p_H does not change even when the digestion-time is five times the ordinary duration. The influence of citrate-mixtures is much more inhibitory than that of phosphate- and acetate-mixtures. The inhibition is energetic especially on the side of the minor p_H's. This accounts for the fact that in citrate-mixtures the optimal reaction has shifted towards the neutral point.

Astronomy. — *"On absorption of gravitation and the moon's longitude."* By Prof. Dr. W. de Sitter. Part I.

(Communicated in the meeting of November 30, 1912).

By absorption of gravitation we mean the hypothesis that the mutual gravitational attraction of two bodies is diminished when a third body is traversed by the line joining the first two. If this absorption exists, it will manifest itself by diminishing the attraction of the sun upon the moon during a lunar eclipse. Therefore, in order to test the reality of our hypothesis, we must compute the perturbations in the longitude of the moon which are a consequence of this decrease of attraction, and compare these computed perturbations with the well known deviations of the observed longitude from that derived in accordance with the rigorous law of Newton. Newcomb, in the last paper from his hand (M. N. Jan. 1909) has put before the scientific world the great problem of these deviations or "fluctuations" in the moon's longitude. They can be represented by a term of long period, for which Newcomb finds an amplitude of 12″.95 and a period of 275 years (great fluctuation), upon which are superposed irregular deviations (minor fluctuations), which amount to not more than ± 4″ in Newcomb's representation. Mr. F. E. Ross, Newcomb's assistant, has afterwards represented these minor fluctuations by two empirical terms having periods of 57 and 23 years and amplitudes of 2″.9 and 0″.8 respectively (M. N. Nov. 1911). The outstanding residuals are very small: after 1850 they seldom reach 1″. In the years before 1850 the minor fluctuations are not so well marked, probably because (owing to the smaller number and greater uncertainty of the available observations) too many years have been combined in each mean result.

The idea of explaining these fluctuations by an absorption of the gravitational attraction of the sun upon the moon by the earth during lunar eclipses, has for the first time been publicly worked out by Mr. BOTTLINGER[1]), the investigation having been proposed as the subject of a prize essay by the philosophical faculty of the University of Munich. I had also towards the end of 1909 commenced a similar investigation, which was however of a preliminary character and, as it did not lead to positive results, was discontinued and not published. The publication of Mr. BOTTLINGER's dissertation led me to resume the investigation.

The decrease of the attraction of the sun upon the moon can be taken into account by adding to the forces considered in the ordinary lunar theory a perturbing force acting in the direction of the line joining the sun and the moon, in the direction away from the sun. If the sun and moon are treated as material points, this force is

$$H = \varkappa \frac{m'}{\Delta^2} = \frac{n_0{}^2 m^2 a'^3}{r'^2} (1-2\alpha)\, \varkappa \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The meaning of the letters is:

m' = mass of the sun,

n', a' = mean motion and mean distance of the earth,

n, a = the same elements of the moon (osculating values),

n_0, a_0 = the mean values of these elements,

Δ, r' = distance of sun from moon and earth,

$\alpha = a_0/a'$ $\qquad m = n'/n_0$.

The effect on the elements of the moon's orbit can be computed by the ordinary formulas. The perturbing forces are:

radial force $H \cos\beta \cos(\zeta-\zeta')$,

transversal „ $H \cos\beta \sin(\zeta-\zeta')$,

orthogonal „ $-H \sin\beta$,

where ζ and ζ' are the selenocentric longitudes of the earth and sun, and β is the selenocentric latitude of the sun, the moon's orbital plane being taken as fundamental plane. For the instant of central eclipse we have $\zeta-\zeta' = 0$. The transversal force therefore changes its sign during the eclipse, and its total effect is very nearly zero. The effect of the orthogonal force is entirely negligible. In the expression of the radial force, we can put $\cos(\zeta-\zeta') = 1$. We have further with sufficient accuracy

$$\beta = s, \quad \zeta = w + 180^\circ, \quad \zeta' = w'.$$

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[1]) K. F. BOTTLINGER. Die Gravitationstheorie und die Bewegung des Mondes. Inaugural-Dissertation (München). 1912.

See also "The Observatory" November 1912.

where

$s =$ the moon's latitude,

$w, w' =$ true longitudes of moon and sun.

The radial force thus becomes $H \cos s$. It is easily verified that the mean motion (whose perturbation must be *twice* integrated to give the perturbation in longitude) is practically the only element which need be considered. We find

$$\frac{dn}{dt} = -\frac{3\,e \sin v}{a\sqrt{1-e^2}}\,H \cos s = -\frac{3n_0^{\,2}m^2}{\alpha}(1-2\alpha)\frac{a_0}{a}\left(\frac{a'}{r'}\right)^2 \varkappa \frac{e \sin v}{\sqrt{1-e^2}} \cos s, \quad (2)$$

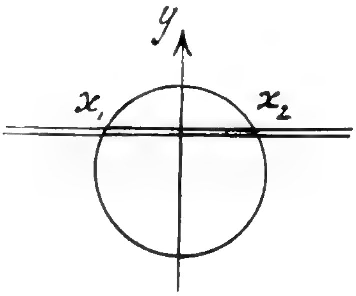
where v is the moon's mean anomaly. For the excentricity e we must use the osculating value. The mean value will be denoted by e_0, as for the other elements.

During the eclipse we can for the coordinates and elements of the moon use their values for the epoch of central eclipse. We then find for the addition to n as the effect of one eclipse:

$$dn = \int_{-T}^{+T} \frac{dn}{dt}\,dt = -3n_0^{\,2}\,m^2\,\frac{1-2\alpha}{\alpha}\left(\frac{a'}{r'}\right)^2 \frac{a_0}{a}\,\frac{e \sin v}{\sqrt{1-e^2}} \cos s \int_{-T}^{+T} \varkappa\,dt, \quad . \quad (3)$$

where the time is counted from the middle of the eclipse, and T is the half duration.

Now assume the absorption of gravitation to be proportional to the mass of the absorbing body. We have then $\varkappa = \mu.\gamma$, where γ is the coefficient of absorption and μ the mass of that part of the earth that is traversed by the "ray of gravitation". This ray of gravitation, i. e. the infinitely thin cone enveloping the sun and moon, which are considered as points, by its motion during the eclipse cuts an infinitely thin disc out of the body of the earth. In the plane of this disc take two coordinate axes, of which the axis of x is parallel to the line joining sun and moon at the instant of centrality. If then ϱ is the density and x_1 and x_2 are the points where the "ray" enters and leaves the earth, we have



$$\mu = \int_{x_1}^{x_2} \varrho\,dx.$$

Further we have

$$dy = \frac{r'}{\Delta} \cdot r \frac{dw}{dt} \cdot dt$$

or

$$dt = \frac{(1+\alpha)\, dy}{r \dfrac{dw}{dt}}.$$

Consequently:

$$\int_{-T}^{+T} \varkappa dt = \frac{(1+\alpha)\,\gamma}{r \dfrac{dw}{dt}} \iint \varrho \, dx \, dy.$$

The double integral must be taken over the entire surface of the above considered section of the earth, and represents the mass of the infinitely thin disc. Its value therefore depends on the distribution of mass within the body of the earth. Like BOTTLINGER I take the distribution according to WIECHERT, i. e. a central core of density $\delta_2 = 8.25$ surrounded by a mantle of density $\delta_1 = 3{\cdot}30$. The radius of the core is $R_1 = 0{\cdot}77\ R$. If we call D the radius of the above considered disc, we can take $D = R \cdot \frac{T_0}{112}$, where T_0 is the half-duration of the eclipse computed with the *mean* elements of the moon's orbit, i. e. the value which is given in OPPOLZER's Canon der Finsternisse, expressed in minutes of time. The number 112 is the maximum of this half-duration.

We then find easily, in the case when the section is entirely in the outer mantle

$$\iint \varrho \, dx \, dy = \pi\, R^2 \delta_1 \left(\frac{T_0}{112}\right)^2,$$

and when it also traverses the inner core (i. e. for $T_0 > 71.5$):

$$\iint \varrho \, dx \, dy = \pi\, R^2 \delta_1 \left\{ 2.5 \left(\frac{T_0}{112}\right)^2 - 0.62 \right\}.$$

Now put, in the first case

$$J_0 = 100 \left(\frac{T_0}{112}\right)^2$$

and in the second case

$$J_0 = 100 \left\{ 2.5 \left(\frac{T_0}{112}\right)^2 - 0.62 \right\}.$$

The function J_0 which is thus defined, is tabulated in Dr. BOTTLINGER's dissertation, with the argument T_0. We have now

$$\int_{-T}^{+T} z\,dt = \frac{(1+\alpha)\,\pi\,R^2\delta_1\gamma}{100\,r\,\frac{dw}{dt}}\,J_0 \quad . \; . \; . \; . \; . \; . \quad (4)$$

and this value must be subtituted in the formula (3). In doing this, we can either express the coordinates and velocities in the osculating elements, or the latter in the former, by the well known formulas

$$\pi = \frac{1}{r} = \frac{1+e\cos v}{a\,(1-e^2)} \qquad \frac{dr}{dt} = \frac{ane\sin v}{\sqrt{1-e^2}}$$

$$r^2\frac{dw}{dt} = a^2n\sqrt{1-e^2}$$

We then find

$$\delta n = -\,q\,J_0\left(\frac{a'}{r'}\right)^2 \cos s\,\frac{a_0^{\,2}n_0}{a^2n}\,\frac{e\sin v}{(1+e\cos v)}, \quad . \; . \; . \; . \quad (5)$$

or

$$\delta n = q\,J_0\left(\frac{a'}{r'}\right)^2 \cos s\,\sqrt{1-e^2}\,\frac{a_0^{\,2}n_0\,\pi\,\frac{d\pi}{dt}}{\left(\frac{dw}{dt}\right)^2} \quad . \; . \; . \; . \; . \quad (6)\,^{1})$$

where we have put

$$q = \frac{3n_0m^2\,(1-\alpha)\,\pi R^2\delta_1}{100a_0a}\,\gamma.$$

We can with sufficient accuracy ²) take in the formula (5) $a_0^{\,2}n_0 = a^2n$, and in the formula (6) $\sqrt{1-e^2} = \sqrt{1-e_0^{\,2}}$. The formulas can, however, not be used for the computations, unless they are so developed as to contain only such quantities as can be easily derived from existing tables.

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¹) The formula (6) is derived by **Bottlinger** from the *vis viva* integral. In this derivation he introduces a couple of approximations, which are unnecessary, and which are the reason why the factor $\sqrt{1-e^2}$ does not appear in his formula. On his page 12 he takes *tan i* for *sin i*. If we retain *sin i* and replace it by its value $\frac{1}{r^2}\frac{dr}{dt}$, the square root drops out of the formula, and consequently the approximation introduced on page 13 in the development of this same root is also unnecessary. We then find $\Delta n = -\frac{3}{a^2n}\,J\,\frac{dr}{dt}$. Now we have $\sqrt{1-e^2} = r^2\frac{dq}{dt}$ and $r = \frac{c}{\pi}$. **Bottlinger**'s formula (I) on page 13 thus becomes $\Delta n = \frac{3\sqrt{1-e^2}}{c}\,\frac{d\pi}{dq}\,J$, and his formula (I) on page (18) then becomes identical to our formula (6).

²) See however the footnote on p. 815.

The coordinates of the moon are developed in the lunar theory in series depending on the four arguments l, l', F and D, where l and l' are the mean anomalies of the moon and sun, F the mean argument of the moon's latitude, and D the difference of the mean longitudes of the moon and sun. For the *mean* opposition we have $D = 0$. The other three arguments are contained, under the names of I, II and III, in OPPOLZER's "Tafeln zur Berechnung der Mondfinsternisse". We have

$$l_1 = \frac{9}{10} II, \qquad l_1' = \frac{9}{10} I, \qquad 2F_1 = \frac{9}{10}(III - 37.66)$$

Denoting the mean longitudes by λ and λ', and the true longitudes by w, w', we have

$$w = \lambda + \delta l + \Delta\lambda, \qquad w' = \lambda' + \delta l',$$

where

$$\delta l = 2e \sin l + \frac{5}{4} e^2 \sin 2l - \gamma^2 \sin 2F$$

represents the elliptic term $\left(\gamma^2 = \sin^2 \frac{1}{2} i\right)$, and $\Delta\lambda$ the sum of all perturbations in longitude. The perturbations in the motion of the earth can be neglected. Then, denoting the values for mean opposition by the suffix 1, we have

$$\lambda_1 - \lambda_1' = 180^\circ, \qquad w_1 - w_1' = 180^\circ + \delta l_1 + \Delta\lambda_1 - \delta l_1';$$

for the instant of central eclipse on the other hand we have

$$w - w' = 180^\circ - \gamma^2 \sin 2F.$$

We now put

$$\Delta = (w_1 - w_1') - (w - w') = \delta l_1 + \Delta\lambda_1 - \delta l_1' + \gamma^2 \sin 2F,$$

Then, $n(1-c)$ and $n(1-g)$ being the mean motions of the perigee and the node, we have, neglecting perturbations 1):

$$\mu = \frac{dw}{dt} = n\left(1 + 2ce \cos l + \frac{5}{2} ce^2 \cos 2l - 2g\gamma^2 \cos 2F\right),$$

$$\mu' = \frac{dw'}{dt} = nm\left(1 + 2e' \cos l' + \ldots\right),$$

The time elapsed between the epochs of mean opposition and central eclipse is then

$$\Delta t = -\frac{\Delta}{\mu - \mu'}$$

At the instant of central elipse we have thus

$$l = l_1 + nc\Delta t, \qquad v = l + \delta l + \Delta l.$$

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1) See however the next footnote.

where $\Delta l = \Delta \lambda - \Delta \omega$, $\Delta \omega$ being the perturbation in the longitude of the perigee. Further we have, to the order of accuracy here required, $dl = dl_1 - 2e\Delta \cos l$. Therefore, neglecting the difference between the perturbations Δl and Δl_1 at the two epochs, and putting $c = (1-m)\, c'$, we find

$$v = l_1 + dl_1' - \gamma^2 \sin 2F_1 - \Delta\omega - (c'-1)\Delta. \quad . \quad . \quad . \quad (7)$$

Now we have approximately $l' = l_1' - m\Delta$, and also $c'-1$ differs not much from m, therefore, if $\Delta\omega$ is neglected, we find from (7)

$$v - v' = l_1 - l_1' - \gamma^2 \sin 2F, \quad \text{or} \quad w - w' = \lambda_1 - \lambda_1' - \gamma^2 \sin 2F.$$

The term $\gamma^2 \sin 2F$ is the reduction from true opposition to central eclipse. Consequently the meaning of these formulas is: The difference of the true longitudes of moon and sun at true opposition is equal to the difference of the mean longitudes at mean opposition.

In the expression for Δ, which only occurs multiplied by the small factor $c' - 1$, we can neglect all perturbations except the evection. This latter is very easily applied by replacing e_0 in dl by $\frac{6}{7} e_0$ (see e. g. TISSERAND III p. 134). We have thus

$$\Delta = \frac{12}{7} e \sin l_1 - 2e' \sin l_1'.$$

We must now develop the quantity

$$K = \left(\frac{a'}{r'}\right)^2 \cos s \, \frac{e \sin v}{1 + e \cos v}.$$

where for v we must introduce the value (7). We can take with sufficient accuracy

$$\left(\frac{a'}{r'}\right)^2 = 1 + 2e' \cos l'.$$

Further we can take $\cos s = 1$, and we put

$$\Delta e = \Sigma \varkappa \cos x, \qquad e_0 \Delta\omega = \Sigma \varkappa \sin x,$$

It appears, in fact, on investigation that all perturbations which need be considered, are of this form. We then find easily

$$K = e_0 \sin l_1 - \left[\frac{1}{12} + \frac{6}{7}(c'-1)\right] e_0^2 \sin 2l_1 + (c'+1)\, ee' \sin (l_1 + l_1') + \Sigma\varkappa \sin (l_1 - x).$$

The perturbations Δe and $\Delta\omega$ are not as such contained in the existing lunar theories. I have therefore derived them, neglecting all perturbations that do not exceed $0.01\, e_0$. The only remaining term is again the evection. Those terms in the perturbing function, which in longitude give rise to the variation, produce a large perturbation in e and ω, but its argument is $x = l \pm 2D$, and consequently the corresponding term in K is zero, since $2D_1 = 0$[1]. The evection-term has the argument $x = 2l - 2D$. The resulting term in K therefore has the same argument as the principal term. Finally I found in this way

$$K = e_0 \{0.858 \sin l_1 - 0.031 \sin 2l_1 + 0.033 \sin (l_1 + l_1')\}$$
$$= 0.0471 \{\sin l_1 (1 - 0.072 \cos l_1) + 0.039 \sin (l_1 + l_1')\} \quad . \quad . \quad (8)$$

In order to verify this result, I have also computed the formula (6). The values of π and $w - \lambda$ expressed in the arguments l, l', D and F were taken from BROWN's lunar theory. From these we easily derive $\dfrac{d\pi}{dt}$ and $\dfrac{dw}{dt}$.

We must then substitute for the arguments their values

$$l = l_1 + cn\,\Delta t \qquad D = 180^\circ + (1 - m)\, n\Delta t$$
$$l' = l_1' + mn\,\Delta t \qquad 2F = 2F_1 + 2g\, n\Delta t$$

The value of Δt is given in OPPOLZER's "Syzygien-Tafeln für den Mond", page 4. The value there given is the interval of time between mean and true opposition. To get the value for the epoch of central eclipse it is sufficiently accurate to omit the term $+0.0104 \sin (2g' + 2\omega')$. The interval thus computed must then be reduced to our unit of time (see below). The developments, which are rather long, finally led to the following formula, where nothing is neglected that can affect the third decimal place:

$$a_0{}^2 n_0 \frac{\pi \dfrac{d\pi}{dt}}{\left(\dfrac{dw}{dt}\right)^2} \cos s = 0.{}^{0}5404 \{0.8075 \sin l_1 - 0.0300 \sin 2l_1$$
$$+ 0.0300 \sin (l_1 + l_1') - 0.0020 \sin (2l_1 + l_1')$$
$$- 0.0033 \sin l'_1 - 0.0050 \sin (l_1 - l'_1)$$
$$+ 0.0016 \sin 2F_1 - 0.0055 \sin 2F_1 \cos l_1$$
$$+ 0.0114 \cos 2F_1 \sin l_1\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Eclipses occur near the node. Consequently $\sin 2F < \frac{1}{2}$. Thus, if we neglect all but the first three and the last term, none of the neglected terms exceeds $\frac{1}{200}$. Further $\cos 2F$ is always included between the limits 1 and 0.866. Therefore if we take $\cos 2F_1 = 0.96$ throughout, we cannot make a larger error than about $\frac{1}{10}$ of the last term. This latter then becomes $0.0110 \sin l_1$ and can be added to the principal term. We thus finally get the formula

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[1] The influence of the variation on the osculating values of a and n, is considerable, but it is the same in all oppositions, so that $a^2 n$ is a constant. The same thing is true of the error which is produced by our taking in μ, in the computation of Δt, the mean instead of the osculating value of n.

$$dn = - q_1 J_0 \{ \sin l_1 (1 - 0.074 \cos l_1) + 0.037 \sin (l_1 + l_1') \}. \quad . \ (10)$$

where

$$q_1 = 0.8185 \times 0.05404 \times q \sqrt{1 - e_0^2} = 0.04473 q.$$

The agreement with (8) is very satisfactory [1]).

We adopt as unit of time the mean interval between two successive eclipses, i. e. 6 synodic months or 177.18 days. Then taking as units of length and of density the earth's radius and the density σ_1 of the outer mantle, we find

$$q_1 = 1262''.\gamma$$

Calling λ the coefficient of absorption in the *C.G.S* system of units, we have $\gamma = R\sigma_1 \lambda$, and therefore

$$q_1 = 2656.''10^9.\lambda.$$

The formula (10) has been used to compute the value of σn for all eclipses occurring in OPPOLZER's Canon between 1703 and 1919. The coefficient q_1 was omitted, the results are therefore expressed in q_1 as unit.

Eclipses occur in groups of six. The interval of time between two successive eclipses of a group is 6 synodic months. In some groups there are only five or four eclipses: we can then still treat the group as consisting of 6 eclipses, if for the missing eclipses we assume $dn = 0$ [2]).

Between each group and the next one or two eclipses are missed out, the interval of time between the last eclipse of one group and the first of the next group being in those cases 11 or 17 synodic months instead of 12 or 18.

Five groups make a Saros of 223 synodic months = 6585.2 days = 18.03 years.

The interval of 6 synodic months being the unit of time, the perturbation in n is derived by simply adding up the individual values of dn, i. e. forming the first series of sums. Then to get the perturbations in longitude we must again form the successive sums of these values of n, after having filled in so many times the final value of n of each group as there are empty places corresponding to the eclipses dropped out between that group and the next, remembering however that for *one* of these missing eclipses we must only take $^5/_6$ of this final value.

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[1]) The difference in the multiplier outside the brackets is produced by the neglect of the influence of the variation in (8) (see preceding footnote).

[2]) In the course of time eclipses drop out at the beginning of the groups and new eclipses appear at the end. The limits of the groups are thus displaced within the Saros. During the interval of two centuries treated in this paper, it is not necessary to take account of this displacement.

In each of the two series of sums we can start with an arbitrary constant.

When the computations were carried out it appeared that always the values of dn summed up over a complete Saros gave a very small total, while the perturbation in longitude showed a very marked periodicity, with the Saros as period.

Accordingly I have divided the total perturbation into two parts: the periodic Saros and the remaining non-periodic part. I call Δn_p and $\Delta\lambda_p$ the increase of the mean motion and the longitude during the pth Saros, if the initial constants for both series of sums are taken zero. The purely periodic part of the perturbation during that Saros is then derived by taking for the initial constant of the first series of sums — i. e. the initial value of the perturbation in n — a value n_0 determined from the condition $37\frac{1}{6}\, n_0 + \Delta\lambda = 0$ $\left(37\frac{1}{6}\right.$ is the length of the Saros in our units of time$\left.\right)$. The perturbation in longitude at the end of the p^{th} Saros is then:

$$\lambda_p = \Delta\lambda_0 + \sum_{k=1}^{p} \Delta\lambda_k + 37\frac{1}{6}\left\{p\,\Delta n_0 + \sum_{k=1}^{p} (p-k)\,\Delta n_k\right\}.$$

where Δn_0 and $\Delta\lambda_0$ are the initial constants of the two series of sums, i. e. the values of n and λ at the beginning of the first Saros. Putting now

$$\Delta\lambda_k = \Delta_0\lambda + (\Delta_1\lambda)_k, \qquad 37\frac{1}{6}\,\Delta n_k = \Delta_0\mathbf{r} + (\Delta_1\mathbf{r})_k,$$

$$37\frac{1}{6}\,\Delta n_0 = -\,\Delta_0\lambda + \frac{1}{2}\,\Delta_0\mathbf{r} + \mathbf{r}_1,$$

we have:

$$\lambda_p = \Delta\lambda_0 + p\mathbf{r}_1 + \frac{1}{2}\,p^2\Delta_0\mathbf{r} + \sum_{k=1}^{p}(\Delta_1\lambda)_k + \sum_{k=1}^{p}(p-k)\,(\Delta_1\mathbf{r})_k, \quad (11)$$

which formula still contains two arbitrary contants $\Delta\lambda_0$ and $\mathbf{r}_1$. If for $\Delta_0\lambda$ and $\Delta_0\mathbf{r}$ we choose the mean values of $\Delta\lambda_k$ and $37\frac{1}{6}\Delta n_k$, the terms under the signs Σ are small and of varying sign. The term containing p^2 is of the nature of a secular acceleration. If we denote the time expressed in centuries by τ, then p is equivalent to 5.55 τ, or $\frac{1}{2}p^2$ to 15.4 τ^2.

The individual values of dn will be given in the second part of this paper. Table I contains the values of Δn, $\Delta\lambda$, $\Delta_1\mathbf{r}$ and $\Delta_1\lambda$ for each Saros.

TABLE I.

Year	Saros	Δn	$\Delta\lambda$	$\Delta_1 r$	$\Delta_1 \lambda$	λ_1	λ_2	$\frac{\lambda_2}{160}$	Newc.
1703.0						+1091	− 628	− 3.9	− 5″4
	I	− 7.5	+1839	+103	−756				
1721.0						0	0	0	− 0.4
	II	− 2.3	+2180	+297	−415				
1739.1						− 647	+ 690	+ 4.3	+ 4.6
	III	2.2	+2299	+300	296				
1757.1						− 878	+1414	+ 8.8	+ 9.1
	IV	−16.9	+2197	−246	−398				
1775.1						− 911	+1954	+12.2	+11.5
	V	−11.8	+2415	− 57	−180				
1793.1						− 972	+2084	+13.0	+12.9
	VI	− 8.3	+2565	+ 74	− 30				
1811.2						− 940	+1925	+12.0	+11.7
	VII	− 6.2	+2537	+152	− 58				
1829.2						− 862	+1430	+ 8.9	+ 8.7
	VIII	−11.1	+2627	− 30	+ 32				
1847.2						− 542	+ 795	+ 5.0	+ 4.1
	IX	−15.7	+2874	−202	+281				
1865.3						− 3	− 3	0	− 1.1
	X	−14.8	+3200	−168	+605				
1883.3						+ 658	−1061	− 6.6	− 6.1
	XI	−21.4	+3135	−413	+540				
1901.3						+1086	2734	−17.1	−10.2
	XII	− 5.3	+3269	+185	+674				
1919.4						+1237	−5066	−31.7	

We have $\Delta_0 r = -382$, $\Delta_0 \lambda = +2595$. If we neglect the term in p^2, and choose the values of $\Delta\lambda_0$ and r_1 so as to make $\lambda_p = 0$ for 1721 and 1865, the perturbation in longitude given under the heading λ_1 results. If we add the term $\frac{1}{2} p^2 \Delta_0 r$, at the same time altering the initial constants so that the perturbation remains zero at the same two epochs, we get the values λ_2 [1]).

The reliability of these results of course depends on the reliability of the individual values of dn. The values of l_1 in two successive eclipses differ by 155°, consequently the values of dn have opposite signs and nearly destroy each other. Therefore, to arrive at a tolerable accuracy in the final perturbation in longitude, it is necessary to compute the individual dn to a much higher accuracy. The sum of the neglected terms in the series (9) will generally not exceed $^1/_{200}$, or in some cases perhaps $^1/_{100}$, of the whole. The maximum value of dn is about 190, we may thus expect on this account an error of one, or in extreme cases, 2 units.

The chief source of uncertainty is the function J_0. This function contains the hypothesis regarding the distribution of mass in the

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[1]) In the original Dutch there was a mistake in the values of λ_1 and λ_2, which has here been corrected. The conclusions remain the same.

body of the earth. If a distrubution differing from WIECHERT's is adopted, the function J_0 is considerably altered. What is the effect of this on the final result can only be decided by actually carrying out the computation with a different hypothesis. This has been done, as will be related in the second part of this paper. Here it must suffice to state that, although there are some differences, the general character of the results is remarkably similar to those of the first computation. It may be mentioned that also my preliminary investigation of 1909, though based on a totally different and only roughly approximate formula, gave results of the same character.

The hypothesis that the sun and moon can be treated as points, is also, of course, only approximate, and it is very difficult to say in how far it affects the reliability of the results. It seemed however better, at the present state of the question, to rest content with this approximation.

The function J_0 however gives rise to errors in still another way. It is tabulated with the half-duration T_0 as argument. This is taken from the Canon, where it is given in minutes of time, and can thus be a half, or in some cases perhaps even a whole minute in error. The resulting error in δn may occasionally amount to 4 units. Thus, neglecting the uncertainty introduced by the hypothesis regarding the distribution of density, the purely numerical error in δn may reach an amount which can be taken to correspond to a mean error of say ± 3 units. The mean error of the perturbation in n after p eclipses is then $\pm 3\sqrt{p}$. For a Saros (30 eclipses) this gives ± 16. Also the m. e. of the second sum (i. e. the perturbation in longitude, if we neglect the fact that sometimes the interval between successive eclipses differs from the normal value) is found to be $\pm \frac{1}{2}\sqrt{6p(p+1)(2p+1)}$. For the Saros this becomes ± 292.

It thus appears that all the values which have been found for Δn might very well be due to accidental accumulation of the inaccuracies of the computations. On the other hand the circumstance that they have the same sign throughout might lead us to consider them as at least partly real; by which I mean as necessary consequences of the adopted hypotheses. The values of $\Delta_1\lambda$ also are not so large that their reality can be considered as certain, but here also the systematic change with the time may be an indication of their being not entirely due to accidental errors of computation. The only thing that can be asserted with confidence is that the values of $\Delta_1 r$ and $\Delta\lambda_1$ are small, and consequently that the non-periodic part of the perturbations in longitude has a smooth-running course: no other irregularities with short periods can exist in the longitude than those which are contained in the periodic part.

This periodic part is very nearly the same in all Saros-periods. It will be given in detail in the second part of this paper. To show its general character I give here in Table II the mean for the last five periods VIII—XII (1829—1919), which are the most important for the comparison with the observations. The first column contains the time t counted in synodic months from the beginning of the Saros. This periodic perturbation can be represented with unexpected accuracy by the formula:

TABLE II.

t	λ_s	Form.	t	λ_s	Form.	t	λ_s	Form.	t	λ_s	Form.	t	λ_s	Form.
0	0	0	41	−521	−523	88	573	−546	129	−34	−36	176	+312	+360
6	75	−84	47	−560	−572	94	−557	−491	135	+64	+45	182	+311	+356
12	−143	−167	53	−578	608	100	−545	−426	141	+133	+120	188	+321	+337
18	−309	−359	59	−654	−631	106	−362	−354	147	+237	+208	194	+305	+306
24	−321	−331	65	−538	−640	112	−319	−273	153	+239	+247	200	+240	+262
30	−441	406	71	−603	−635	118	−216	−190	159	+262	+295	206	+272	+206
36	−487	−474	77	582	−616	124	117	−106	165	+316	+330	212	+174	+140
			83	−577	−583				171	+314	+352	218	+76	+66

$$\lambda_s = -140 - 500 \sin\left[\frac{2\pi t}{223} - 16^\circ 26\right] \quad . \quad . \quad . \quad (12)$$

The values computed by this formula are given in the table under the heading "Form". The constant term, of course, is unimportant, and could be added to the arbitrary constant of integration $\Delta\lambda_0$. It would almost entirely disappear, if the Saros was begun at the end of the third-group, say at about $t = 121$. If the time is expressed in years, the formula becomes

$$\lambda_s = -140 + 500 \sin\left[19^\circ.967\,(t - 1900) + 137.^\circ 1\right] \quad . \quad (13)$$

The course of the perturbation in longitude is remarkably similar in the different periods, the irregularities, i.e. the deviations from the sine-formula, recurring in each period at the same values of t. The coefficient of the sine on the other hand varies from one period to another. For the first eight periods it oscillates between about 350 and 400, in the later periods it increases up to about 600 for the Saros XII (1901—1919).

Comparison with the observations. The excesses of the observed longitude of the moon over the longitude as computed by pure gravitational theory, which have been given by NEWCOMB, must still be corrected by the differences between the new lunar theory of BROWN and HANSEN's theory which has been used by NEWCOMB. The corrections necessary on this account have been collected by BATTERMANN[1]). Out of the 43 terms given by him we need only consider the terms of long periods (14)—(22) and (43). For the discussion of the non-periodic part of the perturbation in longitude we must take account of the terms (16) to (19), which have periods between 128 and 1921 years[2]). I have, however, not applied these terms, the reality of the non-periodic part being too uncertain to warrant much labour to be bestowed on it. For the discussion of the periodic part, we have to consider the terms (14), (15), (20), (21), (22) and (43), which can be written as follows:

(14) $+0''.48 \, sin \, 40^\circ.67 \, (t - 1894.3)$ period 8.84 years
(22) $+0\;.13 \, sin \, 30\;.35 \, (t - 1894.6)$,, 11.87 ,,
(20) $+0\;.24 \, sin \, 20\;.66 \, (t - 1890.7)$,, 17.41 ,,
(43) $+0\;.56 \, sin \, 19\;.35 \, (t - 1892.2)$,, 18.60 ,,
(15) $+0\;.13 \, sin \, 10\;.34 \, (t - 1870.4)$,, 34.76 ,,
(21) $+0\;.28 \, sin \;\; 9\;.69 \, (t - 1877.6)$,, 37.14 ,,

The therm (43) contains the correction given by BATTERMAN in his "Zusatz". It is very similar to the term which was already applied by ROSS, viz: $-0''.50 \, sin \, \Omega = +0''.50 \, sin \, 19^\circ.35 \, (t - 1894.8)$. These corrections must be added to the tabular longitudes, or subtracted from the residuals.

Considering now first the non-periodic part, it is very remarkable that the values of λ_2 as given in Table I are between the years 1703 and about 1894 almost identical to NEWCOMB's great fluctuation, if 160 of our units are taken equal to 1". This is at once apparent from the last two columns of table I, of which the last contains the great fluctuation according to NEWCOMB. Therefore, if we assumed the absorption of gravitation to be the true explanation of the great fluctuation, we should have

$$160 \times 1262'' . \gamma = 1'' \qquad \gamma = 5.10^{-6} \qquad \lambda = 25.10^{-16}.$$

However, after 1894 the similarity ceases. The agreement before that date depends on the assumption of the reality of the values

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[1]) Beobachtungs-Ergebnisse der K. Sternwarte zu Berlin, N°. 13, 1910.

[2]) The most important of these is a correction of 0."85 to the coefficient of the well known Venus-term of 273 years period.

which have been found for $\angle n$ and $\angle \lambda$, especially the negative value of the mean $\angle_0 r$. This latter is equivalent to a secular acceleration of which the coefficient would, with the above value of q, become $-37''$. This, of course, is entirely inadmissible and consequently it is not possible to consider the value of $\angle_0 r$ as real unless we take for q such a small value that the whole effect becomes entirely negligible [1]). The partial agreement of λ_2 with the empirical terms of long period can therefore not be considered as a proof for the existence of an absorption of gravitation.

We now come to the comparison with the observations of the periodic part of our computed perturbation. This comparison was only carried out for the time after 1829. From 1847 to 1912 I had the advantage of being able to make use of a new and careful reduction of the Greenwich meridian observations which Prof. E. F. VAN DE SANDE BAKHUYZEN most kindly placed at my disposal. Prof. BAKHUYZEN applied to the meridian observations the correction for the difference of right ascension of the moon between the epochs of true and of tabular meridian passage, for those years in which this correction had not yet been applied at Greenwich. Then the systematic corrections, which in his former reduction (These Proceedings, Jan. 1912), were taken constant over the whole interval from 1847 to 1910, were derived anew. The following are the systematic corrections finally adopted by Prof. BAKHUYZEN for the observations of the limb:

1847—48	49—57	58—68	69—78	79—98	1899—1911
0″.00	—1″.61	—0″.83	—0″.93	—0″.62	+0″.39

For the observations of the crater Mösting A the correction was derived in two different ways, which gave — 0″.22 and + 0″.34 respectively. The adopted correction is 0″.00. Prof. BAKHUYZEN then formed the means of the meridian observations of the limb, of the crater and the occultations, the latter being taken from NEWCOMB's paper, but corrected by + 0″.18, for reasons explained in his paper of Dec. 1911. The corrected results of the meridian observations and the means thus derived are given in Table VII in the second part of this paper. From these means I then subtracted the theoretical corrections given by BATTERMANN and quoted above. The resulting corrected means which are thus the excesses of the longitude of the moon over the pure gravitational value, diminished by NEWCOMB's great fluctuation, were plotted and a smooth curve was drawn through

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[1]) In my former investigation I was led to a similar conclusion (see "The observatory" Nov. 1912 page 892).

them. From this curve were read off the values given below in Table III under the heading "Obs." If these are compared with the computed perturbation, of which the periodic part is also given in the table under the heading λ_s, there appears at first sight to be

TABLE III.

Year	Obs.	λ_s	Obs. $-\frac{\lambda_s}{500}$	Year	Obs.	λ_s	Obs. $-\frac{\lambda_s}{500}$	Year	Obs.	λ_s	Obs. $-\frac{\lambda_s}{500}$
1829	−0.3	+ 20	−0.3	1865	+3.8	+ 60	+3.7	1892	2.8	340	2.1
35	0.8	−550	+0.3	68	+2.4	−500	3.4	95	3.1	+300	−3.7
41	−0.5	+ 60	−0.6	71	0.0	630	+1.3	98	2.0	+380	−2.8
47	+1.3	+ 10	+1.3	74	−1.8	−350	1.1	1901	+0.5	+ 40	+0.4
50	+1.1	−440	+2.0	77	−2.5	+230	−3.0	04	+1.4	−560	+2.5
53	+1.1	−550	+2.3	80	−1.4	+330	−2.1	07	+2.7	−640	+4.0
56	+2.0	330	+2.7	83	−1.4	+ 50	1.5	10	+4.4	−350	+5.1
59	+3.0	+170	+2.7	86	−2.2	−580	−1.0	12	5.1	+ 70	+5.0
62	+3.8	+270	+3.3	89	−3.0	−630	−1.7				

a certain similarity in the course of the two curves. Mr. BOTTLINGER, whose results on the whole agree with mine, has been led by this similarity to consider the existence of an absorption of gravitation as being established "mit guter Wahrscheinlichkeit". In fact, from about 1840 to 1868 the observed deviations can be very satisfactorily represented by about $\frac{1}{500}\lambda_s +$ a smooth curve, which latter then must either be ascribed to the non-periodic part, or remain unexplained. After 1868, however, the agreement is lost. We have again a partial parallelism between 1886 and 1891, and also the increase after 1908 coincides with an increase of λ_s, but it is impossible so to represent the observed values over the whole interval 1829 to 1912 by λ_s multiplied by a constant coefficient, that the remaining differences form a smooth curve. Still I think we cannot consider the probability of the existence of an absorption of gravitation as established unless the residuals remaining after applying the perturbation produced by this absorption (and which then remain unexplained), are small and form a smooth curve, or at least are less irregular than the original fluctuations. The values of Obs. — $k\lambda_s$ however, whatever value we adopt for k, always are considerably more irregular than the observed values themselves. The sudden fall between 1868 and 1874 coincides with a horizontal stretch (minimum) of λ_s, the quick rise from 1897 to 1906 corresponds to a decrease of λ_s. The effect of absorption cannot have another period than 18.03 years, while in the observed fluctuations periods of different length are certainly present.

It appears to me, therefore, that so far we have no reason to consider the existence of a sensible absorption of gravitation as proved, or even as probable.

(To be continued).

Astronomy. — *"On Absorption of Gravitation and the moon's longitude".* By Prof. Dr. W. DE SITTER. Part II.

(Communicated in the meeting of December 28, 1912).

The conclusions derived in the first part of this paper are entirely confirmed by the second computation, which was already referred to in that part, and which was based on a different hypothesis regarding the distribution of mass in the body of the earth. I now assumed a core of density $\delta'_2 = 20$ and radius $R'_1 = 0.55\ R$, surrounded by a mantle of density $\delta'_1 = 2.8$ [1]. In the same way as before, I put, for $T_0 < 93.5$

$$J_0' = 84.7 \left(\frac{T_0}{112}\right)^2,$$

and for $T_0 > 93.5$

$$J_0' = 84.7 \left\{ 7.1 \left(\frac{T_0}{112}\right)^2 - 4.27 \right\}.$$

The multiplier 100 has been replaced by $84.7 = 100\ \delta_1'/\delta_1$ in order to get the same value of q for both computations. The result of the introduction of this new distribution of mass instead of the formerly assumed one is to increase the amount of absorption for long eclipses and to diminish it for short eclipses. The ratio J_0'/J_0 varies from 0.51 to 1.25. It is smallest for those eclipses in which with WIECHERT's hypothesis the core also contributes to the absorption, while in the new hypothesis the ray of gravitation is situated entirely in the mantle. For the purpose of computation this ratio J_0'/J_0 was tabulated with the argument T_0. We have then

$$dn' = \frac{J_0'}{J_0}\, dn.$$

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[1] This hypothesis has been suggested by recent investigations by Mr. GUTENBERG, which were kindly communicated to me by Dr. FOTTLINGER Mr. GUTENBERG finds that the real distribution of mass is included between the limits given by $\delta'_2 = 20$, $\delta'_1 = 2.8$ and $\delta_2' = 8$, $\delta'_1 = 4.4$. It being my intention to investigate the effect of a change in the function J_0, I purposely took the upper limit, which differs most from WIECHERT's assumption.

With this value of dn' the computation was then carried out in exactly the same way as with dn. Notwithstanding the considerable difference between the functions J_0' and J_0 the general character of the results of the two computations is the same.

The non-periodic part of the perturbation in longitude derived from the new computation is given in Table IV, which is entirely similar to Table I of Part I. We now find $\Delta_0 r' = \quad 230$, $\angle_0 \lambda' = + 2939$. Neglecting the term $- \frac{1}{2} p^2 \angle_0 r'$ and causing the perturbation to vanish for 1721 and 1865 by an appropriate choice of the constants of integration, we find the values given under the heading λ'_1. If the term containing $\angle_0 r'$ is added, we get the value λ'_2. The general character of the perturbation is very similar to that of the first computation. But the correspondence with the "great fluctuation", which was apparent in the first computation, does not exist here.

TABLE IV.

Year	Saros	$\Delta n'$	$\Delta\lambda'$	$\Delta_1 r'$	$\angle_1 \lambda'$	λ_1'	λ_2'
1703.0						+ 747	− 288
	I	−15.2	+1727	334	−1212		
1721.0						0	0
	II	−10.4	+2318	−156	− 621		
1739.1						− 490	+ 315
	III	−21.0	+2346	− 550	− 593		
1757.1						−1180	+ 272
	IV	+ 2.8	+3300	+334	+ 361		
1775.1						−1322	+ 403
	V	−12.3	+3141	−227	+ 202		
1793.1						−1361	+ 476
	VI	− 9.3	+3380	−115	+ 441		
1811.2						−1388	+ 337
	VII	− 1.0	+3466	+193	+ 527		
1829.2						−1444	− 64
	VIII	+14.0	+3896	+751	+ 957		
1847.2						− 877	− 72
	IX	− 1.9	+3452	+160	+ 513		
1865.3						− 3	− 3
	X	− 9.7	+3120	−130	+ 181		
1883.3						+ 699	− 336
	XI	−19.6	+2494	−498	− 445		
1901.3						+ 645	−1655
	XII	+ 9.2	+2630	− 572	309		
1919.4						+ 229	−3566

In the periodic part the agreement between the results of the two computations is even more complete.

With reference to the reliability of these results it must be remarked that the function J_0' has a wider range of variation depending on T_0 than J_0, and consequently the possible error arising from the fact that T_0 is only known to whole minutes is in the second computation much larger than in the first. Accordingly we find that the values of $\angle_1 r'$ in the second computation are considerably larger than the corresponding values of $\angle_0 r$ in the first computation. Also the values of $\angle_1 \lambda'$ are larger than those of $\angle_1 \lambda$. We are thus led to the same conclusion as before, viz: the reality of the non-periodic part of the perturbation is not assured, and the only thing that can be asserted with certainty is that the non-periodic part cannot have any considerable irregularities and that no other periods are possible than the Saros of 18.03 years.

The following tables contain the principal quantities occurring in the computations. Table V gives for each eclipse the values of T_0, l_1, l_1' and those of dn and dn' computed by the formula (10). The first column of the table contains the time t counted in synodic months from the beginning of the Saros. The time $t = 223$ of any Saros is, of course, identical to the time $t = 0$ of the next Saros. The arrangement of the eclipses in groups of six is very clearly shown. The several groups begin at

$$t = 0, \quad 41, \quad 88, \quad 129 \text{ and } 176$$

and end at

$$t = 30, \quad 77, \quad 118, \quad 165 \text{ and } 212.$$

Table VI contains the purely periodic part of the perturbation λ_s and λ_s' according to the two computations. The similarity between the different Saros-periods is very striking. In the mean motion this similarity is even more apparent than in the longitude. The mean motion is not contained in the table, but can easily be derived from the longitudes, as it is the difference of two successive values of λ_s (or λ_s'). We see from this table that in the first computation the amplitude of the periodic part is fairly constant for the first eight periods and begins to increase after the eighth Saros. The difference between the extreme values of λ_s oscillates between 700 and 830 in the periods I to VIII, and then gradually increases up to about 1200 for the Saros XII. In the second computation the difference between the extreme values of λ_s' is more constant and varies between about 950 and 1100.

The remarkable agreement between the results of the two computations justifies the expectation that the general character of the perturbations in longitude produced by an absorption of gravitation will be sensibly the same for any assumed distribution of density within the body of the earth, which is at all within the limits of probability. The conclusions arrived at in Part I are thus not restricted to the particular hypothesis which was there introduced, but have a much wider bearing.

TABLE V.

	Saros I						Saros II					
t	Year	T_0	l_1	l'_1	δn	$\delta n'$	Year	T_0	l_1	l'_1	δn	$\delta n'$
		m	°	°				m	°	°		
0	1703.0	83	223.2	4	+ 58.2	+ 34.9	1721.0	83	220.4	14	+ 55.5	+ 33.3
6	03 5	108	18.1	178	− 49.2	55.1	21.5	105	15.2	189	− 37.0	− 57.7
12	04.0	112	173.0	353	− 26.8	− 33.5	22.0	112	170.1	4	− 36.1	45.1
18	04.5	102	327.9	167	+ 71.0	+ 64.6	22.5	105	325.0	178	+ 84.0	+ 85.7
24	04.9	78	122.8	342	− 56.3	37.2	23.0	79	119.9	353	− 60.6	− 39.4
30												
41	1706.3	74	201.6	117	+ 20.4	15.5	1724.4	65	198.8	128	+ 12.3	+ 10.5
47	06.8	84	356.6	292	+ 7.2	+ 4.2	24.8	82	353.7	302	+ 10.0	+ 6.1
53	07.3	112	151.5	106	− 90.6	−113.2	25.3	111	148.6	117	97.1	−118.5
59	07.8	112	306.4	281	+153.0	+191.2	25.8	112	303.5	292	+159.5	+199.3
65	08.3	76	101.3	95	− 55.2	− 38.6	26.3	82	98.4	106	− 73.9	− 45.1
71	08.7	72	256.2	270	+ 43.0	+ 34.8	26.8	76	253.4	281	+ 54.5	+ 38.1
77												
88	1710.1	93	335.1	45	+ 43.4	+ 22.1	1728.2	92	332.2	56	+ 46.2	+ 24.0
94	10.6	91	130.0	220	− 84.3	− 44.7	28.6	85	127.1	230	− 70.7	− 41.0
100	11.1	111	284.9	34	+182.6	+222.8	29.1	111	282.0	45	+186.5	+227.5
106	11.6	110	79.8	209	−172.5	−205.3	29.6	111	76.9	220	−174.1	−212.4
112	12.1	58	234.7	23	+ 23.8	+ 20.2	30.1	59	231.9	34	+ 24.0	+ 20.4
118	12.5	49	29.6	198	− 8.8	− 7.5	30.6	63	26.8	209	− 12.6	− 10.7
124												
129	1713.4	63	313.6	158	+ 20.9	+ 17.8	1731.5	48	310.7	169	+ 13.2	+11.2
135	13.9	71	108.5	333	− 41.3	− 34.3	32.0	70	105.6	344	− 40.6	− 34.1
141	14.4	111	263.4	148	+182.9	+223.1	32.4	110	259.5	158	+177.7	+211.5
147	14.9	112	58.3	322	−159.6	−199.5	32.9	112	55.4	333	−154.7	−193.4
153	15.4	82	213.2	137	+ 44.0	+ 26.8	33.4	90	210.3	148	+ 55.2	+ 29.8
159	15.9	90	8.1	311	− 11.1	− 6.0	33.9	90	5.2	322	− 6.8	− 3.7
165												
176	1717.2	83	87.0	86	− 78.0	− 46.8	1735.3	78	84.0	97	− 61.2	− 46.4
182	17.7	83	241.9	261	+ 69.4	+ 41.6	35.8	77	239.0	272	+ 51.5	+ 34.5
188	18.2	112	36.8	76	−114.8	−143.5	36.2	112	33.9	86	−106.7	−133.4
194	18.7	112	191.7	250	+ 34.9	+ 43.6	36.7	112	188.8	261	+ 24.6	+ 30.8
200	19.2	76	346.5	65	+ 10.5	+ 7.4	37.2	79	343.7	76	+ 15.1	+ 9.8
206	19.7	67	141.4	239	24.2	− 20.6	37.7	76	138.6	250	− 40.0	− 28.0
212												

TABLE V (*Continued*).

t	Saros III						Saros IV					
	Year	T_0	l_1	l'_1	δn	δn	Year	T_0	l_1	l'_1	δn	$\delta n'$
		m						m	°	°		
0	1739.1	82	217.5	25	50.7	30.9	1757.1	80	214.6	35	+ 43.2	+ 27.6
6	39.6	103	12.4	200	27.8	26.4	57.6	98	9.5	211	17.2	− 12.7
12	40.0	112	167.3	14	45.1	56.4	58.1	112	164.4	25	− 54.1	− 67.6
18	40.5	107	322.2	189	95.8	104.4	58.6	110	319.3	200	+111.0	+132.1
24	41.0	80	117.1	4	− 64.6	− 47.7	59.0	80	114.3	14	− 65.7	− 42.0
30												
41	1742.4	52	196.0	139	+ 6.8	+ 5.8	1760.4	31	193.2	148	+ 2.0	+ 1.7
47	42.9	79	350.9	313	+ 11.5	+ 7.5	60.9	77	348.1	323	+ 12.9	+ 8.6
53	43.4	110	145.8	128	102 9	−122.5	61.4	110	143.0	139	110.7	− 131.7
59	43.8	112	300.7	302	+165.3	+206.6	61.9	112	297.9	313	+170.5	+ 213.1
65	44.3	88	95.6	117	− 93.2	− 51.3	62.4	94	92.8	128	−114.5	− 60.7
71	44.8	80	250.5	292	+ 65.7	+ 42.0	62.8	82	247.7	302	+ 71.8	+ 43.8
77												
88	1746.2	91	329.4	67	+ 48.5	+ 25.7	1764.2	88	326.5	76	+ 47.0	+ 25.8
94	46.7	76	124.3	211	− 48.4	− 33.9	64.7	70	121.5	251	− 35.7	− 30.0
100	47.2	111	279.2	56	+186.3	+227.3	65.2	112	276.4	66	+191.4	+239.2
106	47.6	112	74.1	230	−175.3	219.1	65.7	112	71.3	240	−172.5	−215.6
112	48.1	61	228.9	45	24.8	+ 21.1	66.1	64	226.2	56	+ 26.2	+ 22.3
118	48.6	73	23.8	220	15.9	− 12.6	66.6	80	21.1	230	− 20.5	− 13.1
124												
129	1749.5	26	307.9	180	+ 4.7	+ 4.0						
135	50.0	71	102.8	355	− 42.1	− 34.9	1768.0	70	100.0	5	− 41.3	− 34.7
141	50.5	108	257.6	169	+168.9	+189.2	68.5	105	254.9	179	+153.9	+157.0
147	51.0	112	52.5	344	−149.7	−187.1	69.0	112	49.8	354	−144.7	−180.9
153	51.4	96	207.4	158	+ 61.3	+ 38.6	69.5	101	204.7	168	+ 63.8	+ 55.5
159	51.9	91	2.3	333	− 2.3	− 1.2	70.0	91	359.6	343	+ 1.8	+ 1.0
165												
171	1753.3	73	81.2	108	44.6	− 35.2	1771.3	67	78.5	118	− 34.4	− 29.2
182	53.8	72	236.1	283	+ 37.3	+ 30.2	71.8	67	233.4	293	+ 29.8	+ 25.3
188	54.3	112	31.0	97	98.2	−122.8	72.3	112	28.3	107	− 90.1	−112.6
194	54.8	112	185.9	272	+ 14.4	18.0	72.8	111	183.2	282	+ 4.6	+ 5.6
200	55.2	84	340.8	87	+ 22.5	13.3	73.3	88	338.1	96	+ 29.8	+ 16.4
206	55.7	82	135 8	261	− 56.6	− 34.5	73.7	88	133.0	271	75.2	41.4
212												

TABLE V (*Continued*).

t	Saros V						Saros VI					
	Year	T_0	l_1	l'_1	δn	δn	Year	T_0	l_1	l'_1	δn	$\delta n'$
		m	°	°				m	°	°		
0	1775.1	79	211.9	46	+ 38.7	+ 25 2	1793.1	75	208 9	57	28.6	+ 20.9
6	75.6	93	6.8	220	9.6	4.9	93.6	89	3.9	231	− 3.3	− 1.8
12	76.1	112	161.7	35	− 62.4	− 78.0	94.1	112	158.8	46	− 71.3	− 89.1
18	76.6	110	316.6	210	+118.3	+140.8	94 6	112	313.7	220	+131.2	+164.0
24	77.1	82	111.4	24	− 73.6	− 44.9	95.1	83	108.6	35	− 77.3	− 46.4
30	77.6	39	266.3	199	+ 11.6	+ 9.9	95.6	58	263.5	210	+ 26.1	+ 22.2
41												
47	1778.9	77	345.3	334	+ 15.3	+ 10.3	1797.0	76	342.4	345	+ 16.8	+ 11.8
53	79.4	107	140.1	149	−109.8	−119.7	97.4	104	137.3	159	−107.7	105.5
59	79.9	112	295.0	323	+175.5	+219.4	97.9	111	292.2	334	+176.1	+214.8
65	80.4	98	89.9	138	−129.4	− 95.8	98.4	102	87.1	148	−144.8	−131.8
71	80.9	84	244.8	312	+ 77.4	+ 45.7	98.9	85	242.0	323	+ 78.9	+ 45.8
77												
88	1782.2	85	323.7	87	+ 45.0	+ 26.1	1800.3	80	320.9	98	+ 38.4	+ 24.6
94	82.7	62	118.6	262	− 28.5	− 24.2	00.8	54	115.8	273	− 22 7	− 19.3
100	83.2	112	273.5	76	+191.9	+239.9	01.2	112	270.7	87	+192.2	+240.2
106	83.7	112	68.4	251	−169.3	−211.6	01.7	111	65.6	262	−162.6	−198.4
112	84.2	70	223.3	66	+ 30.2	+ 25.4	02.2	73	220.5	76	+ 33.1	+ 26.1
118	84.7	86	18.3	240	22.6	− 12.9	02.7	93	15.4	251	− 22.5	− 11.9
129												
135	1786.0	70	97.1	15	− 41.4	− 34.8	1804.1	69	94.3	26	− 40.3	− 34.3
141	86.5	101	252.0	190	+136.7	+118.9	04.6	96	249.2	201	+116.6	+ 73.3
147	87.0	112	46.9	5	−138.7	−173.4	05.0	112	44.1	14	−132.6	−165.8
153	87.5	105	201.8	179	+ 62.0	+ 63.2	05.5	108	199.0	190	+ 58.2	+ 65.2
159	88.0	91	356.8	354	+ 6.1	+ 3.2	06.0	91	353.8	4	+ 10.7	+ 5.7
165												
176	1789.4	58	75.6	129	− 25.4	− 21.6	1807.4	44	72.8	139	− 14.7	− 12.5
182	89.8	62	230.5	303	+ 24.9	+ 21.2	07.9	58	227.7	313	+ 20.9	+ 17.8
188	90.3	111	25.4	118	− 79.5	− 97.0	08.4	110	22.5	128	− 69.0	− 82.1
194	90.8	110	180.3	293	− 5.2	6.2	08.8	110	177.4	303	− 14.6	− 17.4
200	91.3	91	335.2	107	+ 37.8	+ 20.0	09.3	95	332.3	118	+ 48.3	+ 28.0
206	91.8	91	130.1	282	− 87.8	− 46.5	09.8	94	127.2	292	−100.7	− 53.4
212					6							

TABLE V (*Continued*).

t	Saros VII Year	T_0	l_1	l'_1	δn	$\delta n'$	Saros VIII Year	T_0	l_1	l'_1	δn	$\delta n'$
		m	°	°				m	°	°		
0	1811.2	72	206.1	67	22.2	+ 18.0	1829.2	67	203.3	77	+ 16.5	+ 14.0
6	11.7	83	1.0	241	1.1	+ 0.7	29.7	77	358.2	252	+ 3.7	+ 2.5
12	12.2	112	155.9	56	80.2	—100.3	30.2	111	153.1	67	— 86.1	—105.0
18	12.6	112	310.8	230	138.6	173.2	30.7	112	308.0	241	+145.7	+182.2
24	13.1	86	105.7	45	87.9	— 50.1	31.2	87	102.9	56	92.3	— 51.7
30	13.6	67	260.7	220	+ 34.8	+ 29.6	31.6	75	257.8	230	+ 50.1	+ 36.6
41												
47	1815.0	76	339.5	355	+ 19.1	+ 13.4	1833.0	75	336.7	5	+ 19.8	+ 14.5
53	15.5	100	134.4	169	—101.6	— 84.3	33.5	94	131.6	180	— 88.6	— 47.0
59	16.0	111	289.3	344	180.1	+219.7	34.0	111	286.5	355	+183.3	+223.6
65	16.4	106	84.2	158	158.7	168.2	34.5	109	81.4	169	170.0	—195.5
71	16.9	87	239.2	333	83.7	+ 46.9	35.0	87	236.2	344	+ 81.7	+ 45.8
77							35.4	35	31.1	158	— 4.8	— 4.1
83												
88	1818.3	74	318.0	108	29.5	+ 22.4	1836.3	67	315.2	119	+ 22.8	+ 19.4
94	18.8	44	112.9	283	15.4	13.1	36.8	39	110.1	293	11.9	— 10.1
100	19.3	112	267.8	97	191.7	+239.6	37.3	111	264.9	108	+186.9	+228.0
106	19.8	110	62.7	272	—155.4	184.9	37.8	110	59.8	283	151.3	—180.0
112	20.2	78	217.6	86	41.8	+ 27.6	38.3	83	214.7	97	+ 49.1	+ 29.5
118	20.7	94	12.5	261	— 19.4	— 10.3	38.8	97	9.6	272	— 15.5	— 10.7
129												
135	1822.1	68	91.3	36	39.1	33.2	1840.1	67	88.5	47	36.9	— 31.4
141	22.6	90	246.3	211	93.1	50.4	40.6	83	243.4	221	+ 69.2	+ 41.5
147	23.1	112	41.2	25	126.0	—157.5	41.1	112	38.3	36	—119.0	—148.8
153	23.6	110	196.1	200	+ 50.6	+ 60.2	41.6	111	193.2	211	+ 41.2	+ 50.3
159	24.0	92	351.0	14	15.6	+ 8.1	42.1	92	348.1	25	+ 20.2	+ 10.5
165	24.5	45	145.9	189	— 9.2	— 7.8	42.6	61	143.1	200	— 18.7	— 15.9
171												
176	1825.4	18	69.8	149	— 1.9	1.6						
182	25.9	54	224.8	324	17.9	+ 15.2	1843.9	51	221.9	335	+ 14.9	+ 12.7
188	26.4	110	19.7	139	— 60.2	— 71.6	44.4	107	16.8	149	— 44.5	— 48.5
194	26.9	110	174.6	313	23.7	— 28.2	44.9	109	171.7	324	— 32.3	— 37.1
200	27.4	99	329.5	128	60.4	47.7	45.4	103	326.6	139	+ 74.3	+ 70.6
206	27.8	95	124.4	302	107.9	— 62.6	45.9	97	121.6	513	—118.6	— 81.9
212												

TABLE V (*Continued*).

t	Saros IX						Saros X					
	Year	T_0	l_1	l'_1	δn	$\delta n'$	Year	T_0	l_1	l'_1	δn	$\delta n'$
		m	°	°				m	°	°		
0	1847.2	60	200.5	88	+ 11.7	+ 9.9	1865.3	51	197.7	99	+ 7.6	+ 6.5
6	47.7	72	355.4	263	4.8	3.9	65.8	65	352.6	274	+ 5.3	+ 4.5
12	48.2	110	150.3	77	— 92.1	—119.6	66.2	110	147.4	88	— 99.8	—118.8
18	48.7	112	305.2	252	—152.4	+190.5	66.7	110	302.3	263	—152.3	—181.2
24	49.2	90	100.1	67	103.5	55.9	67.2	92	97.2	77	—110.5	— 57.2
30	49.7	82	255.0	241	+ 71.9	+ 43.9	67.7	88	252.1	252	— 90.4	+ 49.7
41												
47	1851.0	74	333.8	16	+ 20.6	+ 15.7	1869.1	74	331.0	26	+ 22.4	+ 17.0
53	51.5	89	128.8	191	— 78.3	— 42.3	69.6	80	125.9	201	— 56.1	— 35.9
59	52.0	111	283.7	5	+186.0	+226.9	70.0	111	280.8	16	+188.1	—229.5
65	52.5	110	78.6	180	—171.2	—203.7	70.5	111	75.7	191	—172.2	—210.1
71	53.0	87	233.5	355	+ 79.6	+ 44.6	71.0	88	230.6	5	+ 79.6	— 43.8
77	53.5	53	28.4	169	— 9.9	— 8.4	71.5	65	25.6	180	— 13.2	— 11.2
83												
88	1854.4	58	312.3	130	+ 18.1	+ 15.4	1872.4	42	309.5	140	+ 9.8	+ 8.3
94	54.8	30	107.3	304	— 7.0	— 6.0	72.9	21	104.4	314	— 4.0	— 3.4
100	55.3	110	262.2	119	+181.7	+216.2	73.4	109	259.3	129	+176.3	+202.7
106	55.8	110	57.1	293	147.4	—175.4	73.8	109	54.2	303	—139.6	—160.5
112	56.3	89	212.0	108	+ 58.0	+ 31.3	74.3	93	209.1	119	+ 61.1	+ 31.2
118	56.8	99	6.9	283	— 10.6	— 8.4	74.8	102	4.1	293	— 5.2	— 4.7
129												
135	1858.2	65	85.8	58	— 34.5	— 29.3	1876.2	62	82.9	68	— 31.0	— 26.4
141	58.6	75	240.7	232	+ 45.2	+ 33.0	76.7	64	237.8	242	+ 28.0	+ 23.8
147	59.1	111	35.6	47	—109.7	—133.8	77.2	111	32.7	57	—102.2	—124.7
153	59.6	112	190.5	221	+ 31.9	+ 39.9	77.6	111	187.6	231	+ 20.8	— 25.4
159	60.1	92	345.4	36	+ 24.4	+ 12.7	78.1	94	342.5	46	+ 30.8	+ 16.3
165	60.6	74	140.3	211	— 32.7	— 24.9	78.6	83	137.4	220	— 55.5	— 33.3
176												
182	1862.0	48	219.2	346	+ 12.9	+ 11.0	1880.0	45	216.2	356	+ 10.4	+ 8.8
188	62.4	104	14.1	160	— 36.5	— 35.8	80.5	102	11.2	170	— 27.0	— 24.6
194	62.9	109	169.0	335	— 40.6	— 46.7	81.0	108	166.1	345	48.3	— 54.1
200	63.4	105	323.9	149	+ 84.5	+ 86.2	81.4	108	321.0	159	+ 99.0	+110.9
206	63.9	98	118.7	324	—125.4	— 92.8	81.9	99	115.9	334	—132.1	—104.4
212												

TABLE V (*Concluded*).

t	Saros XI						Saros XII					
	Year	T_0	l_1	l'_1	δn	$\delta n'$	Year	T_0	l_1	l'_1	δn	$\delta n'$
		m	°	°				m	°	°		
0	1883.3	35	194.7	169	+ 2.9	+ 2.5						
6	83.8	58	349.7	284	+ 5.4	+ 4.6	1901.8	54	346.8	294	+ 5.9	+ 5.0
12	84.3	109	144.6	98	—104.5	—120.2	02.3	107	141.7	109	—106.2	—115.8
18	84.8	110	299.5	273	+157.9	+187.9	02.8	110	296.6	284	+163.6	+194.5
24	85.2	96	94.4	87	—126.2	— 79.5	03.3	99	91.5	98	—136.4	—107.8
30	85.7	92	249.3	262	+103.5	+ 53.8	03.8	95	246.5	273	+112.7	+ 65.3
41												
47	1887.1	72	328.2	37	+ 21.7	+ 17.6	1905.1	71	325.4	48	+ 21.6	+ 17.9
53	87.6	71	123.1	212	35.2	— 29.2	05.6	59	120.3	222	— 24.8	— 21.1
59	88.1	111	278.0	26	+189.8	+231.5	06.1	111	275.2	37	+191.0	+233.0
65	88.6	112	72.9	201	—172.8	—216.0	06.6	112	70.1	212	—169.3	—211.6
71	89.0	88	227.8	15	+ 76.9	+ 42.3	07.1	88	225.0	26	+ 73.8	+ 40.6
77	89.5	75	22.7	190	— 17.8	— 13.0	07.6	84	19.9	201	— 24.1	— 14.2
83												
88	1890.4	11	306.7	150	+ 0.8	+ 0.7						
94	90.9	11	101.6	325	— 1.0	— 0.8						
100	91.4	107	256.5	139	+165.4	+180.3	1909.4	104	253.7	150	+150.7	+147.7
106	91.9	109	51.4	314	—135.1	—155.3	09.9	108	48.6	325	—127.2	—142.5
112	92.4	98	206.3	129	+ 64.7	+ 47.9	10.4	103	203.5	139	+ 67.0	+ 63.6
118	92.8	102	1.1	303	+ 1.9	+ 1.7	10.9	103	358.4	314	+ 8.1	+ 7.7
129												
135	1894.2	57	80.1	78	— 25.7	21.8	1912.3	50	77.2	89	— 19.4	— 16.5
141	94.7	54	235.0	253	+ 19.8	+ 16.8	12.7	40	232.2	264	+ 10.4	+ 8.8
147	95.2	111	29.8	68	— 94.3	—115.0	13.2	110	27.1	78	— 84.9	—101.0
153	95.7	110	184.7	242	+ 10.1	+ 12.0	13.7	109	182.0	253	+ 0.4	+ 0.5
159	96.2	95	339.6	57	+ 36.8	+ 21.3	14.2	97	336.9	67	+ 44.0	+ 30.4
165	96.6	90	134.5	231	77.5	— 41.9	14.7	94	131.8	242	— 92.5	— 49.0
176												
182	1898.0	44	213.4	6	+ 9.7	+ 8.2	1916.1	42	210.7	17	+ 7.9	+ 6.7
188	98.5	97	8.3	181	— 16.5	— 11.4	16.5	92	5.6	192	— 8.8	— 4.6
194	99.0	108	163.2	356	— 56.7	— 63.5	17.0	108	160.5	6	— 64.2	— 71.9
200	99.5	110	318.1	170	+111.1	+132.2	17.5	111	315.4	181	+120.5	+147.0
206	1900.0	100	113.0	345	—138.4	114.9	18.0	100	110.3	355	—140.5	—116.6
212	00.5	15	268.0	159	+ 1.9	+ 1.6	18.5	45	265.2	170	+ 15.4	+ 13.1
218												

TABLE VI.

t	Saros I			Saros II			Saros III			Saros IV		
	Year	λ_s	λ'_s	Year	λ_s	λ'_s	Year	λ_s	λ'_s	Year	λ_s	λ'_s
0	1703.0	0	0	1721.0	0	0	1739.1	0	0	1757.1	0	0
6	03.5	+ 9	− 12	21.5	− 3	− 29	39.6	− 11	− 32	57.6	16	61
12	04.0	− 31	− 79	22.0	− 43	− 96	40.0	− 50	− 91	58.1	− 49	−135
18	04.5	− 98	−179	22.5	−119	−208	40.5	134	−206	58.6	−136	−277
24	04.9	− 94	−215	23.0	−111	−234	41.0	−122	−217	59.0	−112	286
30		−147	−288		−164	−300		−175	−275		−154	−337
41	1706.3	−244	−422	1724.4	−261	−421	1742.4	272	−381	1760.4	−231	431
47	06.8	−276	−479	24.8	−302	−476	42.9	−318	433	60.9	−271	−481
53	07.3	−301	−532	25.3	−333	−525	43.4	353	−478	61.4	298	522
59	07.8	−417	−688	25.8	−460	−693	43.8	491	−646	61.9	436	695
65	08.3	−380	−663	26.3	−418	−661	44.3	−463	−607	62.4	−403	−655
71	08.7	−398	−677	26.8	−450	−674	44.8	−528	−619	62.8	−485	−675
77		−373	−656		−438	−649		−528	−589		−495	−652
88	1710.1	−327	−617	1728.2	−416	−603	1746.2	−528	−534	1764.2	−513	−610
94	10.6	−258	−574	28.6	−357	−554	46.7	−479	−479	64.7	−476	−561
100	11.1	−274	−576	29.1	−369	−546	47.2	−479	−457	65.2	−475	−542
106	11.6	−107	−355	29.6	−195	−311	47.6	−292	−208	65.7	−282	284
112	12.1	−113	−339	30.1	−195	−288	48.1	−281	−178	66.1	−262	−241
118	12.5	− 95	−303	30.6	−171	245	48.6	−245	−127	66.6	−216	−176
124		− 86	−274		−159	−212		−225	89		−190	124
129	1713.4	− 78	−250	1731.5	−149	−184	1749.5	208	− 57		−178	− 81
135	13.9	− 48	−203	32.0	−134	−140	50.0	−183	− 15	1768.0	−152	− 29
141	14.4	− 59	−191	32.4	−150	−130	50.5	−200	− 8	68.5	−167	− 12
147	14.9	+103	+ 44	32.9	+ 12	+ 91	51.0	− 48	+189	69.0	− 28	+162
153	15.4	+115	+ 80	33.4	+ 19	+119	51.4	46	+199	69.5	− 34	+155
159	15.9	+171	+143	33.9	+ 82	+177	51.9	+ 17	+247	70.0	+ 24	+204
165		+216	+200		+138	+231		+ 78	+294		+ 83	+254
176	1717.2	+299	+304	1735.3	+241	+333	1753.3	+190	+380	1771.3	+193	+346
182	17.7	+266	+314	35.8	+235	+347	53.8	+206	+392	71.8	+218	+367
188	18.2	+303	+365	36.2	+281	+395	54.3	+260	+434	72.3	+273	+413
194	18.7	+225	+273	36.7	+220	+310	54.8	+216	+353	72.8	+237	+346
200	19.2	+182	+225	37.2	+184	+255	55.2	+185	+290	73.3	+206	+285
206	19.7	+149	+184	37.7	+163	210	55.7	+178	+240	73.7	+205	+240
212		+ 92	+123		+102	+137		+114	+156		+129	+154
223		− 12	+ 11		− 10	+ 3		− 3	+ 5		10	4

TABLE VI (*Continued*)

	Saros V			Saros VI			Saros VII			Saros VIII		
t	Year	λ_s	λ'_s	Year	λ	λ'_s	Year	λ_s	λ'_s	Year	λ_s	λ'_s
0	1775.1	0	0	1793.1	0	0	1811.2	0	0	1829.2	0	0
6	75.6	— 26	— 59	93.6	— 40	— 70	11.7	— 46	— 75	29.7	— 54	— 91
12	76.1	62	—113	94.1	84	—142	12.2	— 91	—150	30.2	—104	—179
18	76.6	—160	255	94.6	—139	—303	12.6	—216	—325	30.7	—241	—372
24	77.1	—140	—256	95.1	—123	—300	13.1	—203	—327	31.2	—232	—383
30	77.6	—194	302	95.6	—184	343	13.6	—278	—379	31.6	—315	—446
41		—271	—368		—248	—382		—351	—419		—376	—494
47	1778.9	—313	404	1797.0	—283	—403	1815.0	—391	—441	1833.0	409	—520
53	79.4	340	—430	97.4	—301	—412	15.5	—412	—450	33.5	—422	—532
59	79.9	—476	576	97.9	427	527	16.0	524	543	34.0	524	—591
65	80.4	437	—502	98.4	—377	—427	16.4	—476	—416	34.5	—443	—426
71	80.9	527	—524	98.9	472	—459	16.9	—577	—458	35.0	—532	457
77		540	—500		—488	—445		—594	—453	35.4	—539	—442
83		—553	—477		—504	—431		—611	448		—551	—431
88	1782.2	—564	—459	1800.3	—517	—419	1818.3	—625	—444	1836.3	—561	—422
94	82.7	—532	409	00.8	—494	—380	18.8	—613	416	36.8	—550	—392
100	83.2	—528	—384	01.2	—494	—371	19.3	—616	—401	37.3	—551	—372
106	83.7	—333	—119	01.7	—302	—109	19.8	—427	—147	37.8	—365	—124
112	84.2	—307	— 65	02.2	—272	— 48	20.2	—394	— 78	38.3	—330	— 56
118	84.7	—251	+ 14	02.7	—209	+ 39	20.7	—319	+ 19	38.8	—246	+ 42
129		—189	+117		—136	+177		—216	+179		—121	+201
135	1786.0	—155	+173	1804.1	— 96	+252	1822.1	—160	+266	1840.1	— 53	+288
141	86.5	—163	+194	04.6	— 96	+293	22.6	—143	+319	40.6	— 21	+344
147	87.0	— 34	+334	05.0	+ 20	+407	23.1	33	+423	41.1	+ 80	+441
153	87.5	— 44	+301	05.5	+ 4	+355	23.6	— 49	+369	41.6	+ 62	+389
159	88.0	— 8	+331	06.0	+ 46	+369	24.0	— 15	+375	42.1	+ 84	+388
165		+ 66	+364		+ 98	+388	24.5	+ 35	+390	42.6	+127	+397
171		+124	+397		+151	+407		+ 76	+397		+151	+390
176	1789.4	+172	+425	1807.4	+195	+423	1825.4	+110	+403		+169	+384
182	89.8	195	+437	07.9	+233	430	25.9	+149	+408	1843.9	+193	+377
188	90.3	+253	+470	08.4	+292	+455	26.4	+206	+428	44.4	+232	+383
194	90.8	+231	+406	08.8	+282	+398	26.9	+203	+377	44.9	+227	+341
200	91.3	+204	+336	09.3	+257	+323	27.4	+176	+298	45.4	+189	+261
206	91.8	+215	+286	09.8	+234	+276	27.8	+209	+266	45.9	+226	+252
212		+138	+189		+157	+176		+133	+172		+144	+161
223		— 3	+ 11		+ 16	— 7		+ 3	0		— 6	— 6

TABLE VI (*Concluded*).

t	Saros IX			Saros X			Saros XI			Saros XII		
	Year	λ_s	λ'_s	Year	λ_s	λ'_s	Year	λ_s	λ'_s	Year	λ_s	λ'_s
0	1847.2	0	0	1865.3	0	0	1883.3	0	0		0	0
6	47.7	— 66	— 83	65.8	— 78	78	83.8	— 81	— 65	1901.8	— 88	— 71
12	48.2	—127	—162	66.2	151	151	84.3	157	—125	02.3	170	—137
18	48.7	—280	—361	66.7	324	—343	84.8	337	—295	02.8	358	—319
24	49.2	—280	—369	67.2	345	—354	85.2	360	—287	03.3	—383	—306
30	49.7	—384	—433	67.7	—476	422	85.7	—509	—359	03.8	544	—401
41		—442	470		—551	—455		—592	—392		—632	456
47	1851.0	—474	—490	1869.1	—592	—473	1887.1	637	—410	1905.1	680	486
53	51.5	—486	—495	69.6	—610	—474	87.6	—661	—410	05.6	—707	498
59	52.0	—576	—542	70.0	—684	—511	88.1	720	—440	06.1	—759	—531
65	52.5	—480	—362	70.5	570	—319	88.6	589	—238	06.6	—620	—331
71	53.0	—555	—386	71.0	629	337	89.0	—631	252	07.1	—650	—342
77	53.5	—550	—365	71.5	—608	313	89.5	596	—224	07.6	—606	—313
83		—555	—352		—600	—298		—579	—209		586	—298
88	1854.4	—559	—341	1872.4	—593	—286	1890.4	—565	—197		—569	—286
94	54.8	—546	—313	72.9	575	—263	90.9	—547	—181		—549	—271
100	55.3	—540	—291	73.4	—561	243	91.4	—530	—166	1909.4	—529	—256
106	55.8	—352	— 53	73.8	—371	— 20	91.9	—348	+ 29	09.9	—359	— 93
112	56.3	—312	+ 5	74.3	—321	+ 42	92.4	—301	+ 69	10.4	—316	— 73
118	56.8	—214	+ 99	74.8	210	+135	92.8	—189	+157	10.9	—206	— 11
129		53	+257		16	+298		+ 20	+322		+ 10	+180
135	1858.2	+ 35	+343	1876.2	+ 90	+387	1894.2	+134	+412	1912.3	+128	+272
141	58.6	+ 88	+398	76.7	+165	+449	94.7	+222	+480	12,7	+227	+347
147	59.1	+186	+487	77.2	+268	+535	95.2	+330	+565	13.2	+336	+431
153	59.6	+174	+443	77.6	+269	+496	95.7	+344	+535	13.7	+360	+414
159	60.1	+194	+438	78.1	+291	+483	96.2	+368	+517	14.2	+385	+397
165	60.6	+239	+446	78.6	+344	+486	96.6	+429	+520	14.7	+454	+411
176		+261	+415		+338	+431		+398	+449		+412	+347
182	1862.0	+273	+398	1880.0	+335	+401	1898.0	+381	+410	1916.1	+388	+312
188	62.4	+298	+393	80.5	+343	+379	98.5	+374	+379	16.5	+372	+283
194	62.9	+290	+352	81.0	+323	+333	99.0	+350	+337	17.0	+348	+250
200	63.4	+238	+264	81.4	+255	+233	99.5	+270	+231	17.5	+259	+145
206	63.9	+270	+262	81.9	+286	+244	1900.0	+301	+258	18.0	+291	+197
212		+177	+167		+185	+150	00.5	+193	+170	18.5	+182	+122
218		+ 84	+ 72		+ 84	+ 56		+ 77	+ 83		+ 85	+ 60
223		+ 6	— 7		0	— 22		— 11	+ 11		+ 7	+ 4

Finally we give in Table VII the new reduction of the meridian observations by Prof. Bakhuyzen, which was referred to above. The column $M-N_2$ contains the excess of the observed correction to the tabular longitude of the moon over Newcomb's "great fluctuation". The systematic corrections mentioned in Part I have already been applied. For the years 1905 to 1912 two results are given; the upper one is derived from the observations of the limb, the lower from the crater Mösting A. The third column contains the means of the numbers of the second column and the results from the occultations, i. e. Newcomb's minor fluctuations. The latter were however corrected by $+0''.18$ for reasons stated in Prof. Bakhuyzen's paper (these Proceedings, Jan. 1912). For the years 1905.5 to 1908.5 the mean given depends on the observations of the limb and the crater alone. From these means I have subtracted the sum of the corrections for the difference between the theories of Hansen and Brown, which were given in Part I of this paper. This sum was computed by a graphical process, of which I estimate the maximum error at about $\pm 0''.05$. The thus corrected mean is given in the fourth column. The second decimal, which has no real value, has been dropped. The last column gives the residuals remaining after subtracting Ross's empirical formula, without its constant term $-0''.18$, viz.:

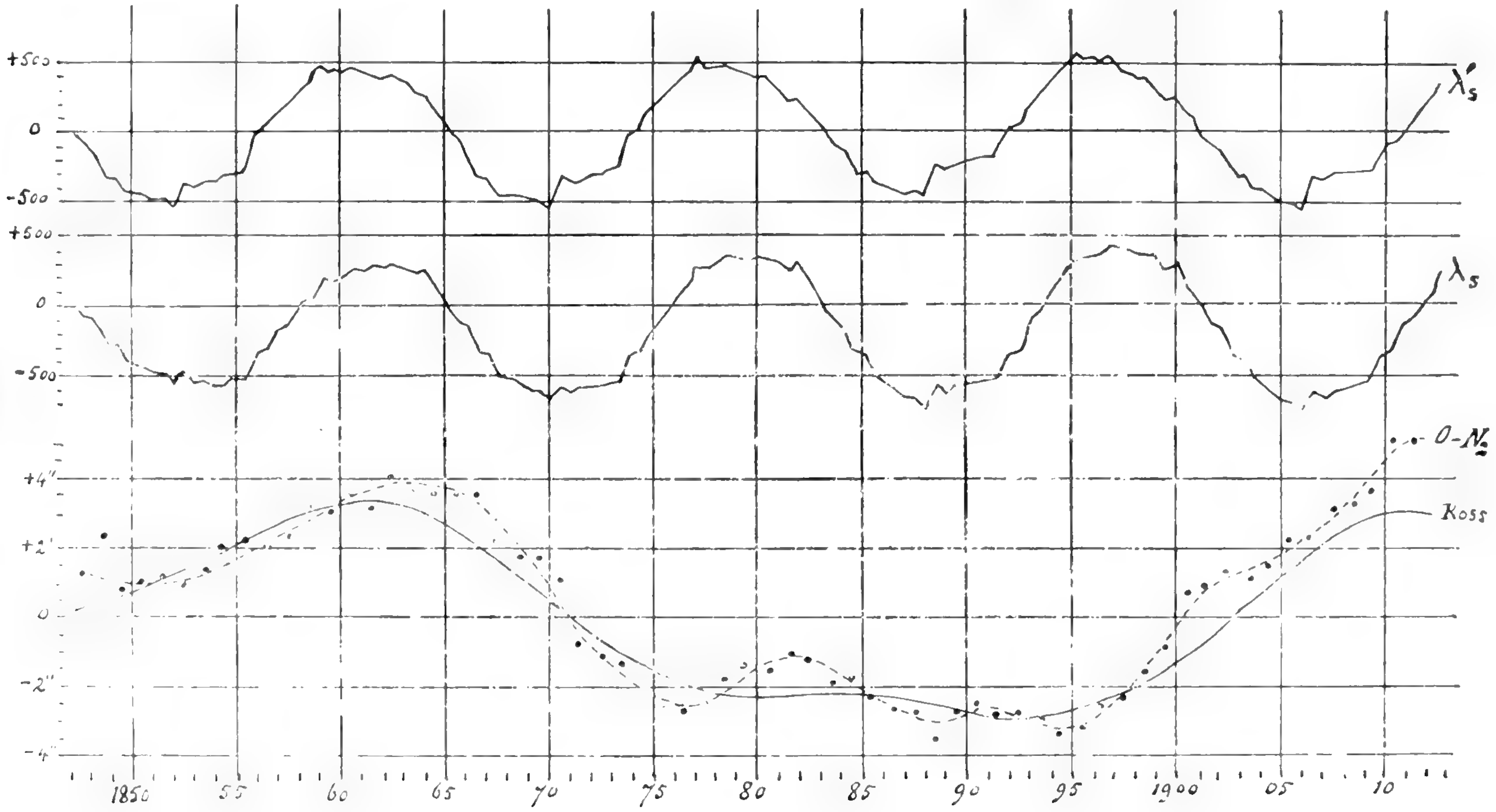
$$+ 2''.9 \, sin \, 6^\circ.316 \, (t-1844.5) + 0''.8 \, sin \, 15^\circ.65 \, (t-1880)$$

It will be seen that these residuals, although small, are as a rule somewhat larger than those found previously by Ross himself and by Bakhuyzen. The explanation of this is as follows. The residuals ∠-Ross given by Bakhuyzen in 1911 (these Proceedings Jan. 1912, p. 691) showed a marked period of nine years, which entirely disappears by the application of the perturbational corrections (14) and (22). The term (43) is nearly identical to the term which was already applied by Ross, and consequently does not affect the residuals to any appreciable extent. The terms (20), (15), and (21) however, especially (21), produce a considerable increase of the residuals. No doubt it would be possible by a small adjustment of Ross's formula considerably to improve the representation, but it is evident that a perfect agreement with the observations can never be reached by a formula containing only two terms. If a new empirical formula were to be derived it would, of course, be necessary first to correct the term of long period, and to apply the corresponding corrections to the theory. It seems opportune to defer such an investigation until the moon's longitude for the next few years will be

TABLE VII.

	M—N₂	Mean Obs.—N₂	Corr^d mean	⊿ Ross.
1847.5	+0"08	+0"89	+1"3	+0"8
48.5	+1.22	+1.66	+2.3	+1.6
49.5	+0.26	+0.28	+0.8	0.0
50.5	+0.31	+0.76	+1.0	0.0
51.5	+1.37	+1.18	+1.1	0.1
52.5	+1.20	+1.15	+1.0	—0.5
53.5	+1.95	+1.42	+1.4	0.4
54.5	+2.29	+1.94	+2.0	—0.1
55.5	+1.57	+1.94	+2.2	—0.2
56.5	+1.40	+1.75	+2.0	0.7
57.5	+2.48	+2.39	+2.4	0.6
58.5	+3.71	+3.70	+3.2	0.0
59.5	+3.83	+3.96	+3.1	0.4
60.5	+5.17	+4.64	+3.6	—0.1
61.5	+4.78	+4.14	+3.2	0.3
62.5	+5.11	+4.60	+4.0	0.5
63.5	+4.21	+3.70	+3.7	0.4
64.5	+2.83	+2.96	+3.6	0.5
65.5	+2.04	+2.42	+3.6	—0.8
66.5	+1.52	+2.26	+3.6	—1.3
67.5	+0.56	+0.93	+2.2	0.3
68.5	+0.30	+0.75	+1.8	0.4
69.5	+0.39	+1.10	+1.8	0.9
70.5	+0.39	+0.64	+1.1	—0.7
71.5	—1.26	—1.18	—0.7	0.6
72.5	—1.21	1.40	1.0	—0.4
73.5	—1.70	—1.65	—1.3	—0.4
74.5	—2.27	—2.14	—2.0	0.7
75.5	—2.40	—2.25	—2.5	—1.0
76.5	—1.89	—1.90	—2.7	—1.0
77.5	—0.87	—1.28	—2.4	—0.6
78.5	+0.32	—0.44	—1.7	+0.2
79.5	—0.23	—0.26	1.4	—0.6
80.5	—0.33	—0.76	—1.5	—0.5
81.5	0.16	—0.78	—1.1	+0.9
82.5	—1.39	—1.30	1.2	+0.8

	M—N	Mean Obs.—N	Corr^d mean	⊿ Ross.
1883.5	—2"41	2"20	—1"9	+0"1
84.5	2.30	2.10	1.7	+0.2
85.5	2.46	2.38	2.2	0.2
86.5	2.60	—2.60	—2.6	0.4
87.5	3.11	—2.76	2.8	0.6
88.5	—3.64	—3.47	3.4	—1.2
89.5	—2.50	2.90	2.6	—0.3
90.5	—2.70	—2.95	—2.5	0.0
91.5	—3.65	3.28	2.8	0.2
92.5	—3.78	3.09	—2.8	0.2
93.5	—3.02	—2.76	2.9	—0.3
94.5	—2.32	—2.56	3.3	—0.7
95.5	—1.95	—1.98	—3.1	—0.6
96.5	—1.55	—1.28	2.5	0.2
97.5	—0.89	—1.34	2.3	—0.3
98.5	0.84	—1.07	1.5	—0.2
99.5	—0.39	—0.80	0.7	—0.6
1900.5	—0.12	+0.04	+0.7	+1.5
01.5	—0.26	—0.08	+0.9	+1.1
02.5	—0.33	—0.42	1.4	—1.1
03.5	—0.17	+0.32	+1.2	+0.4
04.5	+0.59	+0.94	+1.6	+0.3
05.5	+1.97 +1.53	+1.73	+2.3	+0.6
06.5	+2.42 +1.43	+1.78	+2.4	+0.2
07.5	+2.39 +2.63	+2.42	+3.1	+0.5
08.5	+2.64 +3.01	+2.65	+3.3	+0.6
09.5	+3.21 +3.12	+3.16	+3.8	+0.9
10.5	+5.32 +4.36	+4.84	+5.1	+2.0
11.5	+5.57 +5.04	+5.30	+5.1	+1.9


+500
0
-500
λ'ₛ
+500
0
-500
λₛ
+4"
+2"
0
-2"
-4"
O-N.
Ross
1850
55
60
65
70
75
80
85
90
95
1900
05
10

known, or at least until we know how long the increase, which began a few years ago, will last.

The accompanying diagram shows for the years 1847 to 1912 the excess of the observed longitude of the moon over NEWCOMB's great fluctuation, i. e. the number contained in the fourth column of Table VII. Ross's curve is also given, (including the constant term — 0".18). The broken line is the smooth curve mentioned in Part I from which the values given in Table III were read off. The diagram also contains the purely periodic part λ_s and λ'_s of the perturbation in longitude produced by the absorption of gravitation on the two hypotheses regarding the distribution of density within the earth.

Chemistry. — "*The equilibrium Tetragonal Tin ⇄ Rhombic Tin.*"

By Prof. ERNST COHEN. (Communicated by Prof. VAN ROMBURGH).

(Communicated in the meeting of November 30, 1912).

It has struck me, and from several quarters my attention has been called to it, that in a communication from Mess^rs SMITS and DE LEEUW [1]) "On the system Tin" there occur a number of mistakes which require rectification.

1. The relation between the existence of a transitionpoint tetragonal tin ⇄ rhombic tin at 200° and the method of preparation of the so-called *corn-tin* or *grain-tin* has been first pointed out in the paper which I have published in 1904 with Dr. E. GOLDSCHMIDT [2]). From the communication of Mess^rs SMITS and DE LEEUW the reader might conclude that they (or SCHAUM) have first noticed this connection.

2. In the paper which I published in 1904 with Dr. E. GOLDSCHMIDT, a conclusion was drawn, from the experiments of WERIGIN, LEWKOJEFF, and TAMMANN [3]) as to the situation of the said transition point, which proved to be erroneous. Dr. DEGENS has pointed this out [4]) and as in my opinion he was quite right. I have hastened to rectify my error in the section of ABEGG's Handbuch der anorganischen Chemie [Vol. **3**, (2) 532 (1909), special p. 552] edited by myself. Evidently, the recent literature on this subject has not been known to Mess^rs SMITS and DE LEEUW, for they still base their communication on my paper that appeared five years previously.

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[1]) These Proc. XV, p. 676.

[2]) Chem. Weekblad **1**, 437 (1904), special p. 446. Zeitschr. f. physikal. Chem. **50**, 225 (1904), special p. 234.

[3]) Drud. Ann. **10**, 647 (1903).

[4]) Dissertation, Delft 1908, p. 38.

3. Mess$^{\text{rs}}$ SMITS and DE LEEUW write:1) "Why in reference to these experiments COHEN and GOLDSCHMIDT give **195**° for the point of transition in the *"Chemisch Weekblad"*, and **170**° in the *"Zeitschrift für physikal. Chemie"* is quite unaccountable." The difficulty disappears immediately when one refers to the said paper2): it then appears that the following sentence has escaped Mess$^{\text{rs}}$ SMITS and DE LEEUW's notice: "Wir setzen hier vorläufig 170°, doch beabsichtigen wir auf die genaue Bestimmung dieser Temperatur noch später zurückzukommen. In der Figur steht irrtümlich 195°." 3)

I will refer again to the transition: tetragonal tin $\rightleftarrows$ rhombic tin as soon as the investigations announced in my above paper shall be concluded.

Utrecht, November 1912. VAN 'T HOFF-*Laboratory*.

Physiology. — *"On localised atrophy in the lateral geniculate body causing quadrantic hemianopsia of both the right lower fields of vision"*. By Prof. C. WINKLER.

(Communicated in the meeting of November 30, 1912).

In 1904 BEEVOR and COLLIER 4) observed blindness in the upper quadrants of both the left fields of vision by an invalid, who after death proved to be the bearer of a focus in the right hemisphere, through which the surroundings of the calcarine fissure, from the occipital pole to the confluence with the parieto-occipital fissure were destroyed.

This observation is one of the few, in which quadrantic-hemianopsia responded to a focus, which chiefly destroyed the cortex, although the optic radiation, as shown in the drawings of BEEVOR and COLLIER, here too was not spared in the least; on the contrary it was destroyed to an important extent (especially the medio-ventral part).

BEEVOR and COLLIER pointed out, that already at that time in the literature there was sufficient ground to suggest, that foci in the dorso-lateral division of the strata sagittalia of the occipital lobe can cause blindness in the lower quadrants of the crossed optic fields. On the other hand foci in the ventro-medial division of these strata

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1) These Proc. XV, p. 677.

2) Chem. Weekblad **1**, 437 (1904), special p. 449.

3) Zeitschr. für physikal. Chemie **50**, 225 (1904), special p. 236, note 2.

4) C. E. BEEVOR AND JAMES COLLIER. A contribution to the study of the cortical localisation. A case of quadrantic hemianopsia with pathological examination. Brain. 1904. XXVI p. 153.

sagittalia can cause quadrantic hemianopsia in the crossed upper fields of vision (Henschen, Förster, Wilbrand etc.)[1]

Von Monakow[2]) proceeds still more in the here taken direction. If the dorsal division of the occipital lobe (Upper Cuneus, $O_1 - O_3$) incl. the dorsal part of the optic radiation is destroyed, then exclusively the dorsal layer of the lateral medullary capsule of the lateral geniculate body degenerates, and of this body the fronto-medial part.

On the contrary after destruction of the ventral convolution of the occipital lobe (ventral lip of the calcarine fissure, the Gyrus lingualis, the Gyrus occipito-temporalis) it gives rise to a secondary degeneration of the ventral division of the geniculo-cortical radiation and degeneration of the ventro-lateral part (cauda) of the lateral geniculate body.

The projection of the retina on the cortex could no longer be interpreted as simple as Henschen had taught us. It was not limited only to the surroundings of the calcarine fissure and had to be regarded from a different point of view.

It had to be borne in mind that in each lateral geniculate body there was already a first field of projection for the two homonymous retinal halves. Another projection, secondary to this, took place through the geniculo-cortical radiation, which united this body with the cortex. But in a particular way.

As long as the dorsal division of the radiation and the caput of this body did not show secondary change, the vision in the lower crossed quadrants of the fields of vision was intact. (Beevor and Collier).

As long as the ventral division of the radiation and the cauda of the body lacked these changes, the vision in the upper crossed quadrants of the fields of vision could remain intact.

The radiation from this body spreads itself however to a greater area of the cortex than to the surroundings of the calcarine fissure only. Without doubt also the upper Cuneus, $O_1 - O_3$, i. e. the whole

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[1] S. E. Henschen. Pathologie des Gehirns. Upsala 1890-94 and 1903 Cf Sur les centres optiques cérébraux. Rev. gén. d'Ophth. Paris 1894. Revue critique de la doctrine sur le centre cortical de la vision Congr. int. de Médecine. Paris 1900. La projection de la rétine sur la partie corticale calcarine. Sem. méd. 1903.

Wilbrandt. Hemianopische Gesichtsfeldformen. Wiesbaden. 1890.

Wilbrandt und Sänger. Neurologie des Auges. 3 Bde 1900 1904.

Förster. Unorientirtheit, Rindenblindheit, Andeutung von Seelenblindheit. Arch. f. Opth. 1890 and Wilbrandt. Doppelversorgung der Macula lutea and der Förster'sche Fall von doppelseitiger homonymer Hemianopsie. Beitr. zur Augenheilkunde (Festschr. für Förster.)

[2] Von Monakow. Gehirnpathologie. 1905. S. 757.

of the occipital pole has to be taken in account as VON MONAKOW desires, but most probably even more.

The retinal projection on the cortex, secondary to that of the lateral geniculate body is therefore without doubt much more complicated than HENSCHEN had figured to himself.

In 1909 I myself[1] could prove that the geniculo-cortical radiation and the geniculate body reacted differently, if by dorsally situated foci the dorso-lateral division of the strata sagittalia was cut through, than they did, if ventrally situated foci destroyed the ventro-medial division of these strata in the occipital pole. In the first case, with incomplete quadrantic hemianopsia of the lower fields of vision, the dorsal division of the radiation and the medial part of the geniculate body was greatly, but not altogether degenerated.

In the second case the degeneration took place in the ventral division of the radiation and the cauda of the body. Both degenerations were incomplete. At present I can communicate two new cases, this time of complete partial atrophy of the lateral geniculate body (cauda or caput), of which one with exquisite quadrantic hemianopsia, and through which I am obliged to extend even more than MONAKOW did, the areae of the cortex for the lateral geniculate body.

I.

Nephritis. Attack of unconsciousness on Dec. 9th 1910, followed by transitory sensory aphasia, alexia and **permanent quandrantic hemianopsia in the lower right fields of vision,** *which in July 1911 is tested through the ophthalmologist. In January 1912 second insult, which causes death. Autopsia: Old haemorrhagic cyst in the Gyrus temporalis II and the Gyrus angularis, sectioning completely the dorsal optic radiations. Fresh bleeding immediately next to this in the dorsal strata sagittalia.*

Miss C. P. S....., 37 years, is the eldest of 9 children, of which 5 are still living. The mother of this family died 50 years old of apoplexy, the father 75 years old of nephritis. Mental or nervous diseases did not exist in the family.

No abusus alcoholicus, no syphilis. Before this present illness she had nothing to complain of.

On the 9th of December 1910, she all at once fell unconscious, remained unconscious for 10 days. After coming to, she spoke with much difficulty, she could not find the words, asked for "sour" (zuur) when she meant "butter milk" (karnemelk), etc.

She soon regained a certain quantity of words, although she did not understand everything allright, but even now (July 1911) she names with difficulty the objects, which she recognises well. Especially proper names and nouns she often uses in the wrong way. Moreover after the attack she could not read, partially, as she says, because she soon grew tired, partially because she did not understand much of what she read.

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[1] C. WINKLER. De achterhoofdskwab en de half-blindheid. Psych. en Neurol. Bladen. 1910 Bl. 1—16.

Lastly after the attack she had been paralysed on the right side, but the lameness had passed off completely after three weeks.

Afterwards she often had been giddy, in March, on the 4th of June and on the 15th of June; but this always happened at the beginning of the menses, which were very irregular after the attack. She noticed that after the attack she did not see very well to the right: it seemed as if white spots were there. The electric light on the market-place seemed to hang lower than formerly to her, and now and then it was, as if brown spiders hung in front of the right eye. Since the 9th of December she sees worse through the right eye. She also often complains of headache, vomitting at the same time. Moreover the urine contains $4\,^0/_{0}$ albumen and many cylinders covered with epithelium of the kidneys.

On account of these complaints she was brought into my ward of the University Hospital (Binnen-Gasthuis).

The patient looks very ill, is a woman of middle height. Anaemic. Much arteriosclerosis. Somewhat enlarged heart. The second tone over the valvula aortae is loud. Pulse 90—120.

Her attitude is active, she takes interest in her surroundings, is well orientated in time and in space, sleeps calmly, eats sufficiently. She can walk and makes every movement.

Nowhere on the trunc or extremities any trouble of motility or sensibility is to be found. Except a lowered abdominal reflex at the right side, all the reflexes of the extremities are within normal limits. No sign of Babinski. There are impediments in speach. She understands simple commands without an yexception and follows them out. Her abundance of words is unlimited but she often misspeaks herself. Most of the objects are well named; they are always well recognised. Now and then she has to think long over them and after all uses the wrong word for them.

She recognises every letter of the alphabet and pronounces them correctly. Also short words. She can read loud, but she reads paraphatically and the longer words are regularly badly reproduced. She does not comprehend the reading or only insufficiently. To comprehend the reading she repeats it several times loudly and then as a rule she does not understand it, she forgets many things. Yet she can do light work. She manages her little affair in pottery.

The smell is not affected.

The pupils are equally wide, the right one does not react on light as correctly as the left. She cannot converge and the reaction of the pupils by convergence is not to be seen.

The vision of the right eye is $^1/_6$; of the left eye $^1/_2$.

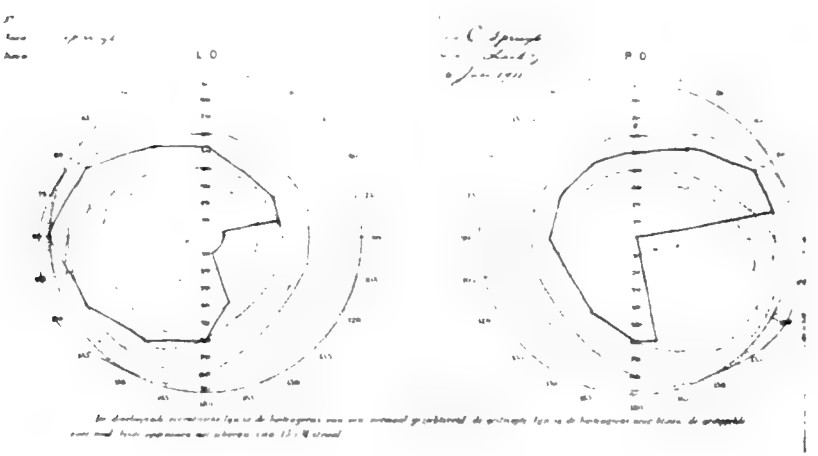
There is quadrantic hemianopsia in both the lower quandrants of the right fields of vision (s. figure).

Dr. Smit, the ophthalmologist writes about the fundus oculi: "There is no trace of papillitis. On the right the borders of the papilla are clearly limited, but there have been bleedings and there is still some oedema of the retina (retinitis albuminurica). On the left the papilla is also clearly limited, but here too are rests of haemorrhages.

There is exquisite hemianopsia in the lower quadrants of the right fields of vision. That the macula vision is lost in the right anoptic sector is probably due to the bad vision of that eye.

The eye-movements, especially by their turning to the right and more so of the left eye, are limited. The left eye deviates to the temporal side. It is impossible to direct both eyes to one point.

The hearing has not been strongly disturbed, certainly not on one side only. A ticking watch can be heard on both sides at a distance of 1 Meter.



Field of vision on July 6th 1911.

The diagnosis was made of nephritis with retinitis albuminurica and a focus in the left Gyrus angularis, cutting through the dorsal strata sagittalia.

July the 11th she left the hospital. On the 10th of January 1912 she was brought in unconscious and died three days later.

The account of the section shows: Hypertrophia cordis with nephritis interstitialis chronica and a focus in the left hemisphere, in the Gyrus temporalis II and the Gyrus angularis. The brown coloured focus spreads itself out in a straight direction along the distal third of the fissura t₁, and follows this along its ascending branch. The dorsal bounder of the Gyrus temporals II and the ventral Gyrus angularis are sunken in (s. fig. 1 and 2). On the section the focus proves to be a cyst with orange coloured walls, sectioning the strata sagittalia, in the neighbourhood of the retro-lenticular internal capsule and sectioning them completely in more distal slides (fig. 6 and 7). More distally, it soon retracts from the strata.

There is however a second fresh focus in the strata sagittalia, an haemorrhagy of bright colour, consisting of scarcely altered blood corpuscles (See fig. 7 in y).

In resuming the clinical data, it is not to be doubted that the second fresh focus caused the letal ending insult on the 10th of January 1912 and that the first apoplectic cyst responds to the insult of the 9th of December 1910, which brought forth the quadrantic hemianopsia as well as the secondary degenerations.

The importance of this observation lies in the first place in the fact, that a quadrantic hemianopsia of both the right lower fields of vision, noted with all possible precaution, is caused by a focus cutting "*completely*" through the dorso-lateral division of the strata sagittalia. Therefore too the secondary degenerations are of great importance. They lasted for 13 months and made alterations proximally in the lateral geniculate body and distally in the occipital lobe.

As the reproduction of the WEIGERT—PAL preparation [1]) (fig. 6 and 7) and photo 1 and 2 show, the two foci are thus situated that the older cuts the dorsal division of the strata sagittalia over the whole width.

This focus — the important one of the two — reaches close up to the lateral geniculate body (fig 6, pointed out by the first line through fig. 1 and 2) and stretches, cutting through the strata sagittalia, along the dorsal boundary of the cornu inferius and posterius (fig. 7, pointed out by the first following line through fig. 1 and 2), where the fresh focus too is found. It ends about 2 c.m. proximally from the distal end of the cornu posterius. Nowhere the ventro-medial division of the strata is affected directly by the focus. In fig. 6 and in fig. 7, this is intact.

According to the destruction by the focus, totally different fibre-systems are affected and a massive degeneration towards the occipital pole takes place.

The degenerated mass of fibres has been drawn on a more distally situated section (s. fig. 8, line 8 through fig. 1 and 2) 1 c.m. distally from the focus [1]). In this is visible, that the tapetum-fibres are very soon restored after their transsection, showing nearly a normal tapetum and forceps posterior round the very wide ventricle. In a less degree this is also the case with the stratum sagittale internum. It has fewer fibres than normal, and between them are spread degenerated fields in different spots. But the loss of fibres in the stratum sagittale externum is enormous. No normal fibres are to be found in it. This mighty black layer in WEIGERT—PAL preparations is here replaced by a white band, *as well in the dorsolateral as in the ventro-medial division.*

Smaller white stripes, coming from the degenerated band round the ventricle penetrate to far into the medullary cones of the convolutions, surrounding the calcarine fissure, also to the praecuneus and to the gyrus angularis. The gyri occipito-temporalis and fusiformis have suffered least.

The massive degenerated ring round the ventricle is always found distally from the ventricle-end till the occipital pole. About $^1/_2$ c.m. behind this end (s. fig. 9, line 9 from fig. 1 and 2) the distal point of the restored stratum sagittale internum is still touched and lies as a black island within the white degenerated mass of the stratum sagittale externum, while nearly all the medullary cones of the convolutions are degenerated and only fibrae arcuatae seem to be left.

The praecuneus has suffered least. In the section, which falls about 1 c.m. from the occipital pole (s. fig. 10, last line through fig. 1 and 2) it is likewise. From the massive centre degenerated stripes penetrate *in every convolution.*

All this proves that perception in the upper fields of vision is still possible, notwithstanding the stratum sagittale externum in the occipital pole is missing. If therefore the fibres, used for visual perception are to be looked for in that layer, as seems probably to me,

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[1]) Al these figures have been drawn with the greatest care; they are enlarged $2^1/_2$ times and reduced to $^7/_{12}$ of their size at the reproduction. Photos would have shown the same things, but drawings are more instructive as combinations of several sections are possible.

those which are spared here, do not at all belong to the occipital pole, but they must issue from far more proximal parts of the Gyrus occipito-temporalis.

This conclusion is the more valuable, if we look at the influence which the focus has had on the geniculo-cortical radiation and on the lateral geniculate body.

To make this clear I have drawn in fig. 4 a normal section of the surroundings of this body and in fig. 3 a cell-preparation[1]) of the same, to make comparison possible.

In these figures one sees the lateral geniculate body, which shows on frontal sections the form of a shoe (s. fig. 3) and in which can be distinguished a dorso-medial part: the caput, and a latero-ventral one: the cauda.

Within its own fibre-capsule covering the whole of it, (s. fig. 4) layers of fibres — laminae medullares — are alternately followed by layers of cells. The cells in the ventral layers are large, those in the dorsal ones much smaller, although, especially in the capital part large cells penetrate in these dorsal layers. The size of the dorsal cells differs a great deal between themselves. Many of them are very small.

In the normal fibre preparation the cauda contrasts but little against the caput, because the radiation of the optic tract has already begun in this proximal section.

On the dorso-lateral side the lateral geniculate body is covered by the triangular area of **Wernicke** through which the geniculo-cortical radiation penetrates. In the dorsal part of this area (s. fig. 4) the fibre-direction is totally different from the transverse sectioned fibres of its ventral part.

A rather thick layer of very thin subependymal fibres surrounds the area of **Wernicke** against the ependym of the ventricle. As soon as the geniculo-cortical radiation has freed itself from this area, it opens its way in elegant curvings through the fronto-occipital bundle and the retro-lenticular division of the internal capsule to the stratum sagittale externum. So it seems at least, although nobody will dare to make a decided conclusion about the origin of these fibres, crossing here in all directions.

If we compare the above described area of the normal brain with an identical of our quadrantic hemianopsia, it then follows, (not to mention the degenerations in the fronto-occipital bundle, in the mere proximally situated parts of the corona radiata, etc.) that the dorsal layers of the geniculo-cortical radiation, and more in particular of the area of **Wernicke**, are totally degenerated. The ventral division of this fibre-area on the other hand, is not much injured, neither is the neigbbouring dorsal and ventral part of the proper medullary capsule of the lateral geniculate body (s. fig. 6). In the cauda of the body we find intact laminae medullares. In the caput (in its dorso medial part) the proper medullary capsule is dorsally and ventrally gone as well as the striae medullares. All the cells of this caput are (s. fig. 5) vanished, the dorsal as well as the large ventral ones. The layers in which they were situated are to be seen as thick layers of glia. The whole body

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[1]) The cell-preparations of this body have been drawn with the camera of Zeiss; they are enlarged 20 times and reduced to $^{7}/_{12}$ of their size by the reproduction. Idem with the retro-lenticular area.

is reduced to almost half its normal size[1]), but in its cauda the small dorsal and the large ventral cells (s. fig. 6) are completely intact; there too the striae medullares as well as the proper capsule are on the whole untouched.

The conclusion is readily made: the possibility of sight in the upper quadrants is due to the conservation of the cells and fibres in the cauda of the lateral geniculate body, their projection on the cortex being preserved by the *ventral* layer of the area of WERNICKE and of the geniculo-cortical radiation.

But where do these cells find their projection on the cortex? Not in the occipital pole which in my opinion was totally separated by the focus from the lateral geniculate body, as is shown by the complete degeneration of the stratum sagittale externum and all the medullary cones of the occipital convolutions (only fibrae arcuatae remained). Perhaps from the gyrus occipito-temporalis, its medulla being but partly cut through by the focus (s. fig. 7). Distally from it (s. fig. 9) the medullary cones of the temporal circonvolutions were normal, those of the occipital lobe (s. fig. 9) were degenerated. Proximally from it this convolution with normal medullary cone contributed to the forming of the intact ventral division of the strata sagittalia.

The answer to the question where the field of projection of the lateral cells of this body was situated, was brought to me by a very remarkable right hemisphere, given to me by Professor BOLK. He had found it by accident in the corpse of a woman of whose antecedents nothing was known.

II.

This right hemisphere carries the rests of a very old pathological process, which has reduced on the transition of the basal temporal and occipital lobe all the convolutions with their medullary cones to a thin membrane. When the pia mater was removed it was torn near the cuneus. (s. fig. 11). The occipital pole is intact. On the middle of the cuneus the defect begins with a sharp edge. The proximal end of the cuneus, of the gyrus lingualis and of the gyrus fusiformis, as well as the medial part of the gyrus occipito temporalis (as far as near to the f. rhinica) are replaced by a thin membrane (s. fig. 11, 13, 14, 15 and 16).

The series of sections show the following[2]). The first remarkable alteration is drawn in fig. 16 (pointed out by the line 16 on fig. 11 and comparable with fig. 9 of the first observation). Thrice the distal end of the defect has been cut. Firstly in A in the depth of the fiss. calcarina. There the cortex is gone and the

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[1]) The enlargement is similar to that of the normal figure. (s. fig. 3).

[2]) In order to give an easy survey the sections are reversed and drawn as if they came from a left hemisphere.

medulla of the circonvolution lies uncovered. The line of Gennari ends on both sides sharply against the defect, is not atrophied, even mightier than usual and formed by thicker fibres; secondly in B, where ventrally from the f. pariëto-occipitalis the medulla of the cuneus lies uncovered and in C. where the defect begins in the gyrus fusiformis.

In the white matter opposite the fissura calcarina a triangular degenerated field is to be seen. It is situated for the greater part ventrally, but also a bit laterally round the sectioned distal end of the strata sagittalia

In figure 15 (pointed out by line 15 of fig. 11 and comparable to fig. 8 of the first observation, the defect is found distally from the confluence of the fiss. calcarina and f. pariëto-occipitalis. All the basal convolutions are missing.

Cuneus, lingualis, fusiformis, as well as the medial border of the ventricle are entirely gone. The medial medullary cone of the g. occipito-temporalis lies uncovered. The degenerated field is larger, lies partly in the ventral, partly already in the latero-dorsal division of the stratum sagittale internum, but also in the stratum sagittale externum, especially there where the ventral division of it passes into the lateral. For the rest the stratum sagittale externum is seen quite distinctly here (in fig. 8 totally gone), a proof that this area consists of more fibres than the geniculo-cortical radiation only (all gone in fig. 8).

In fig. 14 (pointed out by line 14 of fig. 11 and comparable to fig. 7) the splenium corporis callosi is sectioned.

Except a rest of the Cornu Ammonis no convolutions are to be found ventrally from the cornu inferius. The greater part of the gyrus occipito-temporalis is gone. The intact ventral strata sagittalia, as were found in fig. 7 are missing. The degenerated field (due to the defect) lies laterally and dorsally from the ventricle in both the strata sagittalia.

A great part of the dorsal stratum sagittale externum is intact. In fig. 7 exactly this large layer was totally destroyed and therefore also the geniculo-cortical radiation to the occipital lobe.

In fig. 13 (pointed out by the lines 13 of fig. 11, comparable to fig. 6) the retro-lenticular area is sectioned [1]).

As if this section were the negative of that reproduced in fig. 6, one hardly finds here normal fibres in fields, which were there the best preserved In the ventral part of the geniculo-cortical radiation and of the area of Wernicke all the fibres are gone. The ventral and lateral part of the proper capsule of the lateral geniculate body scarcely consist of normal fibres, the striae medullares in the cauda are gone, and the body is reduced to half its normal size.

On the other hand the dorsal part of the geniculo cortical radiation and the area of Wernicke, the dorso-medial proper capsule and the striae medullares in the caput of the geniculate body are only relatively changed [1]).

The same reverse is shown in the cell-preparations of the body itself. Latero-ventral, in the cauda of the body not one cell is to be found.

Thick layers of neuroglia, where once the cells were alternate with less thick layers of neuroglia (now representing the striae), but all cells, the dorsal as well as the ventral, have disappeared. On the other hand, the dorso-medial part, the caput of this ganglion contains well ranged cell layers, small dorsal ones as

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[1]) Here, as well as before, purposely I do not point out several other degenerations. To make things still less complicated I do not even mention the influence upon the pulvinar of both these foci.

well as a number of ventral large cells. This geniculate body is in every respect the negative of fig. 5.

The result of this observation is clear enough: The important defect in the occipital lobe above mentioned, was not sufficient to produce an atrophy of the dorso-medial division of the lateral geniculate body. The cauda on the other hand lost all the cells and fibres. From our first observation we learned that the cauda remained uninjured, when the focus (s. fig. 6 and fig. 7) totally destroyed the dorsal layer of the strata sagittalia. There (according to the spot of degeneration in our second observation in fig. 14) the geniculo-cortical radiation from the ventral occipital convolutions is already situated dorsally from the cornu inferius.

Moreover on the same sections in our first observation the ventral strata sagittalia are intact, and exactly these are completely missing in the second (s. fig. 13). New was to me the exquisite total loss of all the cells and fibres, either in the lateral, either in the medial half of the geniculate body, as is found in both these observations, although I possess many other partial atrophies of it after occipital-lesions.

Generally spoken, lesions of the medio-ventral occipital convolutions cause atrophy of the latero-ventral part of the geniculate body, but in my cases it has never been a total one.

As long as the gyrus occipito-temporalis proximally from the calcarine fissure is uninjured, not all the laterally situated fibres disappear, but cells often remain in the ventral, occasionally also in the dorsal layers. [1]) Only after the knowledge of such extremes as above described, I have learned to appreciate the incomplete atrophies. Wedges turning their base to the dorsal part of the geniculate body, fall out. Their localisation differs by the place of the focus, although they never touch the dorso-medial part of it, as long as the focus only destroys the ventro-medial occipital convolutions.

In this way e. g. must be considered the ventral occipital focus with atrophy in the cauda of the lateral geniculate body, described by myself in 1910. At present I complete this observation referring to the same figures in order to describe that geniculate body exactly.

III.

A basal defect in the left hemisphere (s. fig. 17, also Psych. and Neurol. Bladen 1910, p. 16 more precisely the photos on plate IV and fig 12 on plate V) elimi-

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[1]) Nearly the same can be said of dorsally situated foci (mutatis mutandis) which section the optic radiation either close to the geniculate body or further off. I shall refer to this later on.

nates the O_3, the gyrus lingualis and fusiformis to the confluence of the calcarine fissure with the parieto-occipital fissure (s. Psych. Bladen Pl. IV, fig. 6). Also a part of the gyrus occipito-temporalis, lying more proximally, is injured.

Through this lesion the ventral division of the geniculo-cortical radiation as well as that of the area of Wernicke is degenerated, but in less degree its most ventral layer (cf. Ps. Bladen, Pl. V, fig. 12).

The geniculate body belonging to this is drawn in fig, 18. It is smaller than normal, but not as far reduced as in both the former observations. The proper capsule is not changed dorso-medially and the same can be said of its cells, dorsal as well as the ventral ones, belonging to the caput of the ganglion.

The cauda is for the greater part atrophied but not the most laterally situated division of it. There, ventral and dorsal cells are to be seen within an almost normal capsule. Between caput and cauda, not or only little changed, one finds in the middle a part, where all is detroyed: the dorsal and ventral cells, the striae medullares, the proper fibres and the proper capsule.

In this case an example is shown of an *incomplete* atrophy of the cauda of the lateral geniculate body, incomplete because the focus did destroy the ventral occipital convolutions, but had not touched the gyrus occipito-temporalis far enough proximally. Therefore the most ventral layers of the geniculo-cortical radiation and the most lateral parts of the cauda remained free from degenerative atrophy.

Recapitulating I come to the following conclusions:

1. Vision in the upper quadrants of the field of vision is possible, notwithstanding the total loss of all the cells and fibres in the medial (caput) division of the crossed lateral geniculate body, as long as the cells and fibres of the cauda (origin of the ventral geniculo-cortical radiation) are intact.

2. It is not sufficient that the ventral occipital convolutions are destroyed to make all the cells disappear out of the lateral (cauda) division of the geniculate body. This only occurs when more proximally situated parts of the gyrus occipito-temporalis are destroyed.

3. The cortical areae belonging to the lateral geniculate body are not only limited to the cortex of the occipital lobe.

Chemistry. — *"On the occurrence of metals in the liver"*. By Prof. L. van Itallie and Dr. J. J. van Eck. (Communicated by Prof. Einthoven).

(Communicated in the meeting of November 30, 1912).

In the analysis of organs as to the presence of metallic poisons, we found in the liquid obtained after destruction of 170 grams of liver, kidney and heart, in addition to traces of arsenic and copper, as much zinc as corresponds with 80 mgs. of zinc oxide per kilogram of organs. As there was no reason to suppose that a poisoning with a zinc salt had been attempted the literature was consulted to see whether anything was known as to the occurrence of zinc in the human body. This investigation gave a positive result: Communications have been made by LECHARTIER and BELLAMY [1], and by RAOULT and BRETON [2]) from which it appears that the human liver may contain 10—76 mgs of zinc per kilogram. The quantity might be dependent on the age, the state of health and the nature of the food of the persons from which the liver is derived.

As the method of investigation did not appear to us correct in every respect and as the number of livers tested was comparatively small and as, moreover, the results could not be taken as applying to Holland without further evidence, we have investigated a number of human livers of Dutch origin. We have also extended the investigation to the occurrence of arsenic and copper.

As regards the presence of arsenic, the results of BLOEMENDAL [3]) are opposed to those of the French investigators. Whereas the latter assume the presence of normally-occurring arsenic, according to BLOEMENDAL the liver does not normally contain the same.

As to the distribution of copper in the animal and vegetable organism, investigations have been carried out by LEHMANN [4]). There was reason to suppose that the "charring process" employed by him had caused the results to be too low; moreover, figures of Dutch origin, are also wanting here.

For the destruction of the organic matter we, with a few modifications, made use of the process devised by KERBOSCH in the pharmaceutical laboratory at Leiden. This method has the great advantage that the organic substance is completely destroyed, the only reagents used being sulphuric and nitric acids which can be obtained absolutely free from arsenic.

For this purpose, a current of hydrochloric acid is passed for some hours through sulphuric acid heated at 250—270°, whereas nitric acid can be obtained free from arsenic by distillation. In a check-experiment where 25 cc. of sulphuric acid and 250 cc. of nitric acid had been used and of which 5—6 cc. of liquid were left after distillation, no arsenical mirror could be obtained in a modified Marsh-apparatus. From previous investigations, it had already appeared [5]) that the limit of sensitiveness may be taken as 0.0001 mg. of arsenic.

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[1]) Compt. rend. de l'Ac. der Sc. **84**, 1877, p. 687—690.

[2]) Idem. **85**, 1877, p. 40—42.

[3]) Arsenicum in het dierlijk organisme. Dissertatie Leiden 1908.

[4]) Arch. f. Hygiene **24**, 1895.

[5]) BLOEMENDAL l. c.

As to the exact *modus operandi* of the quantitative determinations, we refer to the more detailed communication to be published elsewhere.

The results of our investigations are collected in the annexed table, augmented with the *data* furnished to us as to the origin of the livers.

HUMAN LIVERS.

Age	Sex	Occupation	Residence	Course of death	Number of mgs. per kilo of liver, calculated as:		
					As	Cu	Zn
Still-born					—	26.1	73.9
Some hours					—	30.0	52.2
5 weeks	m.		Leiden		0	8.0	55.7
3 months	m.		„	Acute enteritis	0	18.9	55.0
3½ years	m.		Rijnsburg	Diphtheria	trace	10.6	67.8
5 „	m.		Leiden	„	0.06	2.9	—
21 „	f.	Servant	„	Morbus Basedowi	0	5.7	36.1
24 „	f.		Woudrichem	Miliary tuberculosis	0	11.2	79.6
28 „	m.	Greengrocer	Den Haag		0	4.8	—
28 „	f.		Noordwijk	Pneumonia	0	14.8	56.2
32 „	m.	Navvy	Friesland	Septicaemia	0.03	6.0	50.6
35 „	f.		Hazerswoude	Carcinoma	0	5.0	17.7
36 „	f.	Housewife	Leiden	„	trace	17.7	60.5
37 „	m.	Roadman	Den Haag		2.63[1]	3.8	54.3
39 „	m.	Gardener	Voorhout	Kidney tuberculosis	trace	3.2	79.4
43 „	m.	Dealer	Nieuwkoop	Brain bleeding	trace	6.15	44.5
40-50 „	m.	Goldsmith	Leiden	Tumour in stomach	trace	10.0	62.3
50 „	f.		Vlaardingen	Tumour in kidney	0	13.8	64.6
70 „	f.		Leiden	Apoplexy	0	7.4	55.9
70 „	m.	Casual labourer	„	Hypertroph. prostat.	0.1	10.6	26.7
74 „	f.		„	Apoplexy	0.015	9.0	53.0
76 „	f.	None	„	Rib fracture	0.5	9.1	86.8
83 „	f.		„	Heart disease	trace	3.8	35.0
86 „	m.		„	Arteriosclerosis	0	8.0	41.1

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[1] Before death, the deceased had used Pilulae Blaudii c. Acido arsenicos. as a medicine.

In the investigation of the liver of a new-born calf were found, per kilo, 31 mgs. of copper and 81.1 mgs. of zinc.

From the results obtained the following conclusions may be drawn:

1. Arsenic is not a normal constituent of the human liver.
2. Copper and zinc appear to occur regularly in the human liver.
3. They are already deposited in the liver during the foetal stage and, as regards copper, even in a larger quantity than in the following period.
4. Otherwise, there seems to exist no relation between the copper and zinc content of the liver and the age, sex, occupation and place of residence.
5. The figures given by LEHMANN for the copper content are comparatively low. His maximum figure of 5 mg. per kilogram of liver is, as a rule, exceeded in Holland.

Pharmaceutical Laboratory
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Chemistry. — "*Equilibria in ternary systems. IV*". By Prof. SCHREINEMAKERS.

(Communicated in the meeting of November 30, 1912).

In the previous communication we have observed the changes when at a constant temperature there is a change of pressure, and from this deduced the saturation lines of a solid substance F under their own vapour pressure. We will now briefly consider the case that, at a constant pressure, there is a change in temperature. At a constant temperature a reduction of pressure causes an expansion of the gas region and a contraction of the liquidum region; under a constant pressure the same happens on elevating the temperature.

A system that exhibits at a constant temperature a maximum vapour pressure (minimum), has at a constant pressure a minimum boiling point (maximum).

At a constant temperature, the influence of the pressure on the situation and form of the saturation line of F is generally small unless at temperatures close to the melting point of F; at a constant pressure the influence of the temperature is usually much greater and the movement of the line, therefore, much more rapid. Yet, as a rule, the liquidum line will move more rapidly than the saturation line unless indeed the latter is on the point of disappearing.

At a constant temperature, the saturation line of F may disappear on increasing or reducing the pressure; this depends on whether, on melting, an increase or a decrease of the volume takes place. Under a constant pressure it disappears at an elevation of temperature only.

From all this it follows that most of the diagrams described above which occur at a constant temperature on reduction of pressure will also, as a rule, form at a constant pressure by an elevation of temperature. At a constant temperature, the liquid and the gas of the three-phase equilibrium $F + L + G$ each proceed along an isothermic-polybaric curve which we have called the saturation line of F under its own vapour pressure and the vapour line appertaining thereto.

Under a constant pressure, the liquid and the gas of the three-phase equilibrium $F + L + G$ each proceed along a polythermic-isobaric curve. As these solutions saturated with F can, at a given pressure, be in equilibrium with vapour and consequently boil at that temperature we will call these lines the boiling point line of the solutions saturated with F and the vapour line appertaining thereto.

The saturation line of F under its own pressure may be circumphased [fig. 7 (I) and 11 (I)][1] as well as exphased [fig. 12 (I) and 13 (I)]. The same applies to the boiling point line of the solutions saturated with F, with this difference, however, that fig. 13 (I) does not occur. The saturation line of F under its own vapour pressure exhibits a pressure maximum and minimum; the boiling point line of the solutions saturated with F a temperature maximum and minimum. These are, however, so situated that the arrows of the figs. 7 (I), 11 (I) and 12 (I) should point in the opposite direction.

We will refer later to these curves in various respects.

We can also unite these boiling point lines with their correlated vapour lines for different pressures, in a same plane. We then obtain a diagram analogous to fig. 14 (I) in which the arrows, however, must point in the opposite direction. If the pressure axis is taken perpendicularly to the plane of drawing, the spaceal representation gives two planes, namely the boiling point plane of the solutions saturated with F and the correlated vapour plane.

We will now consider still in another way the saturation lines under their own pressure and the boiling point lines of the liquids saturated with a solid substance.

We assume that a solid substance F of the composition α, β, and

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[1] The number (I) placed behind a figure signifies that a figure from the first communication is intended.

$1-\alpha-\beta$ is in equilibrium with a liquid L of the composition x, y and $1-x-y$ and with a vapour L of the composition x_1, y_1 and $1-x_1-y_1$. We call the volumes of these phases v, V, and V_1, their entropies η, H, and H_1, their thermodynamic potentials ζ, Z and Z_1.

As equilibrium conditions we find:

$$\left.\begin{array}{c} Z-(x-\alpha)\dfrac{\partial Z}{\partial x}-(y-\beta)\dfrac{\partial Z}{\partial y}=\zeta \\[2ex] Z_1-(x_1-\alpha)\dfrac{\partial Z_1}{\partial x_1}-(y_1-\beta)\dfrac{\partial Z_1}{\partial y_1}=\zeta \\[2ex] \dfrac{\partial Z}{\partial x}=\dfrac{\partial Z_1}{\partial x_1} \quad \text{en} \quad \dfrac{\partial Z}{\partial y}=\dfrac{\partial Z_1}{\partial y_1} \end{array}\right\} \quad . \; . \; . \; . \; . \; . \quad (1)$$

From this we find:

$$[(x-\alpha)\,r+(y-\beta)s]\,dx+[(x-\alpha)s+(y-\beta)t]\,dy=AdP-BdT \quad . \; (2)$$

$$[(x_1-\alpha)r_1+(y_1-\beta)s_1]\,dx_1+[(x_1-\alpha)s_1+(y_1-\beta)t_1]\,dy_1=A_1dP-B_1dT \; (3)$$

$$rdx+sdy=r_1d_1+s_1dy_1+\left(\frac{\partial V_1}{\partial x_1}-\frac{\partial V}{dx}\right)dP-\left(\frac{\partial H_1}{\partial x_1}-\frac{\partial H}{\partial x}\right)dT \quad (4)$$

$$sdx+tdy=s_1dx_1+t_1dy_1+\left(\frac{\partial V_1}{\partial y_1}-\frac{\partial V}{\partial y}\right)dP-\left(\frac{\partial H_1}{\partial y_1}-\frac{\partial H}{\partial y}\right)dT \quad (5)$$

If we only want a relation between dx, dy, dP, and dT then from the previous equations we deduce:

$$[(x-\alpha)r+(y-\beta)s]\,dx+[(y-\alpha)s+(y-\beta)t]dy=AdP-BdT \, . \quad (6)$$

$$[(x_1-x)r+(y_1-y)s]dx+[(x_1-x)s+(y_1-y)t]dy=CdP-DdT \, . \; (7)$$

In this:

$$A=V-v+(\alpha-x)\frac{\partial V}{\partial x}+(\beta-y)\frac{\partial V}{\partial y} \quad B=H-\eta+(\alpha-x)\frac{\partial H}{\partial x}+(\beta-y)\frac{\partial H}{\partial y} \, .$$

$$C=V_1-V+(x-x_1)\frac{\partial V}{\partial x}+(y-y_1)\frac{\partial V}{\partial y} \quad D=H_1-H+(x-x_1)\frac{\partial H}{\partial x}+(y-y_1)\frac{\partial H}{\partial y} \, .$$

In order to obtain the saturation line of the solid substance F under its own vapour pressure we call in (6) and (7) $dT=0$: we then obtain:

$$[(x-\alpha)\,r+(y-\beta)\,s]\,dx+[(x-\alpha)\,s+(y-\beta)\,t]\,dy=AdP \quad (8)$$

$$[(x_1-x)\,r+(y_1-y)\,s]\,dx+[(x_1-x)\,s+(y_1-y)\,t]\,dy=CdP \quad (9)$$

The correlated vapour line is obtained by interchanging in these relations the *quantities* relating to vapour and liquid. In order that the pressure in a point of the saturation line under its own pressure may become maximum or minimum dP in (8) and (9) must be $=0$. Hence:

$$[(x-\alpha)\,r+(y-\beta)\,s]\,dx+[(x-\alpha)\,s+(y-\beta)\,t]\,dy=0\,. \quad (10)$$

$$[(x_1-x)\,r+(y_1-y)\,s]\,dx+[(x_1-x)\,s+(y_1-y)\,t]\,dy=0\,. \quad (11)$$

This means that in this point the saturation line under its own vapour pressure comes into contact with the isothermic-isobaric saturation line of F (10) and with the liquidum line of the heterogeneous region LG (11).

We can satisfy (10) and (11) by:

$$\frac{y-\beta}{x-\alpha}=\frac{y_1-y}{x_1-x} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

This means that the three points representing the solid substance F, the liquid and the vapour are situated on a straight line. Hence, we find that on a saturation line of a solid substance F under its own vapour pressure, the pressure is maximum or minimum when the three phases (F, L, and G) are represented by points of a straight line, or in other words, when between the three phases a phase reaction is possible.

If we imagine before us the equation of the correlating vapour line we notice that when the pressure in a point of the saturation line under its own vapour pressure is at its maximum or minimum, this must also be the case in the corresponding point of the correlated vapour line. It then also follows that the correlated vapour line, the vapour saturation line of F and the vapour line of the heterogeneous region LG meet in this point.

The previous remarks apply, of course, also to the boiling point line of the solutions saturated with F; in (6) and (7) dP must then be supposed $=0$.

Hence we conclude:

When solid matter, liquid and gas have such a composition that between them a phase reaction is possible (the three figurating points then lie on a straight line) then, on the saturation line of the saturated solutions under its own pressure, the pressure is at its maximum or minimum; on the boiling point line this will be the case with the temperature. The same applies to the vapour lines appertaining to these curves. In each of these maximum or minimum points the three curves come into contact with each other.

The properties found above have been already deduced by another way in the first communication.

We will now investigate the saturation line of F under its own vapour pressure in the vicinity of point F. First of all, it is evident that one line may pass through point F.

For if in (8) we call $x=\alpha$ and $y=\beta$ it follows that $dP=0$; (9) is converted into:

$$[(x_1-\alpha)\,r+(y_1-\beta)\,s]\,dx+[(x_1-\alpha)\,s+(y_1-\beta)\,t]\,dy=0\,. \quad (13)$$

We thus find a definite value for $\frac{dy}{dx}$; at the same time it appears from (13) that in point F the saturation line under its own vapour pressure and the liquidum line of the heterogeneous region LG meet each other. It further appears from (13) that the tangent to the saturation line in F under its own vapour pressure and the line which connects the points F with the vapour phase are conjugated diagonals of the indicatrix in point F. (The same applies, of course to the boiling point line of the saturated solutions).

If accidentally, not only the liquid but also the vapour still has the composition F, therefore, when not only $x=\alpha$ and $y=\beta$, but also $x_1=\alpha$ and $y_1=\beta$, then $\frac{dy}{dx}$ becomes indefinite.

In this case, however a maximum or minimum vapour pressure appears in the ternary system LG; we will refer to this later.

From (6) and (7) we deduce for $x=\alpha$ and $y=\beta$:

$$\frac{(BC-AD)\,dT}{A}=\{(x_1-\alpha)\,r+(y_1-\beta)\,s\}\,dx+\{(x_1-\alpha)\,s+(y_1-\beta)\,t\}\,dy \quad (14)$$

This relation determines the change in temperature dT around point F; this is always differing from 0 unless one chooses dx and dy in such a manner that the second member of (14) becomes nil. According to (13) this signifies that, starting from F, one moves over the tangent to the liquidum line of the heterogeneous region LG.

We now choose dx and dy along the line which connects the point F with the vapour phase; for this we put:

$$dx=(x_1-\alpha)\,d\lambda \quad \text{and} \quad dy=(y_1-\beta)\,d\lambda \quad . \quad . \quad . \quad . \quad (15)$$

We then obtain from (14)

$$(BC-AD)\,dT=(V-v)\{(x_1-\alpha)^2\,r+2\,(x_1-\alpha)(y_1-\beta)\,s+(y_1-\beta)^2\,t\}\,d\lambda \quad (16)$$

In this we have replaced A by the value $V-v$, which A obtains for $x=\alpha$ and $y=\beta$.

Let us investigate the sign of:

$$K=BC-AD=(H-\eta)\,C-(V-v)\,D.$$

Now, C is the increase in volume when a quantity of vapour is generated from an indefinitely large quantity of liquid; D is the increase in entropy in this reaction. Hence so long we are not too close to temperatures at which critical phenomena occur between liquid and vapour, C is as a rule large in regard to $(V-v)$; $H-\eta$ and D are *quantities* of about the same kind. If now $V<v$, then K is for certain positive; if, however, $V>v$, then K is, as a rule, also still positive on account of the small value of $V-v$ in regard to C. We will, therefore, in future always put K positive; should it become negative the necessary alterations can readily be introduced.

We now distinguish two cases.

a. $V>v$, dT and $d\lambda$ have the same sign;

b. $V<v$, dT and $d\lambda$ have the opposite sign.

Now, it follows from (15) that $d\lambda>0$ signifies that one is moving from point F towards the vapour phase. From this we conclude:

The part of a saturation line passing through the point F of the substance F under its own vapour pressure and situated in the vicinity of F moves at an increase of temperature:

a. if $V>v$, towards the vapour phase appertaining to point F.

b. als $V<v$, away from the vapour phase appertaining to point F.

From (6) and (7) instead of (16) we can deduce also:

$$K\,dP=(H-\eta)\,\{(x_1-\alpha)^2\,r+2\,(x_1-\alpha)\,(y_1-\beta)\,s+(y_1-\beta)^2\,t\}\,d\lambda. \quad (17)$$

From this we conclude:

The part of a boiling point line of the saturated solutions of F situated in the vicinity of F moves, on increase of pressure, always more towards the vapour phase appertaining to point F.

In order to get a better knowledge of the saturation line of F under its own vapour pressure which passes through the point F and of the boiling point line of the saturated solutions of F we will also introduce in our formulae terms with dx^2, $dx\,dy$, and dy^2. In order to simplify the calculations a little we will assume provisionally that the vapour consists of one component only.

We, therefore call in our previous formulae $x_1=0$ and $y_1=0$. Our equilibrium conditions (1) then are converted into:

$$Z-x\frac{\partial Z}{\partial x}-y\frac{\partial Z}{\partial y}=Z_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

$$Z_1+\alpha\frac{\partial Z}{\partial x}+\beta\frac{\partial Z}{\partial y}=\zeta. \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

We now write for (18), T being kept constant:

$$(xr+ys)\,dx+(xs+yt)\,dy+\frac{1}{2}\left(r+x\frac{\partial r}{\partial x}+y\frac{\partial s}{\partial x}\right)dx^2+$$

$$+\left(s+x\frac{\partial s}{\partial x}+y\frac{\partial t}{\partial x}\right)dx\,dy+\frac{1}{2}\left(t+x\frac{\partial s}{\partial y}+y\frac{\partial t}{\partial y}\right)dy^2\ldots=$$

$$=\left(V-V_1-x\frac{\partial V}{\partial x}-y\frac{\partial V}{\partial y}\right)dP+\ldots \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

From (19) follows:

$$(\alpha r+\beta s)\,dx+(\alpha s+\beta t)\,dy+\frac{1}{2}\left(\alpha\frac{\partial r}{\partial x}+\beta\frac{\partial s}{\partial x}\right)dx^2+$$

$$+\left(\alpha\frac{\partial s}{\partial x}+\beta\frac{\partial t}{\partial x}\right)dx\,dy+\frac{1}{2}\left(\alpha\frac{\partial s}{\partial y}+\beta\frac{\partial t}{\partial y}\right)dy^2+\ldots$$

$$=\left(v-V_1-\alpha\frac{\partial V}{\partial x}-\beta\frac{\partial V}{\partial y}\right)dP+\ldots\ldots \qquad (21)$$

Let us now deduce (21) from (20) after having substituted in (20) $x=\alpha$ and $y=\beta$: we find:

$$\frac{1}{2}\,r\,.\,dx^2+s\,dx\,dy+\frac{1}{2}\,t\,dy^2+\ldots=A\,dP+\ldots\ldots \qquad (22)$$

in which the coefficients of $dP\,.\,dx$ and $dP\,.\,dy$ are nil, whereas for the sake of brevity we write the coefficient of dP in (21) $-(A+C)$. A and C then have herein the same values as in our former equations. Then, however, we assume $x=\alpha$, $y=\beta$, $x_1=0$, and $y_1=0$.

From (22) follows dP of the order dx^2 and dy^2, here from (21) at first approximation:

$$(\alpha r+\beta s)\,dx+(\alpha s+\beta t)\,dy=0 \qquad (23)$$

In connection with (13) it appears from this that the liquidum line passing through point F and the saturation line of F under its own vapour pressure come into contact with each other.

If we eliminate dP from (21) and (22) we obtain:

$$(\alpha r+\beta s)\,dx+(\alpha s+\beta t)\,dy+\tfrac{1}{2}\left(\alpha\frac{\partial r}{\partial x}+\beta\frac{\partial s}{\partial x}+r+\lambda r\right)dx^2+$$

$$+\left(\alpha\frac{\partial s}{\partial x}+\beta\frac{\partial t}{\partial x}+s+\lambda s\right)dxdy+\tfrac{1}{2}\left(\alpha\frac{\partial s}{\partial y}+\beta\frac{\partial t}{\partial y}+t+\lambda t\right)dy^2=0 \quad (24)$$

in which $\lambda=\dfrac{C}{A}$.

For the liquidum line passing through point F we find:

$$(\alpha r+\beta s)\,dx+(\alpha s+\beta t)\,dy+\tfrac{1}{2}\left(\alpha\frac{\partial r}{\partial x}+\beta\frac{\partial s}{\partial x}++r\right)dx^2$$

$$+\left(\alpha\frac{\partial s}{\partial x}+\beta\frac{\partial t}{\partial x}+s\right)dxdy+\tfrac{1}{2}\left(\alpha\frac{\partial s}{\partial y}+\beta\frac{\partial t}{\partial y}+t\right)dy^2=0\,. \quad 25)$$

For the sake of brevity we write (24) and (25) as follows:

$$aX+bY+\tfrac{1}{2}(c+\lambda r)X^2+(d+\lambda s)\,XY+\tfrac{1}{2}(e+\lambda t)\;Y^2=0\,. \quad (26)$$

$$aX+bY+\tfrac{1}{2}\,cX^2+dXY+\tfrac{1}{2}\,eY^2=0\,. \quad (27)$$

Equation (26) now relates to the saturation line, under its own pressure, passing through F, (27) on the liquidum line of the heterogeneous region LG passing through F.

Now the curvature of (27) is given by:

$$\frac{2abd-a^2e-b^2c}{(a^2+b^2)^{3/2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

that of curve (26) by:

$$\frac{2abd-a^2e-b^2c-\lambda(a^2t+b^2r-2abs)}{(a^2+b^2)^{3/2}} \quad . \quad . \quad . \quad . \quad . \quad (29)$$

As (28) and (29) have the same denominator we, in order to compare the curvatures of both curves, only want the numerators. For the sake of brevity we write:

$$2\,abd-a^2e-b^2c=Q \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

and

$$2\,abd-a^2e-b^2c-\lambda\,(a^2t+b^2r-2\,abs)=Q-\lambda S \quad . \quad (31)$$

If, by means of the known values of a and b we calculate the value of S we find:

$$S=(rt-s^2)\,(\alpha^2r+2\,\alpha\beta s+\beta^2t)$$

hence, S is always positive.

In order to find the direction of the curvature we calculate the coordinates ξ and η of the centre of the curved circle and ascertain at which side of the tangent this centre is situated. Therefore, we call the origin of the coordinate system the point which in this case represents the vapour, O. We now find the following: the liquidum line is curved in the point F towards O when $Q<O$; it is curved in F away from Q if $Q>O$.

A consideration of Q shows that this can be positive as well as negative; hence, the liquidum line can be curved in F, away from O as well as towards O.

In order to find the saturation line under its own vapour pressure we will consider two cases.

Owing to the small value of $V-v$, λ will generally have a large positive value. In Fig. 1, wherein for the moment we disregard the curve $d'Fe'$, the liquidum line is represented by dFe; the point O is supposed to be somewhere to the left of this curve dFe so that this is curved towards O; Q is consequently negative.

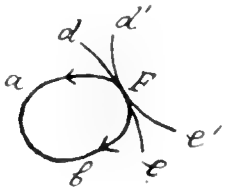

Fig. 1.

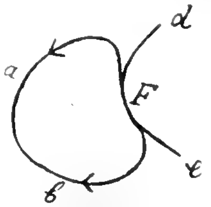

Fig. 2.

From this it follows at once that $Q-\lambda S$ is also negative and that the saturation line under its own vapour pressure, namely the curve Fab, must possess a curvature stronger than that of the liquidum line. It further follows from our previous considerations that they must intersect also the line OF somewhere between O and F so that they must exhibit a form as indicated schematically in fig. 1. The change in pressure along this curve is determined in F by (22), from which it follows, that, starting from F, dP is positive whether towards a or towards b. The pressure in F is, therefore a minimum one and increases in the direction of the arrows. The solution with maximum vapour pressure is, of course, in this case situated on the intersecting point of this curve with the line OF.

We will now disregard the liquidum line dFe of fig. 1 and suppose it to be replaced by $d'Fe'$ which is curved in another direction: Q is, therefore, positive so that $Q-\lambda S$ can be positive as well as negative. If the liquidum line is not curved too strongly $Q-\lambda S$ will be negative and the saturation line under its own vapour pressure again exhibits a form like the curve aFb of Fig. 1. If however the liquidum line is curved very strongly and λ is not too large, then $Q-\lambda S$ can also become positive, so that both curves in F are bent in the same direction. This has been assumed in Fig. 2 wherein dFe represents the liquidum line and aFb the saturation line under its own vapour pressure. As in this case, Q is larger than $Q-\lambda S$ it follows, as assumed in Fig. 2, that in the vicinity of F the curve dFe must be bent more strongly than the curve aFb.

$V<v$. λ has, therefore, generally a large negative value. In the same way as above we find that Figs. 3 and 4 can now appear. The saturation line under its own vapour pressure is again represented by aFb, the liquidum line by dFe. In Fig. 3 are united two cases, namely a liquidum line dFe curved towards O and another $d'Fe'$ curved in the opposite direction. We must remember also that the line OF must intersect the saturation line somewhere in a point situated at the other side of F than the point O. $\varDelta$ now being negative, it further follows from (22) that the pressure of $\varDelta$ must now decrease towards a as well as towards b; hence, the arrows

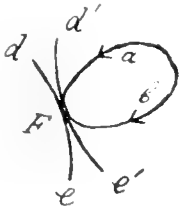

Fig. 3

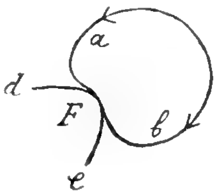

Fig. 4.

again indicate the direction in which the vapour pressure increases.

The previous considerations relate to the saturation line under its own vapour pressure; in a similar manner we may likewise investigate the boiling point line of the saturated solutions. We must then in (26) replace λ by μ in which $\mu=\frac{D}{B}=\frac{D}{H-\eta}$.

Instead of $Q-\lambda S$ we must then consider $Q-\mu S$. μ is now always positive and as regards absolute value smaller than λ. Further we must replace AdP in (22) by BdT. As, moreover, the line OF must intersect the boiling point line of the saturated solutions in a point between O and F, we re-find the cases represented in figs. 1 and 2 in which aFb now represents the boiling point line of the saturated solutions. If, however, the arrows must indicate the direction of an increasing temperature one must imagine them to point in the opposite direction.

If we compare the values of $Q-\lambda S$ and $Q-\mu S$ in regard to each other, we may search for the different situations of the saturation line under its own pressure, and for the boiling point line of the saturated solutions in regard to each other, in the vicinity of point F. I will, however, not go in for this now; I will, however, refer to it when discussing the value of $\frac{dP}{dT}$ in the vicinity of the point F. Whether all conceivable combinations are actually possible is difficult to predict. Perhaps a solution might be found by introducing the condition of equilibrium of VAN DER WAALS and expressing the different *quantities* in the a and b of VAN DER WAALS, which must then be considered as functions of x and y.

We will now deduce the vapour saturation lines under their own pressure and the boiling point lines of the saturated solutions yet in another manner.

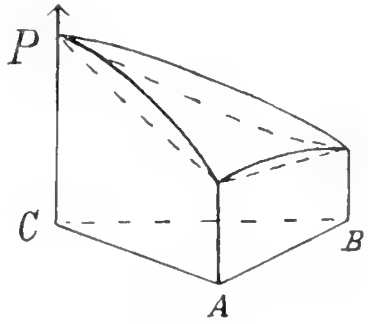

Fig. 5.

In order to find the saturation line, under its own pressure, of a definite temperature T we take the vapour- and the liquidum surface of this temperature T; we then obtain fig. 5 in which the pressure axis is taken perpendicularly to the component triangle ABC. The liquidum surface is represented by the drawn, the vapour plane by the dotted lines. If the vapour contains only two of the components the vapour side reduces itself to a curve situated in one of the border planes; if it contains but one single component it reduces itself to a single point. Like in our former considerations, we further assume, provisionally, that in the liquidum side occurs neither a maximum, minimum, nor a stationary point.

We further take, at the assumed temperature T and an arbitrary pressure P, a saturation line of the solid substance F. If we alter the pressure, T remaining constant, this saturation line changes its form. If, to the component triangle, we place perpendicularly the P-axis and if on this we place the different saturation lines we get an isothermic-polybaric saturation surface of F. This surface may lie as in fig. 6 or 7; the component triangle has been omitted from both figures, the arrows point in the direction of increasing pressure. That both cases are possible is evident from what follows:

$V > v$. At the assumed temperature T the substance F will melt at a definite pressure. Because the substance melts with increase of volume the saturation line of F will appear on elevation of pressure, so that we obtain a surface like in fig. 6, namely with the convex side directed downwards.

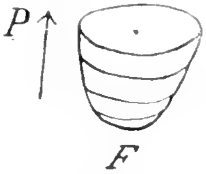

Fig. 6.

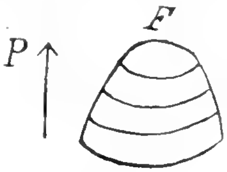

Fig. 7.

$V < v$. At the assumed temperature T the solid substance F will also melt at a definite pressure. Because on melting there is now a decrease of volume, the saturation line of F will now appear on reduction of pressure. We thus obtain a surface like in fig. 7, namely with the concave side directed downwards.

The surfaces of figs. 5, 6, and 7 are isothermic-polybaric; they, therefore, apply only to a definite temperature; if this is changed those surface alter their form and situation. On elevation of temperature the liquidum and vapour surfaces of fig. 5 shift upwards likewise the surface of fig. 6. On elevation of temperature, the surface of fig. 7

moves, however, downwards; as V is smaller than v the correlated melting pressure will fall on increase of the melting temperature of F.

As a small change in the melting point usually causes a very great change in pressure both surfaces of figs. 6 and 7 will generally move much more rapidly than the vapour and liquidum side of fig. 5.

$V > v$. We now suppose the saturation line of fig. 6 to be introduced also in fig. 5; to begin with we assume the point F of the saturation surface to be far below the liquidum side. All points of the section of both surfaces now represent liquids saturated with solid F and in equilibrium with vapour, consequently the system $F + L + G$. As the points of the section all appertain to the same temperature, this section is therefore the previously recorded saturation line of the solid substance F under its own vapour pressure. If we project this section on the component triangle we obtain a curve surrounding point F like the drawn curves in fig. 7 (I) or fig. 11 (I). It is also evident that the pressure must increase in the direction of the arrows of these figures. We now again imagine in fig. 5 the section of liquidum surface and saturation surface; with each point of this section corresponds a definite point of the vapour surface. On the vapour surface is situated, therefore, a curve indicating the vapours in equilibrium with the solutions saturated with F; this curve is the vapour line appertaining to the saturaton line under its own vapour pressure. If this curve is projected on the component triangle we obtain a curve surrounding point F such as the dotted curve of figs. 7 (I) or 11 (I).

If the temperature is increased the liquidum, gas, and saturation surfaces of F move upwards; as the latter surface, however, moves more rapidly than the first, there occurs a temperature where F falls on the liquidum surface so that the solid substance F is in equilibrium with a liquid of the same composition and with a vapour. Like VAN DER WAALS in the binary systems, we may call this temperature the minimum melting point of F.

As the plane of contact *introduced* in F at the saturation surface is horizontal, the saturation surface must intersect the liquidum surface. We notice that this section proceeds from F towards the direction of the vapour surface. If we project this curve on the component triangle we obtain the curve aFb of figs. 1 or 2. The curves de or $d'e'$ of these figures are the sections of the plane of contact in F at the saturation surface with the liquidum side; they are consequently the liquidum lines of the heterogeneous region LG at this minimum melting point of the substance F.

From a consideration of fig. 5 it immediately follows that the vapour lines appertaining to the curves aFb of figs. 8 and 2 are exphased and may, or may not, intersect the saturation line.

If we still increase the temperature a little, the point F gets above the liquidum surface and the saturation line of F under its own pressure becomes exphased. We then obtain fig. 12 (I) in which the vapour line may, or may not, intersect the saturation curve under its own vapour pressure.

If we increase the temperature still a little more, the saturation and the liquidum surface come into contact in a point; it is evident that on the saturation surface of F this point does not coincide with F, but is shifted towards the gas surface. We now have the highest temperature at which the system $F + L + G$ exists. In fig. 12 (I) both lines contract to a point; both points lie with F on a straight line.

$V < v$. We now imagine the saturation surface of fig. 7 to have been introduced in fig. 5 and in such a manner that the point F is situated above the liquidum surface. The section is then again a saturation line of the substance F under its own vapour pressure, which surrounds the point F. In projection we, therefore, again obtain fig. 7(I) or 11(I) with an exphased or circumphased correlated vapour line which has shifted towards the side of the vapour surface.

On increasing the temperature the liquidum and vapour surface shift in an upward direction but the saturation surface of F shifts, however, downwards. At a definite temperature, the minimum melting point temperature of F (point F) arrives at the liquidum side and it is now evident that the saturation line under its own vapour pressure has shifted, starting from F, from the gas surface. In projection we thus obtain the curves $a\,F\,b$ of fig. 3 or 4. The correlated vapour line has, of course, shifted towards the side of the gas surface and may be either exphased or circumphased.

What will happen at a further increase of temperature will now be readily understood.

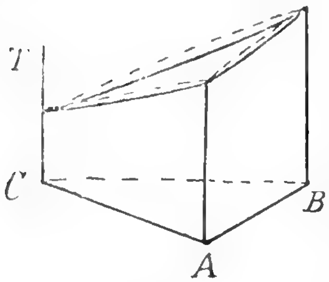

Fig. 8.

In order to find the boiling point line of the solutions saturated with F, for a definite pressure P, we take the vapour surface and the liquidum surface for this pressure P; we then obtain fig. 8 in which the temperature axis is taken perpendicularly to the component triangle ABC. The liquidum surface is represented by the drawn, the vapour surface by the dotted lines. In order to act in accordance with our determined assumption that C is the component with the highest vapour pressure the boiling point of C has been taken lower than that of A and B.

We now also take a polythermic-isobaric saturation surface of F. At the assumed pressure P, there exists, for an entire series of temperatures, at each temperature a definite saturation line of F. If these are put on a temperature axis, the polythermic-isobaric saturation surface is formed which we can represent by fig. 7 in which however, we must imagine P to be replaced by T; we will call this figure fig. 7*a*.

The figs. 7*a* and 8 apply only to one definite pressure; if this is altered they change their situation and form. On increase of pressure both surfaces of fig. 8 move upwards; the saturation surface of the figure 7*a* can move upwards as well as downwards. This depends on whether on melting, there is an increase or decrease of volume. As however, a change in pressure causes, as a rule, a comparatively small change in the melting point of a substance, the movement of the saturation surface of the substance F will be slower than that of the two surfaces in fig. 8.

We now imagine the saturation surface of the fig. 7*a* to be introduced in fig. 8 and in such a manner that the point F lies above the liquidum side. The section is then the boiling point line of the solutions saturated with F; the correlated vapour line has, as seen from the figure, shifted towards the vapour surface. A projection on the component triangle gives a circumphased boiling point line of the solutions saturated with F and a circumphased and an exphased vapour line. We thus again obtain the figures 7 (1) or 11 (1) in which however, the arrows, indicating the direction of increasing temperatures, must be supposed to point in the opposite direction.

On further increase in pressure, the point F first arrives at the liquidum surface, then the liquidum surface comes into contact with the saturation surface of F from which follow the previously described boiling point lines of the saturated solutions and their correlated vapour lines.

In place of the saturation surface of F we could also have considered the vapour saturation surface of F and its movement in regard to the vapour surface of the system $L\,G$. We will refer later to the vapour saturation surfaces of a solid substance, in connection with another investigation.

We have already stated above that the vapour surface, when the vapour contains two components only, reduces itself to a vapour curve, and to a point when the vapour contains only one component.

This causes that many of the properties already mentioned may be deduced and expressed in a much more simple manner. I will refer to this later when discussing the vapour pressures and boiling points of aqueous solutions saturated with salts and double salts, which in some cases have been determined experimentally.

(*To be continued*).

Chemistry. — "*Equilibria in ternary systems.*" III. By Prof. SCHREINEMAKERS.

(Communicated in the meeting of Dec. 28, 1912).

In the previous communications [1]) we have assumed that in the system liquid-vapour occurs neither a maximum or minimum, nor a stationary point; we have also limited ourselves to the appearance of two three-phase triangles.

We will now discuss first the case that in the ternary system occurs a point with a minimum vapour pressure.

Let us imagine that in fig. 1 (1) the liquidum line de and the vapour line d_1e_1 of the heterogeneous region LG surround the saturation line of F, so that we get a diagram as in fig. 1. The saturation line of F is here surrounded by the liquidum region L, this by the heterogeneous region LG and this in turn by the vapour region. All liquids saturated with F therefore occur at the stated P and T in a stable condition.

On reduction of pressure, the liquidum region contracts so as to disappear simultaneously with the heterogeneous region LG in a point. This point represents for the stated temperature, the liquid and the vapour which, at the minimum pressure of the system liquid + gas can be in equilibrium with each other. This point may occur without as well as within the saturation line of F. As at lower temperatures the region FL is generally large, but small at temperatures in the vicinity of the melting point of F, the said point will appear, at high temperatures, usually without, and at lower temperatures as well within as without the saturation line of F.

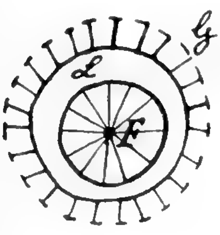

Fig. 1.

We now first consider the case where the point with a minimum vapour pressure falls outside the saturation line of F, or in other words that the liquidum and the heterogeneous region disappear in a point outside the saturation line of F.

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[1]) These Proc. p. 700 and 853.

If starting from fig. 1 we now reduce the pressure, the liquidum line of the heterogeneous region approaches the saturation curve of F and meets this at a definite temperature. The diagram now formed may be deduced from fig. 2 (1) if we suppose the saturation curve of F therein to be surrounded by the curves de and d_1e_1. The diagrams appearing on further reduction of the pressure can be represented by figs. 3 (1), 4 (1), 5 (1), 6 (1), or 3 (1), 8 (1), 9 (1) and 10 (1). In each of these figures, however, the curves de and d_1e_1 must be imagined to be bent in such a manner that they entirely surround the liquidum region; they finally disappear in the point with the minimum pressure.

From this it now follows that the liquid as well as the vapour of the three-phase equilibrium $F + L + G$ proceeds along a closed curve like in fig. 7 (1) or 11 (1); the saturation line under its own pressure is, therefore, again circumphased and the correlated vapour line circumphased or exphased.

If we consider temperatures very close to the melting point of F, we find as in the first communication, that the saturation line under its own vapour pressure becomes exphased and that we obtain diagrams such as in figs. 12 (1) and 13 (1).

We now consider the case where the point with minimum vapour pressure falls within the saturation line of F, or in other words, that the liquidum and the heterogeneous region disappear in a point within the saturation surface of F.

We again start from fig. 1 and reduce the pressure first of all until the liquidum and saturation curve come into contact, then until both curves intersect. We now obtain a diagram as in fig. 3 (1) in which, however, the saturation curve of F is supposed to be surrounded by the heterogeneous region $L\,G$.

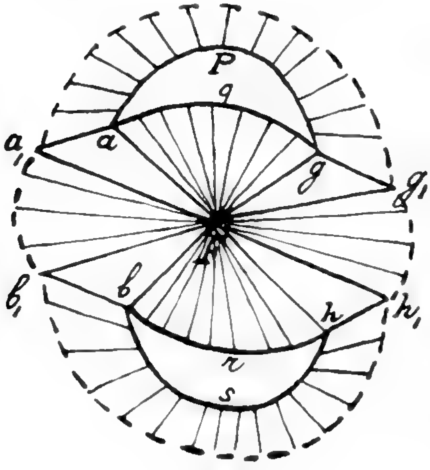

Fig. 2.

On further reduction of pressure, the liquidum line of the heterogeneous region and the saturation line of F may once more come into contact, so that on further reduction of pressure two new three-phase triangles are formed; we then obtain a diagram such as fig. 2 with four three-phase triangles. The liquidum region now consists of the two isolated pieces $apgq$ and $brhs$, the heterogeneous region likewise of two isolated parts, namely of a_1g_1gpa

and b^1h^1hsb, whereas the vapour region forms a coherent whole.

In fig. 2 we find the following equilibria:

Curve a^1g^1 represents vapours in equilibrium with liquids of the curve apg;

Curve b^1h^1 represents vapours in equilibrium with liquids of the curve bsh;

Curve a^1b^1 and g^1h^1 represents vapours in equilibrium with the solid substance F;

Curve apg represents liquids in equilibrium with the vapours of the curve a^1g^1;

Curve bsh represents liquids in equilibrium with vapours of the curve b^1h^1;

Curve apg (and brh) represents liquids saturated with the solid substance F.

If, at the temperature and the pressure applying to fig. 2, we join the components, then, according to the situation of the figurating point, there is formed within:

the gasregion . . . . an unsaturated vapour:
the liquidum region an unsaturated solution;
$apgg_1a_1$ . . . . a vapour of a_1g_1 + a liquid of apg;
$bshh_1b_1$ . . . . a vapour of b_1h_1 + a liquid of bsh;
a_1b_1F . . . . a vapour of a_1b_1 + solid F;
g_1h_1F . . . . a vapour of g_1h_1 + solid F;
$aqgF$ . . . . a liquid of aqg + solid F;
$brhF$ . . . . a liquid of brh + solid F;
aa_1F . . . . vapour a_1 + liquid a + solid F;
bb_1F . . . . ,, b_1 + ,, b + ,, F;
gg_1F . . . . ,, g_1 + ,, g + ,, F;
hh_1F . . . . ,, h_1 + ,, h + ,, F.

On further reduction of pressure, the liquidum line apg and hsb which surrounds the liquidum region contracts still more so that on the one side the points a and g coincide at a pressure P, this will be likewise the case with their conjugated points a_1 and g_1; the two triangles Fa_1a and Fg_1g then coincide along a straight line and the pressure P for the system $F+L+G$ is a minimum pressure. The same applies when the two triangles Fbb^1 and Fhh_1 coincide.

After the four three-phase triangles have disappeared from fig. 2 owing to reduction of pressure, the vapour saturation line of F composed in Fig. 2 of the two branches a_1b_1 and g_1h_1 forms a closed curve which surrounds the heterogeneous region LG as well as the saturation line of F. Hence, at these pressures only unsaturated vapours and those saturated with solid F can occur in the stable condition.

From a consideration of the equilibrium $F+L+G$ it appears that the saturation curve of F under its own vapour pressure is a curve surrounding the point F, on which however, now occur two points with a maximum vapour pressure. The same applies to the correlated vapour curve surrounding the former curve. Each maximum or minimum point of the one curve lies with the correlated maximum or minimum point of the other curve and the point F on a straight line.

We have assumed above that when the liquidum and the heterogeneous region disappear in a point within the saturation line of F two three-phase triangles, as in fig. 2. appear. We may, however, also imagine that the liquidum line of the heterogeneous region LG in fig. 1 contracts in such a manner that it intersects the saturation line of F in two points only; only two three-phase triangles are then formed.

The saturation line of F under its own vapour pressure and the correlated liquidum line are then both circumphased and exhibit one point with a maximum and one with a minimum vapour pressure. When the liquidum region disappears at one temperature within and at another temperature without the saturation point of F, it will, at a definite temperature disappear in a point of the saturation line. Among all solutions saturated at this temperature with F and in equilibrium with vapour there will be one which is in equilibrium with a vapour of the same composition. The saturation line of F under its own vapour pressure and the correlating vapour line then meet in the point with the minimum vapour pressure.

We have noticed above that there exist saturation lines of F under their own vapour pressure which exhibit two vapour pressure maxima and two minima. Such curves must, of course, be capable of conversion into curves with one maximum and one minimum; this takes place by the coincidence of a maximum and a minimum of the first curve causing the part of the curve situated between these two points to disappear. The two other parts then again merge in each other.

We have deduced above the saturation line under its own vapour pressure with two maxima and two minima in the assumption that the liquidum region disappears somewhere within the saturation line of F. We may also however, imagine similar cases if this disappearance takes place in a point outside the saturation line of F. We have only to suppose that in fig. 1 the liquidum line of the heterogeneous region LG contracts so as to disappear in a point outside the saturation line of F.

After the contact of the liquidum and saturation lines two points of intersection appear; if now no further contact takes place, these points finally coincide in a point of contact so that the saturation line under its own vapour pressure exhibits but one maximum or minimum.

If, however, after the appearance of the first two points of intersection a second point of contact occurs we obtain four points of intersection of which, at first two, and afterwards the other two coincide in a point of contact, so that in all four of these points are formed. The saturation line under its own vapour pressure then exhibits two maxima and two minima.

By way of a transition case it might happen that the second point of contact, which appears after the formation of the two first points of intersection, coincided with one of these points so that a point of the second order was formed. On further change of pressure two points of intersection then again occurred, which finally coincided in a new point of contact. The saturation line under its own vapour pressure then represents the transition form between that with one maximum and one minimum and that with two maxima and two minima.

After what has been stated it will surely be unnecessary to consider the case where, in the system liquid-vapour, a vapour pressure maximum or a stationary point occurs; we will refer to this and to a few peculiar boiling point lines perhaps later.

We will now just consider what happens if we take the compound F only and apply heat. If we imagine F placed in a vacuum at a low temperature a portion of this compound F will evaporate and there is formed the equilibrium: solid $F +$ vapour F. On increase of temperature the vapour pressure of F is raised; in a P,T-diagram we thus obtain a curve such as aK of fig. 3, namely the sublimation curve of the substance F. At a definite temperature T_k and a pressure P_k an infinitely small quantity of liquid is now formed; this, of course, has not the composition F but another composition K. As only an infinitely small amount of liquid has formed as yet, the vapour still has the composition F. The point K is, therefore the terminal point of the sublimation line, called by VAN DER WAALS in his binary systems the upper sublimation point of the compound.

If we increase the temperature, say, to T'', more of the compound melts; there is then formed the three-phase equilibrium $F + L + G$ in which neither L nor G have the composition F. L and G have such a composition that we can form from both the solid substance F, the three figurating points are, therefore, situated on a straight

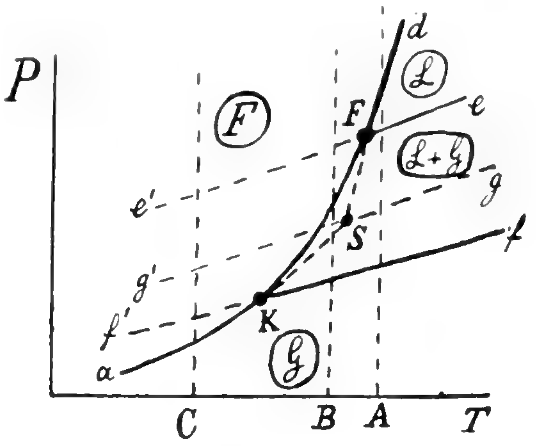

Fig. 3.

line. Besides, L and G are always present in quantities equivalent to the reaction $L + G \rightarrow F$; L and G are, consequently, present in such amounts that from both we can form F without any L or G remaining.

As a rule, the three-phase equilibrium $F + L + G$ can exist, at the temperature T' with a whole series of pressures, namely, with the pressures occurring on the saturation line under its own vapour pressure of the solid substance F at the temperature T'. As in this particular case a phase reaction is possible between the three phases or in other words, as the points F, L, and G lie on a straight line, the three-phase equilibrium exists here only at a definite pressure, namely, the maximum or minimum pressure which occur at the temperature T' on the saturation line of F under its own vapour pressure. In this particular case it is the minimum pressure, as will appear later.

At a further increase of temperature more of the substance F keeps on melting and L and G alter their composition; we will regulate the volume in such a manner that there is but an infinitely small amount of vapour which, of course, does not affect the pressure. If we represent the pressure and temperature graphically, a curve is formed such as curve KF of fig. 3.

Finally we now arrive at a temperature and correlated pressure at which all solid F has fused; as particularly at the last moments, we have taken care that but infinitely little vapour is present, the liquid now has the composition F; the vapour has quite a different composition D.

As the solid substance F and the liquid now have the same composition we have attained the melting point of F. If now we regulate the temperature and pressure in such a manner that the solid matter F remains in equilibrium with its melt the system proceeds along the melting point line Fd of fig. 3. Here, it has been assumed that the volume v of the solid substance is much smaller than the volume V of its melt. If this is not the case, the melting point line Fd starts from F towards lower temperatures. In binary systems, VAN DER WAALS has called the initial point F of the melting point line, the minimum melting point of the solid substance F.

Hence, we have forced the substance F to proceed along:

a. the sublimation line aK

b. the three phase line KF

c. the melting point line Fd

we can, however, consider still other lines.

In the upper sublimation point K we have solid $F +$ vapour $F +$ infinitely little liquid. We now increase the volume until the solid substance F has been converted totally into vapour, or else we remove the solid substance. We then have the system: vapour $F +$ infinitely little liquid or we may also say, a vapour F which can be in equilibrium with a liquid. If the temperature is increased the vapour F will continue to exist; it is then, however, no longer in equilibrium with liquid. In order, to again form an infinitely small quantity of liquid, or in other words to again bring the vapour in equilibrium with a liquid, it will generally be necessary to increase the pressure.

Hence, at an increase in temperature, one can always regulate the pressure in such a manner that a vapour of the composition F is in equilibrium with an infinitely small quantity of liquid which, of course, changes its composition with the temperature. If pressure and temperature are represented in fig. 2, the curve Kf of this figure is formed.

In the minimum melting point F we can start from the system solid $F +$ liquid $F +$ infinitely little vapour after we have first eliminated the solid substance F thereof. If now, we elevate the temperature, the pressure may be always regulated in such a manner that this liquid of the composition F is in equilibrium with an infinitely small quantity of vapour which, of course, changes its composition with the temperature. The corresponding PT-line is represented in fig. 3 by the curve Fe.

As, on the line eF, a liquid of the composition F is in equilibrium with vapour we will call this line the evaporation line of F. On the line Kf a vapour of the composition F is in equilibrium with liquid; we will, therefore, call Kf the condensation line of F. The metastable prolongations of Fe and Kf are represented in the figure by Fe' and Kf'. Hence, in point F three curves coincide namely, the melting point line (Fd), the evaporation line (Fe) and the three-phase line (FK); in point K three curves also meet, namely, the sublimation line (aK), the three-phase line (KF) and the condensation line (Kf).

The metastable prolongations of the sublimation line aK and the melting point line dF intersect in a point S; at this temperature T_S and pressure P_S now occurs, in a metastable condition, the equilibrium: solid $F +$ liquid $F +$ vapour F. If now the substance F behaved as a simple substance which can only yield a liquid and a vapour of the same composition, S would represent the triple point of the substance F; owing to the occurrence of the three-phase equilibrium $F + L + G$ this triple point is, however, metastable here. Through this metastable triple point S now also passes, besides the sublimation and the melting point curve of F, the evaporation line $g'Sg$ of F. This represents the equilibrium liquid $F +$ vapour F occurring in the metastable condition; on this curve $g'Sg$ liquid and vapour, therefore, have the composition F and not, as on $f'Kf$, only the vapour, and as in $e'Fe$ only the liquid. We will call the curve $g'Sg$ the theoretical evaporation line.

In order to find what conditions of the substance F are represented by the points of the different regions we take this substance in a condition answering to a point of the sublimation line aK. We then have solid $F +$ vapour F. From a consideration of what takes place on supply or al withdraw of heat, or on increase or decrease in volume we now deduce: to the right and below the line aK occurs the vapour region, to the left and above the line aK is found the solid region of F.

Acting in a similar manner with the points of the other lines, we find that four regions may be distinguished, namely, a gas region indicated in the figure by an encircled G, a solid region indicated by an encircled F, a liquidum region indicated by an encircled L and a liquidum-gas region indicated by an encircled $L + G$. Hence if the substance F is brought to a temperature and under a pressure corresponding with a point of the solid region, the substance F is solid; if brought to a temperature and under a pressure corresponding with a point of the liquidum-gas region, F is resolved into liquid and gas etc.

We will also consider fig. 3 just once more in connection with the previously mentioned saturation lines of F and the liquidum and vapour lines of the heterogeneous region $L+G$. For this, we first choose a temperature T_A corresponding with point A of fig. 3 and a very high pressure so that we find ourselves in the solid region. On the pressure being reduced we arrive from the solid region into the liquidum region, then into the liquidum-gas region and finally into the gas region. If we choose a temperature T_B corresponding with point B of fig. 3, the substance F on reduction of pressure first traverses the solid region, then the liquidum-gas region and finally the gas region. Reduction of pressure at the temperature T_C transfers the substance from the solid region to the gas region.

We now start from the temperature T_A and a very high pressure: the corresponding diagram then consists of fig 1 (1) wherein, however, is still wanted the gas region and the heterogeneous region $L+G$ of this figure. It is now evident that the compound F can only exist in the solid condition; it can, of course, be in equilibrium with a liquid, but this liquid cannot form unless to the compound is added a little of at least one of its components. The pure compound F which we have still under consideration can only occur in the solid condition.

On reduction of pressure, the saturation line of F contracts so as to coincide finally with point F of fig. 1 (1). At this pressure occurs, therefore, the equilibrium solid F + liquid F, so that in fig. 3 we proceed from the solid region to a point of the melting point line Fd. The heterogeneous region $L+G$ of fig. 1 (1) may, or may not, have appeared at this pressure; in any case, however, it has not yet extended to the point F of this figure.

As, on further reduction of pressure, the saturation line of F disappears from fig. 1 (1) (in order to keep in with fig. 3 we take $V>v$) F is now situated in the liquidum region of fig. 1 (1). Hence, in fig. 3 we must also arrive in the liquidum region. As on further reduction of pressure the gas region of fig. 1 (1) is further extended, the liquidum line ed of the heterogeneous region passes, at a definite pressure, through the point F. This means that the liquid F can be in equilibrium with vapour. This is in agreement with fig. 3; therein we proceed from the liquidum region to the line Fe.

On further reduction of pressure, the heterogeneous region $L+G$ shifts over the point F; the compound F is now resolved into a liquid of the liquidum line and into a vapour of the vapour line which on further decrease in pressure always change their composition. Hence the compound F traverses the liquidum gas region which is in agreement with fig. 3. This will continue until on further reduction of pressure the vapour line of the heterogeneous region passes through point F. This means that a vapour F can be in equilibrium with a liquid; this again is in harmony with fig. 3; therein we proceed from the liquidum gas region to the curve Kf. On still further reduction of pressure the gas region of fig. 1 (I) moves over the point F so that, in harmony with fig. 3 the compound F can occur only in the state of vapour.

Between the liquidum line $d\,e$ and the vapour line d_1e_1 of the heterogeneous region $L+G$ of fig. 1 (I) is situated the projection of the line of intersection of the liquidum and the vapour side of the ζ-surface. This line indicates a series of solutions which each can be in equilibrium with a vapour of the same composition; all these liquids and vapours, however, are metastable and break up into a liquid of the liquidum line and a vapour of the vapour line of the heterogeneous region $L+G$. We will call this line of intersection the theoretical liquidum-vapour line.

As this theoretical line passes, at a definite pressure, through the point F, there exists at this pressure the equilibrium: liquid $F +$ vapour F in a metastable condition; hence, we have a point of the theoretical evaporation line Sg of fig. 3 and it is, moreover, evident that this must be situated in the liquidum-gas region of fig. 3.

We now choose a temperature T_B lower than T_A; this will cause the saturation line of F to disappear at T_B at a lower pressure than at T_A. We now choose T_B so low that, on lowering the pressure the saturation line of F has not yet disappeared when the liquidum line of the heterogeneous region passes through the point F; T_B is, therefore lower than the minimum melting point of F. If we now choose a very high pressure, the corresponding diagram will then consist of fig. 1 (I) wherein, however, the gas region and the heterogeneous region $L+G$ are still wanting. On reducing the pressure fig. 1 (I) is formed first, then fig. 2 (I) and further fig. 3 (I); at these pressures the compound F still occurs in the solid condition so that it finds itself in the solid region of fig. 3. At a definite pressure the metastable part of the liquidum line $d\,a\,b\,e$ situated between the points a and b in fig. 3 (I) will pass through the point F; this means that a liquid of the composition F may be in equilibrium with vapour; this is only possible in the metastable condition for in the stable condition F only occurs as a solid. Hence, in fig. 3 we find ourselves in the solid region on a point of the metastable curve $e'F$.

On further reduction of pressure there is now formed from fig.

3 (I) the figure 4 (I) or 8 (I); we first choose T_B in such a manner that on lowering the pressure, the vapour saturation line has not yet disappeared when the vapour line of the heterogeneous region passes through the point F. So as to be in harmony with fig. 3, T_B has been chosen lower than the minimum melting point and higher than the upper sublimation point of the compound F. In consequence of this, fig. 3 (I) is converted into fig. 4 (I) on reduction of pressure, and afterwards at a definite pressure into fig. 5 (I). At this pressure the as yet solid compound F melts with formation of the vapour m_1 and the liquid m; hence in fig. 3 we proceed from the solid region to a point of the three-phase line KF.

On further decrease of pressure F is resolved into liquid and gas; in fig. 3 we, therefore, proceed from the line KF to the liquidum gas region. On further reduction of pressure the vapour curve $e_1 d_1$ of fig. 5 (I) passes, at a definite pressure through the point F; this means that a vapour of the composition F can be in equilibrium with a liquid. The compound F then passes, in fig. 3, from the liquidum-gas region to the line Kf. On further decrease of pressure is now formed fig. 6 (I), the point F lies now in the vapour region so that the compound F can only still occur in the state of vapour.

In fig. 3 we, therefore, proceed from the line Kf to the gas region.

Between fig. 3 (I), in which we assume the metastable part $a\,b$ of the liquidum line $d\,a\,b\,e$ to pass through the point F, and fig. 5 (I), in which we assume the vapour line $d_1 e_1$ to pass through F. there must, of course, lie another one where the theoretical liquidum vapour line passes through point F. This means that, in fig. 3, we must find, at the temperature T_B, between the curves $e'F$ and Kf a point of the curve $g'Sg$. If this theoretical vapour curve already passes through the point F before fig. 5 (I) is formed through reduction of pressure, the point of intersection of $g'Sg$ with the vertical line then lies in the point B of fig. 3 above the three-phase line; if, however, this theoretical line passes through the point F when, through reduction of pressure, fig. 5 has formed, the above point of intersection in fig. 3 lies below the three-phase line. These results, as follows from fig. 3, are in harmony with this figure.

The situation of the metastable sublimation line KS and of the metastable melting point line FS may be found in this manner. Here, we will just determine the situation of the triple point S. In this point there exists an equilibrium between solid $F +$ liquid $F +$ vapour F.

The equilibrium liquid $F +$ vapour F requires that the theoretical liquidum vapour line passes through point F; if this equilibrium occurs in the stable condition, the liquidum and the vapour line of the heterogeneous region must then also pass through the point F; this is the case when, incidentally, a ternary maximum, minimum or stationary point occurs in F. If, however, this equilibrium appears in the metastable condition, the liquidum and vapour line of the heterogeneous region do not pass through F which is then situated between these two. As, from the equilibria solid F + liquid F + vapour F and solid F + vapour F, it follows that the saturation and the vapour saturation line of F coincide to one point in F, the metastable triple point S must be situated in the liquidum gas region of fig. 3.

We now choose a temperature T_e (fig. 3) lower than the upper sublimation point T_k of fig. 3; the vapour saturation line of F has, therefore, not yet disappeared when the vapour line of the heterogeneous $L + G$ passes through the point F. Starting from high pressures and then reducing the same there is first formed fig. 1 (I) wherein, at first, the gas and heterogeneous regions are still wanting, then figs. 1 (I), 2 (I) and 3 (I) which is now converted into 8 (I); then are formed figs. 9 (I) and 10 (I) and finally a figure which we will call 10a and which is formed from fig. 10 when the vapour saturation line of F coincides with the point F.

During this lowering of the pressure, as shown from the figures, the substance F only occurs solid in the stable condition; the substance F, therefore, traverses the solid region of fig. 3. Not until the pressure has been so reduced as to form fig. 10a can solid F be in equilibrium with vapour F. We then proceed in fig. 3 from the solid region to a point of the sublimation line $a\ K$.

On continued reduction of pressure the vapour saturation line of F disappears from fig. 10a, so that F lies within the gas region; hence, F can occur only in the form of vapour, so that in fig. 3 we proceed to the vapour region.

In the conversion of fig. 3 (I) into fig. 8 (I) the substance F passes through different metastable conditions. On reduction of pressure the metastable piece $a\ b$ of the liquidum line passes through the point F first, then the theoretical liquidum-vapour line and then the metastable piece $a_1\ b_1$ of the vapour line of the heterogeneous region $L + G$. This also agrees with fig. 3; on lowering the pressure at the temperature T_e we meet in the solid region, successively, the metastable curves $e'\ F$, $g'\ S$, and $f'\ K$.

When in a system liquid-gas a liquid and a vapour of the same composition are in equilibrium, we will call this a singular point of the system $L+G$. The appearance of such a point has no influence on fig. 3 unless this accidentally coincides with the point F of one of the previously examined figures. Such a singular point, that at each T occurs only at a definite P, proceeds in the component triangle along a curve which may happen to pass through F. If this should take place, and if this point is a statonary point, then, in the case of the correlated P and T, the vapour and liquidum line of the heterogeneous region $L+G$ and the theoretical liquidum vapour line pass through F; if this point is a maximum or minimum one these three lines coincide in F. From this it follows that in fig. 3 the singular point must always lie simultaneously on the lines $g' S g$, $e' F e$ and $f' K f$. The coincidence of a singular point with the point F therefore causes the above three curves of fig. 2 to have one point in common; from other considerations it follows that they get into contact with each other.

This point of contact may lie in the solid as well as in the liquidum-gas region; in the first case, the system liquid F + vapour F is metastable, in the second case it is stable.

This point of contact may — but this is not very likely — also coincide with point S of fig. 3. The system solid F + liquid F + vapour F would then occur in the stable condition and the sublimation and melting point curves would then continue up to the point S.

(To be continued).

Mathematics. — *"On complexes which can be built up of linear congruences"*. By Prof. JAN DE VRIES.

(Communicated in the Meeting of December 28, 1912).

§ **1.** We will suppose that the generatrices a of a scroll of order m are in (1,1)-correspondence with the generatrices b of a scroll of order n, and consider the complex containing all the linear congruences admitting any pair of corresponding generatrices a, b as director lines. The two scrolls admit the same genus p; as the edges of a complex cone are in (1,1)-correspondence with the generatrices a, b on which they rest, p is also the genus of all the complex cones[1]. The rays of a pencil are arranged in a correspondence (m, n) by the generatrices of the scrolls $(a), (b)$; so in general the complex is of order $m+n$.

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[1] For $m=n=1$ (two pencils) we get the *tetrahedral complex*. In a paper *"On a group of complexes with rational cones of the complex"* (Proceedings of Amsterdam, Vol. VII, p. 577) we already considered the case of a pencil in (1,1)-correspondence with the tangents of a rational plane curve.

The double edges of a complex cone are rays resting on two pairs a, b; they belong to a congruence contained in the complex, of which congruence both *order* and *class* are equal to the number of double edges of the cone.

Evidently any point common to two corresponding generatrices a, b is a *principal point*, the plane containing these lines a *principal plane* of the complex. If one of the scrolls is plane, the bearing plane is a *principal plane* too; if one of them is a cone, the vertex is a *principal point*[1].

Any point P of a principal plane is *singular*, the pencil with vertex P lying in that plane forming a part of the complex cone of P. The same degeneration presents itself for any point of each of the given scrolls; so these surfaces are loci of *singular points*. Likewise any plane through a generatrix a or b and any plane through a principal point is *singular*.

By means of one scroll only can also be obtaine complexes consisting of linear congruences. So we can arrange the generatrices of a scroll in groups of an involution I and consider any pair of any group as director lines of a linear congruence[2].

In the following lines we treat the *biquadratic complex* which can be derived in the manner described above from *two projective reguli*. After that we will investigate the particular cases of plane scrolls or cones.

§ **2.** We use the general line coordinates x_k, introduced by KLEIN, which are linear functions of the coordinates p of PLÜCKER and satisfy the identity $(x^2) = \sum\limits_6 x_k^2 = 0$, while $\sum\limits_6 x_k y_k = 0$ or $(xy) = 0$ indicates that x and y intersect each other.

Then a regulus is characterized by the six relations

$$a_k = p_k \lambda^2 + 2q_k \lambda + r_k,$$

satisfying the conditions:

$$(p^2) = 0, (r^2) = 0, (pq) = 0, (qr) = 0, 2(q^2) + (pr) = 0.$$

Likewise we represent the second regulus by

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[1] In our paper "*Sur quelques complexes rectilignes du troisième degré*" (Archives Teyler, 2nd series, vol. IX, p. 553—573) we have considered among others the case that one of the scrolls is a pencil whilst the other is formed by the tangents of a conic.

[2] This has been applied to a developable in our paper "*On complexes of rays in relation to a rational skew curve*" (Proceedings of Amsterdam, vol. VI, p. 12) and on a rational scroll in "*A group of complexes of rays whose singular surfaces consist of a scroll and a number of planes*". (Proceedings of Amsterdam, vol. VIII, p. 662).

$$b_k = p'_k \lambda^2 + 2q'_k \lambda + r'_k .$$

Then we find for the rays x of the congruence with director lines a, b

$$(p x) \lambda^2 + 2 (q x) \lambda + (r x) = 0,$$
$$(p' x) \lambda^2 + 2 (q' x) \lambda + (r' x) = 0,$$

which we abridge into

$$P\lambda^2 + 2Q\lambda + R = 0 \quad , \quad P'\lambda^2 + 2Q'\lambda + R' = 0.$$

By elimination of λ we get the equation of the *biquadratic complex* under discussion. It is

$$(PR' - P'R)^2 = 4 (PQ' - P'Q) (QR' - Q'R),$$

or, what comes to the same,

$$(PR' - 2QQ' + P'R)^2 = 4 (PR - Q^2) (P'R' - Q'^2).$$

From this ensues that the complex can be generated in two different ways by *two projective pencils of quadratic complexes*. This is shown by the equations

$$PR' - P'R = 2 \mu (PQ' - P'Q),$$
$$\mu (PR' - P'R) = 2 (QR' - Q'R)$$

and

$$PR' - 2QQ' + P'R = 2 \mu (PR - Q^2),$$
$$\mu (PR' - 2QQ' + P'R) = 2 (P'R' - Q'^2).$$

The equation $(ab) = 0$ expressing the condition that two corresponding generatrices a, b have a point in common, gives rise to a biquadratic equation in λ. So there are *four principal points* and *four principal planes*.

§ **3.** We now occupy ourselves with the congruence of the rays x each of which rests on *two pairs* of homologous generatrices (λ). For such a ray x the two equations

$$P\lambda^2 + 2Q\lambda + R = 0 \quad , \quad P'\lambda^2 + 2Q'\lambda + R' = 0$$

must be satisfied for the same values of λ; so we have the condition

$$\left|\begin{matrix} P & Q & R \\ P' & Q' & R' \end{matrix}\right| = 0.$$

This equation leads to a *congruence* (3,3). For the quadratic complexes $PQ' = P'Q$ and $PR' = P'R$ have the congruence $P = 0$, $P' = 0$ in common and the latter congruence does not belong to the complex $QR' = Q'R$.

This result is in accordance with the fact that the complex cones (and curves) must be rational and have to admit therefore *three double edges* (and *three double tangents*).

Both the characteristic numbers of the congruence can also be found as follows. A plane through any point A_0 of the generatrix a_0 and the corresponding generatrix b_0 cuts both reguli respectively in a conic α_0^2 and a line β_0. On these sections the other pairs of corresponding lines a,b determine two projective ranges of points (A), (B). As these arrange the rays of a pencil in the plane $(A_0 b_0)$ in a correspondence (1,2), the lines AB envelop a *rational curve* of *class three* with β_0 as *double tangent*. Each of the three lines AB passing through A_0 rests on two pairs a,b and belongs therefore to the congruence.

The curve of class three just found and the pencil with A_0 as vertex form together the *complex curve* of plane $(A_0 b_0)$. Likewise the *complex cone* of A_0 breaks up into this pencil and a rational cubic cone.

Any point and any tangential plane of the quadratic scrolls (a), (b) is *singular*. Moreover the points of the principal planes and the planes through the principal points are *singular*.

§ 4. If we add the relation $(p'r') = 0$ to the conditions enumerated in § 2, it follows from $2(q'^2) + (p'r') = 0$ that the coordinates q'_k also determine a line, which is to cut p' and r' on account of $(p'q') = 0$, $(q'r') = 0$ without belonging to the regulus. So it lies either in the plane τ through p' and r' or on a quadratic cone with the point of intersection T of p' and r' as vertex.

In the first case each line of τ belongs to the complex and even *twice* as it cuts two generatrices of the regulus (a). In other words: τ is a *double principal plane*.

In the second case an analogous reasoning shows that T is a *double principal point*.

§ 5. In the two latter particular cases the complex has lost the property of corresponding *dually with itself*. On the contrary this property is still preserved by the complex generated by two projective reguli the first of which consists of the tangents of a conic α^2 (in plane α) and the second is formed by the edges of a *quadratic cone* β^2 (with vertex B).

The range of points B_0 on the section β_0^2 of β^2 and α is in (1,1)-correspondence with the system (a). So the points B_0 are in (2,2)-correspondence with the points of intersection A_0 of the generatrices a and the conic β_0^2. So the complex admits *four principal points*, each of which bears a *principal plane*.

Furthermore α is a *double principal plane*, B a *double principal point*.

The complex cone of point P has PB for double edge; for PB cuts two generatrices a and at the same time the corresponding lines b. So the congruence (3,3) of the general case must break up here into a (1,0), a (0,1) and a (2,2).

In order to check this we consider the correspondence between the points $A = a_1 a_2$ and the corresponding planes $\beta = b_1 b_2$. If A describes a line, a_1 and a_2 generate an involution; as b_1 and b_2 do then likewise, β will rotate about a fixed axis. So the correspondence (A, β) is a *correlation*. Therefore plane α contains a conic a_0^2, each point A_0 of which is incident with the trace b_0 of the homologous plane β_0. So each point A_0 is the vertex of a pencil belonging to the complex and lying in plane β_0. These pencils generate a *congruence* (2, 2). For their planes envelop a quadratic cone with vertex B, two tangential planes β_0 of which pass through the arbitrarily chosen point P; so the lines connecting P with the homologous points A_0 belong to the congruence in question, which evidently is *dual in itself*.

§ **6**. We will now suppose that the tangents a of the conic α^2 in plane α and the tangents b of the conic β^2 in plane β are in (1, 1)-correspondence. Then the congruence with any pair of corresponding tangents a, b as director lines generates once more a complex of order four, evidently *not* dual in itself.

By the correspondence (a, b) the points of the line c common to α and β are arranged in a (2,2)-correspondence. The *four* coincidencies are *principal points* of the complex and the lines a, b concurring in any of these points determine a *principal plane* So we have indicated four sheaves of rays and four fields of rays belonging to the complex.

The planes α and β are also fields of rays of the complex; for any line s of α is cut on c by two lines b but also by the corresponding lines a; so s belongs twice to the complex.

We account for this by saying that α and β are *double principal planes.*

The complex cone of any point P meets c in four points, i. e. in the four principal points; so we deal with a *biquadratic complex.*

The *complex cone* is rational, its edges corresponding one to one to the tangents of α^2; therefore it has to admit *three double edges.* Likewise the *complex curve* of any plane has to admit *three double tangents.*

§ **7**. In order to investigate this more closely we consider the relationship between any point A of α, as point common to two tangents a_1, a_2, and the point B common to the corresponding tangents b_1, b_2.

If A describes a line l_A its polar line with respect to α^2 will rotate about a fixed point, whilst the pair a_1, a_2 generates an involution. But then b_1, b_2 must also generate an involution, so that B describes a line l_B. So the point fields (A), (B) are in projective correspondence (collinear, homographic).

By projecting the field (A) out of any point P unto β we obtain in β two projective collocal fields, admitting three coincidencies. So the congruence of the lines AB is of *sheaf degree* (order) *three*. Its *field degree* (class) however is *one*; for if A describes the section of α with any plane Π, B will arrive once in Π, i. e. Π contains only *one* line AB.

The congruence (3, 1) found here is generated, as we know, by the *axes* (= biplanar lines) of a twisted cubic γ^3, i. e. any line AB lies in two osculating planes of γ^3.

Evidently any line AB is double edge of the complex cone of any of its points P. However the complex rays through A form the pencil $A(\alpha)$ counted twice and the pencils determined by the lines b_1, b_2; for B the analogous property holds.

§ **8.** Evidently the *three double edges* of the *complex cone* of P are the mutual intersections of the *three osculating planes* of γ^3 passing through P.

Likewise the *complex curve* in Π has for *double tangent* the axis of γ^3 lying in that plane, the other *two double tangents* coinciding with the intersections of Π with α and β. For, each of the lines b', b'' which concur in the point $c\Pi$ determines a complex ray lying in Π, which lines coincide both with $\alpha\,\Pi$.

An *osculating plane* Ω of γ^3 contains ∞^1 axes, enveloping a conic ω^2. Any plane Ω is *singular* for the congruence (AB). So the complex curve in Ω is the conic ω^2 counted twice.

As the congruence (3,1) cannot admit singular points, no point bearing more than three planes Ω, no complex cone can degenerate but those corresponding to the principal points and the points of the principal plane. We already remarked this for α and β; for any point of a single principal plane the complex cone breaks up into a pencil and a rational cubic cone.

The complex cone of any point of the *developable* with γ^3 as cuspidal edge admits an edge along which two sheets touch each other (the plane section has two branches touching each other). For any point of γ^3 the cone possesses an edge along which two sheets osculate each other (the section has two branches with a common point of inflexion touching each other).

A *cuspidal edge* connects any point A_0 of α^2 with the corresponding point B_0 of β^2. The locus of the line A_0B_0 is a *biquadratic scroll,* of which α and β contain two generatrices. Any point of this scroll admits a complex cone with a *cuspidal edge.*

Evidently the biquadratic scroll is *rational,* so it has a *twisted cubic* as *nodal curve*: For any point P of this curve the complex cone has *two cuspical edges.*

By replacing the two conics α^2, β^2 (as bearers of flattened reguli) by two quadratic cones we obtain a complex evidently dually related to that treated above.

If α^2 and β^2 touch the line $c = \alpha\beta$ whilst c corresponds to itself in the relationship between a and b, the complex degenerates into the special linear complex with axis c and a cubic complex. Evidently the same holds for the general biquadratic complex (§ 2) if the reguli admit a common generatrix corresponding to itself.

Chemistry. — "*On the system phosphorus*". By Prof. A. SMITS, J. W. TERWEN, and Dr. H. L. DE LEEUW. (Communicated by Prof. A. F. HOLLEMAN).

(Communicated in the meeting of November 30, 1912).

In a previous communication on the application of the theory of allotropy to the system phosphorus [1]) it was pointed out that the possibility existed that the line for the internal equilibrium of molten white phosphorus is not the prolongation of the line for the internal equilibrium of molten red phosphorus, in consequence of the appearance of critical phenomena below the melting-point of the red modification. The latter could namely be the case if the system αP—βP belonged to the type ether-anthraquinone, which did not seem improbable to us.

This supposition was founded on the following consideration. In the first place it follows from the determinations of the surface-tension carried out by ASTON and RAMSAY [2]), that the white phosphorus would possess a critical point at 422°. Hence the critical point of

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[1]) Zeitsch f. phys. Chem. **77**, 367 (1911).

[2]) J. Chem. Soc. **65**, 173 (1894).

Cf. also SCHENCK, Handb. ABEGG III$_3$ 374.

the pseudo-component αP will probably lie below 422°. The melting-point of the pseudo-component βP lies certainly above the melting-point of the red modification, hence above 610°, so that we arrive at the conclusion that the melting-point of the second pseudo-component is probably situated more than 200° above the critical point of the first pseudo-component.

In the second place the liquid white phosphorus, which must be considered as a supersaturate solution, contains no appreciable quantity of the phosphorus insoluble in carbon disulphide even at higher temperatures from which it may be inferred that the solubility of βP, or of mixed crystals containing βP, in liquid αP is exceedingly slight.

In these considerations we arrive accordingly at the conclusion that in the system phosphorus exactly those conditions are satisfied which a system must satisfy if there is to be a chance for the appearance of critical phenomena by the side of the solid substance.

Experiment has really taught us that the pseudo system of the phosphorus belongs to the type ether-anthraquinone.

It is true that in a pretty extensive investigation in which pure white phosphorus in capillaries of infusible glass was suddenly immersed in a bath of high temperature, a critical phenomenon could not be observed, because the observation is very much hampered by the deposition of a red solid phase, which always precedes, but yet phenomena appeared which pointed to the existence of a critical point below the melting-point temperature of the red phosphorus.

Though the observed phenomena will be more fully discussed in a following communication, we may already mention here that among others it was found that on sudden immersion of a capillary with white phosphorus in a bath of 450°, at first solid red phosphorus deposited, and that then the liquid suddenly totally disappeared, in which a shock was felt in the hand in which the iron bar was held, on which the capillary was suspended by means of a copper wire. At the moment of the shock the whole capillary filled with solid red substance, which, however did not consist of the well-known red phosphorus, for if the capillary was removed from the bath of 450°, and suddenly immersed in a bath of 510°, it appeared that already at this temperature melting took place, so 100° below the unary melting-point of the red phosphorus. The perfectly colourless liquid, however, which originated at 510°, was strongly metastable, and the velocity of crystallisation being rather great at this temperature, the formed liquid became soon solid again.

It now appeared that this phenomenon must be explained as follows. At high temperature, i. e. at about 300°, the velocity of crystallisation of the red phosphorus is so great that it begins to be deposited. This velocity of conversion, however, is not so great as is generally thought, for even at 330° the vapour tension of the rapidly heated white phosphorus, which contained pretty much red solid substance, appeared to be still the same as that of the liquid, because the liquid still present was sufficient to control the vapour tension. How long this will continue of course depends on the relative volumes occupied by the solid and the liquid phosphorus and by the vapour.

In the experiment with the capillary the velocity of heating is so great that even at considerably higher temperatures liquid white phosphorus still continues to exist by the side of the solid red mass. If, however, the temperature rises above the temperature of the first critical endpoint p of the pseudo-binary system, the liquid becomes so strongly metastable that it suddenly disappears, and then the red solid substance deposits from the fluid phase formed, through the whole of the capillary.

If the capillary is immersed in a bath of 620°, a colourless liquid is obtained, which exhibits something particular when cooled exposed to the air, which was already observed by STOCK and GOMOLKA [1]). They say namely: "Kühlt man die Schmelze recht langsam ab, so fängt sie bei etwa 580° an feste, rote Teilchen auszuscheiden: der Vorgang macht den Eindruck einer Kristallisation. Bei etwa 570° überziehen sich dann *plötzlich*[2]) die Wände des Glasrohres auf ihrer ganzen Länge (auch oberhalb der Flüssigkeit) mit rotem Phosphor, welcher in der Hitze sehr dunkel, bei Zimmertemperatur leuchtend purpurrot aussieht. Beim Öffnen des abgekühlten Rohres merkt man, dass es auch farblosen Phosphor enthält".

STOCK and GOMOLKA cooled down slowly, but we found that the phenomenon became more distinct, when the capillary is cooled by exposure to the air. It is then seen that red solid substance deposits in the liquid, the vapour space and also the glass wall remaining perfectly colourless there on account of the fact that the liquid which deposits from the vapour, is perfectly colourless. At a given moment a violent phenomenon is observed in the capillary, while at the same moment very clearly a shock is felt. The liquid has disappeared, and the inner wall of the capillary is covered everywhere, also at the place where before the vapour was found, with a solid, red substance, containing rather great quantities of αP.

This phenomenon is explained by means of the following consi-

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[1]) Ber. 42, 4510 (1909).

[2]) The italics are ours.

deration. The second critical end-point q of the pseudo-system lies below the melting-point of the red phosphorus. If now the temperature of the capillary has fallen below this critical endpoint, the liquid has become strongly metastable, and hence at a given moment it will suddenly be converted to a fluid phase, from which solid red substance will be deposited, also there where before the colourless vapour was found.

That the solid substance formed in this way is not in internal equilibrium follows most clearly from this that on being rapidly heated it does not show the melting-point of red phosphorus, but melts at a lower temperature, e. g. at 583°. As will be shown in a following communication, this behaviour also admits of an easy interpretation, just as the phenomena observed by STOCK [1]) on sudden cooling of phosphorus vapour heated to different temperatures. These phenomena are not strange, on the contrary, they were to be expected in virtue of these considerations, and thus afford a not inconsiderable support to the theory.

An important question which remained to be answered, was this: *"can it be experimentally demonstrated that in contradiction to what was assumed up to now the vapour pressure line of molten white phosphorus and that of molten red phosphorus do not belong to the same curve?"* If the system phosphorus really belongs to the type ether-anthraquinone, the vapour pressure line of molten white phosphorus is *not* the prolongation of the vapour pressure line of molten red phosphorus.

To find this out the vapour tension of molten white phosphorus was determined up to the temperature of 338° by means of the manometer of JACKSON [2]), as has already been described by Messrs. SCHEFFER and TREUB [3]).

Further by the aid of a new apparatus, which will be described later, the vapour pressure line of molten red phosphorus was determined, in which it appeared that the triple point pressure of red phosporus amounts to almost 50 atmospheres. To answer the question proposed above the vapour tension, which the liquid white phosphorus would possess at the triple point temperature of the red phosphorus (610°), was calculated from the observations by the aid of the integrated relation:

$$lnp = -\frac{a}{RT} + \frac{b}{R} \log T + C$$

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[1]) Ber. **45**, 1514 (1912).

[2]) J. Chem. Soc. 99, 1066 (1911).

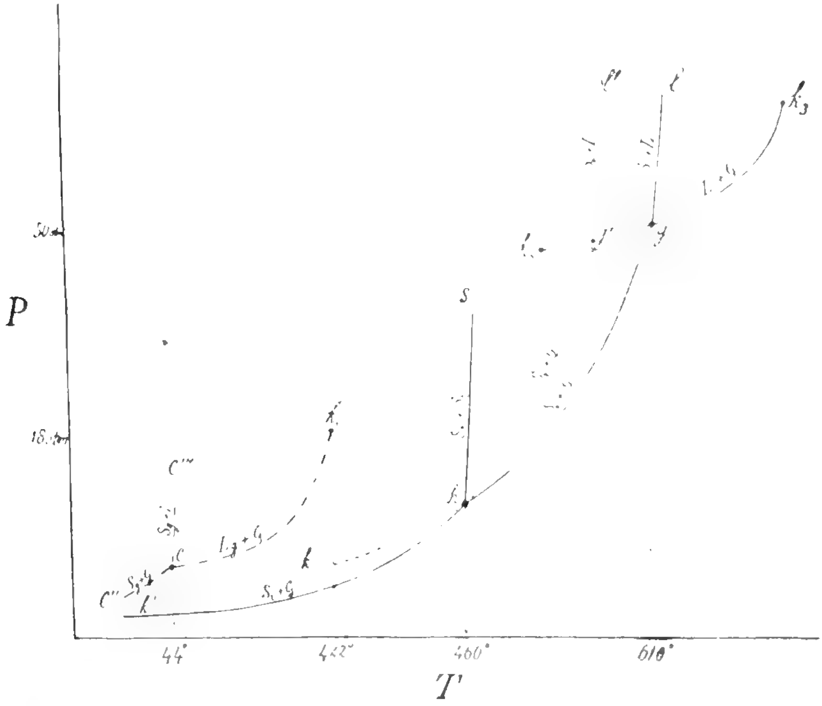
[3]) Verslag Kon. Akad. v. Wet. 25 Nov. 1911, 529.
Zeitschr. f. phys. chem. **81**, 308 (1912).

by putting $Q = a + bT$ in the formula

$$\frac{d \ln p}{dT} = \frac{Q}{RT^2}.$$

If we had to do with one and the same vapour pressure line, about 50 atm. would have to be found for that pressure.

If on the other hand the pseudo system exhibits the type *ether-anthraquinone*, and the vapour pressure line of the liquid white phosphorus possesses a critical point below 610°, the prolongation of that line above this critical temperature will of course have no physical significance, but if this prolongation points to a pressure *higher* than 50 atmospheres at 610° the question put above will be answered by this. The result of the extrapolation was that at 610° the pressure would amount to about 350 atmospheres. This result is so convincing that it shows the erroneousness of the earlier view with perfect certainty, so that it may be considered indisputable already now that the view about the type of the pseudo-system has been correct [1].



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[1] Also the system cyanogen has been investigated and conforms entirely to that of phosphorus. In the same way as for phosphorus we have succeeded in showing by means of experiments of solidification that we have to do with different kinds of molecules, which can be in equilibrium with each other in solid and liquid cyanogen.

We will conclude this communication with the schematic *PT*-figure of the phosphorus; the connection between the unary and the pseudo-binary system will be treated in a following publication.

When the calculated critical temperature 422° for liquid white phosphorus is correct about 18 atmospheres follows from the vapour pressure line for the critical pressure. The critical point is indicated by k_1, in the drawing. The vapour pressure line of molten red phosphorus exhibits probably a peculiarity that has never been met with as yet, viz. two critical points k_2 and k_3, the former of which is metastable.

It is of course also possible even probable that unmixing takes place in the pseudo-system between p and q, so in the metastable region. The point k_2 might, therefore, lie at even lower temperature and pressure than the point k_1. Possibly the continued investigation may give an indication with regard to this too.

It may finally be pointed out that when we apply VAN DER WAALS's equation,

$$log \frac{Pk}{p} = f\left(\frac{T_k}{T} - 1\right)$$

and write

$$log\, p = -\frac{fT_k}{T} + C$$

3,94 is found for the value of f.

This equation does not represent the observed vapour pressure line as well as the former, the cause of this may be that f is not constant as has been found indeed with several substances.

Anorg. Chem. Laboratory of the University.

Amsterdam, Nov. 29, 1912.

Mathematics. — *"On loci, congruences and focal systems deduced from a twisted cubic and a twisted biquadratic curve".* III.

By Prof. HENDRIK DE VRIES.

(Communicated in the meeting of November 30, 1912).

17. If we assume that the line l itself is a ray of the complex without however belonging to the congruence deduced from Ω^4, then the two surfaces Ω^{20} and Ω^4 undergo considerable modifications. The surface Ω^{20} has no lowering of order; instead of the regulus, namely, which is the locus of the rays s conjugated to the points of l we now have a quadratic cone (passing likewise through the cone

vertices) whose vertex P_l is the focus of l, because the two conjugated lines of l, which cross each other in general and exactly therefore generate a regulus, now both pass through P; but P_l does not lie on Ω^6, because l is a ray of the complex, but not of the congruence. A generatrix of the cone therefore intersects Ω^6, as formerly a line of the regulus, in six points, from which ensues that l now again is a sixfold line of the surface. And to a plane λ through l corresponds as formerly a twisted cubic through the cone vertices and which now passes moreover through P_l, because l is a tangent of the complex conic lying in λ, but which now again intersects Ω^6, except in the cone vertices, in fourteen points; thus in λ lie **14** generatrices of the surface, so that this is indeed of order $6 + 14 = 20$. The curve k^{12}, the section of the cone with Ω^6, has also 6 nodal points lying on k^3, so that Ω^{20} contains 6 nodal generatrices.

The nodal curve of Ω^{20} undergoes a very considerable modification as regards the points it has in common with l. Through such a point namely must go 2 generatrices of the surface lying with l in one plane; but now l is itself a ray of the complex and three rays of the complex can then only pass through one point when the complex cone of that point breaks up into two pencils; so the only points which the nodal curve can have in common with l are the points of intersection of l with the four tetrahedron faces.

These points which in § 15 we have called S_i coincide with the points which were called $T_i{}^*$ in the same §. Let us assume the plane lT_1. As now again and for the same reason as before nine of the fourteen generatrices of Ω^{20} lying in this plane pass through T_1 (§ 13) the five remaining ones must pass through another point $T_1{}^*$ lying in τ_1 and whose complex conic breaks up into τ_1 and the plane $T_1{}^*l$; now however this point coincides with S_1. For the complex cone of S_1 likewise breaks up into two pencils, of which one lies in τ_1, the second in a plane through $T_1{}^*$ and T_1; now however, to this second pencil evidently belongs our ray l and so indeed the complex cone of S_1 degenerates in this way into τ_1 and a plane through l; so S_1 and $T_1{}^*$ are identical. To S_1, regarded as a focus, a ray s through T_1 is conjugated which lies at the same time on the quadratic cone, thus in other words the ray $P_l\,T_1$; the latter intersects Ω^6 besides in T_1 in 5 more points and the rays s conjugated to these are the 5 generatrices of Ω^{20} through $S_1 = T_1{}^*$ lying in the plane lT_1; the sixth generatrix through this point conjugated to T_1 lies in τ_1, but not in the plane lT_1.

So we see that through S_1 pass five generatrices of Ω^{20} lying in the same plane; *so the four points S_i are* $\frac{1}{2} \,.\, 5 \,.\, 4 = 10$*-fold points* *for the nodal curve; this curve cannot have other points in common with l. So it cuts l in four tenfold points* (i. e. the **40** points of before have changed into four tenfold ones) *and so it is again of order* $40 + 91 = 131$.

Also the surface $\mathbf{\Omega}^4$ undergoes considerable modifications as the conic lying in a plane λ must now always touch the line l. The complex cone for a point P of l contains the ray l; the two tangential planes through l to the cone coincide therefore; from which ensues that for each point P of l the two conics passing through it, coincide. The most intuitive representation of this fact is obtained by imagining instead of the point of contact of a k^2 with l two points of intersection lying at infinitesimal distance; if then on l we assume three of such like points, then through 1 and 2 passes a conic and through 2 and 3 an other differing but slightly from it, so that really through point 2 pass two conics. *The loci of the conics is thus now again a* $\mathbf{\Omega}^4$ *with nodal line l, but this line has become a cuspidal edge,* i. e. whereas formerly an arbitrary plane intersected $\mathbf{\Omega}^4$ along a plane curve with a nodal point on l and only the planes through the four points S_i (§ 15) furnished curves with cusps, now every arbitrary plane of intersection contains a curve with a cusp on l (and with a cuspidal tangent in the plane of the conic through that cusp). Furthermore we must notice that as the points $T_i{}^*$ coincide with S_i, the four nodal points T_i will be found on the nodal line itself, thus forming in reality no more a tetrahedron proper; nevertheless the property of the simultaneous circumscription round about and in each other remains if one likes.

18. The curve of intersection of order eighty of $\mathbf{\Omega}^4$ and $\mathbf{\Omega}^{20}$ is again easy to indicate; it consists of the line l counted twelve times (for a cuspidal edge remains a nodal edge), and of a curve of contact of order 34 to be counted double (§ 15) which has with a plane λ through l fourteen points lying outside l in common and therefore twenty lying on l; these last however can be no others than the four points S_i, for otherwise a generatrix of $\mathbf{\Omega}^{20}$ would have to touch a k^2 of $\mathbf{\Omega}^4$ on l, which could only be possible (as l itself touches k^2) if a generatrix of $\mathbf{\Omega}^{20}$ could coincide with l which is as we know not possible. The curve of contact of $\mathbf{\Omega}^4$ and $\mathbf{\Omega}^{20}$ passes thus five times through each of the four points S_i which corresponds to the fact that five generatrices of $\mathbf{\Omega}^{20}$ touch in S_i, the degenerated conic (viz. the pair of points S_i, T_i) lying in the plane lT_i.

The method indicated in § 14 to determine the number of torsal lines of the first kind undergoes no modification whatever; we can however control this method here because we have to deal here with a cone instead of a regulus. The first polar surface of P_l namely with respect to Ω^6 is a Ω^5 containing k^3 one time, and therefore cutting Ω^6 along k^3 counted twice and a residual curve of order 24, so that the circumscribed cone at the vertex P_l is of order 24. Now this cone cuts the quadratic cone $[P_l]$ in 48 edges, so 48 edges of $[P_l]$ touch Ω^6 and therefore k^{12}. The number of torsal lines of the first kind is thus indeed 48, and that this same number must now be found in general follows from the law of the permanency of the number.

These numbers 6 and 48, as well as the number of points (namely 40) which the nodal curve of Ω^{20} has in common with l can be controlled with the aid of the symmetrical correspondence of order 70 existing between the planes λ through l (§ 16). To the 140 double planes σ belong, as we saw before, the planes through l and the nodal lines and those through l and the torsal lines of the first kind, together appearing there at a number of 54, but representing 60 double planes. The nodal curve of Ω^{20} has with l only the 4 points S_i in common which however count for 10 each and which have the property that five of the six generatrices through each of those points lie in one plane; such a plane is thus undoubtedly a manyfold plane of the correspondence, the question is only how many single double planes it contains. Now there lie in the plane lT_1, e.g. 9 generatrices through T_1 cutting l in different points; through each of the last pass five other generatrices, and so we find so far 45 planes conjugated to the plane lT_1.

Now we have moreover the plane through l and the 6th generatrix through S_1 (lying in τ_1); however by regarding, just as we have done at the beginning of § 16, a plane λ in the immediate vicinity of lT_1 and in which thus five generatrices cut each other nearly in one point of l we can easily convince ourselves that this plane counts for 5 coinciding planes conjugated to lT_1. To lT_1 are conjugated $45+5=50$ planes *not* coinciding with lT_1 and thus 20 planes coinciding with lT_1; i. e. just as in the general case a plane λ through two generatrices cutting each other on l counts for two double planes, so here each plane lT_i containing five such generatrices counts for 5×4 double planes; so the four planes lT_i represent 80 double planes, and they furnish with the 60 already found the 140 double planes as they ought to.

As by the transition to a ray of the complex all numbers have remained unchanged, the surface Ω^{20} contains now again 58 torsal lines of the 2nd kind; the $4 \times 131 = 524$ points of intersection of Ω^4 with the nodal curve of Ω^{20} lie now however a little differently. The points T_i remain 36-fold for the nodal curve and they therefore furnish $4 \times 72 =$ **288** points of intersection, the 58 torsal lines of the 2nd kind give **58**, the 6 nodal edges give $3 \times 6 =$ **18** other ones; the 4 points $S_i = T_i^*$ however absorb each of them 40 points of intersection. Let us namely imagine our figure variable and in particular l continuously passing into a complex ray, we then see how the 4 points T_i^* tend more and more to S_i, but at the same time how the 40 points of intersection of l with the nodal curve group themselves more and more into 4 groups of 10 in such a way that each group is as it were attracted by one of the points S_i; now each of those 40 points counts for 2, each point T_i^* for 20 points of those we looked for; so on the moment that T_i^* as well as the 10 points of the corresponding group coincide with S_i this point counts for 40, so the four together for **160** and the sum of the four numbers printed in heavy type is again 524.

19. More considerable are the modifications if finally we now assume that l becomes a ray of the congruence; nothing is to be noticed at Ω^4, as l remains a ray of the complex, but the other locus becomes a surface Ω^{18}, for which l is only a fivefold line. The regulus of before is namely now again replaced by a cone $[P_l]$, but the vertex itself P_l now lies on Ω^6, because l is a ray of the congruence, thus itself a generatrix. It even appears twice as a generatrix; for the cone cuts Ω^6 according to a k^{12} which has now a. o. also a nodal point in P_l and to this nodal point the line l corresponds twice. A generatrix of the cone $[P_l]$ cuts Ω^6 in P_l and in five other points; so through the corresponding focus on l pass five generatrices not coinciding with l, i. e. *l is a fivefold line.*

To a plane λ through l a twisted cubic is conjugated containing the four vertices of the cones and P_l and cutting Ω^6 in 13 points more; so in a plane λ lie besides l 13 generatrices, i. e. *our surface is a Ω^{18} of order 18 with a fivefold line l.*

Among the generatrices of the cone $[P_l]$ there are two touching k^{12} in P_l and likewise among the twisted cubics; the foci of the former are the points of intersection proper of l with two generatrices coinciding with l, the planes conjugated to the latter being the connecting planes; thus two particular torsal planes and pinch points (see § 20).

The line $P_l T_i$ is a generatrix of the cone $[P_l]$ and it cuts Ω^6 besides in these two points in four more; the corresponding four rays s pass through $S_i = T_i^*$ and lie in the plane $l T_i$ whilst the ray s conjugated to T_i lies in τ_i, but not in $l\,T_i$; so the points S_i are $\frac{1}{2}\,.\,4.3 = 6$-fold points for the nodal curve and others this curve can evidently not have in common with l. So it has 24 points united in 4 sixfold points in common with l, and as there are in a plane ε through l $\frac{1}{2}\,.\,13.12 = 78$ points not lying on l *the order of the nodal curve now amounts to* $24 + 78 = 102$. The number of nodal points of a plane section of Ω^{18} amounts thus now to $102 + 6 + 10 = 118$, and from this ensues for the class $18.17 - 2.118 = 70 = \varepsilon_1\beta$; the formula $\varepsilon\sigma = 2\,.\,\varepsilon_1\beta - 2\,.\,\varepsilon g$ furnishes therefore $\varepsilon\sigma = 2\,.\,70 - 2\,.\,18 = 104$ torsal lines of both kinds.

The formula

$$\varepsilon = p + q - g$$

now again applied to determine the number of generatrices of the cone $[P]$ touching k^{12} and thus of the number of torsal lines of the first kind gives the following results. The plane of the condition p cuts k^{12} in 12 points; through each of these passes a generatrix of the cone cutting Ω^6 besides in P_l in four points more; so the number p is equal to 48, a and likewise q. The line of the condition g cuts the cone in two points and through each of these passes a generatrix of that cone, on which lie besides P_l five points of k^{12}; so g is $= 2.20$, and thus $\varepsilon = 2.48 - 2.20 = 56$. Among these however are included the six nodal lines counted twice; *the number of torsal lines of the first kind amounts thus to* $56 - 2 \times 6 = 44$.

To control this we again consider the first polar surface of P_l with respect to Ω^6, a Ω^5 touching Ω^6 in P_l and passing through k^3. The intersection with Ω^6 consists therefore of k^3 counted twice and a residual curve of order $30 - 2.3 = 24$ which however is projected out of P_l by a cone of order 22 only, because P_l itself is a nodal point of that curve (for Ω^6 and Ω^5 touch each other in P_l); this cone has with the cone $[P_l]$ 44 generatrices in common, and these touch k^{12}.

The number of torsal lines of the 2^nd^ *kind of* Ω^{18} *amounts to* $104 - 6 - 44 = 54$.

The correspondence of the planes λ through l is now of order 52 with 104 double planes. For, in a plane λ lie besides l thirteen generatrices of Ω^{18} and through each of the 13 points in which these cut l four others pass; so to each plane λ $4 \times 13 = 52$ others are conjugated. The double planes are 1. the planes through the 44 torsal lines of the first kind; 2. the planes through the 6 nodal edges, each counted twice; 3. the 4 planes $l\,T_i$ each counted twelve times, because in each such like plane 4 generatrices pass through the point S_i (comp. § 18); so we find $44 + 2.6 + 4.12 = 104$ double planes.

And as regards finally the number of $4 \times 102 = 408$ points of intersection of the nodal curve with Ω^4, in the four points T_i lie again 288 (comp. § 18), in the pinch points of the torsal lines of the second kind 54, in those of the six nodal edges 18 and in the four points S_i, which are sixfold for the nodal curve, 48, together $288 + 54 + 18 + 48 = 408$.

20. The two particular pinch points on l which we have found in the preceding § were the two foci of the ray of the congruence l and the two torsal planes the two focal planes; for, in these points l was cut by a ray of the congruence at infinitesimal distance. If henceforth with a slight modification in the notation the line l is called s_0, the focus P_0, then P_0 lies on Ω^6 and it is in general an ordinary point of this surface. Let us assume the tangential plane in this point and in it an arbitrary line t through P_0; then this has two conjugated lines crossing each other, and if therefore a point P describes the line t, the ray s of the complex conjugated to P will generate a regulus to which also belongs our ray s_0, a ray of the congruence. As however t is a tangent of Ω^6, a second generatrix of the regulus lying at infinitesimal distance from s_0 will belong to the congruence, however without cutting s_0. If however, we now imagine the complex cone at point P_0 and if we intersect it by the tangential plane, we find two lines t which are at the same time lines s, viz. rays of the complex, and whose two conjugated lines cut each other. Now the lines s conjugated to the points P of t will describe two cones containing also s_0, and having their vertices on s_0 whilst we know out of our former considerations that these vertices are nothing but the foci of the two rays t; and now s_0 will be cut in each of these foci by a ray of the congruence at infinitesimal distance; the two cone vertices are thus the foci of s_0. So: *we find the foci of a ray s_0 of the congruence by determining the focus P_0 (lying on Ω) of s_0, by intersecting the complex cone of this point by the tangential plane in P_0 to Ω^6, and by taking the foci of the two lines of intersection t. And the two focal planes are the tangential planes through s_0 to the complex cones of the foci.*

If P_0 is a point of the nodal curve k^3 of Ω^6 then s_0 is a double ray of the congruence (§ 12); the complex cone of P_0 intersects the two tangential planes of P_0 in twice two rays t, so that we now have on s_0 two pairs of foci and through s_0 two pairs of focal planes; and as the focal surface of the congruence is touched by each ray of the congruence in the two foci, so each double ray will touch the focal surface four times. The four tangential planes are the focal planes, however in such a way that if one pair of foci is called F_1, F_2 the focal plane of F_1 is tangential plane in F_2 and reversely.

Let P_0 be a point of k^4, lying as a single curve on Ω^6; then s_0 is the tangent to k^4 in P_0 and it belongs to the congruence. The complex cone of P_0 intersects the tangential plane in this point to Ω^6 according to s_0 itself and an other generatrix; so of the two foci of s_0 point P_0 is one whilst the other is the focus of the second generatrix of the complex cone of P_0 lying in the tangential plane; and of the two focal planes the osculation plane of k^4 in P_0 is one, because this really contains two rays of the congruence intersecting each other in P_0 and lying at infinitesimal distance (viz. two tangents of k^4); so it touches the focal surface in the other focus, i. e. the surface of tangents of k^4 which is of order 8 envelops the focal surface, and the curve k^4 itself lies on the focal surface.

The question how the cone vertices T_i bear themselves with respect to the congruence, is already answered in § 11; Ω^6 intersects the plane τ_i according to a plane k^6 and the rays s conjugated to these form a cone of order 9 with the vertex T_i and with three nodal edges and three fourfold edges, the latter of which coincide with the three tetrahedron edges through T_i.

Let us assume an arbitrary point P of k^6, then to this a ray s through T_i is conjugated; now the complex cone of P degenerates into a pair of planes, of which τ_i is one component, whilst the other passes through T_i, and this degenerated cone cuts the tangential plane in P to Ω^6 along the tangent t in P to k^6 and according to an other line t^* through P. To that tangent the point T_i is conjugated as focus, so that for each ray of the congruence through T_i this point itself is one of the foci, the other being the focus of the line t^*.

In order to find the focal plane of the considered ray s in the point T_i we should have to know according to the preceding the complex cone of T_i which is in first instance entirely indefinite; let us however bear in mind that in the general case that complex cone is at the same time the locus of the ray s conjugated to the points of the tangent t; then in this case also we can have a definite cone, viz. the cone which replaces the regulus if the line l passes into a complex ray s, and which contains in general the four cone vertices and which will contain here, where T_i itself is the cone vertex, the three tetrahedron edges through this point. On this cone lie the two rays s conjugated to the two points of k^6 lying at infinitesimal distance from each other on t, and the plane through these is the focal plane of our ray s in T_i; but those edges of the quadratic complex cone lying at infinitesimal distance lie of course also on the cone of order 9 (see above); so we can say more briefly that for each ray of this cone T_i is one of the foci and the tangential plane to the cone is one of the focal planes.

Each ray of the congruence through T_i, so each generatrix of the cone of order nine with this point as vertex, must have in P_i two coinciding points in common with the focal surface; so T_i is for the focal surface a manifold point, however without the cone of order 9 being the cone of contact; for the tangential planes of this cone touch the focal surface in the foci of its generatrices *not* coinciding with T_i; the cone of contact in T_i is enveloped by the focal planes of this last category of foci.

21. Over against the question which complex rays through T_i belong to the congruence, is the other one which complex rays out of τ_i belong to the congruence. In the preceding we have repeatedly come across these rays. Indeed, any surface Ω^{20} formed by the congruence rays which cut a line l or a complex ray s, and any surface Ω^{18} formed by the congruence rays which cut a congruence ray s contained such a ray as we proved above; we shall now show that all these rays form a pencil. To that end we imagine the tangential plane ϱ in T_i to Ω^6 and we cut it according to the line r by τ_i. We now saw in the preceding that the rays s conjugated to the points of τ_i form a quadratic cone with T_i as vertex and containing the three tetrahedron edges through T_i; if the base curve of this cone lying in τ_i is k^2, then reversely the points of k^2 are the foci of the rays s lying in ϱ and passing through T_i, for the rays s conjugated to the points of a line pass through the focus of that line and the ray s conjugated to a point of τ_i passes moreover through T_i.

If a point P describes one of the rays of the pencil $[T_i]$ lying in ϱ, say s_0, then the rays s conjugated to the points P form the complex cone of the focus P_0 of s_0, which point lies on k^2; this complex cone breaks up however into a pair of planes, viz τ_i and a plane through P_0 and T_i, and the line of intersection t_i of these two planes is the ray of the congruence conjugated to T_i, in as far as this point is regarded as a point of the ray s_0; so the question is how the rays t_i bear themselves when s_0 describes the pencil $[T_i]$ or, what comes to the same, how the planes $T_i t_i$ bear themselves in those circumstances. We shall try to find how many of those planes through an arbitrary ray s_1 pass through T_i. In each arbitrary plane through s_1 the complex conic breaks up into two pencils; one has the vertex T_i, the other a point T_i^* lying in τ_i.

In each plane through s_1 lies however one such point T_i^*; but if S_1 is the point of intersection of s_1 with τ_i, then also the complex cone of S_1 breaks up into a pair of planes of which one component is of course again τ_i, the other being a plane through $S_i T_i$; so S_1 is itself a point T_i^*, and the consequence of this is that T_i^* describes a conic k^{*2} which passes in the first place through S_1 and in the second place, as is easy to see, through the three cone vertices lying in τ_i; for if a plane through s_1 passes also through a second vertex, then the complex conic breaks up into the two pencils at T_i and at that second cone vertex.

All rays through a point T_i^* of k^{*2} cutting s_1 are according to the preceding rays of the complex; from this ensues reversely that the complex cones of all points of s_1 in τ_i have the same base curve, namely k^{*2}. If now the degenerated complex cone of a point of k^2 is to pass through s_1, then that point must evidently lie also on k^{*2} and of such points there exists apart from the three cone vertices lying in τ_i, only one; in the pencil $[T_i]$ there is thus only one ray for which the (degenerated) complex cone of its focus passes through an indicated ray s_1, i. e. the second components of the complex cones of the foci of the rays of the pencil $[T_i]$ form a pencil of planes, or *the rays of* τ_i *belonging to the congruence form a pencil.*

The axis a of the pencil of planes must of necessity cut the curve k^2; for, if this were not so, then an arbitrary plane through a would cut k^2 in two points, and then the complex curve in that plane would break up into three pencils (among which one at T_i is always included) instead of into two. This objection does not exist when a cuts the curve k^2 in a point A; for then each plane through a cuts k^2 besides in A in only one point T_i^* more, and A itself is a point T_i^* for the plane through a which touches k^2. *The axis a is simply that line which has the property that the complex cones of its points have as common base curve the conic k^2 itself:* for, for each plane through a the point T_i lying on k^2 must lie at the same time on k^{*2}, so k^2 and k^{*2} coincide.

For each ray of the pencil $[A]$ lying in τ_i point A is evidently one focus and τ_i the corresponding focal plane, for each ray is cut in A by an adjacent one of the pencil; the other focus is the second point of intersection T_i^* with k^2 and here the second focal plane passes through T_i. *The focal surface must therefore touch* τ_i *along the conic k^2; the point A itself is however a singular point, for here any plane through a is a tangential plane.*

For the tangent in A to k^2 the two foci coincide evidently with

A: the focal planes, however, do not coincide, for one is τ_1 and the other connects the tangent to T_1.

22. Order and class of the focal surface can be immediately determined by means of two dualistically opposite equations of SCHUBERT, viz.

$$\varepsilon\sigma p^2 = \sigma p g_e + \sigma p h_e - \sigma\widehat{pe}.$$

and

$$\varepsilon\sigma e^2 = \sigma e g_p + \sigma e h_p - \sigma\widehat{pe}\ ^{1}).$$

We conjugate to each ray g of the congruence all other rays as rays h, we then obtain a set of ∞^4 pairs of rays and we can apply to these the two equations just quoted. The symbol σ indicates that the two rays of a pair must intersect each other, ε that they lie at infinitesimal distance and p^2 that the point of intersection p must lie in two planes at a time, thus on an indicated line; so $\varepsilon\sigma p^2$ is evidently the order of the focal surface. The condition $\sigma p g_e$ indicates the number of pairs which cut each other, whilst the point of intersection p lies in a given plane and the ray g likewise in a given plane; now there lie in a given plane **14** rays of our congruence, thus **14** rays g; each of these intersects the plane of the condition p in one point and through each of these pass 5 more rays of the congruence; $\sigma p g_e$ is therefore $14 \times 5 = 70$, and $\sigma p h_e$ means the same and is thus likewise $= 70$.

With $\sigma\widehat{pe}$ we must pay more attention to the point of intersection of the two rays and to the connecting plane than to the rays themselves; $\sigma\widehat{pe}$ indicates namely the number of pairs of rays which cut each other and where the point of intersection lies on a given line and at the same time the connecting plane passes through that line; this number is evidently the third of the three characteristics of the congruence, thus the rank, however multiplied by 2 because each pair of rays of the congruence represents 2 pairs gh; so $\sigma\widehat{pe}$ is $= 80$, *so that the order of the focal surface is equal to* $70 + 70 - 80 = 60$.

$\varepsilon\sigma e^2$ indicates the number of pairs of rays at infinitesimal distance whose connecting plane passes through 2 given points, so through a given line, i. e. the class of the focal surface. Now $\sigma e g_p$ indicates the number of pairs of rays whose connecting plane passes through a given point, whilst also the ray g passes through a given point. So there are 6 rays g and in the plane through one of those rays and the point of the condition e lie besides g still 13 others; $\sigma e g_p$

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[1]) SCHUBERT l. c. page 62.

and $\sigma e h_p$ are thus each = 6 × 13 = 78, and $\sigma p e$ was 80, so the class of the focal surface = 78 + 78 − 80 = 76.

I may be permitted to point out in passing a slight inaccuracy committed by SCHUBERT on page 64 of his "Kalkül" where he gives formulae for order and class of the focal surface of a congruence taking the number $\widehat{\sigma p e}$, called by him c, only once into account: in PASCAL-SCHEPP's well known "Repertorium" vol. II, page 407 we find indicated the exact formulae, with the rank number r counted twice.

In a congruence of rays appear in general ∞^1 rays whose two foci coincide: these too are easy to trace in our congruence. For, according to § 20 in order to find the foci of an arbitrary ray s_0 we must apply in the focus P_0 the complex cone and the tangential plane to Ω^6 and intersect these by each other: the foci of the lines of intersection are the foci of s_0 and the tangential planes through s_0 to the complex cones of the foci the focal planes. So as soon as the complex cone of P_0 touches the tangential plane Ω^6 along a line t, the two foci of s_0 will coincide in the focus of t and the focal planes will coincide in the tangential plane through s_0 to the complex cone of the only focus.

The points P_0 whose complex cones touch Ω^6 are to be found again with the aid of SCHUBERT's "Kalkül". We conjugate the two rays s, along which the complex cone of a point P_0 of Ω^6 cuts the tangential plane in that point, to each other; so we obtain in that manner a set of ∞^2 pairs of rays and we apply to it the formula:

$$\varepsilon \sigma p = \sigma g_e + \sigma h_e + \sigma p^2 - \sigma p e \; {}^{1)};$$

The left member namely indicates the number of coincidences whose points of intersection lie in a given plane, that is thus evidently the order of the curve which is the locus of the points P_0 to be found. σg_e indicates the number of pairs of rays whose component g lies in a given plane; this plane cuts out of Ω^6 a plane curve k^6 which possesses no other singularities than three nodes and which is so of class 6 . 5 — 2 . 3 = 24, and all the complex rays in this plane envelop a conic; so there lie 48 complex rays g in this plane touching Ω^6. If we apply in one of the points of contact the tangential plane to Ω^6, then there lies in it one ray h: so σg_e is 48 and likewise of course σh_e.

With σp^2 we must trace the number of pairs of rays whose points of intersection lie in two given planes at the same time, thus on a given line; this line intersects Ω^6 in six points and in the tangential

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1) SCHUBERT l. c. page 62.

plane lie two rays of the complex cone and thus also two pairs gh, because each of the two rays can be either g or h; so $\sigma p^2 = 12$. For $\sigma p e$ finally the point of contact must lie in a given plane, the tangential plane must pass through a given point; so we can either apply the tangential planes in the points of a plane section of Ω^6 and determine the class of the developable enveloped by it, or we can construct the circumscribed cone and calculate the order of the curve of contact. The latter is the simplest; for the curve of contact is the intersection of Ω^6 with the first polar surface of the vertex of the cone and therefore of order $6 . 5 - 2 . 3 = 24$, because the first polar surface contains the nodal curve k^3 and the latter counted twice separates itself from it. But the two complex rays through the point of contact and in the tangential plane count again for two pairs and so $\sigma p e = 48$, from which ensues $\varepsilon \sigma p = 48 + 48 + 12 - 48 = 60$: *so there lies on Ω^6 a certain curve k^{60} of order 60 having the property that the rays s conjugated to its points have coinciding foci and focal planes.*

We can ask how the curve k^{60} will bear itself with respect to the four cone vertices T_i, where the complex cone becomes indefinite. We now know however out of § 21 that in the plane τ_i only one ray with coinciding foci lies, viz. the tangent in A to k^2; *so k^{60} will pass once through the four cone vertices.* That for that tangent in A to k^2 the two focal planes do not coincide, is an accidental circumstance, which is further of no more inportance; this result was based namely on the supposition that through an edge of the cone passes only one tangential plane of that cone; however, for the point A the complex cone breaks up into a pair of planes whose line of intersection is just the tangent in A to k^2, the tangential plane through that line to the cone is thus in first instance indefinite.

The rays of the congruence with coinciding foci determine a scroll of which we will finally determine the order. To that end the scroll must be intersected by an arbitrary line and we now know that all rays of the congruence meeting a line l form a regulus Ω^{20} and that the foci of those rays are situated on a curve k^{12} lying on Ω^6 and passing singly through the 4 cone vertices. It is clear that to a point of intersection of k^{12} and k^{60} a ray corresponds with coinciding foci and cutting l, with the exception of the cone vertices; for, to T_i is conjugated as regards k^{60} the tangent in A to k^2, on the other hand as regards k^{12} the connecting line of the point of intersection of l and τ_i with A, as we now know. Now k^{12} is, as we know, the complete intersection of Ω^{20} with a regulus; *so* the complete number of points of intersection of k^{12} and k^{60} amounts to 120. If we set apart from these the four cone vertices, we then find as result that *the rays of the congruence with coinciding foci form a regulus of order* 116. The curve k^{60} intersects τ_i besides in the three cone vertices lying in this plane in 57 points more, lying of course on the section k^6 of Ω^6 and τ_i; to each of these points a ray through T_i is conjugated with coinciding foci; *the* 4 *cone vertices are thus for the surface* Ω^{116} *57-fold points.*

Physics. — *"Some remarkable relations, either accurate or approximative, for different substances."* By Prof. J. D. VAN DER WAALS.

(Communicated in the meeting of November 30, 1912).

In a previous communication (June 1910 These Proc. XIX p. 113 I pointed out the perfectly accurate or approximative equality of the ratio of the limiting liquid density to the critical density, and the ratio of the critical density to that which would be present for T_{cr}, p_{cr} and v_{cr}, if $\frac{pv}{RT}$ should always be equal to 1. With the symbols used there

$$2(1+\gamma) = \varphi s$$

I have added the factor φ, which must then be equal to 1 or must differ little from 1.

The rule given there has attracted some attention. For first of all Dr. JEAN TIMMERMANS has informed me that he has found this rule entirely confirmed for six substances, for which the observations made were perfectly trustworthy. For a seventh substance there was a great difference, but he thought that for this real association might perhaps occur, as is the case for acetic acid [1]. Besides this rule has also been adopted by KAMERLINGH ONNES and KEESOM in their recent work for the Encyklopädie: Die Zustandsgleichung. The rule is indeed apt to rouse some astonishment, because it pronounces the equality between two quantities, which, at least at the first glance, have nothing in common.

It is to be expected that this approximative equality will have to be explained by the way in which the quantity b varies with v; but it is seen at the same time that perfect equality cannot be put

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[1] The numerical values have been communicated in the "Scientific Proceedings of the Royal Dublin Society", October 1912.

generally. There is, indeed, a remarkable difference for invariable molecules, i.e. for such for which the quantity b does not change. Then the quantity $s = \frac{8}{3}$ and $\frac{v_k}{b} = \frac{v_k}{v_{lim}} = 3$. In this case φ is not 1, but $\frac{9}{8}$. If there exists a rectilinear diameter for substances with such molecules, $\gamma = \frac{1}{2}$.

Perfect equality or almost perfect equality can therefore, only be expected for substances for which b greatly varies with the volume. Thus for substances for which s is about equal to 3.77, the value of γ is about equal to 0.8 or 0.9. The following remarks are the result of my investigation to get more certainty about this question.

According to the formula:

$$2(1+\gamma) = \frac{v_k}{v_{lim}} = \varphi s$$

is

$$r\frac{b_g}{b_{lim}} = \varphi s$$

or

$$\frac{b_g}{b_{lim}} = \varphi\frac{s}{r} = \varphi\frac{s^2}{sr} = \varphi\frac{64}{27}\frac{(f-1)}{sr}$$

or

$$\frac{b_g}{b_{lim}} = \frac{f-1}{3}\left(\frac{8}{9}\frac{8}{sr}\varphi\right).$$

Now the thought has forced itself upon me to put $\frac{8}{9}\frac{8}{sr}\varphi = 1$ and hence also

$$\frac{b_g}{b_{lim}} = \frac{f-1}{3}.$$

The relation $\frac{8}{9}\frac{8}{sr}\varphi = 1$, or $\varphi = \frac{9}{8}\frac{rs}{8}$ is satisfied for substances for which b is constant. Then $rs = 8$, and as we saw above $\varphi = \frac{9}{8}$. For substances with variable value of 8, $rs < 8$ and φ decreases, but comparatively slowly. Not before $rs = 7\frac{1}{9}$, φ would be $= 1$, and for substances for which rs has this value, the rule

$$2(1+\gamma) = s$$

would be perfectly accurate. If $rs > 7\frac{1}{9}$, $2(1+\gamma) > s$, and not before $rs < 7\frac{1}{9}$, $2(1+\gamma) < s$.

The rule at which we arrive when we put $q = \frac{9}{8}\frac{rs}{8}$, viz.

$$\frac{b_g}{b_{lim}} = \frac{f-1}{3}$$

is satisfied for substances for which b is invariable. Then of course $\frac{b_g}{b_{lim}} = 1$ and $f = 4$ or $\frac{f-1}{3} = 1$. For all other substances $f > 4$, and $\frac{f-1}{3} > 1$; the first member of the equation, viz $\frac{b_g}{b_{lim}}$ is then, of course, also always greater than 1. Later on we shall set ourselves the task to inquire into the theoretical reason for this relation. But for the present we shall accept it as perfectly accurate, and see to what conclusions it leads. If we write $\frac{27}{64}s^2$ for $f-1$, we get:

$$\frac{b_g}{b_{lim}} = \frac{9}{64}s^2 = \left(\frac{3}{8}s\right)^2$$

The value of s can, therefore, not be smaller than $\frac{8}{3}$. For $\frac{b_g}{b_{lim}} = 2$, and so for $f = 7$, $s = \frac{8}{3}\sqrt{2} = 3{,}77$; a value which moreover already follows from the equaliy $\frac{s^2}{f-1} = \frac{64}{27}$ put above. For $\frac{b_g}{b_{lim}} = 3$, to which $f = 10$ would belong, s would be $= \frac{8}{3}\sqrt{3}$, or $s = 4{,}62$. But so high a value of f or s has only seldom been found. If before in the absence of a leading idea, I assumed a still greater ratio for $\frac{b_g}{b_{lim}}$, this was a mistake.

From:

$$\frac{b_g}{b_{lim}} = \frac{9s^2}{64}$$

follows

$$r\frac{b_g}{b_{lim}} = \frac{v_k}{v_{lim}} = \frac{9}{8}\left(\frac{sr}{8}\right)s = \frac{\varrho_{lim}}{\varrho_k} = 2(1+\gamma)$$

Of course we find back the rule from which we have started but with a determined value for the factor q. As I showed before

$sr < 8$, but for by far the majority of the closely investigated substances $(sr > 7\frac{1}{9}$. For them $\frac{2(1+\gamma)}{s}$ must be > 1. But the possibility of $\frac{2(1+\gamma)}{s} < 1$ is not excluded even for normal substances. Yet we should not lose sight of the fact that it has not yet been investigated in how far the existence of quasi-association has influence on the rule of the rectilinear diameter. A close investigation about the value of rs for different substances, and comparison of the value of γ following from this with the experimental data is, therefore, very desirable.

If from the knowledge of the value of $\frac{b_g}{b_{lim}}$ we want to determine the value of r, the given relations are not sufficient for an *accurate* determination. The relation

$$\frac{b_g}{b_{lim}} = \frac{9}{r^2}\left(\frac{sr}{8}\right)^2$$

or

$$\frac{b_g}{b_{lim}} = \frac{9}{r^2}\left[\frac{(f-1)r^2}{27}\right].$$

indeed, holds. As, however, the value of the factor of $\frac{9}{r^2}$ is not accurately known, and as we only know that this factor is smaller than 1, and the smaller as $\frac{b_g}{b_{lim}}$ is greater, we can only give a value for r below which it must remain. Thus for $\frac{b_g}{b_{lim}} = 2$ the value of r is below $\frac{3}{\sqrt{2}} = 2{,}12$. Already with the formula $\frac{8}{rs} < 1$, or $r < \frac{8}{s}$, or $r < \frac{8}{s}$ we arrive at the given value for r. If we, namely, put $s = \frac{8}{3}\sqrt{\frac{b_g}{b_{lim}}}$

$$r < \frac{3}{\sqrt{\frac{b_g}{b_{lim}}}}.$$

Only in the case that b is invariable, the sign $<$ must be replaced by the sign $=$. But even for such a great variability of b that the value of rs would have decreased to $7\frac{1}{9}$, r would still amount to the $\frac{8}{9}$ part of the value calculated according to the above formula. It is, indeed, very remarkable that already with such slight variability of b as will be the case for $\frac{b_g}{b_{lim}} = 2$, $\frac{V_{cr}}{V_{lim}}$ diminished so greatly that the value changes from 3 to about 2; whereas $\frac{b_{cr}}{b_g}$ only decreases to about 0.95 or 0.96, as I calculated before.

Let us now proceed to inquire whether a theoretical reason can be given for the above mentioned relations. That though they may possibly not be quite rigorously accurate, they will hold with a high degree of approximation, cannot be denied.

That b varies with v I have had to admit immediately when I tested the equation of state given by me by the observations of ANDREWS, in which even volumes occur which are smaller than b_g. And I have long been of opinion that this diminution of b with smaller volume does not mean a real diminution of the molecule, but that this diminution of b would only be an *apparent diminution*. I have tried to subject the hypothesis of an apparent diminution to the calculation by what I have called the overlapping of the distance spheres. Then the factor 4 in the expression $b = 4$ times the volume of the molecules diminishes. The value of $\frac{b}{b_g}$ has then the form of a series according to ascending powers of $\frac{b_g}{v}$, and I have at least brought the factor of the 1st power, and also that of the 2nd power in a formula, which, however, required such laborious and lengthy calculations for the second power that I abandoned them hopeless. VAN LAAR has carried out the computations, and calculated the value of the coefficient belonging to the 2nd power, and expressed the opinion that the series would consist of as many as some 20 terms. Afterwards BOLTZMANN has supplemented the calculations, and shown that the value of $\frac{b}{b_g}$ would have the form of a quotient with series of terms with ascending powers of $\frac{b_g}{v}$. More and more the conviction took hold of me that this apparent diminution does not exist. I have not yet obtained perfect certainty that it does not exist. But already before by the application of the form of $\frac{b}{b_g}$ with not too great a degree of density, in which some three terms will suffice, I have repeatedly found that the calculated coefficients are much too great. To this comes that the coefficients thus calculated must be of the same value for all substances, at least if a spherical shape is assigned to all of them. Attempts to determine them when the shape deviates from the spherical form have not yet been tried by anybody, but it may be expected that they will not differ much from those that have been calculated for the spherical shape. A contribution of importance for the decision of the question whether or no apparent-diminution exists will be furnished by the experimental determination of the equation of state of a monatomic substance. If we should have to conclude to diminution of b with decreasing value of v also for these substances, this diminution of b will certainly have to be called a quasi-diminution, unless one would assign a constitution for which real diminution is possible also to an atom.

A second view of the cause of the diminution of b with v would of course be obtained if one should have to ascribe compressibility to a molecule, and if one did not explain this compressibility by a diminution in size of the atoms, but by their coming closer together. If this is to be the cause, the diminution of b must not be found for a monatomic molecule. To decide this it would be desirable to give so considerable and judicious an extension to the investigations for such substances as those of ANDREWS for carbonic acid.

That a molecule consisting of atoms might be compressible in consequence of the approach of the atoms seemed a hypothesis to me worth investigating. And I carried this out in my communications in 1901 published in these proceedings. I arrived at a formula there, which may be considered as the equation of state of a molecule consisting of two or three separate parts which are in thermal motion. These separate parts may be separate atoms or separate atom groups, which are in close relation at the temperature considered, and of which the component atoms are perhaps in vibration with almost vanishing amplitude and small period.

This formula has the following form:

$$\left\} p + \frac{a}{v^2} + \alpha (b - b_0) \right\{ (b - b_0) = kRT.$$

In this formula b is the volume of the molecules, b_0 the volume of the atoms or atom groups, and the latter would be the volume of the atoms or atom groups when the molecule was compressed as much as possible. The quantity k is equal to $^2/_3$ for a molecule composed of two separate parts, and equal to 1 or $<$ 1 according to the nature of the motion for a molecule consisting of three parts.

I have represented the attraction of the separate parts by $a(b-b_0)$, but I shall henceforth denote it by $a'\frac{b-b_0}{b_0}$, which is hardly more than a change of a formal nature, required to make a' retain the character of a pressure on the unity of surface. Just as $p+\frac{a}{v^2}$ is a pressure directed inward on the unity of area, this is the case with $a'\frac{b-b_0}{b_0}$ and the latter represents the increase of that pressure in consequence of the mutual attraction of the separate atoms or atom groups. It was only after a long hesitation that I dared conclude to this value of the attraction, and when I concluded to it it was only, to quote Prof. RICHARDS, *"with some conviction"*.

It follows from this form for the attraction that it is equal to 0 when the atoms touch, and becomes greater when the space allowed to the motion of the atoms, increases. Moreover I put a' proportional to the temperature. I must acknowledge that these suppositions are not founded on a true insight in the constitution of a complex molecule. But I hoped that the study of the consequences of these hypotheses which seemed probable to me, and the comparison of these consequences with experience might contribute to the knowledge of the properties of such a complex molecule. And so far as I could then compare with what was known on other grounds, the impression I obtained, was not entirely unfavourable. And now I have been induced to reconsider the conclusion at which I had arrived, to see if it leads to the relations which I have drawn up in the beginning of this communication. But in this respect I have not obtained perfect certainty yet. I have repeatedly discussed some difficulties which confronted me, with my son—but these discussions have not yet led to an undoubted result. At the moment I shall confine myself to communicating the proposed relations. Later we hope to be able to derive a rule from the state of motion of the atoms in a molecule, which will perhaps lead to the form:

$$\frac{b_g}{b_{lim}}=\frac{f-1}{3}=1+\sqrt{k}$$

when k represents the number of degrees of freedom for the motion of the parts of the molecules divided by the number of degrees of freedom for the progressive motion of the molecule as a whole, viz. 3. From this would follow $f=6{,}448$ for 2-atomic substances, and $f=7$ for triatomic substances, or perhaps this ought to be expressed as follows: for molecules with an axis of symmetry

$f = 6{,}448$. In the absence of such an axis $f = 7$ or $f > 7$. But this is still entirely uncertain.

If the given relations are assumed to be perfectly correct, the reduced equation of state assumes the following form:

$$\left(\pi + \frac{3}{\mathbf{v}^2}\frac{b_g}{b_{lim}}\right)\left(v - \frac{1}{r_{cr}}\frac{b}{b_g}\right) = T\,\frac{8}{3}\sqrt{\frac{b_g}{b_{lim}}}.$$

For b constant, and so also $\frac{b_g}{b_{lim}} = 1$ and $r_{cr} = 3$ we find back the same form as occurs in Continuiteit p. 127. This form is found from:

$$\left(\pi + \frac{f-1}{\mathbf{v}^2}\right)\left(\mathbf{v} - \frac{1}{r_{cr}}\frac{b}{b_g}\right) = Ts.$$

If in this equation we put π, $\mathbf{v}$ and $T = 1$, we find:

$$\frac{b_{cr}}{b_g} = r_{cr}\left(1 - \frac{s}{f}\right).$$

a relation, which had already been found before.

Mathematics. — "*On metric properties of biquadratic twisted curves*". By Prof. JAN DE VRIES.

(Communicated in the meeting of December 28, 1912).

§ **1**. The quadratic surfaces Φ^2 of a pencil cut the imaginary circle γ^2_∞ common to all spheres in the groups of an involution of order four. The lines r_∞ joining two points of the same group envelop a curve of class three. Any of these lines r_∞ is the axis of a pencil of parallel planes cutting a determinate surface Φ^2 of the pencil according to circles.

Such a plane cuts the base ϱ^4 of the pencil (Φ^2) in four concyclic points. So we find: *the planes cutting a biquadratic twisted curve of the first species in four concyclic points envelop a curve of class three lying at infinity.*

§ **2**. Let l be the axis of a pencil of planes. Any plane A cuts ϱ^4 in four points which will be denoted by 1, 2, 3, 4, whilst M_k will indicate the centre of the circle $l\,m\,n$. We consider the locus of the quadruples of centres M and take first the particular case where 1, 2 are fixed points and line l is a bisecant of ϱ^4.

As the centres M_3 and M_4 (of the circles 124, 123) lie in the plane Δ normally bisecting line 1,2 the locus (M) consists of a curve lying in Δ and of the locus of the centres M_1, M_2. But the latter consists of two different curves, as the points M_1, M_2 never coincide during the rotation of A about l. For a coincidence of M_1, M_2 requires that the circles 234 and 134 coincide; as 1 and 2 are fixed points, this only happens when 1, 2, 3, 4 are concyclic, but then the four points M_k belong to different branches of the locus.

§ **3.** The locus of the points M_3, M_4 situated in $\angle$ passes *six* times through the midpoint M_0 of 1,2, for the sphere on 1,2 as diameter cuts ϱ^4 elsewhere in six points. So this locus is of order *eight* and will be indicated by μ^8.

The plane Γ_∞ at infinity contains the centres of four circles determined by the points of ϱ^4 at infinity. The remaining four points common to Γ_∞ and μ_8 originate from two nodes generated as follows. If A touches γ^2_σ the point of contact is the pole of the line at infinity of A with respect to all the "circles" lying in that plane; so M_3 and M_4 coincide then in that point of contact, but belong to different branches.

Through l pass three planes containing four concyclic points; in the centre of each of the three corresponding circles 1234 the curve μ^8 has a node.

By assigning to M_3 and M_4 respectively the points 4 and 3 we establish a correpondence (1,1) between the curves μ^8 and ϱ^4; so these curves have the same genus. As the singular points of a curve of *genus one* are equivalent to 20 nodes, the sixfold point M_0 and the five nodes already obtained form the singular points of μ^8. So this curve is of *rank sixteen*; its four tangents through M_0 originate from the four tangential planes of ϱ^4 through l in which planes M_3 and M_4 coincide.

§ **4.** The locus of M_1 (and likewise that of M_2) is a twisted sextic μ^6; its points at infinity are the points of ϱ^4 at infinity and the points of contact of γ^2_∞ with planes through l.

Evidently it has five points in common with l; so it is *rational* and of *rank ten*.

The three curves μ^8, μ_1^6, μ_2^6 concur in the centres of the circles lying in the three cyclic planes through l. Furthermore each curve μ^6 has still one point in common with μ^8. For in the plane A touching ϱ^4 in 1 (or in 2), M_1 (M_2) is at the same time one of the points M_3, M_4; for 3 1 gives 124 324 and therefore M_3 M_1.

§ **5**. In the case of an arbitrary line l the locus of the points M is a *twisted curve* μ^{20}. Any plane A through a point at infinity of ϱ^4 furnishes three points of Γ_∞ lying in different directions, and on γ^2_∞ the curve has *two fourfold points*. Moreover it possesses *three fourfolds points* in the cyclic planes through l.

As any plane A bears four points M none of which generally lies on l, μ^{20} has with l *sixteen points* in common. Each of the eight tangential planes of ϱ^4 furnishes a tangential plane of μ^{20}; so this curve is of *rank forty*.

It is of *genus one*, for one can assign the point M_k to each point k of ϱ^4. So the generally known formulas

$$r = m(m-1) - 2(h+D) - 3\beta,$$
$$p = \tfrac{1}{2}(m-1)(m-2) - (h+D+\beta),$$

where we have $r = 40$, $m = 20$, $D = 30$, $p = 1$, give $\beta = 0$, $h = 140$.

So the curve has no cusps, but 140 *apparent double points* (bisecants through any point).

§ **6**. If the points 1, 2, 3, 4 of ϱ^4 form an *orthocentric group*, their plane A cuts all the Φ^2 according to orthogonal hyperbolas: then all the planes parallel to A furnish orthocentric groups.

The planes cutting a director cone of Φ^2 in two edges normal to each other envelop a cone of the second class. So two concentric director cones determine four planes cutting the two corresponding Φ^2 and therefore all the Φ^2 of the pencil in orthogonal hyperbolas. From this ensues: *there are four systems of parallel planes cutting* ϱ^4 *in orthocentric groups.*

§ **7**. We consider in any plane A through l the *orthocentres* O_k of the triangles lmn, which four points lie with the points 1, 2, 3, 4 on an orthogonal hyperbola ω^2.

Evidently ω^2 is the section of A with a Φ^2 through ϱ^4; now we can bring through l a second plane cutting that Φ^2 in an orthogonal hyperbola (§ 6). So any point of l lies on two curves ω^2, i. e. l is double line of the locus of the curves ω^2. Therefore: *the locus* (O) *of the orthocentra* O_k *lies on a surface* Ω^4 *with double point* l.

In order to determine the degree of (O) we remark that in a plane A through a point at infinity of ϱ^4 three points O lie at infinity in the same direction, which proves that Γ_∞ contains *four threefold points* of (O). If A touches the circle γ^2_∞, the point of contact I is separated harmonically by γ^2_∞ from any point of the tangent, i. e. of the line at infinity of A. So all the perpendiculars of the triangles lmn concur in I and I is a *fourfold point* of (O). But then the curve is of *order twenty*.

If two points k coincide in a plane A the same happens with two points O_k. So through l pass *eight* tangential planes of ω^{20} and as l contains evidently *sixteen* points of this curve, ω^{20} is of *rank forty*.

It is of *genus one* on account of the (1,1)-correspondence between the point k of ϱ^4 and O_k.

From $p=1$, $r=40$, $m=20$ and $D=24$ (as there are two fourfold and four threefold points) we find (§ 5) $\beta=0$, $h=146$. So the curve has 146 *apparent double points*.

§ **8**. If l joins the points 1 and 2 of ϱ^4 the locus of the points O consists of three curves. For the points O_1 and O_2 always remain separated, if A rotates about l. But on the contrary O^3 and O^4 belong to the same curve; for the difference between the points 3 and 4 disappears as soon as A is tangential plane.

We now can determine the order of the curve (O_1) as follows. We look out in the first place for triangles 234 rectangular in 2. To that end we consider the cubic curve ϱ^3_∞ which is the projection of ϱ^4 out of 2 on the plane at infinity. On each line through the trace 1_∞ of 21 we determine the points H_∞ separating harmonically the projections of 3 and 4 from the circle γ^2_∞. As ϱ^3_∞ cuts the polar of 1_∞ in three points, 1_∞ is threefold point of (H) and this curve a quintic. Its points of intersection with ϱ^3_∞ are 1_∞ counted thrice, six points on γ^2_∞ and an other sextuple forming three pairs of traces of mutually rectangular lines 23, 24. So through 1,2 pass three planes for which the angle 324 is a right one; therefore 1 is a *threefold point* of curve (O).

If line 34 is normal to 12, the point O_1 lies on 1,2. So line 34 generates a hyperboloid if A rotates round l; so by means of a section normal to 1,2 it is immediately clear that there are two chords 34 at right angles to 12.

So five points O_1 lie on l; therefore (O_1) is a *rational curve* ω_1^6 *of order six with a threefold point*. The line l is the bisecant of ω_1^6 passing through the threefold point. Moreover we find $r=10$. $h=7$, $\beta=0$.

Evidently there are three positions of A for which 312 is a right angle; so the points 1 and 2 are *threefold* on the locus of the points O_3, O_4. From this ensues that this locus is a *curve* ω^8 *with two threefold points*.

As 34 happens to be tangent four times, ω^8 is of *rank sixteen*.

Evidently it is of *genus one* (see § 3). Furthermore we have $D = 8$ (two double points on γ^2_x), $h = 12$, $\beta = 0$.

The surface Ω^4 (§ 7) containing the three curves $\omega^8, \omega_1^6, \omega_2^6$ has threefold points in 1 and 2. For, all orthogonal hyperbolas pass through these points. Two of these hyperbolas break up into the line $l = 1,2$ and a chord 3,4 at right angles to it.

§ **9**. If l has only point 1 with ϱ^4 in common the locus of the points O consists of an ω^6 containing the points O_1 and an ω^{14} containing the three other points O; this follows immediately if we consider the points at infinity.

We determine the order 14 of the latter curve independently by means of the number of times that one of the points O lies on l. The planes containing two chords at right angles in 1 envelop a *cone* of *class six*; for the chord 12 is intersected at right angles by three chords and bears three planes in which the chords 13 and 14 are normal to each other (§ 8). So the triangle $1ik$ is rectangular in 1 for *six* positions of Λ and in each of these cases a point O coincides with 1.

The chords of ϱ^4 intersecting l form a *scroll* of *order five* with l as double director line. So there are five chords normally cutting l, each case of which furnishes a point O on l. So we find an ω^{14} with *sixfold point* 1, through which point passes still a *fivefold secant*. It is of *genus one*, as we can assign the point O_k to the point k of ϱ^4. From $m = 14$, $D = 25$, $r = 28$ (on l six tangents rest) we then derive $\beta = 0$, $h = 52$.

The curve ω^6 has l as fivefold secant, is therefore *rational* and of *rank ten* ($h = 10$, $\beta = 0$).

Now the surface Ω^4 has a *threefold point* in 1.

§ **10**. We still consider the scroll, locus of the lines of EULER, $e_k = M_k O_k$, lying in the planes Λ.

Between the points of the curves μ^{20} and ω^{20} exists a correspondence (1,1). By projecting the corresponding points M and O out of an arbitrary line a we generate a correspondence (20.20) between the planes of pencil (a). Of the 40 coincidencies 4 lie in each of the planes through a and one of the two points I, each of these points being fourfold point of μ^{20} and of ω^{20}. In each of the other coincidencies lies a line e resting on a. So the *scroll* (e) is of *order* 32.

We can verify this by means of the locus of the centres of gravity G_k of the triangles $l\,m\,n$. It passes three times through each of the four points of ϱ^4 at infinity and is therefore of *order twelve*. As this curve is also in (1,1)-correspondence with μ^{20}, whilst it never happens that G_k and M_k coincide, the reasoning given above leads here anew to the order 32 of G.

§ **11**. A twisted biquadratic curve ϱ^4 of the second species lies on one quadratic surface Ψ^2 only. It can be considered as partial intersection of Ψ^2 with the cubic scroll Σ^3 generated by the bisecants b of ϱ^4 cutting a given bisecant b_0. Each point of b_0 bears two bisecants b, b' and the plane (b, b') passes through the single director line g of Σ^3.

The pairs b, b' determine an involution on g, the double points of which lie in two double tangential planes of ϱ^4.

Reversely the line common to any two double tangential planes of ϱ^4 is single director line of a Σ^3; for the bisecants lying in these planes are cut by one bisecant b_0 only and this line is the double director line [1]) of Σ^3.

We now determine the number of orthogonal pairs b, b'.

Any edge of a director cone Λ^3 of Σ^3 is at right angles to three other edges; so the planes of the orthogonal pairs envelop a cone of class three. On Λ^3 the pairs b, b' determine an involution and the planes of the pairs of edges pass through an edge parallel to g. From this it follows that g bears three [2]) orthogonal pairs b, b'.

As the lines g form a congruence, there are ∞^2 planes Ω containing orthogonal bisecants; so these planes envelop a surface Ω^3 of class three. The planes intersecting Ψ^2 in orthogonal hyperbolas are parallel to the tangential planes of a cone of the second class and envelop therefore a conic ${}^2\Omega$ at infinity. Evidently a common tangential plane of ${}^3\Omega$ and ${}^2\Omega$ cuts ϱ^4 in an orthocentric group. So: *the planes of the orthogonal quadrangles inscribed in ϱ^4 envelop a developable of class six.*

§ **12**. We consider once more the locus of the quadruples of orthocentres in the planes Δ through a line l. If Δ contains a point

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[1]) The lines g form a congruence (6,3).

[2]) If Σ^3 is represented by the equation

$$(ax + by + cz + d)x^2 = (a'x + b'y + c'z + d')y^2$$

we find for any pair b, b' the equations

$$y = \pm \lambda x\,,\; ax + by + cz + d = \lambda^2 (a'x + b'y + c'z + d').$$

So the orthogonal position of the lines (λ) and $(-\lambda)$ requires evidently

$$(c'\lambda^2 - c)^2 (1 - \lambda^2) + (a - a'\lambda^2)^2 - \lambda^2 (b - b'\lambda^2)^2 = 0.$$

So there are three orthogonal pairs.

of σ^4 at infinity, the centres O_1, O_2, O_3 lie in the same direction at infinity and give rise to a *threefold* point at infinity. As we have found in the case of ϱ^4 (§ 7) γ^2_∞ contains *two fourfold points* of O. But Γ_∞ bears two points O more, originating from the two *trisecants* of σ^4 meeting l. For if in a plane Δ the points 1, 2, 3 are collinear, the three perpendiculars of the flattened triangle **124** are parallel. Then the four orthocentra lie on the normal q through **4** on the trisecant: so q is *quadrisecant* of the curve (O) and the *order* of (O) is 22.

There are six tangents of σ^4 meeting l and therefore as many tangents of ω^{22} doing likewise; as ω^{22} has evidently 18 points in common with l, this curve is of *rank* 42. As it corresponds in genus to σ^4 and its singular points are equivalent to 24 double points, we find by means of the formulas given above $\beta = 0$, $h = 186$.

§ **13.** If l contains the points 1, 2 of σ^4, the locus (O) breaks up into three different curves. As in § 8 we find here through 1, 2 three planes bearing chords 23, **24** normal to each other, so 2 is *threefold point* of (O_1).

But now the line **34** describes a cubic scroll (with double line l) if Δ rotates about l; so 12 is cut orthogonally by *three* chords.

So we find for (O_1) and (O_2) two *rational* curves of *order seven*.

The locus of O_3 and O_4 is once more an ω^8 with *two threefold points*.

The three curves are situated on a surface Ω^5 forming the locus of the orthogonal hyperbolas **1234**. For, in the three planes Δ bearing a chord **34** normal to $l = 12$, the hyperbola degenerates into these two chords and l; so l is *threefold line* from which ensues moreover that 1 and 2 are fourfold points.

So we may conclude that for an arbitrary position of l the corresponding orthogonal hyperbolas form a surface of order five with l as threefold line.

Let us still consider the case that l is a *trisecant*, containing the points 1, 2, 3 of σ^4. Then O_4 is always at infinity and each of the remaining three points O describes its own curve.

If **4** coincides with 1, O_1 is at infinity, which also happens if Δ contains a point of σ^4 at infinity and if Δ touches γ^2_∞. From this we conclude that each of the points O_1, O_2, O_3 describes a *rational* curve of *order seven*, with *threefold* points in two of the points 1, 2, 3.

In fact each of the points 1, 2, 3 is vertex of a rectangular triangle for three positions of Δ, or more exactly of two suchlike triangles; for, if **14** is normal to the trisecant, 1 is orthocentre of **124** and of **134**.

Farthermore there are 3 × 6 positions of A for which O coincides with 4, leading to a point common to σ^4 and (O).

From this we may still conclude that the planes in which the quadrangle 1234 admits one right angle envelop a surface of *class* 36. As to this we have to bear in mind that any plane through a trisecant of σ^4 having the vertex of the right angle on that trisecant must be counted twice as tangential plane.

Likewise we find that the planes for which the quadrangle 1234 admits two equal adjacent sides envelop a surface of *class* 33.

§ **14**. Let us finally consider the locus of the centres M_k of the circles circumscribed to the triangles $l\,m\,n$ in the planes A through l.

Each of the two trisecants cutting l furnishes again a point at infinity; each of the planes through a point of σ^4 at infinity determines three points of Γ_∞ and each of the tangential planes of γ^2_∞ through l contains a fourfold point at infinity. So we find a curve μ^{22}, cutting l in 18 points, with the *rank* 42.

If l is the *bisecant* 12, the points M_3 and M_4 generate a *plane curve* μ^{18} with the midpoint M_0 of 12 as *sixfold* point; for the sphere with 12 as diameter determines on σ^4 the vertices of six rectangular triangles with 12 as hypothenuse. As we can once more assign M_3 and M_4 to the points 4 and 3, μ^{18} is like σ^4 of *genus zero*. So its singular points are equivalent to 26 double points. So it must possess besides the double points on γ^2_∞ and the sixfold point M_0 still *four* double points more. These can only originate from concyclic groups 1, 2, 3, 4. So we conclude: *the planes cutting σ^4 in four concyclic points envelop a surface of class* 4.[1]

So the curve μ^{22} corresponding to an arbitrary line l has *four* fourfold points in the centres of the circles each of which contains a quadruple of points of σ^4.

As it cuts Γ_∞ in *two* fourfold points more, we get $D = 36$. By means of $r = 42$ and $p = 0$ we find $\beta = 0$, $h = 174$.

If l is trisecant 123, each of the points M_1, M_2, M_3 describes a plane curve of *order seven* with a *sixfold* point.

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[1] This is in accordance with the results obtained by Mr. M. STUYVAERT in his *inaugural dissertation* (Étude de quelques surfaces algébriques engendrées par des courbes du second et du troisième ordre, Gand, 1912; see Chap. I, Sur les plans coupant un système de lignes en six points d'une conique).

Mathematics. — *"On the correspondence of the pairs of points separated harmonically by a twisted quartic curve."* By Prof. JAN DE VRIES.

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§ 1. We indicate by P and Q two points, lying on a chord of a *twisted quartic curve of the first kind,* separated harmonically by this curve ϱ^4. As any point P lies generally on two chords, in the correspondence (P, Q) to any point P two points Q are conjugated.

If P moves along a line l, Q describes a curve λ^6 of *order six.* For any plane A through l cuts ϱ^4 in four points S_k and contains therefore six points Q_{kl}, where Q_{kl} lies on a chord S_kS_l and is harmonically conjugated to the points P_{kl} common to that chord and l. If l is an arbitrary line, Q never lies on l when A rotates about l.

The line $Q_{13}Q_{23}$ is separated harmonically from l by $P_{12}S_3$ and S_1S_2. By assuming a position for A in which S_1 and S_2 coincide with Q_{12} we find for $Q_{13}Q_{23}$ a tangent of λ^6 separated harmonically from l by $P_{12}S_1$ and $P_{12}S_3$, whilst an other tangent of λ^6 takes the place of $Q_{14}Q_{24}$. So each of the eight tangential planes of ϱ^4 contains two tangents of λ^6; so the *rank* of this curve is sixteen.

Moreover we find that λ^6 has *eight* points in common with ϱ^4.

§ 2. The line p connecting the two points Q, Q' conjugated to P describes a regulus A^2 if P moves along l. For p is the polar line of P with respect to ϱ^4, i. e. the intersection of the polar planes of P with respect to any two quadratic surfaces through ϱ^4, and these polar planes describe two projective pencils.

Let us now consider one of the two lines p cutting l. The corresponding point P bears two chords S_1S_2 and S_3S_4 lying in the plane $A = lp$. The points Q_{12} and Q_{34} lie on p, the points Q_{13}, Q_{23}, Q_{14}, Q_{24} lie on a line m through P harmonically separated from l by the chords S_1S_2 and S_3S_4. As λ^6 lies on the regulus A^2, m is a line of A^2. Any tangential plane of A^2 contains therefore a quadrisecant of λ^6 and both the reguli of A^2 are arranged by λ^6 in a correspondence $(2, 4)$. Evidently the quadrisecants q are the polar lines of l with respect to the quadratic surfaces through ϱ^4.

§ 3. If we assume for l a *chord* of ϱ^4, the locus of Q breaks up into four parts, i. e. the chord l itself, the tangents r and r' in the points R, R' common to l and ϱ^4, and a *twisted cubic* λ^3. The polar line p now connects a point Q of l with the point Q' of the second chord k passing through P. This line describes a regulus having with A^2 the line l in common. So the locus of $Q' = kl$ is a curve λ^3 through R and R', as l is to have two points in common with it and R and R' correspond amongst other points with themselves; the curves λ^3 and ϱ^4 have four more points in common.

§ 4. If l is a unisecant of ϱ^4 in R, the locus (Q) degenerates into the tangent r and a λ^5. Any plane through l contains besides R three points Q; of these two must be combined with R, if the plane contains the tangent r. The quadrisecants q of l become here trisecants; for r rests on each of the polar lines q of l (§ 2). The plane qr touches ϱ^4 in R and contains therefore two points Q united in R. In relation with the results obtained we conclude from this that by the correspondence (P,Q) to a unisecant of ϱ^4 a twisted curve of *order five* is conjugated having a node in the point common to the unisecant and ϱ^4, the nodal tangents lying in the plane lr.

So the curve is of *rank ten*. Through l pass six common tangential planes of ϱ^4 and λ^5.

§ 5. The vertices T_k of the four quadratric cones containing ϱ^4 are *singular points* of the correspondence (P,Q). For T_1 bears ∞^1 chords and the corresponding points Q lie on the conic τ^2_1 common to the polar plane $\tau_1 = T_2T_3T_4$ of T_1 and the quadratic cone with T_1 as vertex.

To the line T_1T_2 as locus of points P correspond in the first place the two *conics* $\tau_1{}^2$ and $\tau_2{}^2$ and moreover the *line* T_3T_4 *counted twice*. For the points S_k in any plane through S_1S_2 form a complete quadrangle of which T_1 and T_2 are diagonal points; in the third diagonal point Q_{13} and Q_{24} coincide, whilst of the remaining four points Q two lie in τ_1 and two in τ_2. So to any point of T_1T_2 correspond two points of T_3T_4 and inversely.

If l contains the point T_1 only, the six points Q lying in a plane λ through l consist of two points in τ_1 and on $\tau_1{}^2$ and of four points lying on the line common to λ and the polar plane of l with respect to the cone projecting ϱ^4 out of T_1. Then the curve (Q) breaks up into the *conic* $\tau_1{}^2$ and a *plane curve* λ^4. In the two tangential planes of the cone passing through l the two points Q lying on $\tau_1{}^2$ coincide with two of the remaining four in a point of intersection of $\tau_1{}^2$ and λ^4 where the latter is touched by the edge of contact.

§ 6. Let us now consider the surface of the points Q corresponding to the points P of a plane Π. If S_k are the points common to Π and ϱ^4, the six lines S_kS_l form the intersection of Π with the locus under discussion. So it is of *order six*. As it contains at the same time the lines touching ϱ^4 in S_k, these points are nodal points. To the two points of τ_1^2 lying in $\boldsymbol{H}$ correspond two points Q coinciding with T_k, whilst to the point of $\boldsymbol{H}$ lying on T_kT_l two points on $T_m T_n$ correspond. From this ensues that the four points T have to be also nodes of $\boldsymbol{H}^6$.

So to a plane corresponds a *surface of order six with eight nodes and ten lines.*

§ 7. Let us now consider the correspondence between two points P,Q separated harmonically by a *twisted quartic curve of the second kind* σ^4. As P bears three chords of σ^4, it is conjugated to three points Q. To the points P of a line l correspond the points Q of a twisted curve λ^6; for each plane through l contains six points Q.

The three points Q corresponding to P lie in the polar plane of P with respect to the quadratic surface H^2 through σ^4. The plane $\boldsymbol{H}$ rotates about the polar line l' of l, if P moves along l. So l' is a trisecant of λ^6.

The scroll of the chords of σ^4 cutting l is of order nine; so nine of these chords also intersect l'. To these nine belong the two trisecants of σ^4 cutting l, each of which represents three chords; they have to meet l', as they lie on the hyperboloid H^2 and are at the same time trisecants of λ^6. The remaining three chords cutting l and l' determine the three points Q on l'.

§ 8. Each of the six tangential planes of σ^4 passing through l contains a point and two tangents of λ^6; so this curve is of *rank twelve* and rests in *six* points on σ^4. By S_k we represent the points of σ^4 lying in a plane drawn through l; the chord $b = S_1S_2$ is paired to the chord $b' = S_3S_4$ and now we consider the correspondence between the points P and P' in which b and b' intersect l. As P bears three chords we find a (3,3). If b and b' intersect l in the same point P, only the third chord through P furnishes a point P' not coinciding with P; from this ensues that the coincidencies of the (3,3) coincide by two in a double coincidency. So through l three planes pass for which b and b' intersect in l; the line h separating l harmonically from b and b' then contains four out of the six points Q, the remaining two lying on b and b'.

So the curve λ^6 admits three quadrisecants.

§ 9. Let l be a chord of σ^4 and S_1 and S_2 the points it has in common with σ^4. Through any point P of l pass two more chords

b, b' of σ^4. So the locus of the points Q lies on a cubic scroll Λ^3 with double line l.

In the plane bl two points Q coincide in S_1, two other ones in S_2, whilst Q_{12} lies in l and Q_{34} in b. If P moves along l, $q = Q_{12}Q_{34}$ describes a cubic scroll Φ^3 with double line l; for through Q_{12} pass two lines q, q' to the points Q_{34} of the chords b, b' concurring in the point P corresponding to Q_{12}.

The scrolls Λ^3, Φ^3 have the trisecants t_1, t_2 of σ^4 passing through S_1 and S_2 in common. For if P coincides with S_1, t_1 becomes a chord b and, as Q_{12} coincides then with S_1, at the same time a line q.

As l is nodal line for both scrolls, these surfaces have still a twisted cubic λ^3 containing the points Q_{34} in common. In the planes touching σ^4 in S_1 and S_2 the point Q_{34} coincides with the point of contact; so S_1S_2 is a chord of λ^3. This curve intersects σ^4 in the two points the tangents of which intersect S_1S_2; it has for chords the single director lines of the scrolls Λ^3, Φ^3.

So by the transformation (P, Q) the *chord* l passes into the system consisting of l itself, the tangents s_1, s_2 and a *twisted cubic.*

Evidently a *trisecant* t is transformed into that line to be counted thrice and the tangents in the three points it has in common with σ^4.

If l touches σ^4 in S_{12}, the scroll Φ^3 becomes a cone with nodal edge l. In the osculating plane of σ^4 in S_{12} q lies along l; so this plane is common tangential plane of Λ^3 and Φ^3, having still in common the trisecant through S_{12}. The residual intersection λ^3 touches in S_{12} the tangent of σ^4.

§ **10.** If l is unisecant of σ^4 in S the curve λ^6 breaks up into the tangent s of σ^4 in S and a curve λ^5. The polar line l' of l becomes chord of λ^5, s being one of the three chords cutting l and l'. The plane $l'S$ touches H^2 in S and is therefore polar plane of $P \equiv S$; it contains the tangent s and the trisecant of σ^4 on which S lies. Of the three variable points Q common to λ^5 and a plane through l', two coincide with S and only one lies outside S.

Any plane through l contains besides S three points Q and has therefore in S two points with λ^5 in common. Also the plane $l'S$ not passing through l has in S two points in common with λ^5; so S is a node of λ^5. The plane ls contains beside S only one point Q; so it passes through the nodal tangents of the node. So to a unisecant corresponds a *twisted quintic with a node.*

The curve is of *rank eight,* through l passing four common tangential planes of σ^4 and λ^5.

Mathematics. — *"On a line complex determined by two twisted cubics."* By Prof. JAN DE VRIES.

(Communicated in the meeting of November 30, 1912).

§ 1. We will indicate the chords of the given twisted cubics ϱ^3, σ^3 by r, s.

Any plane π contains three chords r and three chords s, therefore nine points $P \equiv rs$. In the *focal system* (P,π) each point has in general *one* focal plane, each plane *nine* foci $(\alpha = 1,\ \beta = 9)$.

If π rotates about the line l, the points determined on l by two complanar chords r, s are conjugated to each other in a correspondence $(3,3)$. As each point of coincidence furnishes a point $P \equiv rs$, l contains *six* points P, the focal planes of which pass through l; so the third characteristic number of (P,π) is *six* $(\gamma = 6)$.

Let b represent one of the ten common chords of ϱ^3 and σ^3. Any point B of b admits ∞^1 focal planes, i.e. all the planes β through b. Any plane β admits four foci not lying on b, whilst at the same time any point B of b is focus. So the lines b are loci of *singular foci* and *singular focal planes*.

If P is assumed on ϱ^3, s is a definite chord of σ^3, whilst r may be any line connecting P with an other point of ϱ^3; then any plane through s can figure as focal plane π in which P counts for two of the nine foci. So the curves σ^3 and ϱ^3 are *singular curves* for the focal system (P,π).

§ 2. The polar planes of P with respect to the ∞^2 quadratic surfaces through ϱ^3 have a point R on r in common; P and R can be said to be separated harmonically by ϱ^3. If P describes any line l, the polar planes of P with respect to three quadratic surfaces of the net not belonging to the same pencil rotate about three definite lines and describe therefore three projective pencils. So the locus of R is a twisted cubic λ^3, intersecting ϱ^3 in four points; for on the four tangents r_0 of ϱ^3, resting on l, the point conjugated to P is every time the point of contact R_0 [1]).

We indicate by S the point on s harmonically separated from P by σ^3 and consider the relationship between R and S.

To any plane Σ as locus of S corresponds a cubic surface H^3 of

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[1]) This generally known involutory cubic transformation has been investigated thoroughly by Dr. P. H. SCHOUTE (Nieuw Archief voor Wiskunde, 2nd series, vol. IV, 1900, p. 90).

points P; as H^3 intersects the twisted cubic λ^3 described by P when R moves along l in nine points, the correspondence (R,S) is of order *nine*.

A point of coincidence of R and S can only present itself when r and s coincide, i. e. on a common chord b. On any of the ten b the pairs (P,R) and (P,S) generate two involutions, of which H_1, H_2 may represent the common pair. By assuming R in H_k, we find H_l for P and H_k for S; so H_1 and H_2 are points of coincidence of (R,S). So this correspondence admits *twenty coincidencies* lying in pairs on the *ten* common chords b.

As a point R_0 of ϱ^3 corresponds to each point P of the tangent r_0 of R_0, R_0 corresponds to each point S of the twisted cubic $\sigma_0{}^3$ into which r_0 passes by the transformation (P,S); evidently $\sigma_0{}^3$ has four points in common with σ^3.

Consequently the curves ϱ^3 and σ^3 are *singular curves* of the correspondence (R,S).

If R describes the tangent r_0 of ϱ^3, P remains in the point of contact of r_0; so the point S^* conjugated to P is singular and corresponds to all the points of r_0. Evidently the locus of S^* is the rational twisted σ^9 into which ϱ^3 passes by the transformation (P,S).

So the correspondence (R,S) admits *two singular twisted curves of order nine*, σ^9 and ϱ^9.

As the developable with ϱ^3 as cuspidal curve cuts σ^3 in 12 points σ^3 and σ^9 have twelve points in common; likewise ϱ^9 rests in 12 points on ϱ^3.

§ 3. We now consider the lines $p = RS$. If P describes the line l, p generates a scroll of order six; for we found above that the plane $\pi = P_p$ passes through l in six positions (§ 1).

The line p generates a *complex*. We determine the number of lines p belonging to a pencil with vertex L and plane λ.

If R describes a ray l of pencil (L, λ), S generates a curve intersecting λ in nine points (§ 2); we conjugate to l the nine lines l' connecting these points with L. In this manner we get in the pencil a correspondence (9,9) each coincidence of which furnishes a line p connecting two points R and S corresponding to each other. So:

The complex (p) *is of order eighteen.*

Evidently the 20 points H are *principal points* of the complex; each complex cone passes through these 20 points.

§ 4. Any point R_0 of ϱ^3 is singular, for it bears the lines p connecting it with the points S of the corresponding curve $\sigma_0{}^3$ (§ 2) and so its complex cone degenerates. Consequently the curves ϱ^3 and σ^3 lie on the *singular surface* of the complex.

The edges of the ∞^1 cones projecting the curves σ_0^3 from their corresponding point R_0 as vertices form a *congruence* of which we will determine order and class.

The locus of the curves σ_0^3 is the surface Σ^{12} into which the developable with ϱ^3 as cuspidal curve is transformed by (P,S).

The cubic cones with an arbitrary point M as vertex and ϱ^3 and σ^3 as director curves, intersect in 9 edges, each of which connects a point S of σ_0^3 with a point R' of ϱ^3; if R' coincides with the point R_0 to which σ_0^3 corresponds we have to deal with a ray of the congruence passing through M. We will conjugate these 9 points R' to R_0. The line MR' cuts the surface Σ^{12} mentioned above in 12 points S lying in general on different curves σ_0^3; so to R' correspond 12 points R. The correspondence (R_0, R') has therefore 21 coincidencies, i.e. the *order* of the congruence is 21.

Any plane μ contains 3 points R_0 and each of the corresponding curves σ_0^3 has 3 points S with μ in common; so the class is 9.

So the lines S_0R form a congruence (21,9) and an other congruence of the same type is formed by the lines S_0R. The two congruences admit successively ϱ^3 and σ^3 as *singular curve.*

§ 5. Any point S^* of the rational σ^9 (§ 2) is the vertex of a pencil of complex rays p the plane of which contains the corresponding tangent r_0. So the curves ϱ^9 and σ^9 lie also on the *singular surface.*

The ∞^1 pencils with vertices S^* form a *congruence* which we will study more closely.

In any plane μ lie 9 points S^*; the tangents r_0 corresponding to these points determine 9 rays p lying in μ; so the congruence is of *class nine.*

To any point S^* we make to correspond the 9 points S' of σ^9 which can be projected out of the arbitrary point M in a point of the corresponding tangent r_0. The line MS' cuts 4 tangents r_0, so S' is conjugated to 4 points S^*. As any coincidency S' S^* is due to a ray of the pencil with vertex S^*, M bears 13 lines RS^*, i.e. the congruence is of *order thirteen.*

So the complex contains *two congruences* (13,9) each of which is built up of ∞^1 pencils. They admit successively σ^9 and ϱ^9 as *singular curve.*

§ 6. To the complex (p) belongs the system of generatrices of the developable determined by ϱ^3 and σ^3. Any tangent r_0 cuts four tangents s_0 and reversely; so the points of contact R_0 and S_0 of the tangents conjugated to each other in this way are in correspondence (4,4). By projecting the pairs of this correspondence out of a line a, the pencil of planes (a) is arranged in a correspondence (12,12). As each coincidency furnishes a line $p = R_0 S_0$ resting on a the *developable* under discussion is of *order* 24; it has ϱ^3 and σ^3 for *fourfold curves.*

Any chord r^* of ϱ^3 meeting σ^3 belongs to the complex, for in the common point of r^* and σ^3 the points P and S coincide. The chords r of ϱ^3 cutting a line l generate a scroll of order four with ϱ^3 as nodal curve; so the locus of the chords r is a scroll of order 12. On the latter surface ϱ^3 is a *sixfold curve,* for through any of its points pass the common edges of the two cones projecting ϱ^3 and σ^3.

So the complex (p) contains *two scrolls of order twelve,* the generatrices of which are chords of one of the curves ϱ^3, σ^3 and secants of the other.

Let p^* be a chord of ϱ^3 not meeting σ^3; then the tangent r_0 in one of the points R_0 common to ϱ^3 and that chord must contain the point P. If P moves along that tangent, S describes a curve $\sigma_0{}^3$; the cone projecting the latter curve out of R_0 has 6 edges in common with that of which ϱ^3 is director curve. So any point of ϱ^3 bears 6 rays p^*. As an arbitrary chord r can be cut by chords p^* in its points common to ϱ^3 only, so all in all by 12, the locus of the chords under discussion is of order 12.

So the complex contains *two scrolls of order twelve,* built up out of chords of one of the curves ϱ^3, σ^3.

Physics. — "*Determinations of the refractive indices of gases under high pressures.*" Second communication. "*On the dispersion of air and of carbon dioxide.*" By Prof. L. H. SIERTSEMA. (Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated in the meeting of November 30, 1912).

4. *The dispersion of air.*

This has already been repeatedly determined both for the visible spectrum and for the ultra-red and ultra-violet rays. The results, however, diverge considerably, and, moreover, the dispersion has never been measured under high pressure.

Through the kindness of Prof. KAMERLINGH ONNES compressed air was placed at my disposal with which dispersion determinations were made in exactly the same way as those for hydrogen described in a former paper.

In the following Table are given the results of three series of observations. For the meaning of the symbols employed reference may be made to the corresponding Table for hydrogen published in the paper just mentioned.

Air.

Pressure in atm.	Temperature.	k_b (mean)	$\lambda_b = 0.546$ $\lambda_a = 0.644$	$\lambda_c = 0.509$	$\lambda_d = 0.472$	$\lambda_e = 0.436$	$\lambda_f = 0.405$
			$\frac{k_a}{k_b}$	$\frac{k_c}{k_b}$	$\frac{k_d}{k_b}$	$\frac{k_e}{k_b}$	$\frac{k_f}{k_b}$
71.4	12.75°C.	823.52	0.84350	1.07697	1.16423	1.26722	1.37179
71.4	12.90	821.23	0.84346	1.07702	1.16418	1.26724	1.37176
70.6	13.19	810.84	0.84352	1.07697	1.16420	1.26718	1.37175
66.4	13.42	759.81	0.84350	1.07697	1.16419	1.26727	1.37183
48.7	13.58	559.27	0.84352	1.07698	1.16421	1.26716	1.37177
31.9	13.67	359.50	0.84339	1.07701	1.16417	1.26725	1.37171
67.7	9.25	790.70	0.84345	1.07697	1.16415	1.26723	1.37187
67.6	10.15	787.92	0.84349	1.07698	1.16419	1.26735	1.37191
66.2	10.35	766.84	0.84353	1.07695	1.16414	1.26724	1.37184
49.2	10.75	567.32	0.84351	1.07698	1.16411	1.26723	1.37178
32.2	10.95	367.70	0.84350	1.07695	1.16414	1.26721	1.37175
101.9	12.75	1170.71	0.84343	1.07698	1.16418	1.26729	1.37203
101.8	12.80	1168.50	0.84340	1.07699	1.16412	1.26732	1.37204
100.0	13.03	1147.43	0.84338	1.07700	1.16419	1.26732	1.37204
82.8	13.39	947.50	0.84337	1.07699	1.16415	1.26729	1.37207
65.5	13.89	745.71	0.84339	1.07704	1.16427	1.26728	1.37206
39.6	13.96	446.50	0.84328	1.07697	1.16415	1.26725	1.37199

The values obtained for the various gas densities are pretty well constant, just as was found to be the case with hydrogen. The deviations are not any more one way than the other, and we can therefore conclude that the dispersion of air is constant up to pressures of about 100 atm.

The mean values are:

$\frac{k_a}{k_b}$	$\frac{k_c}{k_b}$	$\frac{k_d}{k_b}$	$\frac{k_e}{k_b}$	$\frac{k_f}{k_b}$
0,84345	1,07698	1,16417	1,26725	1,37188
± 1,7	± 0,6	± 1,0	± 1,2	± 3,1

Hence we get for the dispersion constants

	λ (vac.)	$c = \frac{n-1}{n_b-1}$
a	0.64403	0.99446 ± 0.000020
b	0.54623	1
c	0.50873	1.00304 ± 0.000006
d	0.47234	1.00669 ± 0.000009
e	0.43597	1.01145 ± 0.000010
f	0.40478	1.01662 ± 0.000023

In order to be able to compare these with the results obtained by other observers, dispersion constants for the wave-lengths I used have been obtained from the results given by MASCART[1]), KAYSER and RUNGE[2]), PERREAU[3]), SCHEEL[4]), HERMANN[5]), RENTSCHLER[6]), LORIA[7]), KOCH[8]), CUTHBERTSON[9]), and GRUSCHKE[10]), either by graphical interpolation or by calculation from dispersion formulae given by them; these results are collected in the following Table.

Correspondence between the present results and those given by PERREAU and by KOCH is quite good both with hydrogen and with air. Only at λ = **0,644** does KOCH find a greater dispersion for both gases. For air, the agreement with HERMANN and with CUTHBERTSON is also very good.

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[1]) E. MASCART. Ann. de l'éc. norm. (2) **6** p. 60 (1877).

[2]) H. KAYSER and J. RUNGE. Ann. d. Physik **50** p. 312 (1893).

[3]) F. PERREAU. Ann. d. Ch. et de Ph. (7) **7** p. 325 (1896).

[4]) K. SCHEEL. Verh. d. D. phys. Ges. **9** p. 27 (1907).

[5]) K. HERMANN. Verh. d. D. phys. Ges. **10** p. 477 (1908).

[6]) H. C. RENTSCHLER. Astrophys. J. **28** p. 357 (1908).

[7]) S. LORIA. Ann. d. Physik. (4) **29** p. 619 (1909).

[8]) J. KOCH. Nova acta reg. soc. Scient. Upsaliensis (4) **2** N°. 5. p. 40 (1909).

[9]) C. and M. CUTHBERTSON. Proc. R. S. (A) **83** p. 153 (1909/10).

[10]) G. GRUSCHKE. Ann. d. Physik. (4) **34** p. 807 (1911).

	Mascart	Kayser and Runge	Perreau	Scheel	Hermann	Rentschler	Loria	Koch	Cuthbertson	Gruschke	Siertsema
0.644	0.9949	0.9952	0.9946	0.9948	0.9946		0.9947	0.9955	0.9947	0.9946	0.9945
0.546	1	1	1	1	1	1	1	1	1	1	1
0.509	1.0029	1.0027	1.0030	1.0028		1.0024	1.0023	1.0029	1.0030	1.0034	1.0030
0.472	1.0067	1.0060	1.0064	1.0063		1.0054		1.0070	1.0066	1.0071	1.0067
0.436		1.0103		1.0106	1.0116	1.0089		1.0116			1.0114
0.405		1.0152				1.0143					1.0166

The following interpolation formula was calculated using the method of least squares:

$$c = \frac{n-1}{n_b-1} = 0{,}98086\left(1 + \frac{0{,}0056376}{\lambda^2} + \frac{0{,}00005401}{\lambda^4}\right)$$

in which λ is the wave length in microns.

The degree of accuracy of this formula is evident from the following table:

	$\lambda_{(air)}$	$c_{(cal)}$	$c_{(obs)}$	$\Delta \times 10^5$
a	0.64385 „	0.99451	0.99446	5
b	0.54608 „	1	1	
c	0.50859 „	1.00303	1.00304	— 1
d	0.47221 „	1.00672	1.00669	3
e	0.43585 „	1.01144	1.01145	— 1
f	0.40467 „	1.01660	1.01662	— 2

5. *The dispersion of carbon dioxide.*

In the following table are given results of two series of measurements made with carbon dioxide. The gas used for the first series was only dried over calcium chloride, and contained about 96°/₀ of carbon dioxide. The gas used for the second series was, in addition, distilled several times, and it contained 98°/₀ of carbon dioxide. The measurements were made in exactly the same fashion as in the case of hydrogen and of air.

Carbon dioxide.

Pressure in atm.	Temperature.	k_b (mean)	$\lambda_b = 0.546$ $\lambda_a = 0.644$ $\frac{k_a}{k_b}$	$\lambda_c = 0.509$ $\frac{k_c}{k_b}$	$\lambda_d = 0.472$ $\frac{k_d}{k_b}$	$\lambda_e = 0.436$ $\frac{k_e}{k_b}$	$\lambda_f = 0.405$ $\frac{k_f}{k_b}$
45.2	12.95° C.	1180.44	0.84286	1.07733	1.16499	1.26864	1.37388
45.5	13.47	1185.20	0.84288	1.07733	1.16503	1.26867	1.37397
43.7	13.99	1084.33	0.84290	1.07735	1.16501	1.26867	1.37392
41.5	14.34	983.51	0.84289	1.07735	1.16505	1.26863	1.37387
38.6	14.58	882.68	0.84288	1.07735	1.16503	1.26864	1.37384
37.9	11.94	883.19	0.84289	1.07735	1.16503	1.26869	1.37380
35.1	12.33	783.79	0.84289	1.07736	1.16507	1.26861	1.37379
31.9	12.39	684.53	0.84284	1.07730	1.16502	1.26865	1.37381
31.6	10.99	685.93	0.84286	1.07733	1.16504	1.26867	1.37390
28.0	11.09	586.93	0.84286	1.07739	1.16503	1.26870	1.37393
24.1	11.28	486.18	0.84284	1.07741	1.16496	1.26869	1.37390
24.1	11.75	487.03	0.84287	1.07737	1.16499	1.26864	1.37385
20.0	11.83	387.11	0.84281	1.07735	1.16496	1.26861	1.37393
46.8	14.00	1281.62	0.84276	1.07735	1.16501	1.26876	1.37395
46.9	14.17	1278.52	0.84275	1.07735	1.16497	1.26875	1.37404
46.5	14.25	1248.50	0.84276	1.07735	1.16498	1.26876	1.37405
41.4	14.75	997.38	0.84278	1.07734	1.16496	1.26872	1.37395
34.2	15.00	748.64	0.84280	1.07732	1.16501	1.26874	1.37397
24.8	15.21	498.73	0.84279	1.07732	1.16497	1.26874	1.37395

Just as with the other gases there is here no definite direction to be recognized in the differences, so that we may again conclude that in this case the dispersion is independent of the gas pressure up to the saturation pressure.

The mean values are:

0,84284	1,07735	1,16501	1,26874	1,37391
± 1,2	± 0,6	± 0,8	± 1,2	± 1,7

from which follow these values for the dispersion constants:

	λ *(vac.)*	$c = \frac{n-1}{n_b-1}$
a	0.64403	0.99374 ± 0.000014
b	0.54623	1
c	0.50873	1.00339 ± 0.000006
d	0.47234	1.00742 ± 0.000007
e	0.43597	1.01259 ± 0.000010
f	0.40478	1.01813 ± 0.000013

In the next table these results are compared with values obtained either by graphical interpolation or by calculation from interpolation formulae from the observations of PERREAU [1]), RENTSCHLER [2]), KOCH [3]), STUCKERT [4]), and GRUSCHKE [5]). MASCART's [6]) results, which show irregularities which were not confirmed by subsequent observers, are not included.

λ	Perreau	Rentschler	Koch	Stuckert	Gruschke	Siertsema
0.644	0.9936		0.9938	0.9917	0.9929	0.9937
0.546	1	1	1	1	1	1
0.509	1.0033	1.0020	1.0031	1.0051	1.0033	1.0034
0.472	1.0072	1.0053	1.0071	1.0110	1.0082	1.0074
0.430		1.0096	1.0127	1.0173		1.0126
0.405		1.0154				1.0181

The agreement with PERREAU and KOCH is good, and with GRUSCHKE not quite so good. RENTSCHLER's results deviate considerably, just as with air, and so too do STUCKERT's.

The interpolation formula calculated as before becomes

$$c = \frac{n-1}{n_b-1} \quad 0{,}97781\left(1 + \frac{0{,}0067868}{\lambda^2} - \frac{0{,}00000614}{\lambda^4}\right)$$

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[1]) F. PERREAU. Ann. de Ch. et de Ph. (7) **7** p. 345 (1896).

[2]) H. C. RENTSCHLER. Astrophys. J. **28** p. 357 (1908).

[3]) J. KOCH Nova acta reg. soc. scient. Upsaliensis (4) **2** No. 5, p. 46 (1909).

[4]) L. STUCKERT. Zeitschr. f. Elektrochemie **16** p. 67 (1910).

[5]) G. GRUSCHKE. Ann. d. Ph. (4) **34** p. 810 (1911).

[6]) E. MASCART. Ann. de l'éc. norm. (2) **6** p. 61 (1877).

in which λ represents the wave-length in air. It gives the following differences between observed and calculated values:

	$\lambda_{(air)}$	$c_{(cal)}$	$c_{(obs)}$	$10^5\Delta$
a	0.64385 μ	0.99379	0.99374	5
b	0.54608 „	1	1	
c	0.50859 „	1.00338	1.00339	1
d	0.47221 „	1.00745	1.00742	3
e	0.43585 „	1.01258	1.01259	— 1
f	0.40467 „	1.01811	1.01813	— 2

In this case, too, the theoretical dispersion formula [1]

$$\frac{n^2-1}{n^2+2} = \Sigma \frac{Ne_1^{\,2}}{3m_1(\mathrm{v}_1^{\,2}-\mathrm{v}^2)}$$

even with only *one* erm in the sum, gives quite good agreement. As with hydrogen we obtain from it:

$$c = \frac{n-1}{n \quad 1} = \frac{\frac{1}{\lambda_1^{\,2}} - \frac{1}{\lambda_b^{\,2}}}{\frac{1}{\lambda_1^{\,2}} - \frac{1}{\lambda^2}}$$

and, taking λ as the wave-length in vacuo, we calculate $\lambda = 0{,}07982\,\mu$. The following table gives an idea of the degree of correspondence:

	$\lambda_{(vac.)}$	$c_{(cal)}$	$c_{(obs)}$	$10^5\Delta$
a	0.64403	0.99391	0.99374	+ 17
b	0.54623	1	1	
c	0.50873	1.00334	1.00339	— 5
d	0.47234	1.00741	1.00742	— 1
e	0.43597	1.01258	1.01259	— 1
f	0.40478	1.01823	1.01813	+ 10

A subsequent paper will deal with the absolute values of the refractive indices of air and of carbon dioxide.

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[1]) These proceedings 1911—12 p. 602.

Microbiology. — *"On the composition of tyrosinase from two enzymes".* By Professor Dr. M. W. Beijerinck.

(Communicated in the meeting of December 28, 1912)

The product of the action of tyrosinase on tyrosin is commonly called melanin, whose colour may be jet black, but takes all shades between light brown, pure red, brownish red, sepia and black in experimental conditions. These pigments are of uncommon stability and resist even heating with strong alkalies and sulfuric acid, whereby the black runs somewhat into brown but in chief remains unchanged. Even when boiled with nitric acid the melanin remains almost unchanged. It is accepted that the pigment of the hair and hide of higher animals is associated with these substances and is derived from tyrosin.

Melanin formation by symbiose of an Actinomyces with a bacterium.

On a culture plate of the composition: distilled water, 2 % agar, 0.1 % tyrosin (dissolved in a few drops natriumcarbonate) and 0.02 % K_2HPO_4, on which some centigrams garden soil are sown and which is kept at 30° C., hundreds or thousands of little sods of *Actinomyces* (*Streptothrix*) will develop after two or three days. The tyrosin serves at the same time as source of carbon and of nitrogen. But the agar itself also is attacked by these microbes, although with difficulty, and used as food. This is not surprising as many *Actinomyces*-species can even live on cellulose as source of carbon.

The common bacteria of the soil develop not or hardly on the tyrosin plate and cannot in the given circumstances compete with the slowly growing *Actinomyces* as they do on better media, e.g. on broth agar, where *Actinomyces* never occurs when bacteria are present.

As the delicate threads of this genus enter deep into the agar, the plates may be freed by washing from the bacterial colonies and the adhering soil; then the *Actinomyces* sods can be easily counted. In humus and humus containing soil their number is amazing. When they can freely multiply on plates which are poor in food their growth is unlimited and they produce sods of great extension, even of one or more decimeters in surface, commonly producing very fine mycelial-rings, which by turns bear spores or not. These rings are independent of light and suggest a periodicity in the nutrition not yet fully explained.

In somewhat extensive culture experiments, similar to the above, it may with certainty be expected that at some places brownish red or jet-black spots will originate. The brown spots are caused by the oxidising action of some common soil bacteria, which produce a red or brown-red pigment from tyrosin: the black ones, caused by melanin, which will be more exactly considered here, have quite another origin.

In or near the centrum of these black spots always lies a colony of *Actinomyces*. Streaks on new culture plates of the said composition to obtain a pure culture, give the surprising result, that the organism can vigorously grow on the tyrosin but produces no pigment at all. A more minute examination shows further, that the black plants of *Actinomyces* lie under a thin, glassy, transparent layer of fine rod-bacteria. This layer covers like a crust the jet-black sods of *Actinomyces* and prevents them from producing spores, which does take place on that part of the mycelium, which develops outside the bacterial cover. If from this layer the bacterium is brought into pure culture, which is easily done on brothgelatin- or brothagarplates, it proves to be an extremely delicate polar ciliate rodlet, which forms no spores and strongly liquefies culture gelatin. Streaks of the pure culture on a tyrosin plate produces no melanin at all, so that in this respect the bacterium resembles *Actinomyces*.

It is obvious that we here have a case of pigment formation reposing on the symbiose of the two organisms. Experience shows that this supposition is right: their combined streaks on a new tyrosin plate produce beautiful black spots of any extension. As they can both be very well grown on better media, such as brothagar, the experiment is, the first isolation effected, easy and interesting. The experiment may be improved by providing the culture plates with a better source of carbon beside the tyrosin, for which glucose and peptone proved particularly useful. On the other hand, additions of an ammoniumsalt or of nitrates had no effect.

In order to ascertain which of the two organisms is the real cause of the melanin production, the following experiment was made.

On an agar-tyrosinplate of the said composition, parallel streaks of both organisms were drawn with some millimeters, distance between. The result was not dubious; after a few days the streaks of *Actinomyces* vigorously developed and covered with snow-white spores, but for the rest were quite colourless. The bacterial streaks, on the other hand, which had developed to a thin, hardly visible transparent layer, had become jet-black wherever they were near *Actinomyces*. The following must therefore take place: *Actinomyces* decomposes the tyrosin and produces from it a colourless chromogene which is converted into melanin by the bacterium and easily diffuses through the agar, evidently without spontaneously oxidising at the air.

From the foregoing it is clear that *Actinomyces*, as well as the bacterium, can only be found in garden soil when germs of both species occur in each other's immediate vicinity. To promote this occurrence I have tried first on fit agarplates to grow *Actinomyces* and later floated them with a tyrosin solution, in which the melanin bacterium was present in so great quantity, that it could develop anywhere on the plate, after the tyrosin had diffused.

As the various species of *Actinomyces* are very vigorous, polyphagous microbes, which develop especially in dilute media at the side of the common bacteria, the most different food may be used for the first part of the experiment.

So, an agarplate, only containing some potassiumfosfate and ammoniumsulfate, was sprinkled with a little dry inulin mixed with garden soil. The soon developing flora was washed off under the tap by which the loosely adhering bacterial colonies together with the non-decomposed inulin, were removed. The agarplate was now clear again but in the surface were hundreds of *Actinomyces* colonies which had not been removed by the washing, as they had penetrated too deep into the agar. After treating with the tyrosin solution in which the melanin bacterium was suspended and a renewed cultivation for some days at 30° C., black melanin spots appeared around some six colonies of *Actinomyces*; this species must thus be rather common in the soil.

The tyrosin *Actinomyces* can also very easily be isolated from the roots of the elmtree (*Ulmus campestris*), in whose dead periderm cells an almost pure *Actinomyces* flora occurs, as I demonstrated before [1]). For the development of this flora some of the hairroots are carefully washed, to remove the adhering soil and are then ground in a mortar. The thus obtained brown paste is diluted with water, mixed with the tyrosin bacterium (which however is also rather common on the elm roots themselves), then sown out on a tyrosinplate of the above composition. After a few days numerous colonies of *Actinomyces* develop at 30° C., among which some jet-black ones.

Here it should be called to mind that the two organisms produce no pigment on peptone or broth-containing media, neither each for itself nor in combination. But herefrom cannot be concluded that at their cultivation from peptone no tyrosin originates. Nevertheless the conclusion must be drawn, that if at the splitting of the peptone

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[1]) Centralbl. f. Bakter. 2 Abt. Bd. 6, S. 2, 1900. Arch. Néerl. 1900, p. 327.

tyrosin is indeed formed, it is oxidised in another way but not to melanin.

That this *Actinomyces* must belong to another species than *Actinomyces chromogenes*, so common in our environment, is obvious. The latter namely is characterised by the production of a dark brown pigment from pepton, (but not from tyrosin in which, as I have formerly[1]) shown, under certain circumstances chinon may be found.

Several other species of *Actinomyces* produce blue, red, or yellow pigments, whereby, as to the blue and red, the simultaneous presence of certain varieties of hay bacteria is favourable. In this case it is not tyrosin, but glucose, malates and nitrates that form the chromogeneous food, so that the symbiose is then evidently associated with other factors than those active in the production of melanin from tyrosin.

Hitherto I have not yet been able in liquid cultures with the help of *Actinomyces* and its symbiont to produce a somewhat considerable quantity of melanin. This could not be foreseen as this genus is as common in the mud of moats and canals as in garden soil. But some experiments as the above to find our *Actinomyces* in mud gave no result, so it seems that this species at least is a real inhabitant of the soil.

That pigment production in this case is difficult in liquid media, whereas *Microspira tyrosinatica*, which I described earlier[2]), produces it as readily in liquid as in solid media, is perhaps owing to the general propriety of *Actinomyces* to grow but slowly in solutions probably in consequence of the little tension of the dissolved oxygen. *Microspira*, on the other hand, is as a true water microbe, evidently better adapted to that tension.

Theory of the melanin formation[3]).

In physiological chemistry it is generally accepted that at the tyrosin reaction from the tyrosin first originates homogentisinic acid, ammonia and carbonic acid after the formula

$$\underset{\text{Tyrosin}}{C_9H_{11}NO_3} + O_3 = \underset{\text{Homogentisinicacid}}{C_8H_8O_4} + NH_3 + CO_2$$

and that only afterwards by a new oxidation the homogentisinic acid is converted into melanin.

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[1]) Centralbl. f. Bakter. 2 Abt. Bd 6. S 2, 1900. Arch Néerl. 1900, p. 327. Commonly the chinon is absent, which I did not know in 1900.

[2]) These Proceedings, XIII, 1066

[3]) For the literature see CZAPEK, Biochemie der Pflanzen. Bd. 2, p. 462 and 478, 1905. ABDERHALDEN, Physiologische Chemie, p. 362 and 365, 1909.

This might give a good explanation of the symbiose experiment, supposing that *Actinomyces* produces homogentisinic acid from tyrosin and that the symbiotic bacterium oxidises this acid to melanin. Taken for granted that these two processes are due to two separate enzymes, this conception may be called "the two enzymes theory" of the melanin production.

In order to obtain more certainty regarding the correctness of this suppositon, I made some experiments with the soda salts of the homogentisinic acid ($C_8H_8O_4$) and compared the results with the conversion of the calcium and soda salts of the gentisinic acid ($C_7H_6O_4$). Both substances I owed to the Chemical Laboratory of the Technical University, the homogentisinic acid as lead salt, which I converted into the soda salt, the gentisinic acid in free state. Both behave towards microbes in a corresponding way, but the gentisinic acid oxidises more greater difficulty.

I also received from Professor Pekelharing the lead salt of homogentisinic acid, prepared from urine, but this could not be distinguished from the other.

At the preparation with these substances of neutral or feebly alkaline agar plates, on which the oxidising microbes were to be grown, the difficulty arose that already during the heating at the air a brown colour appeared, which was not the case when cold. It could, however, with certainty be stated that, as was expected, *Actinomyces* produced no pigment from these acids; on the other hand, the symbiotic bacterium gave a dark brown colour, which may finally run into jet-black. As this bacterium produces some alkali, it might seem doubtful whether this alkali might be the cause of the more intense pigment production, or if any oxidising enzyme, produced by the bacterium, were active in this case. By cautiously neutralising the existence of an oxidase, which diffuses in the agar to a relatively great distance from the bacterial colony, could be ascertained. It is clear that the thus found enzyme might be called "homogentisinase". It will be seen by and by that it also occurs in higher plants and perhaps corresponds to the common laccase.

The formerly described *Microspira tyrosinatica* (l.c.) living in the sea and in sewagewater, oxidises tyrosin directly to melanin without intervention of any other organism. That this is done here also by a vigorously active tyrosinase is easily shown with the form living in the sea, the bacterium, when killed by chloroform, being still able to cause the melanin reaction. I think it is proved now, that also in this case the tyrosinase consists of two enzymes, as it is possible with *Microspira* to oxidise the homogentisinic acid to a dark pigment.

In order to ascertain how in this respect the tyrosinase of the higher plants behaves, I took strong tyrosinase preparations derived from the potato, the beetroot and latex of *Euphorbia Lathyris*[1]) which quickly colour tyrosin solutions deep black, and made them act on homogentisinic acid salts. The latex of *Euphorbia Lathyris* is extremely fit for these experiments as it can always be made to drip from the living plant, which supports our winters very well in the garden. A single drop on an agar-tyrosin plate at from 30° to 50° C. forms deep black melanin spots after a few hours already. But homogentisinic acid can also be oxidised with great velocity. For this experiment I used an agarplate of this composition: water, $2^0/_0$ agar, $0.5^0/_0$ natrium homogentisinate, $0.02^0/_0$ NH_4Cl and $0.02^0/_0$ K_2HPO_4. On this plate drops of the latex were put and besides streaks were made of *Actinomyces* and the symbiotic bacterium. After some hours, at 30° C., dark brownish black fields appeared, evidently more readily formed than the black fields from the tyrosin.

After about 24 hours *Actinomyces* also began to grow but no pigment at all appeared, as was to be expected. The symbiotic bacterium did not develop under these conditions. But some broth being added to a like medium the bacterium could grow and oxidised the homogentisinic salt to melanin. So it is certain that also the tyrosinase of *Euphorbia Lathyris* must be a mixture of two oxidising enzymes; one of these, which may preserve the name of tyrosinase, produces homogentisinic acid from tyrosin, the other, "homogentisinase", forms melanin from the acid, and corresponds with the oxidase of the symbiotic bacterium. This enzyme requires no special name as "homogentinase" and "laccase" are probably identic.

Although the "two enzymes theory" of the tyrosinase may be considered as confirmed by what precedes, still it should be called to mind that, when a method of experimenting is used somewhat deviating from the described the above result with *Euphorbia Latyris* is not obtained. Such is, namely, the case when the milky juice of the plant is put on agarplates with homogentisinic acid salt, with addition of broth for the bacteria. Then the surprising fact occurs that the bacterium is active but the latex is not. Whereon this difference reposes is not clear.

Finally it may be mentioned that the existence of two enzymes in the tyrosinase of the beetroot was already made probable by P. C. VAN DER WOLK (Recherches au sujet de certains, processes enzymatiques chez *Beta vulgaris*, Nimègue 1912).

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[1]) The latex of *Euphorbia palustris*, *E. Peplus*, *E. helioscopia*, *E. Mysinitis*, contain no tyrosinase

Mathematics. — *"On Steinerian points in connexion with systems of nine ϱ-fold points of plane curves of order* 3ϱ." By Dr. W. van der Woude. (Communicated by Prof. P. H. Schoute).

(Communicated in the meeting of December 28 1912).

§ 1. In a former communication[1] has been indicated what is the locus of the point forming with eight given points a system of nine nodes of a non degenerated plane sextic curve; here will be treated a more general problem including the preceding one as a particular case.

To that end we remark that by nine arbitrarily chosen points D_1, $D_2, \ldots, D_9$ a curve of order 3ϱ passing ϱ times through these points is determined; in general however this $C_{3\varrho}$ is a cubic curve counted ϱ times. So the problem we propose now is: "Eight points D_1, $D_2, \ldots, D_8$ being given, to determine the locus of the point D_9 under the condition that the nine points D_i can be ϱ-fold points of a curve $C_{3\varrho}$ not degenerating in the manner mentioned.

§ 2. As we shall find by and by this problem is very closely related to the following one: "Let B_1, $B_2, \ldots, B_9$ be the base points of a pencil (β') of cubic curves, and u_3 any curve of this pencil. On u_3 lie (ϱ^2-1) points S each of which forms with B_9 a Steinerian pair[2] of order ϱ. To determine the locus of these points S, if u_3 describes the pencil (β')".

§ 3. We start by treating the first of the two problems.

So the eight points D_1, $D_2 \ldots D_8$ are given and we have to determine the locus of the ninth point D_9 satisfying the condition stated. In the quoted memoir the case $\varrho = 2$ has been treated; for convenience sake we repeat here the principal results.

Then we occupy ourselves with the case $\varrho = 3$ before passing to

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[1] W. v. d. Woude, "*Double points of a c_6 of genus 0 or 1* (Proceedings of Amsterdam, vol. XIII, p. 629)

Compare also Dr. V. Snijder, "*The involutorial birational transformation of the plane of order 17*" (American Journal of Mathematics, vol XXXIII, p. 328).

[2] Two points P and Q of u_3 form a Steinerian pair of order n, if it be possible to inscribe in u_3 one and therefore an infinity of closed polygons with $2n$ vertices, the sides of which pass alternately through P and Q. *Literature*: Steiner (Journal of Crelle, vol. XXXII, p. 182); Küpper (Math. Ann., vol XXIV, p. 1); Schröter (Theorie der ebenen Kurven dritter Ordnung, § 31). For the treatment by means of elliptic functions see Clebsch: Vorlesungen über Geometrie.

the general case of an arbitrary ϱ. But we wish to give just now one theorem where ϱ has already any arbitrary value:

"*If $D_1, D_2, \ldots, D_9$ are ϱ-fold points of a non degenerated curve $C_{3\varrho}$ of order 3ϱ, these points are at the same time the base points of a pencil of curves of order 3ϱ, each of which passes ϱ times through $D_1, D_2, \ldots, D_9$*".

For the proof it will suffice to remark, that the nine points lie on a cubic curve u_3; so the pencil mentioned is represented by

$$c_{3\varrho} + \lambda u_3^{\varrho} = 0.$$

§ 4. By $D_1, D_2, \ldots, D_8$ we will henceforth denote arbitrarily chosen points; we represent by (β') the pencil of curves c_3 passing through them, by B_9 the ninth base point of this pencil. So the principal results, obtained for $\varrho = 2$, are the following:

I. "The locus of the point forming with $D_1, D_2, \ldots, D_8$ a set of nine nodes of a non degenerated [1] c_6 is a curve j_9 of order nine passing three times through $D_1, D_2, \ldots, D_8$".

II. "This curve j_9 is also the locus of the points corresponding with B_9 in tangential point on the curves of pencil (β')".

III. "Let u_3 be any cubic of (β') and c_6 any sextic passing three times through $D_1, D_2, \ldots, D_8$. Then the line joining the last two points common to u_3 and c_6 will meet u_3 for the third time in the tangential point T of B_9 on u_3".

Before continuing our considerations we wish to correct the preceding communication. We have indicated there that B_9 does not lie on j_9: indeed this is so, but one of the proofs — the geometrical one — may give rise to difficulties. Therefore we once more prove here: B_9 does not lie on j_9. To that end we consider j_9 as the locus of the points on any curve of (β') corresponding with B_9 in tangential point. Now B_9 will be a point of j_9, if and only if one of these points coincides with B_9, which only can happen if B_9 is a node for one of the curves of (β'). Of these nodes — the 12 so called "critical points" of the pencil — none however coincides with one of the base points, if — as it is the case here — eight of the base points have been chosen arbitrarily. So B_9 does not lie on j_9.

§ 5. We now pass to the case $\varrho = 3$.

We still denote by $D_1, D_2, \ldots, D_8$ arbitrarily chosen points,

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[1] Here by *non degenerated* is meant a curve not breaking up into a c_3 to be counted twice. In this manner is to be interpreted henceforth the expression *non degenerated* c_6 used now and then.

whilst u_3, β', B_9 and T keep the signification assigned to them in art. 4. Now the question is to determine the locus of the point forming with $D_1, D_2, \ldots, D_8$ a set of threefold points of a non degenerated c_9.

In order to determine a curve c_9 passing three times through $D_1, D_2, \ldots, D_8$ we can imply to it the condition of containing six arbitrary points. Of these six points however no more than two [1]) may lie on u_3; then the last point common to u_3 and c_9 is determined inequivocally. We will show immediately how the latter point can be found; provisionally we start from any c_9 with the eight given threefold points, cutting c_3 in an arbitrarily chosen fixed point X. This c_9 cuts u_3 in two points more; the line connecting these two points has still a third point E with u_3 in common; according to the *Residual Theorem* of SYLVESTER the latter point is a fixed point, i. e. independent from the chosen curve c_9 passing through X. Now we first determine the point E; to that end we choose a c_9 breaking up into a curve r_3 of pencil (β') and a curve c_6 passing twice through $D_1, D_2, \ldots, D_8$ and passing moreover through X. We have seen that this c_6 cuts u_3 in one point Y more, being collinear with X and T (§ 4, III); moreover u_3 and r_3 have B_9 in common. So the point E is the third point of intersection of the line YB_9 and u_3.

If now we fix on u_3 two points X, X' and consider a curve c_9 with threefold points in $D_1, D_2, \ldots, D_8$ and cutting u_3 in X and X', then the last point of intersection of this c_9 and u_3 can be found as follows: we first determine in the manner indicated the point E; then the third point of intersection of the line EX' and u_3 is the point looked out for.

Remark. We have stated, that any c_9 with $D_1, D_2, \ldots, D_8$ as threefold points meets u_3 in three points more; evidently this does not hold if this c_9 breaks up into two curves one of which coincides with u_3. In this case the residual curve of order six must be determined in such a manner that it admits on u_3 nine nodes, eight of which lie in $D_1, D_2, \ldots, D_8$. So we fall back on the case $\rho = 2$, but we can discard this by requiring that D_9 has been determined in such a way that the c_9 under discussion does not break up, neither into a c_3 to be counted thrice nor in two curves c_3 and c_6, the latter of which admits a node in any of its points of intersection with the former..

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[1]) See e.g. SALMON FIEDLER: Höhere ebene Kurven, p. 23.

§ 6. It is now immediately clear that there are four points in which any c_9 with the threefold points $D_1, D_2, \ldots, D_8$ and passing through X can touch u_3, i. e. in any of the four points admitting E as tangential point; likewise that any c_9 with the threefold points $D_1, D_2, \ldots, D_8$ touching u_3 will cut this curve in X.

We now will try to determine X in such a way that it coincides with one of the four points of which E is the tangential point; in that case any c_9 with threefold points in $D_1, D_2, \ldots, D_8$ and touching u_3 in X, will have in X a third point in common with u_3.

Let us suppose that the point X has been determined so as to satisfy the condition mentioned; then we can describe in u_3 closed hexagons the successive sides of which pass alternately through B_9 and X. If we choose B_9 as first vertex and P is the third point of intersection of B_9X and u_3, then there is a closed hexagon with the successive sides B_9B_9T, TXY, YB_9E, EXX, XB_9P, PXB_9 (fig. 1).

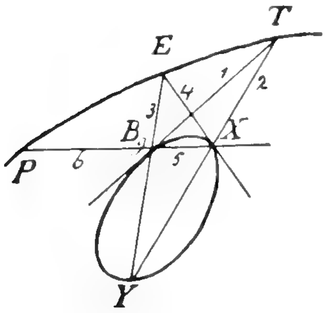

Fig. 1.

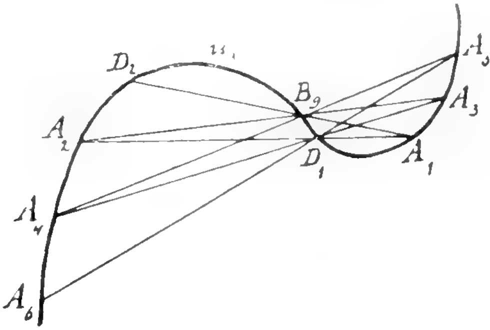

Fig. 2.

So the points X to be determined are the eight points each of which forms with B_9 on u_3 a Steinerian pair of order three. [1]

§ 7. We now choose one point out of these 8 and call it X_1. If we then require that C_9 has threefold points in $D_1, D_2, \ldots, D_8$ and touches u_3 in X_1, we can assume arbitrarily four more points K, L, M, N of this curve, which as we have seen above has in X_1 still a third point in common with u_3. Provisionally we suppose L, M, N to be fixed points but K to describe a right line k through

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[1] That B_9 and the point X satisfying the imposed condition form on u_3 a Steinerian pair of order three can also easily be shown by representing the points of u_3 by means of an elliptic parameter. If β is the parameter value for B_9 and x that for the point X taken provisionally at random, we find for the values corresponding to T, Y and E respectively -2β, $2\beta - x$ and $x - 3\beta$. So the condition that E be the tangential point of X is $3\beta = 3x$. Chiefly for the cases $p = 4, 5, \ldots$ presenting themselves later on the use of this parameter proves to be very convenient. Compare CLESCH: Vorlesungen über Geometrie (p. 615).

X_1 different from the tangent to u_3 in X_1: then the C_9 describes a pencil, one curve of which passes through any point of k. The coincidence of K with X_1 then furnishes a C_9 having in X_1 three points in common with u_3 and two points with k: so this C_9 has a node in X_1 and one of its branches touches u_3. If now we allow L to move along LX_1 to X_1 and afterwards M along MX_1 to X_1, we generate a C_9 having still threefold points in $D_1, D_2 \ldots . D_8$, now admitting a ninth threefold point in X_1 and passing moreover through an arbitrarily chosen point N (compare § 3). So the point X_1 is a point of the curve j_x under discussion. Therefore:

The curve j_x cuts any curve of (β') besides in the base points in 8 *points more. It is at the same time the locus of the points forming with B_9 on the curves of (β') a Steinerian pair of the third order.*

§ 8. In order to determine the curve j_x more closely it is necessary to know the order of multiplicity of the points $D_1, D_2, \ldots . D_8$ on it, i. e. how many times each of these points happens to form with B_9 a Steinerian pair of order three on a curve of (β'). Let u_3 (fig. 2) be once more an arbitrary curve of (β'): then we project B_9 out of D_2 on u_3 (i. e. we determine the third point A_1 common to D_2B_9 and u_3), from this point A_1 we project D_1 on u_3 into A_2, from A_2 we once more project B_9 on u_3 into A_3 and so on, alternately projecting B_9 and D_1. Then we allow u_3 to describe the pencil (β') and determine the loci of the points $A_1, A_2, \ldots . A_n$; then every coincidence of A_6 with D_2 points to a curve out of (β') on which B_9 and D_1 form a Steinerian pair of order three.

So we find for the locus of

A_1: the line D_2 B_9;

A_2: a C_3 with a double point in D_1, not passing through D_2 and
B_9 but cointaining $D_3, D_4 \ldots . D_8$;

A_3: a C_7 with an ordinary point in D_1,
a threefold point in D_2,
double points in $D_3, D_4 \ldots . D_8$,
a fourfold point in B_9;

A_4: a C_{12} with a sixfold point in D_1,
a threefold point in D_2,
fourfold points in $D_3, D_4 \ldots , D_8$,
a double point in B_9;

A_5: a C_{19} with a fourfold point in D_1,
a sevenfold point in D_2,
sixfold points in $D_3, D_4 \ldots , D_8$,
a ninefold point in B_9;

A_6 : a C_{27} with a twelvefold point in D_1,
an eightfold point in D_2,
ninefold points in D_3, D_4 . . ., D_8,
a sixfold point in B_9;
A_{2n} : a C_{3n^2} with a $n(n+1)$-fold point in D_1,
a (n^2-1)-fold point in D_2,
n^2-fold points in D_3, D_4 . . ., D_8,
an $n(n-1)$-fold point in B_9;
A_{2n+1} : a C_{3n^2+3n+1} with an n^2-fold point in D_1,
an (n^2+n-1)-fold point in D_2,
(n^2+n)-fold points in D_3, D_4 . . ., D_8,
an $(n+1)$-fold point in B_9.

We prove this as follows. It goes without saying that the locus of A_1 is the line D_2B_9. Through any point A_1 of this line one curve u_3 of (β') passes and this curve is cut by A_1D_1 for the third time in A_2. In D_1 we draw the tangent to u_3 and we indicate by A_1' the point common to this tangent and D_2B_9. Now if u_3 describes the pencil (β') it will happen twice that A_1 and A_1' coincide; in each of these two cases A_2 coincides with D_1, so that D_1 is a double point of the locus of A_2. This point A_2 describes a rational cubic curve, to be indicated henceforth by α_3, any line through D_1 having only one more point in common with this curve. It contains the points $D_3, D_4, \ldots, D_8$, as D_2B_9 cuts each of the lines D_1D_3, $D_1D_4, \ldots, D_1D_8$ in one point.

Let us now consider the locus of A_3. It is immediately evident that D_1 is an ordinary and D_2 a threefold point of this locus; for α_3 is cut by B_9D_1 in only one, by B_9D_2 in three points; in the same manner we prove $D_3, D_4, \ldots, D_8$ to be double points. So we have still to investigate how many times A_3 coincides with B_9. Let A_2 be once more an arbitrary point of α_3 and u_3 the curve of (β') through A_2; then the tangent of u_3 in B_9 cuts α_3 in three points A'_2. So the points A_2 and A'_2 generate a correspondence (1,3) furnishing — α_3 being rational — 4 coincidences. Any coincidence of A_2 and A_2' gives a coincidence of A_3 and B_9; so A_3 describes a curve of order seven, to be indicated henceforth by α_7, any line through B_9 containing three points more of this locus.

We can prove that B_9 is a fourfold point of α_7 also as follows. In case A_2 coincides with one of the points A_2', A_2 is at the same time the tangential point of B_9 on the curve out of (β') through A_2. So the number of points common to α_3 and the *tangential curve* of B_9 — i. e. the locus of the tangential point of B_9 on any curve of (β') — amounts to four, the common points coinciding with the base points of (β') disregarded: for, the tangential curve is of order four and admits B_9 as threefold point whilst it passes only once through $D_3, D_4, \ldots D_8$. So B_9 is a fourfold point of α_7 and this curve is of order seven. From the number of the double points we deduce that α_7 is rational; this is right, for it corresponds point by point with the line $D_2 B_9$.

As to the locus of A_4 it is immediately clear that B_9 is a double point and D_2 a threefold point on it, while it passes four times through $D_3, D_4, \ldots, D_8$.

The tangential curve of D_1 is cut by α_7 besides in the base points in 6 points more, which implies that D_1 is a sixfold point on the locus of A_4 and that this curve is of order twelve, any line through D_1 containing six more points of it. In the same manner we determine the loci of the points A_5, A_6, A_7, etc. and then the loci of A_{2n} and A_{2n+1} can be found by the Bernoullian method. Provisionally we only still wish to remark, that the locus of A_6 has an eightfold point in D_2, for this proves that the points B_9 and D_1 form two Steinerian points of order three on 8 curves of (β').

§ 9. Let us return to the point we started from. We have seen that the curve j_x under discussion — the locus of the ninth threefold point — is at the same time the locus of the points each of which forms with B_9 a Steinerian pair of the third order. On each curve of (β') lie besides the base points eight points more of j_x; moreover $D_1, D_2, \ldots, D_8$ are eightfold points of j_x.

We have now to investigate whether B_9 lies on j_x or not. This can only happen if on a curve c_3 of (β') the point B_9 coincides with one of the eight points each of which forms with it a Steinerian pair of the third order. However it is easy to prove that a suchlike coincidence of two Steinerian points can only present itself in a node; for the group of the nine inflexions this is immediately evident and for the other groups of Steinerian points of the third order it can be deduced from this by projection. Now B_9 is not a node of a curve out of (β'); so it does not lie on j_x.

As the number of points common to j_x and u_3 amounts to 72 we find:

"*The curve j_x is of order twenty-four; it has $D_1, D_2, \ldots, D_8$ as eightfold points.*"

§ 10. We will enumerate some points of j_x, which curve will be denoted furthermore by j_{24}. It is cut by the line $D_1 D_2$ in eight more points; any point P of these eight determines with $D_1, D_2, \dots, D_8$ a pencil of curves c_9 with threefold points in these nine points. Any other point Q of $D_1 D_2$ determines a curve c_9 of this pencil having ten points in common with that line and breaking up therefore into that line and a curve c_8 with double points in D_1, D_2, P and threefold points in $D_3, D_4, \dots, D_8$. So any point of intersection P of $D_1 D_2$ and j_{24} is at the same time a node of a c_8 forming with $D_1 D_2$ a c_9 with nine threefold points. At first this result may seem astonishing; for we can indicate *eleven* points on $D_1 D_2$ each of which forms with $D_1, D_2, \dots, D_8$ a set of nine threefold points of a c_9, and of these eleven points we find back eight only. But the three other ones prove to determine a c_9 (and therefore a pencil of curves c_9) excluded from the beginning.

To prove this we consider the net $[\delta]$ of curves c_8 determined by the six threefold points $D_3, D_4, \dots, D_8$ and the double points D_1, D_2; the curve of Jacobi of this $[\delta]$ is of order twenty-one and, as it passes five times through D_1, D_2, it is cut by the line $D_1 D_2$ in 11 points more. So $D_1 D_2$ contains 11 points each of which is a node of a c_8 belonging to $[\delta]$.

Now let us consider the curve c_5 passing through D_1, D_2 and admitting $D_3, D_4, \dots, D_8$ as nodes; this completely determined curve cuts $D_1 D_2$ in three points E, F, G more. Each of these points lies on the curve of Jacobi of $[\delta]$, for c_5 forms with the curve c_3 of (β') passing through E a c_8 of $[\delta]$, of which the point E is a node; likewise these two curves form with the line $D_1 D_2$ a curve c_9 of which $D_1, D_2, \dots, D_8$ and E are threefold points. However E does not lie on j_{24}, for this c_9 can be considered as the combination of a c_3 of (β') and a c_6 and this combination has been excluded beforehand (§ 5). But it is evident that E, F, G do lie on the curve j_9 quoted in § 4.

The eight remaining points of intersection of line $D_1 D_2$ and the curve of Jacobi of $[\delta]$ do lie on j_{24}; so on each of the 28 lines $D_i D_k$ can be indicated eight points of j_{24}.

Moreover j_{24} is cut by the conic $D_1, D_2, \dots, D_5$ in eight more points. These lie at the same time on the curve of Jacobi of the net $[\varepsilon]$ of curves of order seven passing twice through $D_1, D_2, \dots, D_5$ and thrice through D_6, D_7, D_8. This curve of Jacobi of order eighteen is cut by the conic $D_1, D_2, \dots, D_5$ in eleven more points; of these however once more three do not lie on j_{24}, i.e. the points common to this conic and the curve c_4 passing once through $D_1, D_2, \dots, D_5$ and twice through D_6, D_7, D_8.

So on each of the 56 conics $D_i\ D_k\ D_l\ D_m\ D_n$ can be indicated eight points of j_{24}.

§ 11. We now treat in a summary way the general case: ϱ is an arbitrary number.

Once more the arbitrarily chosen points $D_1, D_2, \ldots, D_8$ are given and the question is to determine the locus of the point forming with these given points a set of nine ϱ-fold points of a non degenerated curve of order 3ϱ. In the same way as we have used the results obtained for $\varrho = 2$ in the solution of the problem for $\varrho = 3$, we can solve the successive cases $\varrho = 4, 5, \ldots$ by using every time the results obtained in the immediately preceding case. So we consider for $\varrho = 4$ at first a variable c_{12} with fourfold points in $D_1, D_2, \ldots, D_8$ and touching a curve u_3 of pencil (β') in a point X; then we determine the third point of intersection of u_3 with the line connecting the last two points of intersection of c_{12} and u_3, which point is independent of the choice of c_{12}, etc.

But before we state our results more in detail we wish to make a remark. We find, that any point D_9 which can present itself as ninth ϱ-fold point of a non degenerated $c_{3\varrho}$ must coincide with one of the points forming with B_9 a Steinerian point of order ϱ. The locus of the latter points is a curve $c_{3(\varrho^2-1)}$ with (ϱ^2-1)-fold points in $D_1, D_2, \ldots, D_8$. Now however it is evident that this curve degenerates in several cases. So, if e.g. we consider the case $\varrho = 6$, we shall find among the points forming with B_9 on a curve of (β') Steinerian pairs of order six also the points which form with B_9 Steinerian pairs of order two and of order three. So the curve $c_{3(\varrho^2-1)}$, here of order 105, must break up into j_9, j_{24} and a curve of order 72 passing 24 times through $D_1, D_2, \ldots, D_8$. Now the latter curve forms the locus proper of the ninth sixfold point of a non degenerated curve c_{18}. So the two curves of which the first is the locus of the ninth ϱ-fold point, the second that of the point forming with B_9 a Steinerian pair of order ϱ, coincide completely if ϱ is a prime number; if ϱ is no prime number the first curve is a part of the second. So we have found:

"*The locus of the ninth ϱ-fold point coincides completely or partially with that of the points forming with B_9 on the curves of (β') Steinerian pairs of order ϱ. The latter curve cuts any curve of (β') besides in the base points in $(\varrho^2 - 1)$ more points, has the points $D_1, D_2, \ldots, D_8$ for $(\varrho^2 - 1)$-fold points and is therefore of order $3(\varrho^2 - 1)$. The former coincides completely with this curve, if ϱ is a prime; in the opposite case its order and the multiplicity of the base points on it can be easily deduced from the corresponding numbers of the second curve.*"

Physics. — *"On the change induced by pressure in electrical resistance at low temperature."* I. *Lead.* By H. KAMERLINGH ONNES and BENGT BECKMAN. Communication N°. 132^b from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated in the meeting of November 30, 1912.)

§ 1. *Introduction.* The difficulties which encompass the explanation of the variation of resistance with temperature on the lines of the theory of electrons as developed by RIECKE, DRUDE and LORENTZ, and which are of particular import within the region of low temperatures, render it desirable to undertake an investigation of the behaviour of resistance at these temperatures under modification of various external conditions. With that end in view we have already developed in certain directions an investigation of the behaviour of resistance in a magnetic field (and of the closely allied HALL phenomenon). In the present paper we communicate the result of a first investigation of the change of resistance under the influence of uniform hydrostatical pressure. Our first aim had been to trace the connection between pressure coefficient and temperature coefficient. Our data, however, are as yet too few to serve as a basis for deductions — however obvious these may be — affording an explanation by means of vibrators, electrons, dissociation or variation of the mean speed [1]).

The dependence of specific resistance (w_{sp}) upon pressure (p) can, in general, be represented by the formula [2])

$$w_{sp} = w_{1sp}\, e^{-ap-bp^2} \ ,$$

in which a and b are constants, and w_{1sp} is the specific resistance for $p = 1$. When p is not very great, this gives

$$w = w_1 (1 - ap)\left(1 + \frac{1}{3}\beta p\right) = w_1 (1 + \gamma p)$$

for the resistance of a wire which is subjected to uniform hydrostatical pressure, in which

$$-\gamma = a - \frac{1}{3}\beta$$

and β is the compressibility. Hence the variation $\Delta w = w - w_1$, is given by

$$\frac{\Delta w}{w} = \gamma p$$

In the following only γ has been measured.

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[1]) B. BECKMAN, Upsala Univ. Årsskrift 1911, p. 107.

[2]) B. BECKMAN, l.c. p. 16.

The measurement of γ at very low temperatures is one of extreme difficulty. For, at these temperatures, the temperature coefficient is so great that even the smallest fluctuations of temperature can greatly affect the resistance; in this way a slight disturbance of the temperature equilibrium can occasion a variation of the resistance which completely obscures the whole phenomenon of variation with pressure. With the wire we used, for instance, at $T = 20°.3$ K. a pressure of 100 atm. brought about a change in the resistance of only about 0.001 Ω, while a change of 0.0003 Ω was the result of a variation of 0.01 degree in the temperature. And it is pretty obvious that it is a matter of extreme difficulty to re-adjust the temperature to within 0.01 degree of its former value after it has been altered by the heating or cooling of the liquid occasioned by fluctuations in the pressure.

There is a second factor operating which renders the measurement difficult. When the compression has been continued for a long time, elastic after-effects occur which can also attain a value that is a considerable fraction of the magnitude to be observed. Should, therefore, the variation of pressure be distributed over a long period of time in order to disturb the temperature equilibrium as little as possible, this after-action will give rise to a source of error.

Fig. 1.

§ 2. The lead to be subjected to pressure consisted of a turning about 2 metres long and about 0.2 m.m. in diameter. After some practice these long thin turnings could be successfully prepared. Attempts to draw wires of this small cross-section did not meet with success. The wire, a, was wound upon an ebonite cylinder (see fig. 1). To either end was soldered a band, c_1, c_2, rolled from a wire of electrolytic copper; to these bands were soldered the two pairs of leads, d_1, d_2, d_3, d_4. To enable one to subject the lead to pressure it was enclosed in a thick-walled copper cylinder, A_1, closed below by a heavy cap, A_2, (screwed and soldered), and above by a cap A_3 through which two copper capillaries A_4, A_5, pass. One of these capillaries, A_4, is used for filling the cylinder with liquefied gas and for exerting pressure upon the liquid, while the other, A_5, is connected to a manometer and, at the same time, acts as a safety valve, in allowing the liquefied gas to escape in the event of the supply tube getting frozen. This second tube also admits the wires required for the resistance measurements. At the upper end of A_3 these wires pass through a perforated cylinder of ebonite in which they are cemented with marine glue, and this cylinder is held tight against the tube by a screw cap. Resistances were measured by the method of overlapping shunts.

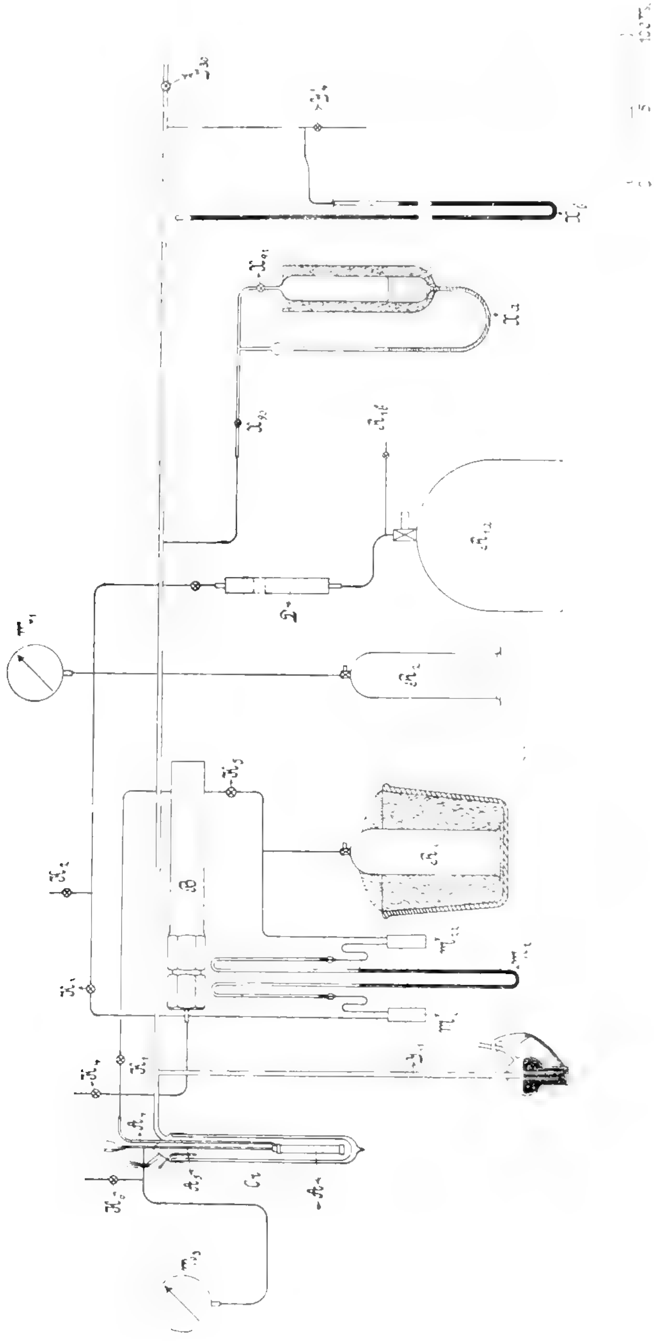

Fig. 2.

The cylinder was immersed in a cryostat, C, consisting of a transparent vacuum glass provided with a pump stirrer (see fig. 2). Fig. 1 shows the latter in aspect and cross section, c_1 is the cylinder and c_2 the piston. The temperature of the bath was regulated and measured by means of the gold resistance thermometer f, also shown in fig. 1. We may refer to earlier diagrams (Comm. No. 83, Pl. IV, and Comm. No. 127. p. 23) in which the same letters have been used, for details of the arrangement Y_{20}, Y_{21}, X_a, X_b, X_{20}, X_{21}, Y'_1, for regulating the pressure under which the liquid in the cryostat vaporises.

When the temperature of the cryostat has been adjusted the same kind of gas as has been liquefied in it is admitted into the experimental cylinder by the tap K_1 through A_4 from the reservoir R_{1a}, which has previously been filled at high pressure. A second reservoir R_{1b} is coupled in parallel with R_{1a} so that gas need be taken from R_{1a} only in sufficient quantity to complete the filling of the cylinder. In this way the reservoir R_{1a} is much longer available for raising the pressure in the experimental cylinder to the highest values. An other reservoir R_2 served as a regulator, and, as gas was added, the pressure was read on the manometer M_1. The tap K_2 was used for the evacuation of the apparatus and connections before the experiments began. The supply of gas was regulated by K_3. Behind K_3 a cylinder R_4 is coupled in parallel with the experimental tube to serve as a buffer; to the inlet tube of this cylinder is coupled not only the experimental cylinder but also the differential manometer, M_2, to which we shall return presently. Through the tap K_4 gas can be allowed to escape from the experimental cylinder and from the buffer. The pressure of the gas they contain can thus be kept at any desired constant value by means of K_3 and K_4. Regulation of the pressure is made according to the indications of the differential manometer, M_2, one side of which is attached to the experimental apparatus and the other to a reservoir R_3 which is maintained at the required constant pressure and is, for that purpose, immersed in ice. To adjust to the desired pressure the differential manometer is first rendered inoperative by opening the tap K_5. Care must be taken in admitting pressure to the manometer that friction does not give rise to difference of pressure between the parts of the apparatus it connects sufficient to cause the mercury of the differential manometer to be blown over. Two steel overflow vessels M_{21}, M_{22}, serve as a safety device. The pressure in the experimental cylinder is read from the manometer M_3, which is connected to A_5. K_6 is a safety valve which comes into operation when A_5 must be used for exhausting.

§ 3. An idea of the degree of purity of the lead is obtained from the values which we give here for the resistance at various temperatures.

TABLE I.

Resistance of the lead wire Pb_I at low temperatures.

T	w
289° K	12.75 Ω
90	3.77
20°.3	0.725
17°.8	0.626
14°.5	0.520

Comparison of these values with those given by KAMERLINGH ONNES and CLAY, Comm. No. 99*c*, shows that the lead now used must hold in solid solution a fairly considerable amount of foreign matter, for the great change in the temperature coefficient exhibited by metals in the presence of small amounts of impurity may generally be attributed to the transition of this admixture to a state of solid solution.

Our measurements were made with liquid oxygen and liquid hydrogen as compressing liquids. The results are contained in Table II. The pressure (p) is given in atmospheres.

TABLE II

Change induced in the resistance of lead Pb_I by compression at low temperatures.

$T = 90°$ K			$T = 20°.3$ K		
p	Δw	$\frac{1}{p}\frac{\Delta w}{w}$	p	Δw	$\frac{1}{p}\frac{\Delta w}{w}$
49.4	— 0.0043 Ω	— 2.35 × 10^{-5}	49.7	— 0.00062	— 1.7 × 10^{-5}
97.8	— 0.0080	— 2.2	97.5	0.00114	— 1.6
102.5	— 0.0085	— 2.2	97.5	— 0.00132	— 1.8
48.5	— 0.0040	— 2.3	98	— 0.00115	— 1.6
97	— 0.0079	— 2.2	97.5	— 0.00131	— 1.8
			97.5	— 0.00114	— 1.6

For the pressure coefficient E. LISELL[1] gives

$$\gamma = -1{,}44 \, . \, 10^{-5} \text{ at } T = 273^\circ \ \text{K}.$$

From our measurements we find

$$\gamma = \ \ 2.25 \, . \, 10^{-5} \text{ at } T = 90 \ \ \text{K}.$$

and $$\gamma = -1{,}7 \ \, . \, 10^{-5} \text{ at } T = 20^\circ.3 \ \text{K}.$$

so that the pressure coefficient has become somewhat greater at the lower temperatures. The increase obtained between 273° K. and 90° K. changes again to a diminution. The accuracy of the measurements is still too small to allow us to attribute any significance to this diminution at the lowest temperatures.

If we consider the decrease $-\angle w$ in the resistance for $p = 100$ atm., we find that it approximates to zero at the lower temperatures. Thus we find for Pb_I:

273° K. for $p = 100$ atm. $-\Delta w = 0{,}017 \ \Omega$
90° K. ,, ,, ,, $-\angle w = 0{,}008$
20°.3 K. ,, ,, ,, $-\angle w = 0{,}001.$

Physics. — "*Isotherms of monatomic substances and of their binary mixtures.* XIV. *Calculation of some thermal quantities for argon*". By H. KAMERLINGH ONNES and C. A. CROMMELIN. Comm. N°. 133*c* from the Physical Laboratory at Leiden.

(Communicated in the meeting of November 30, 1912).

The empirical reduced equation of state for argon, VII. A. 3, published some time ago[2], enables us to calculate a number of thermal quantities which are essential to a knowledge of monatomic substances in general and of argon in particular. These quantities may also be obtained graphically. Calculation by means of an equation which fits the experimental results over the whole region of observation allows, however, a much greater accuracy to be attained.

In the present paper[3] we give values of $\left(\frac{\partial p}{\partial T}\right)_v$, $\left(\frac{\partial^2 p}{\partial T^2}\right)_v$, $\left(\frac{\partial \gamma_v}{\partial v}\right)_T = T\left(\frac{\partial^2 p}{\partial T^2}\right)_v$, $\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p$, (AMAGAT's pression inté-

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[1] E. LISELL: Upsala Univ. Årsskrift 1903.

[2] H. KAMERLINGH ONNES and C. A. CROMMELIN, Proc. June 1912, Comm. N°. 128.

[3] Already indicated in Suppl N°. 23, note 492, p. 146. Preliminary values obtained by C. A. CROMMELIN for some of the quantities here discussed have already been published by E. H. AMAGAT. C. R 9 April, 1912.

rieure [1]), and of REINGANUM's a, $a_R = \left| T\left(\frac{\partial p}{\partial T}\right)_v - p \right| v^2$, calculated as functions of the temperature and of the density from equation VII. A. 3 [2]). The temperature is expressed in KELVIN degrees and is calculated from 0° C.; the pressure is expressed in international atmospheres [3]).

The importance of a knowledge of these quantities especially as functions of the temperature has already been repeatedly insisted upon [4]) so that we need say nothing further here upon that point. We shall only say that according to the chief VAN DER WAALS equation with constant a_W, b_W and R_W $\left(\frac{\partial p}{\partial T}\right)_v$, $\left(\frac{\partial u}{\partial v}\right)_T$ and a_R should be independent of the temperature, and consequently $\left(\frac{\partial^2 p}{\partial T^2}\right)$ should vanish, so that the deviations which they all show may be taken as a measure of the degree to which argon deviates from the simple assumptions regarding molecules accepted by VAN DER WAALS in developing his principal equation.

Agreement, at least approximate, with the chief VAN DER WAALS equation would first be expected in the monatomic substances, and therefore the investigation of these quantities for argon as well as a comparison of the results with those for substances of more complex molecular structure is of the greatest importance.

Consideration of the quantity introduced by REINGANUM [5]).

$$a_R = v^2\left[T\left(\frac{\partial p}{\partial T}\right)_v - p\right] = -\left(\frac{\partial u}{\partial \varrho}\right)_T$$

enables us to see that, as far as the mutual actions of the molecules is concerned, the assumptions upon which VAN DER WAALS founded his chief equation with constant a_W, b_W, and R_W must undergo some modification such as has recently been introduced by VAN DER WAALS in the various developments of the consideration of apparent association. If we retain for the moment the most immediate assumption suitable for monatomic substances such as argon, that the atoms are incompressible, then changes in a_R would be wholly due to deviations of the molecular

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[1]) E. H. AMAGAT, numerous papers in the C. R. collected in "Notes sur la physique et la thermodynamique". Paris 1912.

[2]) For the notations used in this paper see Enc. math. Wiss. V. 10. Suppl. N°. 23.

[3]) Enc. math. Wiss. V. 10. Einheiten. a.

[4]) M. REINGANUM, Diss. Göttingen 1899, Ann. d. Phys. (4). 18 (1905) p. 1008. Suppl. N°. 23, p. 140 sqq.

[5]) M REINGANUM. Diss. Göttingen 1899.

TABLE I.

$\left(\frac{\partial p}{\partial T}\right)_v$.

ϱ_N	+ 20°	0°	− 20°	− 40°	− 60°	− 70°	− 80°	− 90°	− 100°	− 110°	− 113°	− 116°	− 119°	− 122°
20	+0.0764	+0.0766	+0.0768	+0.0770	+0.0773	+0.0775	+0.0777	+0.0779	+0.0781	+0.0784	+0.0785	+0.0786	+0.0787	+0.0788
40	1589	1595	1603	1612	1624	1630	1638	1646	1655	1665	1669	1672	1676	1680
60	2471	2485	2501	2521	2545	2559	2575	2593	2614	2637	2644	2652	2660	2668
80	3409	3431	3457	3490	3531	3556	3584	3615	3650	3690	3703	3717	3731	3745
100				4517	4578	4615	4657	4704	4759	4821	4841	4861	4883	4904
120							5790	5857	5934	6022	6051	6080	6110	6141
140									7173	7292	7331	7371	7411	7453
160									8473	8627	8678	8730	8783	8837
180										1.0030	1.0093	1.0159	1.0227	1.0296
200											1580	1662	1747	1833
220											3142	3243	3348	3455
240												4913	5041	5172
260												6683	6839	6998
280												8568	8757	8951
300												2.0589	2.0817	2.1053
320												2769	3044	3329
340												5136	5467	5810

TABLE II.

$\left(\frac{\partial^2 p}{\partial T^2}\right)$.

ϱ_N	+20°	0°	−20°	−40°	−60°	−70°	−80°	−90°	−100°	−110°	−113°	116°	−119°	−122°
20	−0.00001	0.00001	−0.00002	0.00001	−0.00002	−0.00001	−0.00003	−0.00002	0.00002	−0.00003	−0.00002	0.00003	−0.00003	−0.00003
40	3	3	4	3	6	6	8	9	10	11	11	12	12	13
60	6	7	9	10	14	15	17	19	21	24	26	26	27	28
80	10	12	15	18	24	25	30	35	37	43	43	46	47	48
100				27	35	39	44	51	58	66	68	69	72	74
120							63	73	82	93	97	100	102	106
140									111	126	130	135	138	141
160									144	165	171	175	179	182
180										210	216	223	228	232
200											271	279	285	288
220											334	344	353	358
240												420	432	438
260												512	526	536
280												620	640	653
300												748	775	795
320												899	935	963
340												1079	1125	1165

TABLE III.

$\left(\frac{\partial u}{\partial v}\right)_T \quad T\left(\frac{\partial p}{\partial T}\right)_v \quad p$

ϱ_N	+ 10°	0°	20°	− 40°	− 60°	− 70°	− 80°	− 90°	− 100°	− 110°	− 113°	− 116°	− 119°	− 122°
20	+ 1.150	+ 1.198	+ 1.254	+ 1.314	+ 1.381	+ 1.417	+ 1.454	+ 1.494	+ 1.533	+ 1.579	+ 1.593	+ 1.604	+ 1.620	+ 1.635
40	4.525	4.703	4.905	5.134	5.388	5.523	5.670	5.826	5.990	6.163	6.218	6.273	6.331	6.387
60	9.996	10.37	10.79	11.27	11.82	12.12	12.43	12.77	13.14	13.52	13.64	13.76	13.89	14.01
80	17.44	18.05	18.75	19.55	20.46	20.98	21.53	22.11	22.74	23.42	23.63	24.84	24.06	24.27
100				29.79	31.15	31.92	32.75	33.65	34.62	35.65	35.98	36.31	36.64	36.97
120							45.91	47.18	48.55	50.03	50.49	50.95	51.42	51.90
140									64.38	66.38	67.00	67.63	68.27	68.90
160									81.94	84.54	85.35	86.18	87.00	87.83
180										104.4	105.4	106.5	107.6	108.6
200											127.2	128.5	129.8	131.1
220											150.5	152.2	153.8	155.4
240												177.4	179.4	181.4
260												204.4	206.9	209.3
280												233.2	236.1	239.1
300												263.8	267.4	270.9
320												296.5	300.7	305.1
340												331.3	336.4	341.7

TABLE IV.

$$a_{RN} = \left\{ T\left(\frac{\partial p}{\partial T}\right)_v - p \right\} v^2_N$$

ϑ_N	+ 20°	0°	— 20°	— 40°	— 60°	— 70°	— 80°	— 90°	— 100°	— 110°	— 113°	— 116°	— 119°	— 122°
20	+0.002875	+0.002996	+0.003134	+0.003285	+0.003453	+0.003541	+0.003636	+0.003735	+0.003833	+0.003946	+0.003983	+0.004011	+0.004050	+0.004088
40	2828	2940	3066	3208	3367	3452	3543	3641	3743	3852	3886	3921	3957	3992
60	2777	2880	2997	3131	3282	3366	3454	3548	3649	3756	3789	3823	3857	3893
80	2725	2821	2930	3054	3197	3278	3363	3455	3554	3659	3692	3725	3759	3793
100				2979	3115	3192	3275	3365	3462	3565	3598	3631	3664	3697
120							3188	3276	3372	3474	3506	3539	3571	3604
140									3285	3387	3418	3451	3483	3516
160									3201	3302	3334	3366	3399	3431
180										3223	3255	3287	3319	3352
200											3180	3212	3245	3278
220											3110	3144	3177	3211
240												3081	3115	3150
260												3024	3060	3096
280												2974	3012	3050
300												2931	2971	3011
320												2895	2937	2979
340												2866	2910	2956

TABLE V.

$$\left(\frac{\partial c_v}{\partial v}\right)_T = T\left(\frac{\partial^2 p}{\partial T^2}\right)_v$$

ρ_N	+20°	0°	—20°	—40°	–60°	70°	80°	—90°	—100°	—110°	—113°	—116°	—119°	—122°
20	0.00293	0.00273	0.00506	—0.00233	0.00426	—0.00203	0.00579	—0.00366	—0.00346	—0.00489	0.00320	—0.00471	0.00462	–0.00453
40	879	819	1012	699	1279	1219	1543	1648	1731	1794	1761	1885	1849	1964
60	1759	1912	2278	2331	2983	3046	3283	3479	3635	3914	4162	4084	4160	4231
80	2931	3277	3796	4196	5114	5077	5793	6408	6404	7013	6884	7226	7242	7252
100				6293	7458	7921	8496	9338	0.10039	0.10764	0.10886	0.10839	0.11094	0.11181
120							0.12165	0.13366	14193	15167	15529	15709	15717	16016
140									19213	20549	20812	21207	21264	21304
160									24925	26910	27375	27491	27582	27498
180										34249	34579	35031	35133	35053
200											43384	43828	43916	43514
220											53470	54039	54394	54090
240												65978	66567	66177
260												80430	81051	80984
280												97396	98618	98662
300												1.1750	1.1942	1.2012
320												1.4122	1.4407	1.4550
340												1.6950	1.7335	1.7602

forces from the simple initial assumptions made by VAN DER WAALS. Such changes in a_R might originate from three causes: change in the a_W, in the b_W or in the R_W of the chief equation, as a result of the radius of the sphere of action being but slightly greater than that of the molecule, a circumstance[1] revealed in apparent association.

Since

$$T\left(\frac{\partial^2 p}{\partial T^2}\right)_v = \left(\frac{\partial \gamma_v}{\partial v}\right)_t,$$

the question as to whether $\left(\frac{\partial p}{\partial T}\right)_v$ is independent of the temperature and therefore $\left(\frac{\partial^2 p}{\partial T^2}\right)_v = 0$, is most intimately connected with the question as to whether $\left(\frac{\partial \gamma_v}{\partial v}\right)_T = 0$ or not. For a long time this question remained undecided on account of the lack of experimental data. We now know that, at least for a number of substances, $\left(\frac{\partial p}{\partial T}\right)_v$ is in general a function of the temperature, and that therefore $\left(\frac{\partial^2 p}{\partial T^2}\right)_v$ does not vanish.

If we now compare the behaviour of argon with respect to $\left(\frac{\partial p}{\partial T}\right)_v$ with that of isopentane we find correspondence in many respects.

YOUNG [2]) [3]) deduced from his observations upon isopentane that $\left(\frac{\partial p}{\partial T}\right)_v$ decreases with falling temperature for $v_T < 4.6$ c.c.; at greater volumes up to $v_T = 400$ c.c. it increases with falling temperature, while it remains practically constant at still greater volumes. For argon, for which the volumes are expressed in terms of the normal volume as unit, if the law of corresponding states were accurately obeyed these volumes would correspond to $v_N = 0.00377$ and $v_N = 0.328$ or $\varrho_N = 265$ and $\varrho_N = 3.05$.

The argon observations embraced by VII. A. 3 lie entirely within these limits, and from Table I we see that argon agrees with isopentane within the region of observation. Over the entire region $\left(\frac{\partial p}{\partial T}\right)_v$ falls with increasing temperature. At the lowest argon density

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[1]) This circumstance causes a change in b_W also, cf. H. KAMERLINGH ONNES and W. H. KEESOM, Suppl. N⁰ 23, Nr. **47.**

[2]) M. REINGANUM, Diss. Göttingen. 1899, pg. 42.

[3]) S. YOUNG, Proc. phys. soc. Londen 13 (1895), p. 602.

$\varrho_N = 20$ the diminution becomes extremely small, pointing to constancy at still lower densities. Argon differs from isopentane, however, in this respect that with argon at higher densities far above $\varrho_N = 265$, the increase becomes still more rapid, while the behaviour of isopentane would lead one to expect a diminution in the rate of increase.

From his observations upon isopentane YOUNG[1] deduced the following rule for the behaviour of $\left(\frac{\partial^2 p}{\partial T^2}\right)$:

$$\left(\frac{\partial^2 p}{\partial T^2}\right)_{v < \pm v_k} > 0$$

$$\left(\frac{\partial^2 p}{\partial T^2}\right)_{v > \pm v_k} < 0$$

This rule has already been confirmed for a variety of substances, and is, as far as its second part is concerned, also obeyed by argon.

For carbon dioxide, ethylene and isopentane, REINGANUM found that the quantity $a_R = \left| T\left(\frac{\partial p}{\partial T}\right)_v - p \right| v^2$ is a minimum for v about $\frac{3}{4} v_k$ and at temperatures about 10° above t_k. If the law of corresponding states were strictly true this minimum for argon should be at $\varrho_N = 380$, and therefore outside the region of experiment. Nothing can be done consequently beyond trying to judge from extrapolation, if, and where, the minimum exists. If for this purpose we graph a_R as a function of ϱ_N at $-122°$ and $-116°$, then extrapolation towards higher densities shows that it is probable that these curves would also exhibit a minimum for argon at $v = \frac{3}{4} v_k$.

Physics. — "*On the rectilinear diameter for argon.*" By E. MATHIAS, H. KAMERLINGH ONNES, and C. A. CROMMELIN. Comm. 131*a* from the physical Laboratory at Leiden. (Continued).

(Communicated in the meeting of November 1912).

§ 5. *Results.* The results obtained are given in the following table[2] (p. 961):

The calculated values of the ordinates of the diameter given in this table have been obtained from the equation

$$D_{\xi\Gamma} = 0.20956 - 0.00\,26235\; t_K\,.$$

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[1] l. c.

[2] For the notations, see Suppl. No. 23.

The diameter has been drawn through the points 175°.39 $C_{\text{in K.gr}}$ and — 131°.54 $C_{\text{in K.degr.}}$.

bath	$t_K = T - T_{0°C.}$ Kelvin degrees.	$\varrho_{liq\Gamma}$	$\varrho_{vap\Gamma}$	$D_{\varrho\Gamma}(O)$	$D_{\varrho\Gamma}(C)$	$O-C$
O_2	183.15	1.37396	0.00801	0.69099	0.69006	+ 0.00093
CH_4	— 175.39	1.32482	0.01457	0.66970	0.66970	
CH_4	— 161.23	1.22414	0.03723	0.63069	0.63255	— 0.00186
C_2H_4	— 150.76	1.13851	0.06785	0.60318	0.60508	— 0.00190
C_2H_4	— 140.20	1.03456	0.12552	0.58004	0.57738	+ 0.00266
C_2H_4	— 135.51	0.97385	0.15994	0.56690	0.56507	+ 0.00183
C_2H_4	131.54	0.91499	0.19432	0.55466	0.55466	
C_2H_4	— 125.17	0.77289	0.29534	0.53412	0.53794	— 0.00382

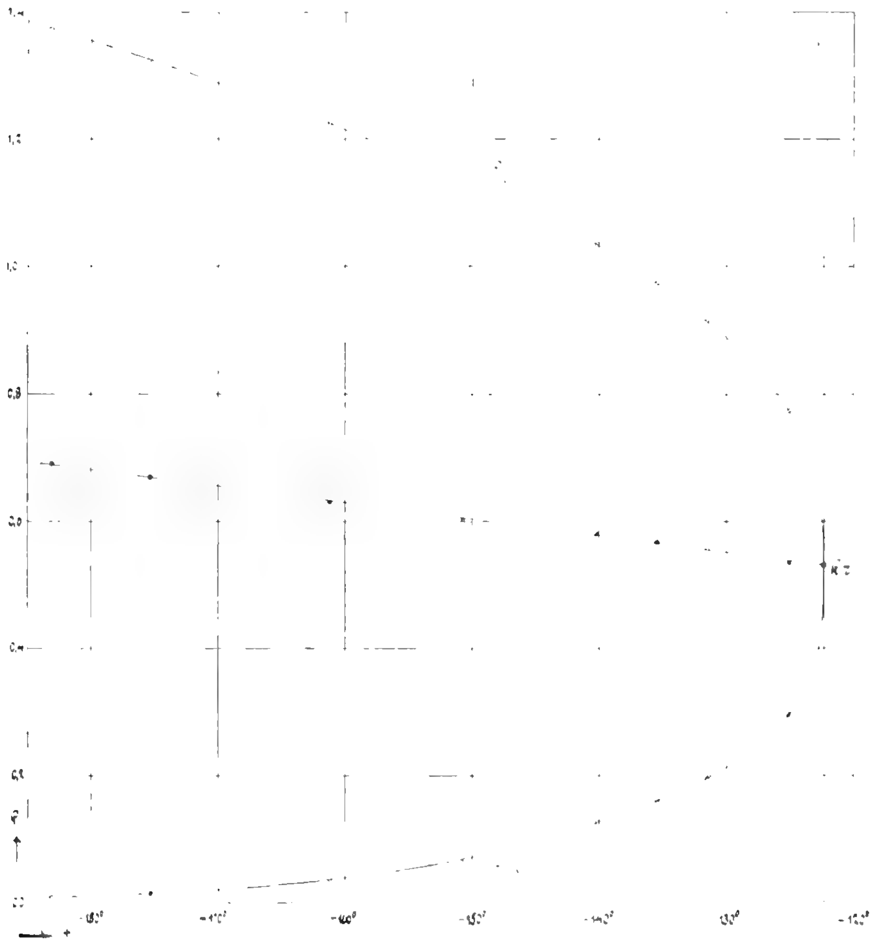

Fig. 2.

§ 6. *Discussion.* The slope of the diameter is given by

$$b_{\mathrm{dr}} = -0.0026235.$$

This coefficient is very large, larger than has been found for any other substance yet investigated with the exception of xenon, for which Patterson, Cripps and Whytlaw-Gray [1]) have found —0.003055. Comparison of the values of this constant for the two monatomic substances argon and xenon again reveals the influence exerted upon it by the values of the critical temperature.

With respect to the critical density the following remarks must be made. If we assume that the diameter remains rectilinear right up to the critical point, we then find

$$\varrho_{\mathrm{kd}} = 0.53078.$$

Using the equation

$$\left(\frac{\partial p}{\partial T}\right)_{\mathrm{vk}} = \left(\frac{dp}{dT}\right)_{\mathrm{koex.k.}}$$

the value

$$\varrho_{\mathrm{k.s.}} = 0.509.$$

was previously found from the argon isotherms. [2]) The difference between these two values is of the same order of magnitude and is in the same direction as the differences found for other substances, carbon dioxide[3]), methyl chloride[4]), sulphur dioxide [5]) amongst others. The fairly large deviation from rectilinearity of the experimental diameter apparent in the neighbourhood of — 125°.17 $C_{\mathrm{in\ K.gr.}}$ agrees well with this behaviour.

3.283 was the value previously [6]) obtained for the critical coefficient on taking $K_{4d} = K_{4s}$ · we now find

$$K_{4d} = 3.424$$

which is therefore slightly greater than that for oxygen [7]) (3.346) If, therefore, we leave $K_{4d} = 3.13$ for helium out of account, oxygen, and not argon, is the substance for which K_{4d} lies nearest the theoretical value, 2.67, deduced from van der Waals's equation.

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[1]) Patterson, Cripps and Whytlaw-Gray, Proc. R. S. (A.) 86 (1912), p. 579.

[2]) C. A. Crommelin. Proc. Dec. 1910, Comm. No. 118*a*, and Thesis for the doctorate, Leiden 1910.

[3]) W. H. Keesom. Proc. Jan. 1904. Comm. No 88; H. Kamerlingh Onnes and W. H. Keesom. Proc. Febr. 1908. Comm No. 104*a*

[4]) C. H. Brinkman, Thesis for the doctorate, Amsterdam 1904.

[5]) E. Cardoso, Arch. sc. phys et Nat. Genève. (4), 34. (1912) p. 127.

[6]) H. Kamerlingh Onnes and C. A. Crommelin. Proc. March 1911. Comm No. 121*a*.

[7]) E. Mathias and H. Kamerlingh Onnes. Proc. Febr. 1911. Comm. No. 117.

The density of the liquid at $-183^\circ.15$ agrees well with the figures given by BALY and DONNAN 1)). The difference is less than 1 %.

Although the deviations of the diameter from rectilinearity are sufficiently small to enable one to say that argon obeys the law of the diameter, they are still too large, and especially too systematic, to be due to experimental errors. As is easily seen from the table and from the accompanying figure, the experimental diameter in the neighbourhood of the critical point exhibits a curvature concave towards the axis of temperature, while at higher temperatures it is convex towards the same axis. The same behaviour has already been observed in other substances, e. g. carbon dioxide 2)).

In fig. 3 are given the reduced density curves and diameters for ether (RAMSAY and YOUNG 3)), isopentane (YOUNG 4)), oxygen (MATHIAS and KAMERLINGH ONNES 5)), xenon (PATTERSON, CRIPPS and WHYTLAW-GRAY 6)), argon and helium (KAMERLINGH ONNES 7)), the reduction from the experimental data has been made by means of the critical density obtained from the diameter.

On a previous occasion it was shown by KAMERLINGH ONNES and KEESOM 8)) how the equations of state for different substances deviate one from another, and how these differences may find expression in deviation functions. On doing this, it appears that substances may be arranged in order so that the deviations of successive substances gradually increase, while it also appears that substances of widely divergent critical temperatures are then found to be in the order of their critical temperatures. The exemplification of this general property afforded by the behaviour of the diameter was noticed by one of us some time ago 9)) and is brought to light in fig. 3 in which the density curves are seen to enclose one another.

If the law of corresponding states were strictly obeyed, then these curves ought to coincide exactly. From the diagram, however, it is seen that this is not the case. The curves enclose one another 10)) in

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1) E. C. C. BALY and F. G. DONNAN, Journ. Chem. Soc. Trans. 81. (1912). p.911.

2) H. KAMERLINGH ONNES and W. H. KEESOM. Proc. Febr. 1908, Comm. N⁰. 104*a*. J. P. KUENEN and W. G. ROBSON, Phil. Mag. (6). 3. 1902. p. 624.

3) W. RAMSAY and S. YOUNG, Phil. Trans. 178, (1887) p. 57.

4) S. YOUNG. Proc. phys. soc. London 1894 1895 p. 602.

5) l c.

6) l.c.

7) H. KAMERLINGH ONNES. Proc. Dec. 1911, Comm. N⁰. 124*b*.

8) Enc. Math. Wiss. V. 10. Suppl. N⁰. 23.

9) E. MATHIAS C. R. 139, (1904), p. 359.

10) In the diagram of N⁰. 36 of Enc. Math. Wiss. V. 10. Suppl. N⁰. 23, is clearly shown the surrounding of the boundary curve for helium by that for isopentane.

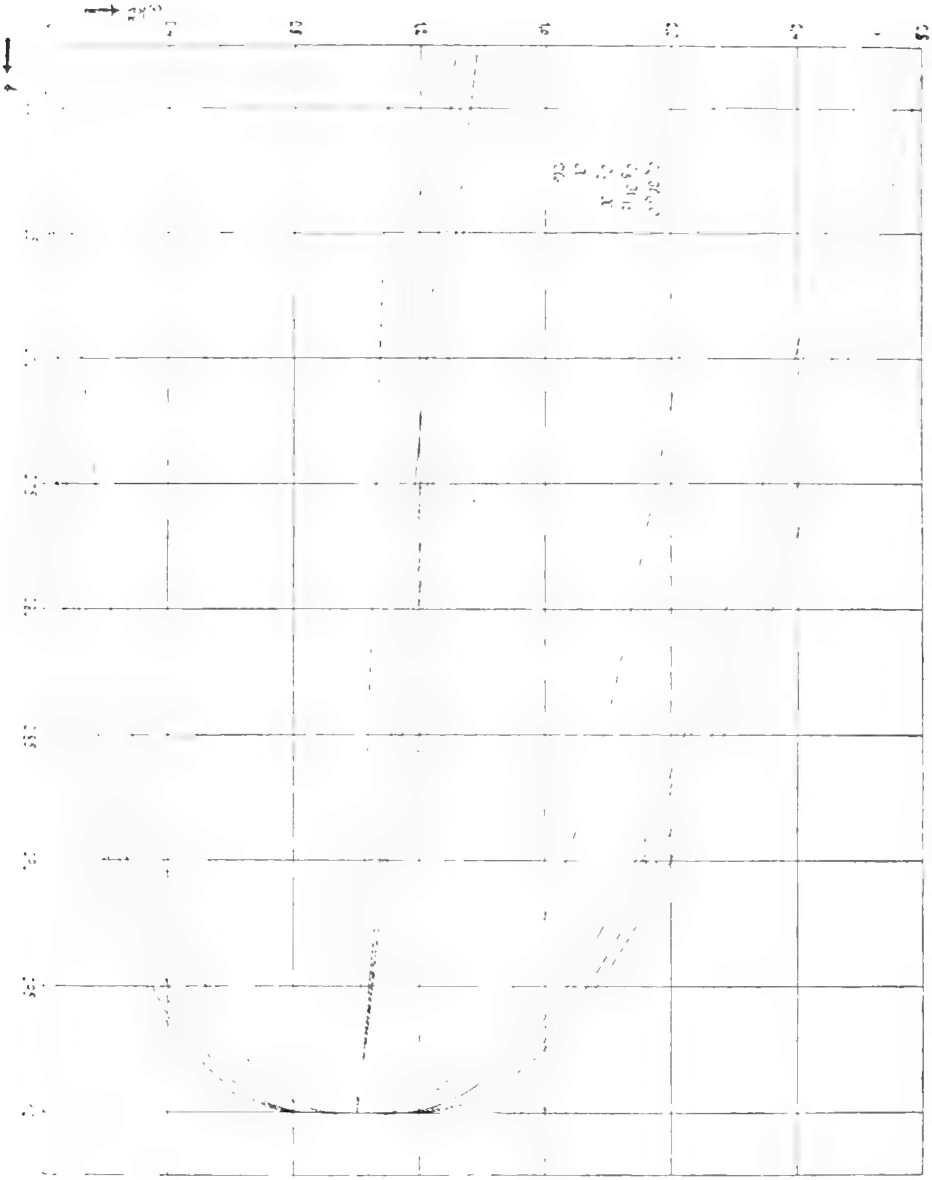

Fig. 3.

such a way that a complex molecular structure and a high critical temperature (circumstances which are usually coexistent) cause divergence between the branches of the curve, while simple molecular structure and a low critical temperature appear to cause them to contract.

Looked at from this point of view, it is of importance to note that the curves for xenon and oxygen so closely correspond that there appears no appreciable difference between the density curves in the diagram, and they have accordingly been represented by a single curve. (The observations for xenon, however, extend only to $t = 0.7$). The cause of this correspondence can well be explained on the assumption[1] that the contracting influence of the simpler molecule and the diverging influence of the comparatively high critical temperature (+ 16°.6 C) have, at least in part, cancelled each other.

Physics. — *Magnetic researches, VII. On paramagnetism at low temperatures (continued).* By H. Kamerlingh Onnes and E. Oosterhuis. Communication N°. 132*e* from the Physical Laboratory at Leiden. Communicated by Prof. H. Kamerlingh Onnes.

(Communicated in the meeting of December 28, 1912).

§ 9. *Crystallized manganese sulphate.* The salt was procured from Merck as puriss. pro analysi. The results were[2]:

TABLE VII.

Crystallized manganese sulphate $MnSO_4.4H_2O$. (I).

T	$\chi . 10^6$	$\chi . T . 10^6$	Limits of H	Bath
288°.7 K.	66.3	19140	10000—17000	Air.
169.6	111.5	18910	8000 - 17000	Liquid ethylene.
77.4	247	19120	6000—16000	Liquid nitrogen.
70.5	270	19030		
64.9	292	18950		
20.1	914	18370	4000—16000	Liquid hydrogen.
17.8	1021	18170		
14.4	1233	17760		

Down to and at nitrogen temperatures, this substance follows pretty much the law of Curie.

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[1] See N°. 34 of Enc. Math. Wiss. V. 10. Suppl. N°. 23.

[2] Prof. Weiss has kindly informed us that in the determination of standards of susceptibility in Zürich, for this substance $\chi = 66.77 . 10^{-6}$ at 14°.2 C. was found.

§ 10. *Anhydrous manganese sulphate.* All the water was driven out of the salt by heating.

The results are given in Table VIII.

With anhydrous manganese sulphate another divergence from the law of CURIE over the whole field of low temperatures was found. Down to nitrogen temperatures, however, it is only a disturbance of the first kind. At hydrogen temperatures a further disturbance shows itself which is not unlike the disturbances with solid oxygen, and at any rate belongs to a kind of disturbances that we have not yet been able to reduce to a definite type. It is remarkable that just as with crystallized ferrous sulphate the presence of molecules of water of crystallization causes a diminution of the quantity Δ' to a very small value in comparison with that of the anhydrous substance, here too Δ' becomes less by the addition of molecules of water of crystallization, and to such a degree, that, if one does not go below nitrogen temperatures Δ' appears to have become $= 0$, whereas with anhydrous salt $\Delta' = 24°$.

TABLE VIII.

Anhydrous manganese sulphate $MnSO_4$. (I). $\Delta' = 24°$.

T	$\chi . 10^6$	$\chi(T+\Delta')10^6$	Limits of H	Bath
293°.9 K.	87.8	27910	6—17 kilog.	Air.
169.6	144.2	27920	5—17	Liquid ethylene.
77.4	274.8	27870	5—16	Liquid nitrogen.
64.9	314.5	27960		
20.1	603	26590	4—16	Liquid hydrogen.
17.8	627	26210		
14.4	636	24420		

If we calculate the number of magnetons for the crystallized salt with $C = \chi T (\Delta' = 0)$ and for the anhydrous with $C' = \chi (T + \Delta')$ and with $\Delta' = 24°$, we find the same number of magnetons in both cases, viz. 29. This is one less than is found in the solution [1].

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[1] P. WEISS. Journal de physique, 1911, p. 976.

§ 11. *Further observations upon ferrous sulphate and ferric sulphate.* After the conclusion of the investigation treated in Comm. N°. 129*b*, we turned to the determination of the water contained in the preparations ferrous sulphate I and ferrous sulphate III.

Prof. VAN ITALLIE kindly investigated the preparations and found that they contained ferric as well as ferrous sulphate. They cannot therefore be taken as a reliable basis for calculations of the number of magnetons, and to make these possible the measurements will be repeated with purer preparations.

The quantitative result arrived at in Comm. N°. 129*b* concerning the appearance of disturbances of the first kind in CURIE's law and the possibility of finding the constant of CURIE for these substances by means of a correction, still retains its value.

As regards the ferric sulphate, which the measurements in § 4 of Comm. N°. 129*b* referred to, the admixture of water may be put at about $^1/_7$ in first approximation. The molecular susceptibility of ferrous sulphate is therefore $^1/_7$ smaller than that of ferric sulphate, so that valency shows its influence in this iron salt also; all this in contradiction to what was observed in § 4.

We must also remark, that the sign and the order of magnitude of the corrections which would be necessary to deduce the number of magnetons for the pure materials from the measurements of the ferrous sulphate I of our Comm. N°. 129*b* and those of the crystallized ferrous sulphate of KAMERLINGH ONNES and PERRIER in Comm. N°. 122*a*, make it seem possible that there is a double analogy between ferrous sulphate and manganese sulphate. Just as in manganese sulphate the number of magnetons in the crystallized and in the anhydrous substance is equal, the same would be found for crystallized and anhydrous ferrous sulphate (viz. 26) (if for the anhydrous substance CURIE's constant is calculated with the help of the correction by $\Delta' = 31°$), and in further analogy with manganese sulphate, this number with ferrous sulphate is also one less than in the solution, if for the latter one may take the number, that has been found by WILLS [1]).

Should the disappearance of $\angle'$ with the introduction of water molecules be ascribable to the increase of distance between the iron atoms which is caused thereby, then it would be possible that with different contents of water of crystallization $\angle'$ decreases with the increase of the number of molecules of water of crystallization. We intend therefore, to examine a salt in this respect, that crystallizes [2])

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[1]) P. WEISS. Journ. de physique 1911. p. 977.

[2]) Compare the investigation of Mlle FEYTIS, C. R. 153, p. 668. 1911 on the

with a series of different numbers of molecules of water of crystallization, and from that to deduce a possible dependence of Δ' upon the density.

§ 12. *Platinum.* A small cylinder of pure platinum from HERAEUS was examined. The susceptibility changes very little with the temperature. On account of its small value it is difficult to determine χ accurately. The results are contained in Table IX.

TABLE IX.

Platinum I.

T	$\chi.10^6$	Limit value of H in Kilogauss.
290°.2 K	0.973	11—17
77.4	1.061	
20.1	1.080	
14.4	1.087	

The value at ordinary temperature lies about the middle of those of OWEN, 0.80 resp. 0.89, HONDA 1.097, KOENIGSBERGER 1.35, FINKE 1.06 (all at 18° C.). If one wished to go so far with the application of the rule $C' = \chi\ (T + \Delta')$ that one applied it to platinum also, then it would follow from this that $\Delta' = 2440°$, and for the number of magnetons n calculated from C'' the value $n = 10$.

§ 13. *Dysprosium oxide* Referring to the data of § 7, we observe that, as will also appear from a further communication of KAMERLINGH ONNES and PERRIER, all the values of χ which occur there must be increased in the ratio of 1 : 1.065. By applying this correction also the difference from the value at ordinary temperature found by Mlle FEYTIS which was stated upon in § 2 of Comm. N°. 122*a* and which was due to an error of calculation, is reduced to a divergence within the limits of accuracy; hence the dysprosium oxide appears to have been about in the same condition as the sample used by her. Our conclusions undergo no change by the correction.

influence of the successive molecules of water of crystallization upon χ. This might be the consequence of a change in Δ' with an unchanged number of magnetons.

§ 14. *Oxygen.* The susceptibility of liquid oxygen has been determined by Kamerlingh Onnes and Perrier by two methods. It has now also been investigated by the attraction method in about the same way as the susceptibility of liquid hydrogen in Comm. N°. 122*a*. An evacuated cylindrical glass tube was hung in the magnetic field and then the repulsion measured that the tube underwent when the surrounding space was filled with liquid oxygen. The value found at $T = 90°.1$ K. agrees well with that in Comm. N°. 116; the small difference at the other temperatures is explained by the fact that the temperatures could not be very accurately ascertained.

In the following table the values found stand beside those of Kamerlingh Onnes and Perrier according to their formula $\chi\sqrt{T} = 2.284.10^{-3}$.

The question naturally arises whether the behaviour of liquid oxygen can also be represented by the formula $C' = \chi(T + \Delta')$. If we assume that $\Delta' = 71°$ this comes out pretty well, as appears from Table XI in which the values of χ are taken from Kamerlingh Onnes and Perrier Comm. N° 116, Table III.

TABLE X.

Liquid oxygen.

T	$\chi.10^6$ *K.O.* and *O.*	$\chi.10^6$ (*K.O.* and *P.*)
90°.1 *K*	241.1	240.6
79.1	258.1	256.8
70.2	270.7	272.6

When the atoms are assumed to be free in the molecule C' gives for the number of magnetons 11 per atom (calculated 11.04),

TABLE XI.

Representation of the susceptibility of liquid oxygen by the formula $\chi(T + \Delta') = C'$, $\Delta' = 71°$.

T.	$\chi.10^6$	$\chi(T+71)\,10^6$.
90°.1 K.	240.6	38760
71.35	269.9	38420
64.9	284.2	38620

and on the hypothesis that in the liquid two gas molecules are rigidly connected it gives 11 per molecule of two atoms.

From $\chi(T + \angle') = 38600$ (the mean of the numbers in the table) with $\angle' = 71^\circ$ one finds for $T = 293^\circ$ K

$$\chi_{293^\circ\ \mathrm{K.}} = 106.0 \times 10^{-6}.$$

This is very close to the value for gaseous oxygen at 20° *C* found by Weiss and Piccard [1]), from which follows 7 magnetons for each of the oxygen atom assumed to be rigidly connected.

Seeing that above 20° *C*. gaseous oxygen follows Curie's law [2]) it seems to be by some chance that our formula with $\angle' = 71^\circ$ gives that figure.

The graphic representation of $^1/\chi$ as a function of T, if our formula actually remained true up to 20° C. would consist of two intersecting lines that have their point of intersection just at the temperature at which the value quoted is determined, which certainly would be a curious coincidence.

Another possibility which Prof. Weiss suggested,in a kind private communication, is that there might be discontinuity in the region between 0° C. and — 183° C. which has not been investigated, by which it remains accidental that the continuation of the line for liquid oxygen cuts that for gaseous oxygen just at 20° C. There is much to be said for this explanation. It is quite possible that the change of density between liquid oxygen and gaseous oxygen makes $\angle'$ into 0. This would be in accordance with what was deduced in § 10 for the influence of the water molecules upon the value of $\angle'$ for manganese sulphate, and moreover quite in accordance with Weiss's idea that the molecular field essentially depends upon the density.

We can further observe, that the change of density, which takes place discontinuously with evaporation, can take place continuously by an indirect transition. In the above line of thought, if we assume that the divergence for liquid oxygen from Curie's law may be defined by a $\angle'$ and pay attention to the change of the number of magnetons which must be assumed in that case, the graph which represents $^1/\chi$ for oxygen of a given density as a function of the temperature would be as in magnetite a succession of straight lines perhaps connected by rounded off pieces. The magnetic equation of state which expresses the susceptibility as a function of density and

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[1]) P. Weiss et A. Piccard. C. R. 155, p. 1234, 1912.

[2]) Prof. Weiss who has particularly investigated this question, kindly tells us that the experimental results of Curie agree so well with Curie's law within the limits of observation errors that Δ' could not be more than $+8^\circ$ or -8°.

temperature (with a view to determining which the experiments of KAMERLINGH ONNES and PERRIER were undertaken (see Comm. N°. 116 § 1) would be given by a series of similar lines, differing for the different densities.

We must not forget that it is by no means established that in the case of oxygen the divergence from CURIE's law is determined by a Δ' which changes with the density, and that it obviously may be due to an association of molecules into complexes with a diminution of the number of magnetons.

However this may be, our attention is again drawn to the important question whether the divergences from CURIE's law depend upon a peculiarity of the atom within the single molecule or from the approach of the molecules up to a very small distance.

In § 3 of Comm. N°. 122*a* by KAMERLINGH ONNES and PERRIER, it is said that preliminary experiments with mixtures of liquid oxygen and nitrogen, which will soon be replaced by better final ones and which were based on the above mentioned association hypothesis, seemed to indicate that bringing the molecules to a greater distance by dilution in the liquid state has no influence of importance upon the divergences from CURIE's law. Here the question is raised in this form: whether Δ' is a quantity which as peculiar to the atom in the single molecule can also be found in the gaseous state or whether it can only be developed by bringing the molecules into immediate vicinity of each other. Further experiments [1]) with oxygen, already planned, must decide this.

(*To be continued*).

Physics. — "*The law of corresponding states for different substances.*" By Prof. J. D. VAN DER WAALS.

(Communicated in the meeting of December 28, 1912).

In the following pages I shall give an account of the result of the researches which I have made of late about the properties of the equations of state for different substances. And I shall communicate in them the simple conclusion at which I have arrived for all the substances for which a chemical combination does not take place, and the molecules continue to move separately, either really isolated, or perhaps joined to groups, if this aggregation (quasi association) behaves in the same way.

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[1]) As this communication is going to press, these experiments have advanced so far, that we may accept with great probability as the result of them, that gaseous oxygen of 90 times the normal density obeys CURIE's law down to — 130° C.

When I discovered the law of corresponding states, I could state the result in two way — and in the beginning I, therefore, hesitated before making a choice between these two ways of expression: 1. if for the different substances $\boldsymbol{\pi}$ and m are equal, $\mathbf{r} = \frac{v}{v_{k_n}}$ is also equal, 2. if for the different substances $\boldsymbol{\pi}$ and m are equal, the volume for all is the same number of times the volume of the molecules. For so far as I saw then these two expressions were both true, and it was after all immaterial whether I chose one form or the other. But the first form was more suitable for experiment and the second form would only be of theoretical value — and so I chose the first form. In order not to get into great difficulties at once, we shall disregard quasi-association for the present, and our result will therefore, at least for the present, be valid only for higher temperatures and not great density.

If we write $p = \boldsymbol{\pi} p_k$, $RT = RT_k m$ and $v = \mathbf{r} v_k$, and if we put $\frac{RT_k}{p_k v_k} = s$, we derive:

$$\left(\boldsymbol{\pi} + \frac{a}{\mathbf{r}^2 p_k v_k{}^2}\right)\left(\mathbf{r} - \frac{b}{v_k}\right) = ms$$

and as we found $\frac{a}{v_k RT_k} = \frac{f-1}{s}$ or $\frac{a}{p_k v_k{}^2} = f-1$, (These Proc. XIII p. 118) we may also write:

$$\left(\boldsymbol{\pi} + 3\,\frac{\frac{f-1}{3}}{\mathbf{r}^2}\left(\mathbf{r} - \frac{b}{v_k}\right) = ms\ .$$

In our latest investigations we have shown that

$$s^2 = \frac{64}{27}(f-1)$$

either quite accurately, or with a high degree of approximation. Substituting this, we find:

$$\left(\boldsymbol{\pi} + 3\,\frac{\frac{f-1}{3}}{\mathbf{r}^2}\right)\left(\mathbf{r} - \frac{b}{rb_g}\right) = m\,\frac{8}{3}\sqrt{\frac{f-1}{3}}$$

or

$$\left(\boldsymbol{\pi} + 3\,\frac{\frac{f-1}{3}}{\mathbf{r}^2}\right)\left(\frac{3\mathbf{r}}{\sqrt{\frac{f-1}{3}}} - \frac{b}{b_g}\,\frac{3}{r\sqrt{\frac{f-1}{3}}}\right) = 8m$$

If we put $\boldsymbol{\pi}$, $\mathbf{r}$, $m = 1$, we find:

$$f\left(\frac{3}{\sqrt{\frac{f}{3}}} - 1 - \frac{b}{rb}\frac{3}{\sqrt{\frac{f}{3}}} - 1\right) = 8.$$

With $f = 4$ and corresponding $r = 3$, we find $\frac{b_k}{b_g} = 1$, and with $f = 7$ we find:

$$\frac{b_k}{b_g}\frac{3}{r\sqrt{2}} = \frac{3}{\sqrt{2}} - \frac{8}{7} = 0,978.$$

As $\frac{b_k}{b_g}$ has been found only little smaller than 1, $\frac{3}{r\sqrt{2}}$ will also differ but little from 1; from $rs < 8$ follows in the case that $s^2 = \frac{64}{27}(f-1)$ is assumed as perfectly accurate, with $rs < 8$:

$$r < \frac{8}{s}$$

or

$$r < \frac{8}{\frac{8}{3}\sqrt{\frac{f-1}{3}}}$$

$$r < \frac{3}{\sqrt{\frac{f-1}{3}}}$$

Hence

$$\frac{3}{r\sqrt{\frac{f-1}{3}}} > 1$$

But it is to be expected that the value of $\frac{3}{r\sqrt{\frac{f-1}{3}}}$ will be only little greater than 1. For $f = 4$ with $r = 3$ we find it exactly equal to 1 and with $f = 7$ we find a value of r little smaller than would follow from $r\sqrt{2} = 3$, namely $r = 2,1213$. We accordingly determined this value at about 2,09. But then we conclude at the same time that if f should have risen to 10, the value of r would descend to below $\frac{3}{\sqrt{3}} = 1,73$. At all events in the equation:

$$\left(\pi + 3\frac{\frac{f-1}{3}}{\mathfrak{r}^2}\right)\left(3\frac{\mathfrak{r}}{\sqrt{\frac{f-1}{3}}} - q\frac{b}{b_g}\right) = 8m$$

the factor q will indeed be somewhat greater than 1, but differ only little from 1.

If we confine ourselves to that part of the whole region where no quasi-association worth mentioning is to be expected, to which part the critical point also belongs, the last equation will hardly change, if we put unity in it instead of $\varphi\frac{b}{b_k}$. And then a rule follows from this holding for all normal substances, so for not *really* associating substances, viz. for given π and m, $\frac{\mathbf{r}}{\sqrt{\frac{f-1}{3}}}$ has the same value. For substances with the same value of $f-1$, $\mathbf{r}$ is therefore also the same and with different value of $f-1$ we have

$$\frac{\mathbf{r}}{\sqrt{\frac{f-1}{3}}}=\frac{\mathbf{r}'}{\sqrt{\frac{f'-1}{3}}}$$

or according to results obtained in These Proc. p. 903.

$$\frac{\mathbf{r}}{\sqrt{\frac{b_g}{b_{lim}}}}=\frac{\mathbf{r}'}{\sqrt{\left(\frac{b_g}{b_{lim}}\right)'}}.$$

Not rigorously valid for the whole region, however. To equal reduced pressure and temperature corresponds a volume which in reduced measure is different for the different substances, when $\frac{b_g}{b_{lim}}$ differs. But if we write the value $\frac{\mathbf{v}}{r\frac{b_g}{b_{lim}}}$ for $\mathbf{r}$, and the value $\frac{v'}{r'\left(\frac{b_g}{b_{lim}}\right)'}$ for $\mathbf{r}'$, we obtain:

$$\frac{v}{b_g\, r\sqrt{\frac{b_g}{b_{lim}}}}=\frac{v}{b_g\, r'\sqrt{\left(\frac{b_g}{b_{lim}}\right)'}}$$

And as we have concluded to the approximate equality of 3, $r\frac{b_g}{b_{lim}}$, $r'\left(\frac{b_g}{b_{lim}}\right)'$ etc. we find as approximate rule: At the same reduced temperature and pressure the same volumes are for all substances the same number of times the molecular volume viz. b_g. If, therefore, we had expressed the law of corresponding states in the second way, it might have been maintained unchanged for all normal substances, at least over a large part of the whole region.

The meaning of equation $\frac{\mathbf{r}}{\sqrt{\frac{b_g}{b_{lim}}}} = \frac{\mathbf{r}'}{\sqrt{\left(\frac{b_g}{b_{lim}}\right)'}}$ is of course this that e.g. for the reduced volume, which in the system in which $f=4$ is put equal to v_1, $v_1 \sqrt{\frac{b_g}{b_{lim}}}$ must be taken in the system, where $\frac{f-1}{3} = \frac{b_g}{b_{lim}}$. Thus the critical volume is equal to $3b_g$, if $f=4$ and the reduced volume is then equal to 1. But in the system in which $f=7$ this volume would have the value of $\sqrt{2}$ in critical measure. That the reduced volume is found $\sqrt{2}$ times larger is due to this that we have divided by a $\sqrt{2}$ times smaller factor.

Hence the different π, m, $\mathbf{r}$ surfaces for substances, for which $\frac{b_g}{b_{lim}}$ might differ, do not cover each other, but they can be made to overlap for the greater part, almost entirely, if we divide the value of $\mathbf{r}$ by $\sqrt{\frac{b_g}{b_{lim}}}$.

Then, however, the border lines, the loci of the coexisting vapour and liquid phases have not been made to cover each other. Not even by approximation, for this locus, which is determined by

$$p\,(v_2 - v_1) = \int_{v_1}^{v_2} p\,dv\,,$$

also requires the knowledge of the properties for smaller volumes, and will, therefore, also demand the knowledge of presence or absence of quasi-association, but especially the knowledge of the course of $\frac{b}{b_g}$. But this will be discussed later.

The cause of the circumstance that the above mentioned properties only hold by approximation is clearly to be seen, if it is borne in mind that the quantity $\frac{b}{b_g}$ in the form found for the equation of state:

$$\left(\pi + 3\,\frac{\frac{b_g}{b_{lim}}}{\mathbf{r}^2}\right)\left(\frac{3\mathbf{r}}{\sqrt{\frac{b_g}{b_{lim}}}} - \frac{b}{b_g}\,\frac{3}{r\sqrt{\frac{b_g}{b_{lim}}}}\right) = 8m$$

is not constant as soon as $\frac{b_g}{b_{lim}} > 1$. If very large volumes are concerned, we may put 1 for it, and even in the critical volume, viz. $r\,b_g$, the difference with 1 is still slight, and we find from:

$$\frac{b_k}{b_g} = r_{kr}\left(1 - \frac{\frac{8}{3}\sqrt{\frac{b_g}{b_{lim}}}}{1 + 3\,\frac{b_g}{b_{lim}}}\right)$$

for $\frac{b_g}{b_{lim}} = 2$ the value of $\frac{b_k}{b_g}$ to be equal to 0,97 or 0,96.

We conclude from this that for the vapour volumes of the border line the rules given above hold with a high degree of approximation. But for the liquid volumes $\frac{r}{\sqrt{\frac{b_g}{b_{lim}}}}$ is smaller than would be calculated if we had retained $\frac{b}{b_g} = 1$, and the density of the liquid greater. The limiting liquid volume is even not b_g, but b_{lim}, and so $\frac{b_g}{b_{lim}}$ times smaller, and the limiting liquid density $\frac{b_g}{b_{lim}}$ times greater.

This must bring about a change in the value of the factor γ. And we can calculate the value of this change.

Let us put

$$\frac{\varrho_{gas} + \varrho_{vl}}{2\varrho_{kr}} = 1 + \gamma\,(1-m)$$

and for b constant

$$\frac{\varrho'_{gas} + \varrho'_{vl}}{2\varrho'_{kr}} = 1 + \tfrac{1}{2}\,(1-m).$$

At very low temperatures the gas densities disappear. With subtraction of the two equations we find:

$$\frac{\varrho_{vl}}{2\varrho_{kr}} - \frac{\varrho'_{vl}}{2\varrho_{kr}} = (\gamma - \tfrac{1}{2})\,(1-m).$$

For $m = 0$ we must introduce the limiting liquid density, and we get:

$$r\,\frac{b_g}{b_{lim}} - 3 = (2\gamma - 1)$$

or

$$r\,\frac{b_g}{b_{lim}} = 2(\gamma + 1)\ ^{1})$$

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1) These Proc. p. 903.

As $r\sqrt{\frac{b_g}{b_{lim}}}$ is somewhat smaller than 3, we get:

$$\frac{3}{2}\sqrt{\frac{b_g}{b_{lim}}} < (\gamma - 1) .$$

Hence the variability of b is the cause that the law of corresponding states does not hold perfectly for all volumes. If this variability was governed by one law, and if accordingly $\frac{b_g}{b_{lim}}$ was the same for all substances, it would hold perfectly. For then the value of $\frac{\mathfrak{r}}{\sqrt{\frac{b_g}{b_{lim}}}}$ and so also of $\mathfrak{r}$ would be the same for given π and m. If the law of the variability of b, hence $\sqrt{\frac{b_g}{b_{lim}}}$, is different, then $\mathfrak{r}$ is indeed not equal for given π and m, but the law of correspondence, as we have stated it here, holds with a high degree of approximation, at least for volumes $> v_k$. Then for given π and m the value of $\frac{\mathfrak{r}}{\sqrt{\frac{b_g}{b_{lim}}}}$ is almost the same or $\frac{v}{v_k\sqrt{\frac{b_g}{b_{lim}}}} = \frac{v}{r\, b_g\sqrt{\frac{b_g}{b_{lim}}}} = \frac{v}{3b_g}$.

As the volume decreases, the law begins to fail. For $v > v_k$ it holds almost good, below this the deviation becomes greater and greater. The value of b_g/b_{lim}, however, does not seem to differ much for the different substances. It is not equal to 1 for any substance, not even for monatomic ones. So substances for which b is constant, are only fictions. When, therefore, in my continuity I calculated the critical circumstances keeping b constant, this did not take place because I thought that b would be invariable, but in the expectation that in the critical volume the quantity b would have changed so little that the influence of the change would be inappreciable. And as we have found now, the quantity

$$\frac{b_k}{b_g} = \frac{3}{\sqrt{\frac{b_g}{b_{lim}}}} - \frac{8}{1+3\frac{b_g}{b_{lim}}}$$

is, indeed, not much smaller than 1 for π and $m = 1$. And even if we should assign to $\frac{b_g}{b_{lim}}$ a value so excessively high as would be the case if we put it at 3 — and substances for which this value would occur will, no doubt, have to be looked upon as fictions —

we should still find $\frac{b_k}{b_q} > 0.93$. The reason, therefore, that even for great densities the law of correspondence is fulfilled by approximation will be owing to this that $\frac{b_q}{b_{lim}}$ does not differ much for the different substances. Moreover the region in which the deviations would become of importance, is inaccessible to experiment; e.g. for the liquid volumes which could coexist with vapour volumes at values of $m < \frac{1}{2}$, or for volumes under an excessively high pressure.

We shall add a few more remarks.

That the coincidence of the surfaces $\frac{\mathbf{r}}{\sqrt{\frac{b_q}{b_{lim}}}} = f(\pi, m)$ for great values of $\mathbf{r}$ entirely disappears for $\mathbf{r}$ very small and near $\mathbf{r}_{lim}$, will be clear if we pay attention to the fact that for $\sqrt{\frac{b_q}{b_{lim}}} = 1$ the surface has no points below $\mathbf{r} = \frac{1}{3}$; for then $v_{lim} = b_q$ and $v_k = 3b_q$. For $\sqrt{\frac{b_q}{b_{lim}}}$ equal to a value greater than 1, $v_{lim} = b_{lim}$ and $v_k = rb_q$, or

$$\mathbf{r}_{lim} = \frac{1}{r}\frac{b_{lim}}{b_q} \quad \text{and} \quad \frac{\mathbf{r}_{lim}}{\sqrt{\frac{b_q}{b_{lim}}}} = \frac{\frac{b_{lim}}{b_q}}{r\sqrt{\frac{b_q}{b_{lim}}}} = \frac{1}{3}\frac{b_{lim}}{b_q}.$$

If e.g. $\frac{b_q}{b_{lim}} = 2$, we have obtained new points for the $\mathbf{r}$ surface, and the surface begins at $\frac{\mathbf{r}}{\sqrt{\frac{b_q}{b_{lim}}}} = \frac{1}{6}$. It will be obvious that in such circumstances with difference of the value of $\frac{b_q}{b_{lim}}$ there can be no question of coincidence. There is only perfect coincidence with equality of $\frac{b_q}{b_{lim}}$. If this value differs, the surfaces almost coincide, indeed, for large value of $\mathbf{r}$, but for very small value of $\mathbf{r}$ the $\frac{\mathbf{r}}{\sqrt{\frac{b_q}{b_{lim}}}}$

ordinates will contract and approach to zero as $\frac{b_g}{b_{lim}}$ becomes larger in a region, however, which is hardly accessible to experiment.

Another remark.

From the circumstance that the $\frac{v}{\sqrt{\frac{b_g}{b_{lim}}}}$ surfaces may be considered to coincide, especially for large value of v, it should, however, not be concluded that the border lines coincide. The top differs already. The top lies at π, m, and v equal to 1, and so $\frac{v}{\sqrt{\frac{b_g}{b_{lim}}}}$ differs; and great differences are even derived for the gas-branch at low temperatures from the relation which holds approximatively, $-l\frac{p}{p_k}=f\frac{1-m}{m}$. Thus we find in the region where the law of the rarefied gases would hold:

$$-l\,\frac{8}{3}m\frac{\sqrt{\frac{b_g}{b_{lim}}}}{v}=\left(1+3\frac{b_g}{b_{lim}}\right)\frac{1-m}{m}.$$

Hence in a region where correspondence would perfectly prevail the border lines differ exceedingly much. This is of course the consequence of the liquid volumes no longer corresponding when $\frac{b_g}{b_{lim}}$ differs, and the construction of the border line also requires the knowledge of these volumes. Where the gas-laws hold, $\frac{pv}{RT}=1$, or $\frac{\pi v}{m}\frac{p_k v_k}{RT_k}=1$, and now we have come to the conclusion that $\frac{RT_k}{p_k v_k}$ for the different substances is equal to $\frac{8}{3}\sqrt{\frac{b_g}{b_{lim}}}$. Then

$$\frac{\pi v}{m}=\frac{8}{3}\sqrt{\frac{b_g}{b_{lim}}}$$

or

$$\frac{\pi}{m}\frac{v}{\sqrt{\frac{b_g}{b_{lim}}}}=\frac{8}{3}$$

A confirmation of the thesis, that the π, m, $\frac{v}{\sqrt{\frac{b_g}{b_{lim}}}}$ surfaces coincide for great value of v.

Now the important question is still left undecided, in how far does the value of $\frac{b_g}{b_{lim}}$ differ for the different substances. We have already stated that it is not probable that there are substances for which this quantity $= 1$. These substances have sometimes been called *perfectly hard* substances, but then it should be borne in mind that since it has appeared that $f > 4$ and $s > \frac{8}{3}$ for monatomic substances, even monatomic substances would not be perfectly hard. For all substances, with our present knowledge we may say without exception, $\frac{b_g}{b_{lim}} > 1$, and probably not very different from 2. Now we might account for about 2 by assuming *quasi-association*. In large volume b_g is the fourfold of the volume of the molecules; hence if the spherical shape is assumed and the diameter is put $= \sigma$, $b_g = 4\frac{\pi}{6}\sigma^3$. The limiting volume of the substance is present when the pressure is infinite at temperatures $T > 0$. Then the molecules must touch, and the volume is only little smaller than σ^3 or $b_{lim} \leqq \sigma^3$. Hence:

$$b_g \geqq \frac{2\pi}{3} b_{lim}$$

or $b_g \geqq 2{,}09\, b_{lim}$.

But on the other hand we should consider that often

$$\frac{b_g}{b_{lim}} < 2.$$

If not the spherical shape was assumed, but as extreme case, a rectangular shape, b_g would be $= 4\sigma^3$, and $b_{lim} = \sigma^3$, and $\frac{b_g}{b_{lim}} = 4$. This will, probably, not be expected by anybody. For ellipsoidal shape we should again find a little more than 2. In this way it seems impossible to me to explain the value of $\frac{b_g}{b_{lim}} < 2$. But we shall possibly discuss this later.

The original theorem of the corresponding states pronounced the equality of the π, μ, r surface. In the form given here it states the superposition of the $\pi, m \frac{r}{\sqrt{\frac{b_g}{b_{lim}}}}$ surfaces. These two forms would coincide, if there was only one single law for the course of b. In the form given here the r ordinates are only $\frac{b_g}{b_{lim}}$ times smaller. But the advantage of the form given here is obvious, when there are different kinds of substances from the point of view of the law of correspondence. First of all it points out the cause for the existence of these different kinds, about which cause the form given originally does not reveal anything. Secondly it appears that attempts to find perfect correspondence between these different kinds must fail, and have certainly no chance of success by variations in the π and m ordinates. And thirdly it shows that the deviation between the different kinds of substances is a gradual one, and the coincidence in the rarefed gas-state is restored.

Physics. — "*On the* HALL-*effect, and on the change in resistance in a magnetic field at low temperatures.* VI. *The* HALL-*effect for nickel, and the magnetic change in the resistance of nickel, mercury and iron at low temperatures down to the melting point of hydrogen*". By H. KAMERLINGH ONNES and BENGT BECKMAN. Communication N°. 132*a* from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated in the meeting of November 30, 1912).

§ 17.[1] *Magnetic change in the resistance of solid mercury.* The resistance was measured of mercury contained in a glass capillary 9 cms. long, and of 0.12 mm. diameter. The capillary was U-shaped, and to either end were fused two glass leading tubes which were filled with mercury. The resistances were measured by the KOHLRAUSCH method of overlapping shunts, in which the main current was $I = 0.006$ amp. The mercury was frozen by blowing cooled hydrogen vapour into the cryostat through a glass tube whose lower extremity reached below the resistance. The resistance was found to be

7,97	Ω	at	$T = 287°,3$ K.
0,1014			$T = 20°,3$
0,0618			$T = 14°,5$

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[1] The sections of this paper are numbered in continuation of those of Comm. N°. 130*c* (Oct. 26, 1912).

TABLE XIX.

Magnetic change in the resistance of mercury.

$T = 20^\circ.3$ K.		$T = 14^\circ.5$ K.	
H in gauss.	$\frac{\Delta w}{w} \times 10^3$	H	$\frac{\Delta w}{w} \times 10^3$
9760	+ 1.3	10270	+ 5.5
10270	+ 1.5	10270	+ 6.5
10270	+ 1.6		

The measurements therefore show an increase of the resistance in the magnetic field. At

$$H = 10000 \text{ and } T = 20^\circ.3 \text{ K} \quad \frac{\Delta w}{w} = +1{,}5 \times 10^{-3}$$

$$T = 14^\circ{,}5 \quad \frac{\Delta w}{w} = +6 \times 10^{-3}$$

were obtained as mean values.

At these temperatures the temperature coefficient of the resistance is very great, and this lessens the accuracy of the above measurements, especially at $T = 14^\circ.5$ K. The large increase occasioned by lowering the temperature from 20° to 14° K. is very striking.

§ 18. *The* HALL*effect for, and the magnetic change in the resistance of, nickel.* The material in the form of a plate of 0.053 mm. thick-

TABLE XX.

HALLeffect for nickel Ni_{pl}.

$T = 290^\circ.5$ K.			$T = 90^\circ$ K.			$T = 20^\circ.3$ K.			$T = 14^\circ.5$ K.		
H	RH	$-R \times 10^4$	H	RH	$-R \times 10^4$	H	RH	$-R \times 10^4$	H	RH	$-R \times 10^4$
3010	18.8	62.4	2980	2.93	9.83	2970	1.48	4.98	4940	2.50	5.06
5170	31.2	60.3	4950	4.58	9.25	5640	2.86	5.08	8250	4.25	5.15
7260	39.3	54.1	7290	6.31	8.65	7260	3.53	4.86	10270	5.19	5.05
9065	43.1	47.6	9110	7.62	8.36	8250	4.08	4.95			
10270	44.9	43.7	10400	8.29	7.98	10270	4.81	4.68			

ness was pure SCHWERTE nickel. H and RH are given in C. G. S. units. I was 0.7 to 0.9 amp.

The results given in Table XX are shown graphically in Figs. 1 and 2.

The HALLeffect for nickel decreases as the temperature falls from ordinary room temperature; this has already been found by A. W. SMITH [1]) to be the case down to liquid air temperatures. According to A. KUNDT [2]) the HALLeffect for ferro-magnetic substances is proportional to the magnetisation and not to the field. Hence, when the magnetisation attains its maximum value, the HALLeffect must also exhibit a state of saturation, that is to say, the curves giving the HALLeffect as a function of the field must show a bend. SMITH's curves, covering a region of temperature from 193° C. to + 546° C., show such a bend, which, as the temperature increases right up to the critical temperature for nickel, is displaced towards the weaker fields, thus corresponding to a diminution of the saturation magnetisation as the temperature rises. At 290° K. our present measurements show this bend clearly at about 5000 to 6000 gauss. At the lower temperatures there is no decided bend visible within the region of fields covered by our observations ($H < 10400$); thus if there are any bends at these temperatures, they must occur at still stronger fields.

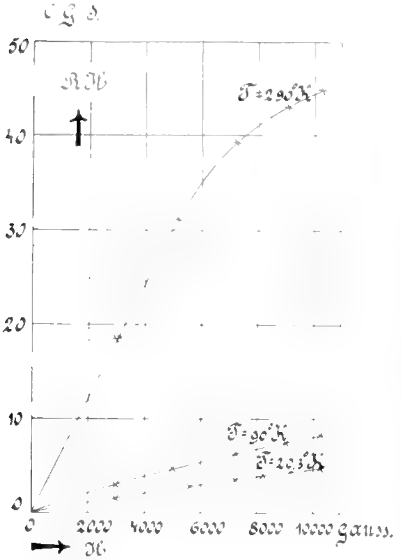

Fig. 1.

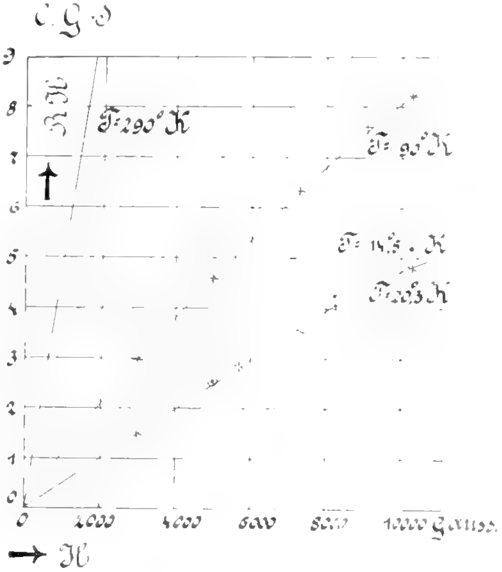

Fig. 2.

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[1]) A. W. SMITH. Phys. Rev. **30**, 1. 1910.

[2]) A KUNDT. Wied. Ann. **49**, 257, 1893

At 14°.5 K. the HALLeffect is strictly proportional to the field, as is also the case at 20°.3 K. as far as $H = 9060$. At 90° K. the HALLcoefficient is a linear function of the field, diminishing as the field increases.

For the HALLcoefficient in very weak fields the relation

$$R_0 = ce^{bT}$$

holds.

The LEDUC quantity $D_L = \frac{R}{w}$, the tangent of the angle of rotation of the equipotential lines in unit field, is here a linear function of the temperature.

The following Table shows the extent to which those relations hold.

TABLE XXI.

R_0 and D_L as functions of the temperature.

T	R_0 obs.	R_0 calc.	D_L calc.	D_L obs.
290° K.	66.0×10^{-4}	67.5×10^{-4}	5.37	5.37
90	11.2	10.5	3.07	3.10
20.3	5.0	5.3	2.22	2.30
(14.5	5.1	5.0	2.28	2.22)

For the nickel plate the magnetic change of resistance was also measured. I was 0.2 to 0.3 amp.

As the resistance of the plate is very small, and the changes were, at the most, 1.5 %, it was not possible to evaluate them with any greater accuracy.

As has also been observed by F. C. BLAKE [1]), G. BARLOW [2]) and C. W. HEAP [3]), there is an increase in the resistance of nickel in the weaker fields ($H < 3000$); in stronger fields the resistance diminishes, and, in the region $5600 < H < 10270$, it does so approximately linearly with the field. This behaviour is, to a large extent, the same throughout the region 290° K. $> T >$ 14°.5 K.

In strong fields the diminution in the resistance is somewhat greater at low temperatures than at ordinary temperature.

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[1]) F. C. BLAKE. Ann. d. Phys. **28**, 449, 1909.

[2]) G. BARLOW. Proc. Roy. Soc. **71**, 30, 1903.

[3]) C. W. HEAP. Phil. Mag. (6) **22**, 900, 1911.

TABLE XXII.

Change in the resistance of nickel in a magnetic field.

$T = 290°.5$ K		$T = 90°$ K		$T = 20°.3$ K		$T = 14°.5$ K	
H	$\frac{\Delta w}{w} \times 10^3$	H	$\frac{\Delta w}{w} \times 10^3$	H	$\frac{\Delta w}{w} \times 10^3$	H	$\frac{\Delta w}{w} \times 10^3$
1750	$+ 0.5$	2270	$+ 2$	1750	$+ 1$	2970	0
2500	$+ 0.5$	2520	$+ 3$	2520	$+ 2$	5640	$- 7$
2970	0	3770	0	3750	0	8250	$- 11$
3750	$- 2$	4950	$- 5.5$	5640	$- 8$	10270	$- 13$
5170	$- 4$	6140	$- 6.5$	8250	$- 12$		
7260	$- 7$	8290	$- 9.5$	9065	$- 13$		
9065	$- 9$	9110	$- 12.5$	10270	$- 15$		
10270	$- 11$	10400	$- 14.0$				
0	$w = 12.2 \times 10^{-4}\,\Omega$	0	$w = 3.63 \times 10^{-4}\,\Omega$	0	$w = 2.25 \times 10^{-4}\,\Omega$	0	$w = 2.23 \times 10^{-4}\,\Omega$

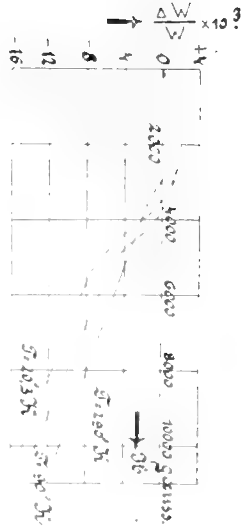

Fig. 3.

§ 19. *Change in the resistance of pure iron in a magnetic field.* As experimental material an iron wire from KOHLSWA, Sweden, was used for which we are indebted to the kindness of Prof. C. BENEDICKS, Stockholm. On analysis the following impurities were found present

C	0,10 %
S	0,007
P	0,028
Si	0,014
Mn	0,03

thus giving a total impurity of about 0,18 %. After analysis the wire was drawn by HERAEUS to a diameter of 0.1 mm.

Before it was drawn the temperature coefficient was $\frac{w_{80^\circ}}{w_{289^\circ}} = 0.14$; afterwards it was $\frac{w_{80^\circ}}{w_{289^\circ}} = 0.17$.

The iron wire was wound non-inductively upon an ebonite cylinder, and was so placed in the magnetic field as to be perpendicular to the lines of force throughout. The method of overlapping shunts was used for determining the resistance. Resistances without field are given in Table XXIII.

TABLE XXIII.

Resistance of pure iron as a function of the temperature.

T	w
288°.0 K.	11.18 Ω
90	2.225
77.5	1.859
20.3	1.129
14.5	1.124

The temperature coefficient of the resistance is very small in the liquid hydrogen region; in liquid oxygen and nitrogen it is large. Resistances were measured at 288° K., 77° K., 20°,3 K. and 14°,5 K. The measurements at 77° K. are not quite trustworthy, and we communicate them only because they are sufficiently accurate to determine the orientation of the temperature curve.

Fig. 4 shows the resistance as a function of the field. The observations at 77° K. are indicated by a broken line.

TABLE XXIV.

Magnetic change in the resistance of iron.

$T = 288°$ K.		$T = 20°.3$ K.		$T = 14°.5$ K.	
H	$\frac{\Delta w}{w} \times 10^4$	H	$\frac{\Delta w}{w} \times 10^4$	H	$\frac{\Delta w}{w} \times 10^4$
990	+ 2.8	1500	— 2.0	990	— 1.7
1500	+ 3.8	2520	— 2.9	2500	— 2.6
2520	+ 5.7	3750	— 2.7	3750	— 3.1
3750	+ 6.0	4940	— 2.2	4940	— 2.4
4940	+ 5.4	6110	— 0.9	6110	— 1.4
6110	+ 3.2	7260	+ 0.7	7260	+ 0.3
7260	+ 0.3	8250	+ 2.6	8250	+ 2.6
8260	— 2.1	9065	+ 3.6	9065	+ 3.6
9065	— 4.7	9750	+ 4.6	9750	+ 4.7
10270	— 9.1	10270	+ 5.2	10270	+ 5.4

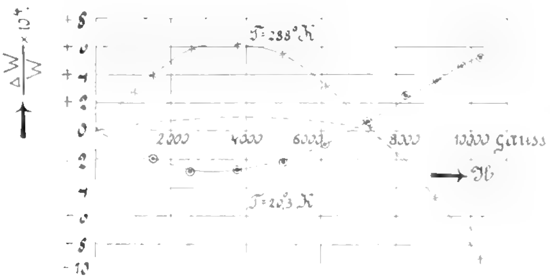

Fig. 4.

At 288° K the resistance increases in weak fields, and decreases in fields greater than 7000. This is in agreement with results obtained by L. GRUNMACH and F. WEIDERT [1]), C. W. HEAP [2]) and others. At liquid hydrogen temperatures this behaviour is reversed, for the resistance diminishes in weaker fields and increases when $H > 7000$. There is a neutral zone at about $H = 7000$.

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[1]) L. GRUNMACH and F. WEIDERT: Verh. d. Deutsch. Physik. Ges. 1906, 359.

[2]) C. W. HEAP: l. c.

Physics. — "*On the* HALL *effect, and on the change in resistance in a magnetic field at low temperatures.* VII. *The* HALL *effect for gold-silver alloys at temperatures down to the melting point of hydrogen*". By BENGT BECKMAN. Communication No. 132*c* from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated in the meeting of December 28, 1912).

This communication is a continuation of Comm. N°. 130*b*.

IV. *Gold-silver-alloys.*

§ 10. Measurements at temperatures of 290° K., 20°.3 K. and 14°.5 K. of the HALL effect for three *Au-Ag* alloys (I, II, III) containing a large percentage of gold were published by KAMERLINGH ONNES and myself in Comm. N°. 129*a*, § 12, and in Comm. N°. 130*c*, § 16. The results of my measurements made on one (I) of these alloys at 90° K. were given in § 9 of Comm. N°. 130*b*. I have since investigated three other alloys containing a greater percentage of silver. and in the present paper the results of these new measurements on the HALL effect for *Au-Ag* alloys are given and are discussed in connection with the former results.

The observational method was the same as was formerly used, viz. the form of the compensation method developed by LEBRET [1]) as used by VAN EVERDINGEN [2]). An iron-clad THOMSON galvanometer was used, with a period of about 4 secs, and a sensitivity of about 1 mm. deflection at 2.5 m. distance for 5×10^{-8} volts. In this method disturbances produced by the thermo-currents arising from the thermo-magnetic effect of VON ETTINGSHAUSEN are completely eliminated only in the case of instantaneous closing of the main current circuit. On account of the comparatively large period of the galvanometer this was not possible in the present experiments; but still, these disturbances were too small in the present case to be observed.

The main current was 0.5 to 1 amp. The plates were circular (11 mm. diam.) with point electrodes. The resistance of the plates was measured as well as the HALL effect.

The alloys were obtained by fusing pure gold and silver in a porcelain crucible, and then rolling them out. They were all submitted to analysis. I am greatly indebted for these analyses to

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[1]) LEBRET, Diss. Leiden 1895. Comm. Leiden N°. 19, 1895.

[2]) E. VAN EVERDINGEN, Comm. Leiden. Suppl. N°. 2. Cf. also H. KAMERLINGH ONNES and B. BECKMAN, Comm. N°. 129a, 1912.

Dr. C. HOITSEMA, Master of the Royal Mint, Utrecht, and to Fil. Lic. G. KARL ALMSTRÖM, Upsala.

In the Tables, H represents the field strength in gauss, R the HALL coefficient in c. g. s. units, w_T the resistance in ohms at the absolute temperature T, and w_0 the resistance at 0° C.

Alloy II contained 10.7 atomic percentages of silver. The thickness of the plate was 0.049 mm.

TABLE XVI.

HALL effect for $(Au—Ag)_{II}$

H	$T = 290°$ K.		$T = 90°$ K.	
	RH	$-R \times 10^4$	RH	$-R \times 10^4$
8250	5.25	6.36	4.26	5.16
9360	—	—	4.96	5.31
9750	6.25	6.41	5.08	5.21
10270	6.51	6.34	5.45	5.31
0	$w = 8.06 \times 10^{-4}\ \Omega$ $\frac{w}{w_0} = 1.03$		$w = 5.43 \times 10^{-4}\ \Omega$ $\frac{w}{w_0} = 0.69$	

Alloy III contained 30 atomic percentages of Ag. The plate was 0.078 mm. thick.

TABLE XVII.

HALL effect for $(Au—Ag)_{III}$.

$T = 290°$ K.			$T = 90°$ K.		
H	RH	$-R \times 10^4$	H	RH	$-R \times 10^4$
8250	5.03	6.10	9065	4.26	4.70
9360	5.70	6.09	9750	4.55	4.67
10270	6.18	6.02	10270	4.83	4.70
0	$w = 9.47 \times 10^{-4}\ \Omega$ $\frac{w}{w_0} = 1.015$		0	$w = 7.71 \times 10^{-4}\ \Omega$ $\frac{w}{w_0} = 0.825$	

Alloy IV contained 69.4 atomic percentages of *Ag*. The plate was 0.083 mm. thick.

TABLE XVIII.

HALL effect for $(Au-Ag)_{IV}$.

H	$T = 287° K$		$T = 90° K$		$T = 20°.3 K$		$T = 14°.5 K$	
	RH	$-R \times 10^4$	RH	$-R \times 10^4$	RH	$-R \times 10^4$	RH	$-R \times 10^4$
9220	5.55	6.02	4.77	5.17	4.12	4.47	4.08	4.43
9760	5.76	5.90	5.12	5.25	4.40	4.51	4.26	4.37
10270	6.20	6.04	5.41	5.27	4.66	4.54	4.55	4.43
0	$w = 9.8 \times 10^{-4} \Omega$ $\frac{w}{w_0} = 1.01$		$w = 8.43 \times 10^{-4} \Omega$ $\frac{w}{w_0} = 0.875$		$w = 7.92 \times 10^{-4} \Omega$ $\frac{w}{w_0} = 0.82$		$w = 7.90 \times 10^{-4} \Omega$ $\frac{w}{w_0} = 0.82$	

Alloy V contained 90.9 atomic percentages of *Ag*. The plate was 0.082 mm. thick.

TABLE XIX.

HALL effect for $(Au-Ag)_V$

H	$T = 290°$ K.		$T = 90°$ K.		$T = 20.°3$ K.		$T = 14.°5$ K.	
	RH	$-R \times 10^4$	RH	$-R \times 10^4$	RH	$-R \times 10^4$	RH	$-R \times 10^4$
9065	6.62	7.31	5.88	6.49	5.22	5.76	5.16	5.69
9760	7.23	7.42	6.30	6.45	5.59	5.73	5.66	5.80
10270	7.52	7.32	6.58	6.40	5.98	5.82	5.86	5.71
0	$w = 5.29 \times 10^{-4} \Omega$ $\frac{w}{w_0} = 1.025$		$w = 3.81 \times 10^{-4} \Omega$ $\frac{w}{w_0} = 0.735$		$w = 3.40 \times 10^{-4} \Omega$ $\frac{w}{w_0} = 0.66$		$w = 3.40 \times 10^{-4} \Omega$ $\frac{w}{w_0} = 0.66$	

Alloy VI contained 97.8 atomic percentages of *Ag*. The plate was 0.093 mm. thick.

TABLE XX.

HALL effect for $(Au-Ag)_{VI}$

H	$T = 290°$ K.		$T = 90°$ K.		$T = 20.°3$ K.		$T = 14.°5$ K.	
	RH	$-R\times10^4$	RH	$-R\times10^4$	RH	$-R\times10^4$	RH	$R\times10^4$
9220	7.10	7.70	6.79	7.37	6.41	6.95	6.38	6.92
9500	—	—	—	—	—	—	6.59	6.94
9760	7.56	7.75	7.22	7.41	6.82	6.99	6.73	6.90
10270	7.95	7.74	7.71	7.51	7.13	6.91	7.09	6.90
0	$w = 25.2\times10^{-5}\Omega$		$w = 12.7\times10^{-5}\Omega$		$w = 8.7\times10^{-5}\Omega$		$w = 8.7\times10^{-5}\Omega$	
	$\frac{w}{w_0} = 1.04$		$\frac{w}{w_0} = 0.525$		$\frac{w}{w_0} = 0.36$		$\frac{w}{w_0} = 0.36$	

In Table XXI are collected my results for alloys of gold and silver. In it are given results for the HALL coefficient R_T, and its temperature coefficient $\frac{R_T}{R_{290}}$, for the LEDUC constant $D_L = \frac{R}{w}$, and for the temperature coefficient of the resistance without a magnetic field. All are expressed in c. g. s. units.

Fig. 1 is a diagram of the electrical conductivity (σ) at $T = 290°$ K. and at $T = 90°$ K. as a function of the atomic percentage of Ag. The unit in which the conductivity is expressed is the reciprocal of the resistance in ohms of a 1 cm. edged cube. The conductivity was calculated from the analyses. (See a previous paper [1]).

At lower temperatures the characteristic curves become steeper. This is strongly marked at hydrogen temperatures as is shown by the measurements of KAMERLINGH ONNES and CLAY [2]) on a gold-silver alloy containing about 0.4 % Ag, and by CLAY's [3]) measurements on Au-Ag alloys with various compositions. The latter measurements have been confirmed by mine, and have been further extended to embrace cases of average and of small content of Au. For these cases, somewhat similar results were obtained as with small content of Ag: the addition of a small quantity of gold to pure silver causes such an enormous decrease in the conductivity that, for

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[1]) BENGT BECKMAN. Upsala Univ. Årsskrift 1911.

[2]) H. KAMERLINGH ONNES and J. CLAY. Comm. n⁰. 99. 1907.

[3]) J. CLAY. Comm. n⁰. 107*d*, 1908.

TABLE XXI.

Substance	Atomic percent. Ag	$R_{290°}$	$R_{90°}$	$R_{20°.3}$	$R_{14°.5}$	$\frac{R_{90°}}{R_{290°}}$	$\frac{R_{20°.3}}{R_{290°}}$	$\frac{w_{90°}}{w_0}$	$\frac{w_{20°.3}}{w_0}$	$[D_L]_{T=290°}$	$[D_L]_{T=90°}$	$[D_L]_{T=20°.3}$
Au	0	7.2×10^{-4}	7.6×10^{-4}	9.8×10^{-4}	9.8×10^{-4}	1.05	1.36	0.285	0.135	3.2×10^{-7}	12.6×10^{-7}	133×10^{-7}
$(Au-Ag)_I$	2.0	6.8	6.6	6.7	6.5	0.97	0.98	0.49	0.30	2.3	4.8	8.03
$(Au-Ag)_{II}$	10.7	5.6	5.25	3.7	3.7	0.82	0.66	0.69	0.585	1.05	1.12	1.23
$(Au-Ag)_{III}$	30.0	5.6	4.7	3.6	3.7	0.77	0.64	0.825	0.755	0.61	0.57	0.52
$(Au-Ag)_{IV}$	69.7	6.0	5.2	4.5	4.4	0.87	0.75	0.875	0.82	0.64	0.64	0.60
$(Au-Ag)_V$	90.9	7.35	6.45	5.75	5.75	0.88	0.79	0.735	0.66	1.45	1.79	1.80
$(Au-Ag)_{VI}$	97.8	7.7	7.4	6.95	6.9	0.96	0.91	0.525	0.36	3.2	6.1	8.5
Ag	100	8.0	8.2	10.15	9.9	1.02	1.27	0.23	0.0091	4.95	23.1	720

instance, an admixture of 2 atomic percentages of gold reduces the conductivity (expressed in the above measure) from 71.10 × 10^6 to

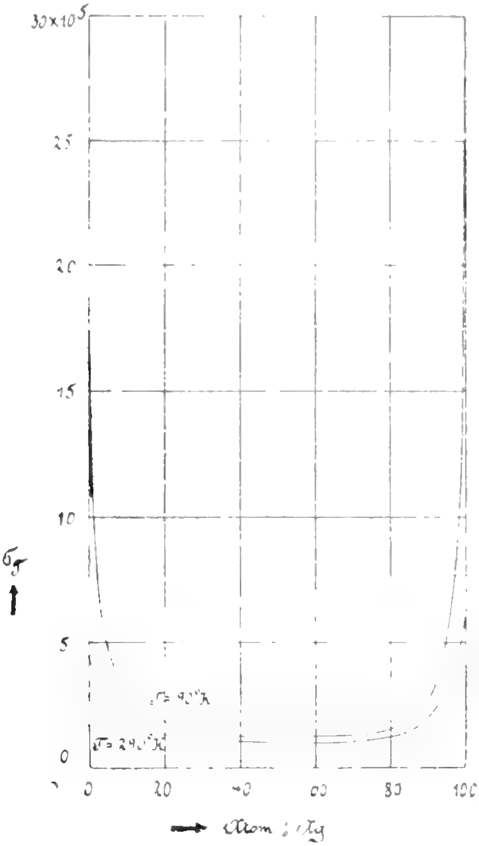

Fig. 1.

1.35 × 10^6. The curves expressing the temperature quotient $\frac{\sigma T}{\sigma_0} = \frac{w_0}{w_T}$ as a function of the atomic percentage follow a similar course. The researches of KAMERLINGH ONNES and CLAY [1]) on various gold wires have shown that the degree of purity of a metal can be very

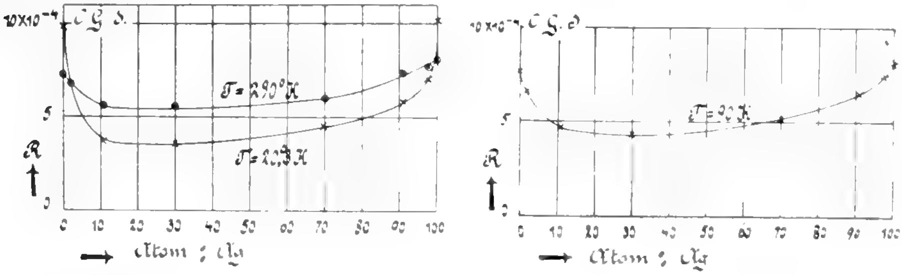

Fig. 2 and 3.

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[1]) See note 3 p. 991.

accurately gauged from a determination of the temperature coefficient of its resistances at hydrogen temperatures.

Figs. 2 and 3 show the HALLcoefficient R_T at temperatures of 290° K., 90° K. and 20°.3 K. as a function of the atomic percentage of *Ag*. The curves resemble those which give the electrical conductivity and the temperature quotient of the resistance as functions of the atomic percentage. (Cf. KAMERLINGH ONNES and BENGT BECKMAN, Comm. N°. 130*c*). When silver is gradually added to pure gold, the HALLcoefficient at low temperatures diminishes, at first rapidly, and then more slowly, until, with a mixture of about equal quantities of *Au* and *Ag*, a large change in the composition occasions only a very small change in the HALLeffect. The lower the temperature the steeper is the descent of the curve. For instance, when a 2 °/₀ admixture of silver is added to pure gold the HALLcoefficient diminishes

at $T = 20°.3$ K from 9.8×10^{-4} to 6.7×10^{-4},
at $T =$ 90° K from 7.6×10^{-4} to 6.6×10^{-4},
at $T = 290°$ K from 7.2×10^{-4} to 6.8×10^{-4}.

Hence a small *Ag* impurity in gold occasions only a small variation of the HALLeffect at $T = 290°$ K. which, however, becomes more appreciable at lower temperatures. On the other hand, as is evident from the measurements of A. VON ETTINGSHAUSEN and W. NERNST [1]), E. VAN AUBEL [2]) and A. W. SMITH [3]), the addition of a small quantity of *Sn* or *Sb* to *Bi*, which exhibits an unusually large HALL-effect, occasions even at ordinary room temperature a great change in the HALL-effect.

In Fig. 4 are shown the curves of the temperature quotients $\frac{R_{90^0}}{R_{290^0}}$ and $\frac{R_{20.3^0}}{R_{290^0}}$ as functions of the atomic percentage of *Ag*. These curves have the same general features as those of Figs. 1, 2, and 3.

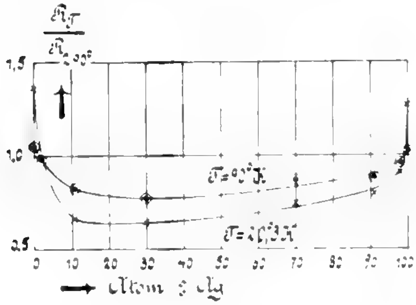

Fig. 4.

In Fig 5 is shown the relation between *R* and *T* for some *Au-Ag* alloys. The course of the curves between 20°K. and 90°K. is not quite certain, as no observations could

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[1]) A. v. ETTINGSHAUSEN und W. NERNST: Wied. Ann. **33**, p. 474, 1888.

[2]) E. VAN AUBEL: C. R. **135**, p. 786, 1902.

[3]) A. W. SMITH: Phys. Rev, **32**, p. 178, 1911.

be made between hydrogen and oxygen temperatures. These portions of the curves are therefore indicated by dotted lines. With *Ag* and

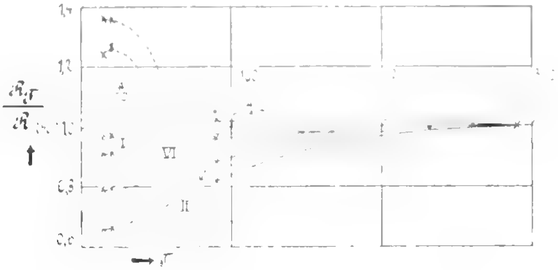

Fig. 5.

Au the HALLcoefficient increases as the temperature falls. This increase takes place chiefly in the temperature region $20° < T < 77°$ K. In the hydrogen region, $20°.3 > T > 14°.5$, R is constant within the limits of accuracy. A very small diminution of the HALLcoefficient is exhibited by the alloy $(Au\text{-}Ag)_I$ with 2 °/₀ *Ag* at low temperatures. At low temperatures alloys with more than 2 °/₀ of *Ag* show a distinct diminution in the HALL effect, which is greatest for alloys of medium concentrations. Thus alloy III with 30 °/₀ *Ag* gives $\frac{R_{20^0}}{R_{290^0}} = 0.64$. With *Au* and *Ag* the ratio $\frac{R_{90^0}}{R_{290^0}}$ differs but very little from 1, while with alloys of medium concentration it differs considerably from 1. Of the alloys with a large percentage of *Au*, a distinct diminution of the HALLeffect at low temperatures is already exhibited by alloy VI, with 2 °/₀ of *Au*.

In fig. 6 is shown the relation between the LEDUC constant $D_L = \frac{R}{w}$ and the atomic percentage of *Ag* at $T = 290°$ K. and $T = 90°$ K. This constant is the tangent of the angle of rotation of the equipotential lines in unit field. The curves are of the same nature as the conductivity-silver percentage diagrams; at lower temperatures they become steeper. When two per cent of *Au* is dissolved in *Ag*, D_L at $T = 20°.3$ K. sinks from 720×10^{-7} to 8.5×10^{-7}. It is worth noting that with alloys of medium concentration D_L is approximately constant throughout the whole temperature region $290° > T > 14°.5$; this holds for $10.7 < x < 90.9$ that is to say, for alloys in which the percentage of neither component is less than 10.

With alloys which may be regarded as dilute solutions, hence for $0 \leq x < 11$ and $90 < x \leq 100$, as a rule R is, to a first approximation, a linear function of the temperature quotient $\frac{w_T}{w_0}$ ($T = 290°$ K, $90°$ K., 20°3 K.. Only the alloys with a large percentage of Ag at $T = 20°,3$ K. are an exception to this rule.

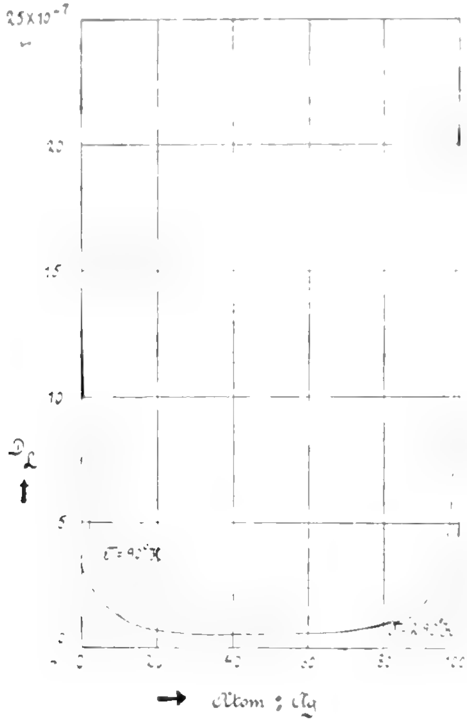

Fig. 6.

At $T = 290°$ K. the Hall coefficient for dilute solutions is proportional to the conductivity $\sigma_{290°}$.

It would undoubtedly be of the greatest importance to systematically extend these investigations of the Halleffect in alloys at low temperatures, which I have, to my regret been obliged to confine to a single series of alloys, and to further investigate alloys of different types. I hope to continue this research as soon as I can find a suitable opportunity.

I gratefully acknowledge my indebtedness to Prof. Kamerlingh Onnes who invited me to undertake these investigations of the Hall effect at low temperatures.

Physics. — "*On the* HALL *effect, and on the change in electrical resistance in a magnetic field at low temperatures. VIII. The* HALL*effect in Tellurium and Bismuth at low temperatures down to the melting point of hydrogen*". By H. KAMERLINGH ONNES and BENGT BECKMAN. Communication N°. 132*d* from the Physical Laboratory at Leiden. Communicated by Prof. H. KAMERLINGH ONNES.

(Communicated in the meeting of December 28, 1912).

§ 20 [1]). *The* HALL*effect in Tellurium.* The measurements were made with a short period WIEDEMANN galvanometer. The primary current was $I = 0.2$ amp. Two plates were investigated, both constructed from the purest MERCK tellurium. The first plate Te_{pI} was compressed in a steel mould, and the second plate Te_{pII} was cast in a steel mould. The first plate was very brittle. Both plates were circular with a diameter of 1 cm. The electrodes were platinum wires $^1/_2$ mm. in diameter, and were fused into the plates. To these platinum wires the leads were then soldered. The specific resistance and its temperature coefficient were different for the two plates; at $T = 289°$K. w_{sp} was twice as great for the first as for the second. The resistance temperature coefficient for Te_{pI} was always negative over the whole temperature region $289° > T > 20°.3$ K. Te_{pII} on the other hand exhibited a minimum in the resistance below $T = 70°$K.

The thickness of the plate Te_{pI} was 1.175 mm., its resistance

at $T = 290°$.K was $w = 0.8\ \Omega$

$20°.3$ $w = 3.0$

and again at $T = 290°$. $w = 1.0$;

at low temperatures therefore the resistance is considerably increased; cooling, moreover, caused an increase in the resistance at ordinary temperature, which is probably due to the production of small fissures.

At $T = 290°$ the specific resistance was 1.95×10^8 c. g. s. We obtained the following results (*RH* and *R* given in c. g. s. units): (see table XXV p. 998).

At $T = 290°$ the specific resistance of Te_{pII} was 1.01×10^8 c. g. s. The plate was 1.88 mm. thick. The change in the resistance with temperature is shown in Table XXVI and in fig. 5 [2]).

Hence, as has already been mentioned, the resistance of the plate Te_{pII} attains a minimum at about 40° to 60° K. This behaviour is somewhat similar to that found by DEWAR to be characteristic of

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[1]) The sections of this Communication are numbered as continuations of Comm. No. 132*a*.

[2]) The diagrams are numbered as continuations of those in Comm. No. 132*a*.

TABLE XXV.

HALLeffect for Te_{pI}

H in gauss	$T = 290°$ K.		$T = 20°.3$ K.	
	RH	R	RH	R
3750	14.65×10^4	39.1	16.1×10^4	43.1
5640	22.4	39.7	—	—
7260	29.0	40.6	31.9	44.2
9065	35.4	39.1	41.4	44.5
10270	40.2	39.1	46.6	45.3

bismuth containing only a slight amount of impurity, and by J. KOENIGSBERGER, O. REICHENHEIM, K. SCHILLING [1]) for a kind of pyri-

TABLE XXVI.

Variation of the resistance of Tellurium, Te_{pII}, with temperature.

T	w
289° K	0.212 Ω
170.8	0.146
162.3	0.144
153.1	0.141
141.8	0.136
90	0.119
80	0.117
69.5	0.113
20.3	0.122
17.7	0.124
14.5	0.126

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[1]) J. KOENIGSBERGER. Jahrb. d. Rad. u. Elektr. **4**, p. 158, 1907.
O. REICHENHEIM. Inaug.-Diss. Freiburg i. Br. 1906.
J. KOENIGSBERGER und K. SCHILLING. Ann. d. Phys. **32**, p. 179, 1910.

tes, for magnetite, metallic titanium and metallic zirconium, a phenomenon explained by J. Koenigsberger by the dissociation of electrons from the atoms.

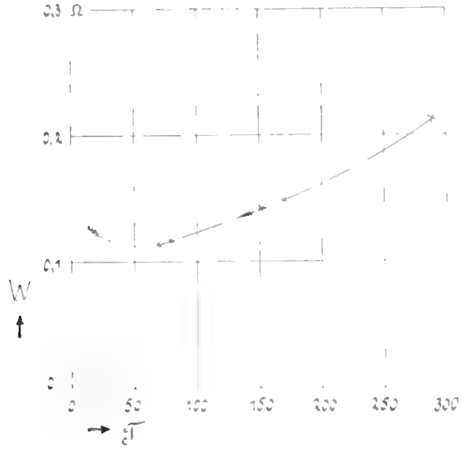

Fig. 5.

With this plate, too, an increase of the resistance was observed on returning to ordinary temperature $T = 290^\circ$ K after having cooled it to hydrogen temperatures. In this case, however, it was much smaller than with Te_{pI}, and was, at the most, 5 %. We obtained the following results:

TABLE XXVII.

Hall effect for Te_{pII}

H in gauss	$T = 291^\circ$ K		$T = 89^\circ$ K		$T = 20.^\circ 3$ K		$T = 14.^\circ 5$ K	
	RH	R	RH	R	RH	R	RH	R
3720	6.90×10^5	185.5	7.85×10^5	210.5	7.98×10^5	214.5	7.85×10^5	211
5680	10.55	186	11.95	210	12.1	213	11.85	208.5
7260	13.6	187		–	15.4	212	15.0	206.5
9065	16.75	185	18.75	207	19.05	210	18.65	205.5
10270	18.85	183.5	21.25	207	21.4	208.5	21.0	204.5

At any definite temperature R is practically constant for various fields; at lower temperatures there is an indication that R diminishes somewhat in the stronger fields; this is most marked at hydrogen temperatures at which R_0 (R for $H=0$) is about 5°/₀ greater than R for $H=10000$.

For both plates the HALLeffect increases at lower temperatures, while the ratio $\frac{R_{20^\circ K}}{R_{290^\circ K}}$ is the same. This is very remarkable, for the plates are completely different with regard to their specific resistance, resistance temperature coefficient and absolute magnitude of the HALLeffect. For both plates the value of the HALLeffect is small compared with that obtained by A. v. ETTINGHAUSEN and W. NERNST[1]), 530, and also by H. ZAHN[2]), and the electrical conductivity is also small. According to the researches of A. MATTHIESEN[3]), F. EXNER[4]), W. HAKEN[5]), J. F. KRÖNER[6]) and others, various modifications of tellurium occur; according to KRÖNER it exhibits dynamical allotropy. The two modifications have very different conductivities. The specific gravity of the plate Te_{pII} was 6.138; this is perhaps connected with the circumstance that it cooled slowly after casting, and that it was subjected to local heating when fusing in the electrodes. For a preparation very quickly cooled KRÖNER gives a specific gravity as low as 5.8. The modification with the lowest specific gravity seems to have the smallest electrical conductivity.

§ 21. *The* HALL*effect in Bismuth crystals.* In Table XIII. Comm. N°. 129*a*, we gave results of measurements of the HALLeffect in bismuth crystals for the case in which the crystalline axis is perpendicular to the field, and the main current runs in the direction of the axis. To these we are now in a position to add results for the case in which the field is parallel, and the main current perpendicular, to the axis. For these measurements we used one of the crystal prisms which had been used by VAN EVERDINGEN (Suppl. No. 2) in his measurements, choosing the most regular of the three (2, 3 and 5 l. c.) which had been found suitable for this purpose (cf. p. 82 l. c.).

In the following Table are given R, H and RH in c.g.s.

At ordinary temperature and in weak fields RH is negative, as was first discovered by VAN EVERDINGEN and subsequently confirmed by J. BECQUEREL[7]).

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[1]) A. VON ETTINGHAUSEN und W. NERNST. Sitz. Ber. Akad. d. Wiss. Wien. **94**, p. 560, 1886.

[2]) H. ZAHN. Ann. d. Phys. **23**, p. 146, 1907.

[3]) A. MATTHIESEN und M. VON BOSE. Pogg. Ann. **115**, 385, 1862.

[4]) F. EXNER. Sitz. Ber. Akad. d. Wiss. Wien. **73**, 285, 1876.

[5]) W. HAKEN. Inaug. diss. Berlin 1910.

[6]) J. F. KRÖNER. Inaug. diss. Utrecht 1912.

[7]) J. BECQUEREL, C. R. 154, p. 1795. June 24, 1912.

In stronger fiields RH becomes positive, as was also found to be the case by VAN EVERDINGEN and BECQUEREL. We may, however, incidentally remark that the initial negative values found by BECQUEREL are much greater than ours, and that with him zero is reached in much stronger fields than with us. This leads us to suspect that the initial negative values we have obtained are to be ascribed to some cause which occasioned their occurrence to a much higher degree in BECQUEREL's experiments; this would be the case, for instance, if our bismuth were purer than his, but still not yet quite free from impurity. If that were the case, then with absolutely pure bismuth we should, perhaps, at ordinary temperature, obtain nothing but increase of RH with the field, the rate of increase being slower in the initial stages.

TABLE XXVIII.

HALLeffect for a Bismuth crystal with its axis parallel to the field.

$T = 290°$ K.			$T = 90°$ K.			$T = 20°.3$ K.			$T = 14°.5$ K.		
H	RH	R	H	RH	R	H	RH	R	H	RH	R
1000	-0.05×10^3	-0.05	1005	$+ 3.4\times10^3$	$+3.4$	1670	$+ 5.2\times10^3$	$+3.11$	2970	$+8.55\times10^3$	$+2.88$
1660	$+ 0.09$	$+0.06$	2490	7.8	3.13	2740	7.95	2.90	5680	15.5	2.73
2970	$+ 0.86$	$+0.29$	4220	12.2	2.89	3720	10.45	2.81	8260	22.1	2.69
3720	$+ 1.57$	$+0.42$	5710	15.9	2.78	5680	15.4	2.71	10270	27.4	2.67
5680	$+ 4.12$	$+0.72$	7300	20.0	2.75	7260	19.3	2.66			
7260	$+ 6.60$	$+0.91$	9110	24.7	2.71	9065	24.0	2.65			
9065	$+ 9.8$	$+1.08$	10320	27.7	2.69	10270	27.2	2.65			
10270	$+11.9$	$+1.19$									

But one can still quite well imagine, however, that at higher temperatures negative values can be obtained in weaker fields in the course of the change which RH as a function of H undergoes with the temperature. The part played by admixture would then be restricted to a displacement of the temperature at which a negative value could still just appear, and this temperature would be higher for bismuth of greater purity than for impure bismuth. This would be analogous to the diminution of the negative effect at lower temperatures in the case discussed in § 14 of Comm. No. 129*c* in which the axis stands perpendicular to the field.

At lower temperatures we found the HALLeffect positive in all fields, which is not what BECQUEREL found to be still the case at liquid air temperatures. It is further worth noting that RH shows no further change with temperature below the temperature of liquid air. This makes it important to amplify the measurements given in Table XIII for the axis perpendicular to the field by others at the temperature of liquid air.

It is seen from Fig. 6 that for fields greater than 2000 gauss at low temperature, and in fields greater than 6000 gauss at ordinary temperature, RH is clearly a strictly linear function of the field. If we write

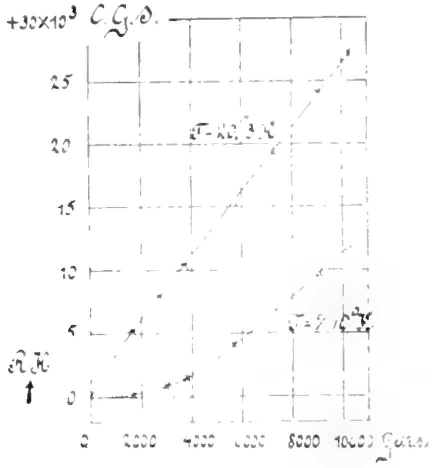

Fig. 6.

$$RH = a'H + b',$$

in this region, we obtain

$T = 290\ ^\circ K$	$T = 90\ ^\circ K$	$T = 20.3\ ^\circ K$
$a' = +1.7$	$a' = +2.56$	$a' = +2.56$
$b' = -5600$	$b' = +1300$	$b' = +1100$

§ 22. *Remark upon the increase in the resistance of bismuth in a magnetic field.* A friendly remark by Prof. H. du Bois leads us to a further development of our ideas concerning the occurrence of a maximum in the isopedals for the increase in the resistance of bismuth.

Our measurements make it probable that the maximum found by Blake at the temperature of liquid air must be ascribed to the presence of impurity or to some modification occasioned, for instance, by mechanical treatment, and that this maximum is not obtained with pure normal bismuth at these temperatures. The values which we obtained at the boiling point of hydrogen make it also certain that neither is a maximum to be found between the temperatures of liquid air and of liquid hydrogen. In the region of hydrogen temperatures a falling off in the rate of increase of the resistance of the bismuth wires is clearly apparent. The existence of this diminution has been proved twice, and on each occasion for different currents (and, as is evident from the table, for various fields). But a maximum, that is to say, a return to smaller values, we have not obtained. From the course of the curves given by Bengt Beckman in Comm. N°. 130*a*, it still remains possible that the phenomenon reaches a limiting value. From various analogous phenomena we might quite well expect something of this kind to happen at extremely low temperatures. In Comm. N°. 129*a* we commented under I, § 2, upon the uncertainty as to whether a maximum is reached at these temperatures, or rather an asymptotic approach would be found to be made to a limiting value, stating that "Perhaps as the purity increases the maximum in the isopedals is displaced towards lower temperatures". The measurements we have made with the plates *Bi* lay further emphasis upon the "perhaps." As the temperature falls to 20° K the plates Bi_{pI}, Bi_{pII}, which were not so pure as the wire, exhibit no diminution in the rate of increase. And yet, on account of the greater impurity suspected in these plates, they should be expected to exhibit a maximum between 14.°5 and 73°.K, if there were a maximum for pure bismuth at temperatures lower than 14°.5 K and if this maximum were displaced towards lower temperatures only by an increase in the purity of the material. In contrast with this we here find that only the diminution in the rate of increase remains between 20° K and 14°5 K. Further experiments upon different bismuth preparations are of course highly desirable.

Botany. — "*Some correlationphenomena in hybrids*". By Miss T. Tammes. (Communicated by Prof. Moll.)

(Communicated in the meeting of November 30, 1912).

In recent years there have been observed also in hybridisation phenomena which show a certain relation between different characters of a plant. Already in 1900 Correns 1) pointed out this relation and called it "Faktorenkoppelung". Some years later Bateson 2) put forward a theory to explain the phenomena observed. According to Bateson, in the formation of gametes in the case of a plant heterozygous for more than one factor, the various possible combinations of factors or genes do not arise in equal numbers. There may be two reasons for this. In the first place some factors may show a certain tendency to remain connected whilst they are however not so completely coupled as to preclude occasional separation. In the second place there can be between different factors a tendency to repulsion.

Some examples of such "gametic-coupling" and "repulsion" or "spurious allelomorphism", as Bateson calls these phenomena, are already known. I too made observations in the course of my investigation on hybridisation that could best be explained by such a genetic correlation. Whilst however the cases known up to the present relate to characters whose presence or absence in the plants investigated is easily determined, this is not so in my inquiry. I have studied characters whose fluctuating variability is very marked, while moreover the distinction between the parental forms for one and the same character already amounts to several genes. The characters are, as Lang 3) expresses it, polymeric. On this account the phenomena become so complicated that a complete analysis is impossible or only possible by most laborious investigation. I have so far therefore taken a shorter course and shall only show in this preliminary paper that the phenomena point to a correlation not only between two but indeed between a greater number of characters.

My observations have been made on the cross already 4) earlier described, between *Linum angustifolium* Huds. and a variety from

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1) C. Correns, Ueber *Lerkoyen*bastarde. Bot. Centr. Bd. 84, 1900, p. 11 of the reprint.

2) W. Bateson, Mendel's Principles of Heredity. 1909, p. 148.

3) Arnold Lang, Fortgesetzte Vererbungsstudien. Zeitschr. f. indukt. Abst. und Vererbungslehre, Bd. V, 1911, p. 113.

4) Das Verhalten fluktuierend variierender Merkmale bei der Bastardierung. Rec. d. Trav. bot. Néerl. Vol. 8, 1911. p. 201.

Egypt of *Linum usitatissimum* L. which I have called *Egyptian flax*. The chief points of difference between these plants are the following: the flower, the fruit and the seed of *L. angustifolium* are smaller than those of *Egyptian flax*, and moreover the colour of the flower is lighter.

The following mean values show this.

	L. angustifolium.	*Egyptian flax.*
Length of petal	8.08 mm	16.20 mm
Breadth ,,	4.45 ,,	13.05 ,,
Length of seed	2.40 ,,	6.08 ,,
Breadth ,,	1.54 ,,	2.94 ,,

By analysis of the second generation I was able to show that the difference in length of the petal of the two forms is caused by at least four factors. This holds good also for the breadth of the petal, while the difference for the length of the seed amounts to at least four and for the colour of the flower to at least three factors. The difference in breadth of the seed is also caused by several factors.[1]

I have attempted to trace the behaviour of the above characters on hybridisation. The first generation was uniform and intermediate in the case of all characters; in the second generation a considerable segretation had occurred. This generation consisted for each of the reciprocal crosses of fully 100 plants. Both groups were separately investigated. Since these however gave exactly the same results, I will only deal with the crossing in which *L. angustifolium* was the father. Of this I have observations of all characters in exactly 100 plants.

The length and breadth of the petal were determined by taking the average values of several flowers; for the determination of the length and breadth of the seed a greater number of seeds were measured, mostly 50 to 100, and the average was taken. The colour of the flower was estimated in the manner described before[2] and expressed numerically. The light colour of the flower of *L. angus-*

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[1] Since the appearance of my above mentioned paper I have succeeded in showing that the factors which cause the difference in the colour of the flower are distributed over both forms and that these forms have no common factors The proof of this was obtained by the appearance of white flowers. The plant was found in much larger culture than the one previously grown. In this case the hybrid thus oversteps the limits of the characters in the parents.

With respect to the factors for the other characters my investigations are not yet complete.

[2] l. c. p. 260.

Length of seed in mm	Breadth of seed in mm	Length of petal in mm	Breadth of petal in mm	Colour of petal
3.144	1.880	9.7	6.3	3
3.186	1.961	10.8	8.0	5
3.186	2.006	10.0	8.3	4
3.224	1.920	9.4	7.0	1
3.242	1.976	9.5	6.4	2
3.281	2.007	10.6	8.0	3
3.305	1.960	9.4	8.5	6
3.321	1.895	10.5	7.8	5
3.383	2.054	11.4	9.4	6
3.387	1.916	10.1	7.5	5
3.405	1.983	9.5	7.7	5
3.449	1.960	10.0	8.0	2
3.450	2.006	11.0	7.0	6
3.451	2.016	10.9	8.3	6
3.458	2.095	9.6	7.0	4
3.473	2.057	11.1	9.2	8
3.482	2.023	11.0	8.3	7
3.495	1.928	11.0	8.5	7
3.501	2.104	10.8	8.9	8
3.511	2.038	10.0	8.0	6
3.529	2.022	11.5	8.0	6
3.530	2.042	9.2	7.3	4
3.552	2.067	10.6	8.0	4
3.557	2.086	11.3	7.5	5
3.562	2.239	10.5	7.0	6
85.064	50.241	259.4	195.9	124

Length of seed in mm	Breadth of seed in mm	Length of petal in mm	Breadth of petal in mm	Colour of petal
3.564	2.130	10.8	8.8	7
3.570	1.993	10.3	8.5	7
3.575	2.149	10.8	7.5	5
3.600	2.126	10.8	8.4	8
3.606	2.077	9.4	6.9	5
3.610	2.224	11.8	8.6	7
3.615	2.088	10.8	8.8	6
3.617	2.080	10.4	8.0	5
3.619	2.150	10.8	7.5	6
3.620	2.112	10.5	7.8	5
3.624	2.137	10.7	8.6	7
3.628	2.246	11.5	9.0	7
3.629	2.333	11.2	7.4	4
3.629	2.157	10.6	8.4	8
3.648	2.013	10.7	8.9	2
3.650	2.145	10.5	8.4	3
3.662	2.226	12.1	8.6	3
3.670	2.081	10.6	7.8	6
3.671	2.050	11.2	7.0	5
3.672	2.036	10.0	6.3	5
3.682	2.193	10.7	6.9	9
3.716	2.267	11.4	8.2	6
3.717	2.331	12.4	9.2	8
3.723	2.183	10.3	7.5	6
3.741	2.141	11.2	8.0	5
91.058	53.668	271.5	201.0	145

Length of seed in mm	Breadth of seed in mm	Length of petal in mm	Breadth of petal in mm	Colour of petal
3.759	2.200	10.8	7.0	4
3.761	2.075	11.0	8.2	5
3.766	2.027	11.5	7.6	5
3.767	2.067	11.2	8.4	6
3.771	2.209	10.4	8.0	9
3.773	2.075	10.0	7.5	4
3.781	2.250	11.2	8.5	6
3.786	2.198	10.1	8.7	10
3.791	2.181	10.2	8.2	7
3.798	2.227	11.0	9.5	7
3.803	2.147	11.8	9.6	6
3.821	2.149	11.3	8.0	8
3.829	2.213	13.0	8.6	4
3.829	2.228	10.0	7.4	7
3.830	2.170	11.0	9.2	8
3.830	2.224	11.2	9.5	6
3.831	2.268	10.5	7.8	7
3.835	2.135	11.5	8.5	5
3.841	2.204	9.5	6.5	5
3.843	2.171	10.6	8.0	4
3.861	2.249	11.7	8.5	5
3.890	2.180	9.8	7.0	6
3.906	2.320	11.5	8.2	8
3.908	2.175	11.3	8.5	4
3.910	2.202	10.0	8.6	4
95.520	54.544	272.1	205.5	150

Length of seed in mm	Breadth of seed in mm	Length of petal in mm	Breadth of petal in mm	Colour of petal
3.915	2.260	10.7	9.0	8
3.922	2.413	10.0	8.4	4
3.922	2.313	11.0	8.5	8
3.923	2.270	10.0	9.1	5
3.926	2.287	10.6	8.2	9
3.933	2.271	11.0	9.5	8
3.940	2.351	11.7	9.8	8
3.948	2.361	12.0	9.2	7
3.949	2.150	11.0	8.8	9
3.968	2.298	10.5	8.0	6
3.988	2.196	10.6	9.5	8
4.016	2.218	9.5	8.2	4
4.031	2.225	11.5	8.2	8
4.139	2.295	11.3	9.7	6
4.140	2.317	11.0	8.0	5
4.154	2.350	12.0	9.5	7
4.167	2.389	11.3	8.0	6
4.188	2.345	11.3	8.6	7
4.238	2.348	11.2	9.3	9
4.244	2.456	11.0	9.4	5
4.274	2.446	11.8	9.8	10
4.335	2.452	13.2	10.7	8
4.350	2.311	11.2	7.5	6
4.381	2.461	12.2	10.0	7
4.420	2.469	11.5	9.9	7
102.411	58.252	279.1	224.8	175

tifolium was represented by 1, the much darker colour of *Egyptian flax* by 10.

I have arranged the observations according to the ascending values of the length of the seed in order to obtain a survey of the mutual relationship of the various characters.

In the preceding table the figures placed in a horizontal row refer to the various characters of the same plant, in the vertical columns those for different plants are given. The whole table is divided into four parts, each containing 25 plants.

From these tables it must now be clear whether there is or is not an inter-relation between the length of the seed and the other characters. If the latter are wholly independent of the former then for each character the values in a vertical direction must follow each other without any regularity; the lowest average, and highest values for each character must be distributed equally over the four tables and the totals of the 4 successive series must be equal or nearly equal or must at least be arranged without any regularity.

On the other hand should there exist an intimate relation between the length of the seed and the other characters such that they behave as a single whole, then these other characters will also be arranged in the tables according to ascending or descending values, except for small deviations due to the influence of external circumstances.

A superficial inspection already shows that for none of the characters are the values in the vertical columns in a sequence; between successive figures a good many irregularities occur. If however the tables are compared with one another, it is seen that in general in the first lower values, in the last higher values are found.

In order to make a comparison easier, I have added the values for the 25 plants of each table. Below are given the totals obtained for the different characters.

Length of seed	Breadth of seed	Length of petal	Breadth of petal	Colour of petal
85.064	50.241	259.4	195.9	124
91.058	53.668	271.5	201.0	145
95.520	54.544	272.1	205.5	150
102.411	58.252	279.1	224.8	175

We see the values for all four characters increase in successive series. It follows therefore that, on the whole, in the plants which have the smallest length of seed, the breadth of the seed and the length and breadth of the petal are small, whilst moreover the flower shows the lighter shades, and conversely a greater length of seed is generally coupled with greater breadth and a larger, more deeply-coloured flower.

In the same way as proceeding from the length of the seed, I have also determined the inter-relations of the other characters. From the above table I have arranged the values in ascending order according to the breadth of the seed and compared the others with it. The same was done starting from the other characters. It is unnecessary to give here the complete tables. Below are set out the totals obtained each time for 25 successive plants.

Arranged in ascending order of breadth of seed	Length of petal	Breadth of petal	Colour of petal
Plant 1— 25	261.3	195.8	121
„ 26 — 50	269.0	204.5	148
„ 51— 75	270.0	205.0	154
„ 76—100	282.8	221.9	171

Arranged in ascending order of length of petal	Breadth of petal	Colour of petal
Plant 1— 25	190.8	121
„ 26— 50	201.3	148
„ 51— 75	211.7	160
„ 76—100	223.4	165

Arranged in ascending order of breadth of petal	Colour of petal
plant 1— 25	124
„ 26-- 50	141
„ 51— 75	150
„ 76—100	178

As is seen the values for successive series of 25 plants in all the above cases increase. There exists therefore a relation not only between the length of the seed and the other characters but the five characters together form a complex of which each part in its development depends somewhat upon all the rest.

Now the nature of the inter-relation of the characters of the flower and seed which have been studied is, as the figures show, such that in general the development of all characters in one plant is in the same direction, since, for example, a long petal shows a distinct tendency to be coupled with a broad petal, with darker shade of flower and with a greater length and breadth of the seed.

From this it might be deduced that here it is only a question of ordinary consequences of slight differences in external conditions in consequence of which the best nourished plants develop more strongly and form larger deeper-coloured flowers and larger seeds, in other words that the relation observed may only be the usual correlation phenomenon of fluctuating varying characters, just as met with in homogeneous material that is in pure forms.

There indeed occurs, as the observations showed, a correlation between the characters in the parent forms and also in the first generation, of the same kind as the relation here described.

In F_2 also this correlation will play a more certain part, but only in a subsidiary way and the phenomenon is chiefly due to another cause. This is already clear from my earlier investigations. Moreover I have also traced the relationships in the offspring. When the relation observed is a phenomenon of correlative variability, then the offspring of each individual of the second generation must exhibit again the same correlationfigure as the whole second generation or at least the offspring of a plant which is extreme for one or more characters must in general deviate much less from the average type than this plant itself. Now this was not the case, for it was found that the relationships as they appeared in the F_2-plant were in the main handed on to the offspring. Some examples having reference to the length, breadth, and colour of the petal will make this clear. The values for four different F_2-plants and their offspring are given in the following table. The first F_2-plant possesses the three characters in an extreme degree, the fourth has extremely small values for them all, the two others show different combination.

	F_2		F_3	
Length of petal	13.2	mm	12.1—14.8	mm
Breadth ,,	10.7	,,	10.3—12.2	,,
Colour ,,	8		7—9	
Length of petal	13.0	mm	12.1—14.0	mm
Breadth ,,	8.6	,,	7.7—9.2	,,
Colour ,,	3		2—5	

	F_2		F_3	
Length of petal	10.0	mm	8.5 11.2	mm
Breadth ,,	9.1	,,	8.3 - 10.1	,,
Colour ,,	5		3 7	
Length of petal	9.5	mm	8.2 —10.0	mm
Breadth ,,	6.4	,,	6.0 7.2	,,
Colour ,,	2		1 2	

The above proves that there is still another relation between the characters in the plants studied in addition to ordinary correlation. The whole phenomenon is only superficially like such a correlation.

Just as any single character which is based on several genes, gives in the second generation a pseudo-curve which shows itself as a curve of fluctuating variability but in which the fluctuating variability plays only a more or less subordinate role, so also here in F_2 an inter-relation of different characters may appear that simulates ordinary correlation, but that is in reality a completely different phenomenon which is only slightly affected by this correlation. I point this out because it seems to me that in studying correlative variability it is of the highest importance to investigate only pure homogeneous material. Since Johannsen has made known to us the "pure lines", it has become clear that much that was formerly thought to be pure material, is a mixture of several forms perhaps also of hybrids. It is possible that the correlation found in such material is not a pure correlation between the fluctuating variability of the characters but is wholly or in part a different correlation phenomenon. This is also the case here. We must assume that here a genetic relation exists between the groups of factors for the different characters. This relation is such that in the formation of gametes in F_2 definite combinations of factors occur preferentially. In general a tendency exists to make the proportion in the number of factors for the various characters such as it was in the original forms or at least to approximate to these. This explains that in F_2 more forms arise in which the characters all deviate in the same direction from the average than should be the case according to the laws of probability.

In the crossing mentioned above the groups of factors for the various characters behave with respect to one another differently from the way in which the factors for one single character behave mutually; for my earlier investigations have shown, that for each of the characters under discussion the genes are mutually quite independent of one another. It is most noteworthy that there exists between the factorgroups for different characters a closer relation than between the factors for the same. Further investigations must show to what extent this phenomenon occurs in other cases and whether it is always coupled with a tendency to preserve the complete image of the parent forms.

In the case here described the genetic correlation is incomplete. As is clear from the tables plants are found, which for some characters more nearly approach the one parental form and for others are nearer to the second. The number in which the different combinations occur, cannot be determined as is done by other investigators for their crossings, also because ordinary correlation plays through it and still further obliterates the separation between the groups. If at all, the ratios could only be found by much more detailed investigation; but it is clear from the foregoing that by this means some insight into the phenomena may be obtained.

The characters mentioned all belong to flower or seed, the fruit might be added since a very close relation exists between the size of the fruit and that of the seed. I am also engaged in tracing the relation of the characters mentioned to those of the vegetative organs. I am, however, prevented by circumstances from completing this investigation in the near future.

The results of the investigation may be summarised as follows:

In hybrids of *Linum usitatissimum* and *L. angustifolium* an incomplete genetic correlation exists between the groups of factors or genes for length, breadth, and colour of the petal and length and breadth of the seed; whereas on the other hand the factors for the same character are completely independent of one another.

The inter-relation is such that there exists a tendency to approximate to the combination of characters as it occurs in the parent forms.

The genetic correlation expresses itself apparently as a phenomenon of the ordinary correlation of fluctuatingly varying characters; the latter correlation which also occurs, plays only through the former.

Botanical Laboratory.

Groningen, 3 Oct. 1912.

Botany. — JOH. H. VAN BURKOM: *"On the connection between phyllotaxis and the distribution of the rate of growth in the stem"*. (Communicated by Professor WENT).

(Communicated in the meeting of November 30, 1912.)

Various investigators have studied the longitudinal growth of the stem. They have for the most part paid attention to the total increase in length of the stem and only a few investigated the distribution of the rate of growth in one or several internodes. Complete investigations, on widely different plants with regard to the distribution of the rate of growth over the whole growing region have so far not appeared. There occur indeed in the literature two important utterances which are based on preliminary observations. The first is the opinion expressed by SACHS[1] that the growth of stems with distinct nodes differs from those with indistinct nodes. If the stem is sharply articulated then according to SACHS each internode shows its own curve of rate of growth. This rate increases from the base of the stem towards the apex, reaches a maximum and decreases again towards the upper node. If the stem has indistinct nodes then the whole growing region yields a single curve of rate of growth of this type.

ROTHERT [2]) has further described this. He speaks of individualised internodes when each internode grows as a separate unit and passes through the great period of growth, whilst in other cases the whole stem passes through this growing-period as one internode. Notwithstanding that these two authors have clearly distinguished two methods of growth, the growth of the whole stem in one growing-period has had most attention paid to it, so that in most text books it is given chief consideration.

This is the circumstance which led me in 1907 to make measurements on various plants in the Botanic Gardens at Utrecht.

With regard to the results of this inquiry which will be shortly communicated in my Dissertation, I wish here to make a brief preliminary statement.

With the aid of a little stamp made for this purpose or of a brush and India ink, linear marks were made on the stem, so that it was divided into zones.

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1) SACHS Jul. 1873. Ueber Wachsthum und Geotropismus aufrechter Stengel. Flora 56 Jahrgang. Regensburg.

2) ROTHERT W. 1896. Ueber Heliotropismus. COHN'S Beiträge zur Biologie der Pflanzen Bd VII.

Immediately on the completion of intervals of time which were as far as possible equal, the length of the zones was measured accurately to $^1/_4$ m.m. I calculated from the increase in length the average rate of growth per m.m. during each separate space of time.

In making the measurements a great difficulty was the determination of the exact boundary of the zones, because the portion of the stem on which the mark had been placed, grew at the same time. I therefore tried to determine as far as possible the middle of the mark. In my later observations, I succeeded in avoiding the error due to this, by marking alternate zones with a lengthwise line. I then took the extremities of the longitudinal mark as the zone-boundary.

Rapid growth also caused this boundary to become indefinite and difficult to determine.

To gain an idea of the errors in my observation, I frequently also measured in the course of my observations the zones which had already been found to have grown out.

I thus obtained numerical data concerning the length of the same zone measured at different points of time.

The greater number of these data were identical, only a few deviated. Calculation showed that the average error was smaller than the expected degree of accuracy.

In *Asparagus officinalis* Linn., *Ginkgo biloba* Linn., *Hedera colchica* Hoch and *Linum usitatissimum* Linn., the whole region of growth formed a single curve of rate of growth, i. e. regularly increasing growth from below upwards and then decreasing growth above this.

Acer dasycarpun Ehrl., *Acer platanoïdes* Linn., *Deutzia scabra* Thbg., *Lonicera tatarica* Linn., *Syringa vulgaris* Linn., and *Viburnum Veitchi* C. H. Wright showed a similar curve of rate of growth with this difference that the zones in which the nodes were situated showed less growth than the zones lying nearest to them.

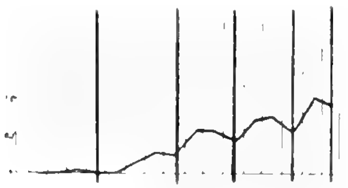

Fig. 1. *Deutzia Scabra* Thbg.
13—17 Juli.

Fig. 1 shows the curve of rate of growth in *Deutzia Scabra* Thbg. from 13th to 17th July 1).

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1) On the abscissae axis the zones have been plotted at equal distances. The thin lines give the division-marks between the zones, the thick lines are the nodes. As ordinates I have plotted the average rates of growth of each zone during a definite space of time.

The rate of growth of the lowest zone of the stem is given in the curve on the left, and that of the uppermost zone on the right.

In *Clematis alpina* Miller, *Clematis recta* Linn., *Eucalyptus Globulus* Labill., *Dahlia variabilis* Dess. *Polygonum cuspidatum* Sieb. et Zucc, *Polygonum Sachalinense* F. Schmidt and *Sambucus niger* Linn. the zones lying below the node had moreover a distinctly slower growth than the others. (See fig. 2).

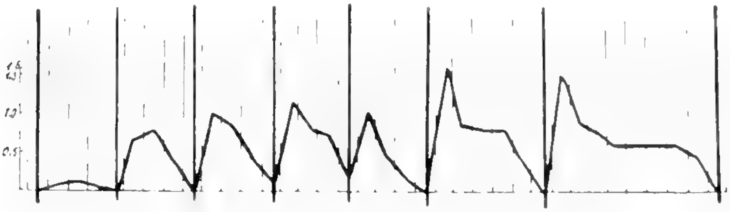

Fig. 2. *Polygonum Sachalinense* F. Schmidt 9—11 May.

In both groups of plants in the beginning the lowest part of each internode grew fastest whilst the rate of growth near the upper end decreased till in the "node-zone" it became very slight or zero (Polygonum).

Afterward the maximal rate of growth was displaced toward the apex and diminished in magnitude.

The zones in which the maximal rate of growth had lasted the longest time, during which period this maximum in the internode also reached its greatest value, increased much more than the uppermost zones in which the maximum lasted only for a shorter time and in which it was moreover much decreased in intensity.

The difference between the first group (Acer etc.) and the second group (Clematis etc.) lies in the rate at which the maximum of growth travels along each internode and the point of time at which it occurs.

In the first group the displacement of the maximum begins in a very early stage of development and the maximum is very quickly found below the node. On the other hand this movement is slow in the plants of the second group, so that for some time, often indeed for a considerable time, the uppermost zones of an internode show less growth than the inferior zones of the same internode.

Since the difference is confined to the moment of time in which and the velocity with which the maximum moves in the direction of the apex, the two groups are not sharply differentiated, and sometimes it is possible to obtain a curve of the rate of growth from plants in the one group which agrees with that from the other group.

I have not yet been able to determine from my observations what factors may influence the movement of the growth maximum. When the maximum chanced to occur just under the node and was therefore measured in the nodal zone, this zone showed the maximum growth.

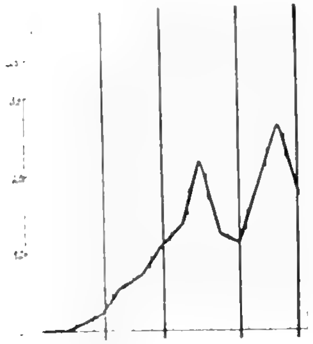

Fig. 3. *Sambucus niger* Linn.
11—16 Mei.

The ascent of the zone of maximal growth from the basal portion of the internode now continued in the lowest zone of the second internode up to the maximum rate of growth of this internode. In this case I found in both internodes one ascent of the rate of growth without diminution in or near the nodal zone (see fig. 3).

Humulus lupulus Linn. showed two different curves of the velocity of growth, namely, some had a regular course (one maximum for the whole growing zone) and some with a decrease at the upper end of some internodes. These divergent results can be brought into agreement by specially noting the movement of the maximum.

Its quick passage into the nodal zone, not only in the undermost growing internode but also in the second internodes, caused the curve of velocity of growth in these internodes to become a regularly ascending line. In the higher internodes the maximum occurred under the nodal zone.

If a sufficient number of growing internodes had been marked on the same stem, I was indeed able to observe this.

I think I have also observed that the movement of the growth maximum in an internode of *Humulus* takes place at about the same time as the maximum of the whole growing region is found in that internode.

I regarded the growth as intercalary, if there was either in the upper or in the lower portion of an internode a short zone which maintained its growth a long time, whilst the middle of the internode was already full grown.

I have observed intercalary growth in *Commelina nudiflora* Linn., *Equisetum limosum* Linn. and *Tradescantia repens* Vand.

In *Commelina* I saw this stage preceded by growth throughout the whole internode with the greatest rate of growth below. The maximal rate did not, however, move towards the upper end but remained situated in the basal portion, whilst in the upper part growth quickly diminished and wholly ceased.

In order to observe well the growth of stems with individualised internodes, external conditions must be favourable. I found that during the days on which the temperature was very low (an average of 10° C.) the curve of rate of growth was almost a horizontal line with scarcely any maxima, and this was also the case with plants which at a higher temperature had a strongly undulating curve.

All plants, which were found to have a lower rate of growth in or also under the nodal zone (to which class plants with intercalary growth also belong) possess complete nodes, that is to say, they show an external thickening round the stem at the point where a leaf is inserted. This *may* happen in plants with alternate leaves, but it *always* occurs in plants with opposite leaves.

On the other hand plants in which ill-defined nodes ("incomplete nodes") are found, show in the growing region a single curve of growth rate and the nodal zones are not differentiated by a smaller rate.

It is therefore seen from these observations that there is here a connection between phyllotaxis and the distribution of growth in the stem.

With regard to the structure of the stem three theories are chiefly put forward. Next to the view that the leaves spring from the stem as independent organs (Strobilus theory) stands the phyton theory, which declares that the stem is composed of the basal parts of the leaves (GOETHE, GAUDICHAUD). ČELAKOVSKY [1]) expressed this view in his caulome theory.

A third opinion regards the interior of the stem as an axis round which there is a layer of leaflike origin.

HOFMEISTER regarded this development as ontogenetic, whilst POTONIÉ [2]) thinks that it has taken place phylogenetically. The pith is according to POTONIÉ the primeval caulome, round which originally xylem and phloem have developed from "leaf feet" (phyllopodia).

ČELAKOVSKY's theory as also those of HOFMEISTER and POTONIÉ, holds that the surface of the stem is composed of parts which belong to the leaves lying above it. DELPINO [3]) has called these parts "leaf-feet" (phyllopodia).

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[1]) ČELAKOVSKY L. T. 1901. Die Gliederung der Kaulome. Bot Zeitung 59er Jahrgang.

[2]) POTONIÉ H. 1912. Grundlinien der Pflanzen. Morphologie im Lichte der Palaeontologie. Jena.

[3]) DELPINO. Atti della reale Università di Genova. Vol IV, Parte II, 1883.

In plants with incomplete nodes there is found to the left and right of the point of attachment of the leaf an area which belongs to a leaf placed above, therefore there are two different phyllopodia.

When we now assume that in plants with alternate phyllotaxis (incomplete nodes) the phyllopodia themselves are subject to the same growth as is also to be seen in the node of the stems (with complete nodes), then parts having a different rate of growth will be adjacent.

The question now arises, how in that case will the rate of growth be distributed over the whole area of growth, when according to this supposition each piece of the stem has the average rate of growth of its component parts.

In order to trace this I have made a calculation for which the known rate of growth of the stem of *Polygonum* was chosen as the startingpoint, because internodes of this plant are very markedly individualised.

I assumed that each leaf only surrounded a fifth part of the circumference of the stem and that the leave were displaced along the stem to the position $^2/_5$.

From the averages of the rates of growth of the five zones thus situated at the same height I obtained a regularly ascending curve with a short descending branch.

Its course agreed with the curve for plants with alternate phyllotaxis.

Although I do not see in this any proof of the theory that the stem may be composed of leaf vases or may be covered with them, yet it is clear in either case that the observed manner of growth is not inconsistent with this.

If this theory is accepted, there is moreover agreement between the growth of plants with complete nodes and those with incomplete ones.

Finally I should like to point out that I have observed in one plant, namely, *Ginkgo biloba* LINN. a difference in growth between three stems, which were in the light and three which grew in the shade.

The number of my observations is too small to warrant any certain conclusion, but nevertheless I consider I have observed that the greater increase in length of the shaded stem must only be attributed to a slight extent to the greater rate of growth, but was more especially due to a longer region of growth, that is to say, each zone grows during a longer period of time.

Physics. — "*Experimental investigations concerning the miscibility of liquids at pressures up to 3000 atmospheres*". By Prof. Ph. Kohnstamm and Dr. J. Timmermans. Van der Waals fund researches N°. 4. (Communicated by Prof. van der Waals).

(Communicated in the meeting of November 30, 1912).

§ 1. The theoretical researches of the last few years have rendered it possible to give a complete classification of the different types of unmixing which are to be expected. Whether these theoretical expectations are in conformity with reality could be ascertained up to now only for a very limited region, on account of the inaccessibility to experiment of the whole region of pressures higher than two or three hundred atmospheres. The wellknown Cailletet tubes are namely useless at higher pressures. We have, therefore, been occupied already for a considerable time in devising an apparatus intended for higher pressures, and we have finally succeeded in constructing such an apparatus, with which we have carried out measerements up to 3000 atm., and which can probably also be used up to 4000 or possibly 5000 atm.

The first problem that was to be solved was, of course, to render the phenomena visible. For, to ascertain the critical phenomena of unmixing, and the phenomena of unmixing in general by means of other properties than those which fall within the scope of direct visual observation, seems hardly possible. Our first attempts to effect this visibility by pressing a thick piece of plate glass *A* (fig. 1) by the aid of a nut *B* fitting round it, against the steel tube which would then contain the substance to be examined, or strictly speaking against the packing enclosed between *C* and *A*, failed entirely. Even the thickest plate glass plates snapped off inexorably, when we tried to screw the nut tight enough to prevent leakage.

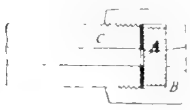

Fig. 1

Led by the figure that Amagat gives for the apparatus of his "méthode des regards", with which he has succeeded in carrying out measurements up to 1000 atm., we resolved to arrange the "windows" in such a way that neither on the front nor on the back side unequal pressures should be exerted[1], but that the whole

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[1] The "windows" used by Amagat have, however, not been constructed according to this principle; they are not cones but cylindres, they bear on the end-plane directed to the observer; Amagat uses celluloid packing between steel and glass. We have, however, experienced that to reach the highest pressures, it should carefully be avoided to make the windows bear on their end-plane.

pressure exerted by the liquid inside the tube on the "window", should be borne by the side-walls. We therefore gave the window the shape of a truncated cone, the basis turned to the side of the liquid, and the smaller plane parallel to the basis quite free and turned to the observer. The conical wall must be ground as carefully as possible into a steel cylindre with conical opening, which is screwed into the steel tube of observation. Fig. 2, where *B* is such a steel cylindre, and *A* the glass cone, will probably make this sufficiently clear. If the cone *A* is ground with sufficient care, and then fastened in *B* with a little cement, an absolutely tight closure is obtained in this way; we have never experienced any trouble owing to leakage between glass and steel, nor has any of the glass cones ever burst in consequence of the high pressure, in such a way that the liquid could be pressed through those windows. We did meet, however, with other difficulties. First of all the difficulty of getting pieces of glass from which the required glass cones could be obtained, without too much loss of time. We

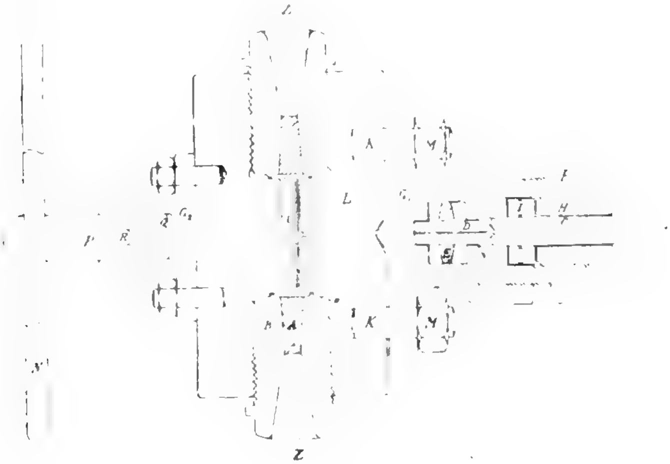

Fig. 2.

first tried to start from thick plates of plate glass (3 cm. thick), but it appeared impracticable to saw or cut off such small pieces (1.5 to 2 cm² area) [1]), that they could serve for further preparation. We then applied to the "Stichtschen Glashandel" at Utrecht, which prepared octogonal rods for us, about 6 cm. long and of a diameter of about 1·5 cm. from the best plate glass. After these rods have been cut off doubly conical (two cones of 3 cm. the bases resting

[1]) When the conus is ready the basis turned to the liquid has a diameter of 12 m.m., the other end-plane a diameter of 10 mm.

against each other), they are cut through in the middle: the planes of section must then be ground once more and polished.

A second circumstance which gave rise to difficulties, and sometimes does so now, is the becoming opaque of the cones. If such a cone which has become opaque, is removed from the cylindre, it appears that innumerable planes of cleavage have arisen at right angles to the axis of the cone, so that it can be easily broken up with the hand into a great number of plane plates. In consequence of these cracks the at first perfectly transparent cone has become quite opaque. It appears that the cones hardly ever or never become opaque with rising pressure. It is probably the consequence of the compressibility of the steel cylindre. This extends with rising pressure, and so the glass cone is driven deeper and deeper into the cylindre. If then the pressure diminishes, the cone cannot return to its first position and is cracked by the immense pressure of the steel cylindre. In agreement with this is the fact that in experiments at higher temperature the cones become opaque still more frequently than at lower temperatures; the difference of the coefficient of expansion of glass and steel then acts in the same direction. Moreover by means of the brass model used for grinding the glass cones into the cylindre, it could be clearly demonstrated that one of the steel cylindres had widened by use. A cylindre made expressly of specially hard nickel-steel yielded better results in this respect. When this was used, the cones were less liable to crack, though even then it occasionally happened. To protect the window from injury as much as possible it is also desirable to diminish the pressure as carefully as possible; a rapid increase of the pressure, on the other hand, rarely, if ever, gives rise to an accident. Though this cleaving of the cones perpendicular to the axis continues to be a drawback, because the preparation and adjustment of new cones always remains a rather lengthy work, the observations themselves are not disturbed by it, if only the experiments are made as much as possible with rising pressure, and decrease of pressure is effected with the utmost care.

At present the apparatus cannot be used for temperatures much above 70°; the Cailletet cement with which the windows are fastened into the steel cylindres, melts at that temperature, or at least rapidly dissolves in the liquid which is in the pressure tube. First of all this renders the liquid turbid, but moreover it gives rise to leakages and breaking of the windows, which are now directly pressed against the steel. We are now trying to find means to apply the windows also at higher temperatures. As to the limit of pressure, we think we have to fix this for the present at about 5000 atm.

§ 2. A second condition which the apparatus has to fulfil, is this that the mixtures which are to be examined, can be properly stirred during the experiment. Of course there can be no question of an electromagnet stirrer inside the heavy steel vessel. The difficulty seemed the greater as during the experiment, and so also during the stirring the steel vessel, which itself is already very heavy, has to remain connected without leakage with the compression pump and the manometer. We have finally succeeded in finding a construction meeting all demands; it rests on the following consideration. The pivot of a high-pressure cock may be turned round, without giving rise to leakages; we can just as well keep this pivot still, and turn the rest of the apparatus round it. Suppose the inlet tube, which connects the vessel of observation with pump and manometer, at the place of this pivot, and arrange the connection in such a way that the observation vessel can turn round this inlet tube as a pivot, then it must be possible to bring about the most efficient form of stirring viz. turning upside down the whole contents of the vessel of observation.

This idea is realized in the construction represented by fig. 2. *C* is the inlet tube of the compression pump, it has a diameter of about 15 mm.; the aperture is about 2 mm. wide. *A* prolongation *D*[1] can be screwed on to the tube *C*, by which a projecting cone is pressed against a conical concavity of *C*. In this way a steel-to-steel closure is obtained, which is quite tight even at the highest pressures. As is shown in the figure, the piece *D* pierces with its carefully finished and polished part through the packing *E*, which is enclosed between two rings, and can be screwed so tightly by means of the gland *F* in connection with the flange *G*, that leaking along this packing is prevented, though the pieces *G* and *F* with this packing can still turn round *DC* as pivot. To prevent *DC* from being pressed outside through the pressure on the end-plane of *D*, *D* is kept in its place by a gland *H*, a ball-bearing adjusted between *D* and *H* making it possible to screw *H* sufficiently tight without making the friction between *D* and *H* so considerable that it would hamper the rotation. The flange *G* is now again pressed against the observation vessel *L* by means of the bolts *K*, which pass through it, and which are screwed into the observation vessel *L*, and the nuts *M*. In this way the same steel-to-steel closure is applied as between *C* and *D*. By means of the handle *N* the pressure vessel *L* can, when everything is mounted and put under pressure, be rotated,

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[1] This tube is only 12 mm externally (and has in correspondence with this also a somewhat smaller opening than C) to make the pressure on the ball-bearings as small as possible.

DC remaining in its fixed position. Thus the two phases in the glass tube *O* change places, passing through each other and becoming perfectly mixed.

The handle *N* cannot be directly fastened to the steel observation vessel *L*. This vessel must namely be surrounded by a thermostat. Quite apart from high or low temperatures, which would make it quite impossible, it would be inconvenient even at the temperature of the room when the handle *N* was *inside* this thermostat. Therefore the connection of the observation vessel *L* with *N* has been effected as follows. The rod *P* connected with the handle (of which only part has been drawn) passes closely fitting through a stuffing box (not drawn in the figure) in the wall of the thermostat, so that *P* can still be moved forward and backward and rotated in the thermostat wall. The rod *P* terminates in a fork *Q*, which in the position drawn in the figure encloses a pin *R*, which is rigidly attached to the flange G_2, which like G_1 is again rigidly connected with *L* by means of bolts and nuts.

So in the position represented in the figure *L* can be rotated by *PN*; if *P* is drawn back in the stuffing box of the wall of the thermostat, *P*, and together with it the thermostat, gets quite clear of *R*, G_2, and *L*.

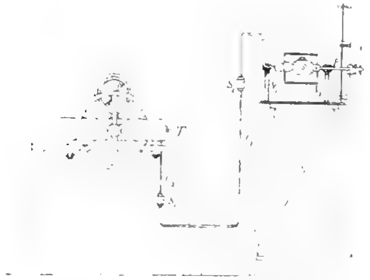

Fig. 3.

The whole arrangement is further elucidated by fig. 3. It exhibits the large SCHÄFFER and BUDENBERG hydrostatic press for 6500 atmospheres, belonging to the VAN DER WAALS-fund with the manometer standing on it. The pump is also connected with the large pressure-balance (not drawn) as a control for the manometer. One of us (K.) hopes soon to give a full description of these apparatus in connection with other experiments. The press is in connection with the tube conduit CC_1C_2, from which it can be shut off if necessary, by means of the high pressure cock *T*. There are two couplings S_1 and S_2 in this tube conduit, to which we shall presently return. Inside the thermostat *C* rests on the bearing V_1, which in its turn rests on the bottom of the sheet iron thermostat. This bearing at the same time fixes the tube *C*, so that the tube is prevented from turning round with the vessel *L*. A second bearer V_2 supports the rod *P*, which is already known to us from fig. 2. Fig. 3 also displays the stuffing box in the wall of the thermostat through which *P* passes. The thermostat is represented in section, the observation vessel is supposed in a position that the windows B are horizontal (hence turned through 90° compared with fig. 2), the position in which the observations are made. The quadrangle in the figure represents a glass window in the back wall of the thermostat (not to render the figure too indistinct it has been drawn much larger than it is in reality); of course a glass window in the front wall corresponds with it. The thermostat has a capacity of ± 40 L., it is provided with a vigorous stirring-apparatus thermoregulator, and thermometer; it rests on a solid stand of L shaped bar-iron.

The coupling S_1 is of no importance for the experiments described here; it only serves to make it possible if required to connect the press with other conduits, and if necessary, to clean the tubes. The coupling S_2, on the other hand, is necessary for the filling of the apparatus, as will appear when the filling is described. Fig. 4 gives a section of these couplings.

Fig. 4.

At the tops of the tubes C_1 and C_2 two cones D_1 and D_2 have been screwed, which exhibit again two cones fitting into each other at their ends. By means of the glands E_1 and E_2 with hexagon, D_1 and D_2 are pressed against each other, and a steel-to-steel closure is again reached tight even at the highest pressures. It is preferable to take the screws with which D_1 is fastened to C_1 and D_2 to C_2 for such couplings with left-handed thread, that when E_1 and E_2 are tightened, D_1 and D_2 are not unscrewed, but on the contrary, are screwed tighter.

In connection with the method of filling another particular of the apparatus deserves being mentioned, which appears from fig. 5. This

Fig. 5.

figure presents a side view of the observation vessel, a section of which was given in fig. 2, with the parts in connection with it, on the supposition, however, that the glass windows are again horizontal (not vertical, as in fig. 2, but in the same position as it is represented on a small scale in fig. 3). So A is again the glass window; the other parts too, for so far as they are visible, are denoted by the same letters. It is clear from the figure that besides the main conduit, in which the observation tube O lies, and the branch conduit, which connects this main conduit with DC, there is another branch conduit in the observation vessel L, at right angles to the two first mentioned. This branch conduit is used for the filling; it is then closed by a tight stopper W, which is again provided with a cone, and which is pressed against the vessel L with steel-to-steel closure by means of an oval flange G_3 laid over this cone, with the nuts and bolts belonging to it. This closure is further made clear by fig. 6, where the flange G_3 is represented seen from above, the line ZZ' corresponding with ZZ' of fig. 2. Fig. 6 also shows the general form of the flange plates G. Fig. 5 finally shows the octagon $L_1 \ldots L_8$ of the observation vessel L, which serves to fix the whole piece sufficiently firmly, when the steel cylindres B are screwed into it, which cylindres themselves have of course also a hexagon. The closure of B on L takes of course again place steel to steel by means of the raised hardened rim of B, which fig. 2 clearly shows in section.

Fig. 6.

We will avail ourselves of this opportunity to express our indebtedness to the instrumentmaker of the VAN DER WAALS-fund, Mr. C. H. STUIVENBERG, for his intelligent assistance in the construction of this apparatus, and particularly in the grinding of the windows.

§ 3. Description of the observations.

When the apparatus described in the preceding paragraphs, is used, care should be taken in the first place that the composition of the examined mixture does not change, and that no impurities can appear, which might have a preponderating influence on the course of the phenomena. This result may be attained by enclosing the mixtures to be examined in a glass tube, closed at the two ends and provided on the side by a capillary (fig. 2, O) as long as possible, which causes the pressure on the liquid inside to be the same as that on the surrounding liquid. This tube has beforehand been filled with a mixture of the required concentration, that of the critical endpoint.

Then the steel tube C is disconnected at S_2, being connected with the observation vessel L at the same time. Now one of the two windows *A* with the cylindre *B* is screwed on, and the glass tube *O* is placed in the vessel *L*. After this through the other window opening the vessel *L* is filled with one of the components, till the liquid begins to flow out at S_2. The tube *C* is then closed at S_2 by means of a wooden peg, the second window is screwed on, and at last the observation vessel *L* is quite filled with liquid through the conduit terminating at *W* (fig. 5). Then *W* is closed. Beforehand the tube conduit C_2C_1 has been quite filled with mercury, which has been poured in at S_2, to prevent contact of the observation vessel *L* with the oil from the press. The wooden peg is quickly removed, and the coupling at S_2 is effected. The steel tube *C* being very narrow, only very little, if any liquid, escapes. Thus the mixture under examination is quite guarded against the influence of contamination, and its concentration changes but exceedingly little on account of the slight compressibility of the investigated liquids, while there can hardly be any question of diffusion through the narrow capillary in the course of the observations. Moreover a slight change in the concentration could not exert an appreciable influence on the results on account of the greatly flattened shape which the liquid-liquid plaits always seem to present.

When the filling is finished, the thermostat is put in its place. An intense metal wire incandescent lamp of 300 candles is placed behind the window in the back wall. In this way, the mixture, particularly the place of the meniscus, can be very clearly observed.

We have confined ourselves in this investigation to plaitpoint observations; as criterion the same phenomenon was taken as was also used by one of us (*T.*) in his observations in Cailletet tubes [1]: while the pressure is kept constant, the temperature is slowly made to oscillate round the plaitpoint temperature, the liquid being continuously stirred. The temperatures are recorded at which the turbidity resp. the transparency sets in, and the mean of all the observations is taken as plaitpoint temperature. Proceeding in this way temperatures of turbidity are always obtained which diverge only some hundredths of degrees when the experiment is repeated. It may also be assumed that the temperature of the mixture follows that of the thermostat very closely, for also the mean of the temperatures of turbidity deviates but a few hundredths of degrees from the mean of the temperatures at which transparency sets in in general. This circumstance proves at the same time that equilibrium is properly secured by the constant stirring of the liquid. This was further confirmed when a glass ball was placed in the glass tube

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[1] These Proc. XIII p. 507.

O. This would have to make the mixing still more thorough, if possible but it did not cause the slightest change of the plaitpoint temperature.

The critical phenomenon preserves its characteristic peculiarities and the same intensity up to the highest pressures that we have examined, which bears further witness to the fact that the plaitpoint concentration changes only very little, so that it remains the same all over the extensive range of pressure and temperature considered here. In this it is absolutely required to keep the pressure perfectly constant during the measurements, as otherwise the VAN DER LEE effect 1) would disturb the observations. It is fortunately, however, easy to distinguish whether the cloudiness which appears in the liquid, is the consequence of the slow cooling of the thermostat or of an abrupt cooling which takes place in the examined liquid itself owing to an expansion by decrease of pressure. In the former case, namely, the cloudiness begins on the outside, and proceeds towards the centre, whereas in the latter case it arises in the centre, and spreads from there in all directions. The sensitivity of the VAN DER LEE effect in these circumstances shows that the equilibrium of pressure between the manometer and the liquid itself sets in almost immediately. A last proof for the accuracy of the measurements in the new apparatus is afforded by the comparison of the results obtained in this way at low pressure with those obtained in Cailletet tubes.

Some values will give an idea of the attainable accuracy.

a. The plaitpoint temperature remains constant, also after the mixture (nitrobenzene + petroleum) under investigation has been in the apparatus for two days, under pressures up to more than 500 atm. As a mean of ten measurements 13.°95 ± 0.°06 was found.

b. The plaitpoint temperature remains constant when the experiment is repeated with different fillings.

Water + triethylamine, critical end-point 18.°35 and 18.°36
The same system in a Cailletet tube yields 18.°33

c. The increase of the plaitpoint temperature per atmosphere is the same for different fillings, and also for determinations in a Cailletet tube. As an example we take the system cyclohexane + aniline.

$\frac{dt}{dp}$ between 1 and 200 k.g. per cm.^{2} yields + 0.0067
in a Cailletet tube was found. + 0.0066

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1) These Proceedings, XIII p. 517.

$\frac{dt}{dp}$ between 1 and 1000 k.g. per cm.^{2} yields

for the first filling	+ 0.0078
for the second filling	+ 0.0079

The temperature determinations were made with thermometers compared with standard ones tested at the Reichsanstalt; the manometrical determinations were controlled with the large pressure balance [1] of the VAN DER WAALS fund; the observations are accurate to about 10 k.g. and 0.°05.

The substances used in these experiments, were identical in preparation and properties with those used by one of us (T.) on a former occasion [2]; only the decane (di-isoamyl) and the tri-ethylamine have been used here for the first time. These two substances have been purified by fractional distillation (the tri-ethylamine over sodium), they presented the following physical constants: Freezing point: Decane — 52°,5 Triethylamine — 114,75; boilingpoint 160°,05 ± 0.10 resp. 89°5 ± 0°02; *d* 0°/4° 0.73852 resp. 0.74585 ± 7.

It may finally be mentioned that all the observations have been made by one of us (T.).

§ 4. Results obtained:

TABLE I.

Hexane + nitrobenzene

Press. in kg. [3] per cm.^{2}	Plaitpointtemp.	$\frac{dt}{dp}$ per kg.
1	20°.81 ± 0°.03	
		— 0°.0164
100	19. 17 ± 0. 04	
		— 0. 0127
250	17. 27 ± 0. 10	
		— 0. 0083
425	15. 82 ± 0. 05	
		— 0. 0051
625	14. 80 ± 0. 05	
		— 0. 0031
825	14. 18 ± 0. 03	

For a comparison we give the results obtained with a Cailletettube:

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[1]) See above p. 1025.

[2]) These Proc. l. c.

[3]) All the pressures and temperatures have been corrected to the standard thermometer and the pressure balance.

TABLE II.

p	T Press. apparat.	T Cailletettube	Difference
1	20°.81	20°.96	+ 0°.15
100	19. 17	19. 23	+ 0. 06
250	17. 27	17. 29	+ 0. 02

The nitrobenzene solidifies (quadruple point)

at — 1°,5 under ordinary pressure

at + 13°,8 under a pressure of 825 kg. per cm² ± 25.

$$\frac{dt}{dp} = +\,0°{,}018.$$

TAMMANN found + 0°,022 for pure nitrobenzene.

TABLE III.

Decane (di-isoamyl) + Nitrobenzene

p	T	$\frac{dt}{dp}$
1	28°.37 ± 0°.04	
		— 0°.0068
100	27. 69 ± 0. 05	
		— 0. 0042
250	27. 06 ± 0. 04	
		— 0. 00245
425	26. 63 ± 0. 07	
		— 0. 0010
625	26. 44 ± 0. 05	
		+ 0. 0004
825	26. 52 ± 0. 04	
		+ 0. 00075
1025	26. 67 ± 0. 03	
		+ 0. 0015
1225	26. 97 ± 0. 07	
		+ 0. 0017
1425	27. 31 ± 0. 05	

The nitrobenzene melts:

at + 1°,5 under a pressure of 1 kg. per cm².

at + 28° under a pressure of 1300 kg. per cm².

$$\frac{\partial t}{\partial p} = +\,0°{,}020.$$

TABLE IV.

American petroleum[1]) + Nitrobenzene

p	T	$\frac{dt}{dp}$
1	13°.95 ± 0°.06	
		+ 0°.0018
100	14. 22 ± 0. 07	
		+ 0. 0017
325	14. 51 ± 0. 09	
		+ 0. 0030
525	15. 11 ± 0. 04	
		+ 0. 0030
725	15. 70 ± 0. 03	
		+ 0. 0033
925	16. 35 ± 0. 05	

The nitrobenzene solidifies at 925 kg. per cm² and 16°.

TABLE V.

Cyclohexane + Aniline

p	T	$\frac{dt}{dp}$
	1st filling[2])	
1	30°.26 ± 0°.07	
		+ 0. 0067
200	31. 60 ± 0. 06	
		+ 0. 0080
400	33. 20 ± 0. 07	
		+ 0. 0077
700	35. 52 ± 0. 10	
		+ 0. 0084
1000	38. 04 ± 0. 10	
	2nd filling	
1	31°.03 ± 0°.04	
		+ 0°.0075
500	34. 77 ± 0. 09	
		+ 0. 00835
1000	38. 95 ± 0. 08	
		+ 0. 0084
1100	39. 79 ± 0. 08	

For a comparison we give the following results obtained with a Cailletet tube:

critical end-point 31°,02 instead of 31°,03,

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[1]) By way of comparison with the preceding binary systems we have also carried out a few observations with this mixture.

[2]) With this first filling the critical concentration was not quite reached; there was a little too much aniline, and it was clearly to be seen how the cyclohexane was dissolved in it.

$\frac{dt}{dp}$ between 1 and 200 atm. 0°.0066 instead of 0°.0067.

The cyclohexane solidifies at 42°,5 under 1200 atm. at 1°.1 under 1 atm. $\frac{dt}{dp} = + 0°.036$.

TABLE VI.

Water + tri-ethylamine

p	T	$\frac{dt}{dp}$
First series 5	18°.36 ± 0°.06	+ 0°.0206
200	22. 37 ± 0. 06	+ 0. 0179
600	29. 53 ± 0. 06	about + 0. 0125
1000	about 34. 5	
Sec. series 5	18. 35 ± 0. 05	+ 0. 0182
600	29. 19 ± 0. 11	+ 0. 0127
1000	34. 26 ± 0. 13	+ 0. 0103
1500	39. 40 ± 0. 20	+ 0. 0080
2000	43. 45 ± 0. 15	

In neither of the series was the critical concentration perfectly reached; hence the discrepancy, which is, however, small, between the results. The critical opalescence was, however, clearly to be perceived. In both cases the experiments had to be broken off on account of the appearance of a leak in the piston of the hydrostatic press.

For a comparison we give the following results obtained in a Cailletet tube, which have not yet been published until now:

Plaitpoint for 5 kg. per cm²: 18°,31 instead of 18°,36 and 18°,38.

$\frac{dt}{dp}$ between 1 and 200 kg. per cm²: 0°,0201 instead of 0°,0206.

Above this pressure the plaitpoint temperature increases greatly; at a pressure of 1100 kg. per cm² the mixture remains homogeneous at every temperature, at least no turbidity sets in up to at least 85°, but a decrease of 10 atm. in the pressure suffices to bring us back to the heterogeneous region. When the temperature rises still higher, we seem to reach the maximum pressure of the plaitpoint line, where the branch which comes from the lower critical end-

TABLE VII.

Water + methylethylketone

p	T		$\frac{dt}{dp}$
225	+ 0°.7		+ 0°.096
250	+ 3.1	± 0.1	+ 0.094
300	+ 7.8	± 0.2	+ 0.086
350	+ 12.1	± 0.1	+ 6.079
400	+ 16.05	± 0.1	+ 0.074
450	+ 19.75	± 0.15	+ 0.069
500	+ 23.2	± 0.1	+ 0.070
600	+ 30.2	± 0.1	+ 0.071
700	+ 37.3	± 0.1	+ 0.068
800	+ 44.1	± 0.3	+ 0.072
900	+ 51.3	± 0.3	+ 0.103
1000	+ 61.6	± 0.3	+ 0.106
1050	+ 66.9	± 0.3	

point joins that proceeding from the upper end-point. For though e.g. at 80° the mixture, homogeneous under a pressure of 1100 kg. per cm². becomes turbid when the pressure falls to 1085 kg. per cm². the pressure must be lowered to 1075 kg. at 86°.5 to reach the heterogeneous region. Moreover a mixture homegeneous at 86°5 and 1075 kg. unmixes no longer on *heating*, as it did before, but on *cooling*; on further cooling, if the same pressure is retained, finally the homogeneous region is again reached.

In the last-mentioned system the observations were less accurate than with the others, because the critical opalescence is almost entirely wanting, and the indices of refraction of the two phases are nearly the same; we think, however, that we are justified in accepting the above results with certainty, at least as far as the general course is concerned, because also another filling, with a somewhat different concentration, gave analogous results. Here too the highest pressure for which there was still question of unmixing is about 1100 kg. per cm²; the plaitpoint then was at about 80°; above this temperature the windows became opaque.

§ 5. Summary of the results.

The preceding determinations sufficiently prove the efficiency of the given method. The material of observation recorded in the tables gives rise to the following remarks.

1. The systems formed by nitrobenzene with a hydrocarbon are not simple cases of retreat as we thought at first [1]; on the contrary they represent cases in which the plait is split up, and belong to case II*b*, in reference to which we had to state in 1909 that we had not found an example of it for normal substances, and about whose possibility for abnormal substances we then ventured to pronounce an opinion only with the greatest reservation [2]).

This conclusion appears with perfect certainty for the system nitrobenzene + decane; the critical end-point (meeting of three-phase line and plaitpoint line) lies here on a branch of the plaitpoint line with negative $\frac{dt}{dp}$; if the plaitpoint line is pursued further, $\frac{dt}{dp}$ becomes zero, and then positive. Accordingly the plaitpoint line passes through a minimum, and this minimum is experimentally realisable: the branchplait exhibits a point where the closed portion gets detached, a homogeneous double plaitpoint, and this lies in the absolutely stable region. The question proposed p. 409 of the Lehrbuch der Thermodynamik [3]) has, therefore, been answered in the affirmative by experiment.

If in this connection the closely related system nitrobenzene-hexane is considered, it appears that it is only owing to an accessory circumstance that the homogeneous double plaitpoint cannot be realized. For here too $\frac{dt}{dp}$ is negative in the critical end-point, but this negative value becomes smaller and smaller; but just before it has become zero, further investigation is prevented by the appearance of the solid phase. So the plaitpoint line becomes metastable by its meeting with the threephase line solid + two liquid phases; we have again a critical end-point, but now the critical point of two "saturated solutions".

The system petroleum + nitrobenzene — if we may compare it for a moment in this connection with a binary system — no more belongs to type II*b*, but to type II*a*. In the critical end-point $\frac{dt}{dp}$ is here positive, the plaitpoint line is intersected by the three-phrase line above the homogeneous double plaitpoint; hence the latter falls

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[1]) These Proc. XII p. 243 and table at p. 239.

[2]) loc. cit. p. 243.

[3]) VAN DER WAALS KOHNSTAMM, Vol. II. Leipzig, Barth. 1912.

in the metastable region inside the transverse plait, and for this reason cannot be realized experimentally.

So we have now realized the succession which we supposed possible in our first communication [1]) for the systems propane + methylalcohol, isobutane + methylalcohol, pentane [2]) + methylalcohol, but about which we could then only pronounce a guarded opinion in the absence of further experimental material to prove the point. We now hope before long to be able to ascertain also for the system propane + methylalcohol whether it really belongs to case II*b*, or to case I.

2. In the second place we have been able for the first time to fully demonstrate a case of type I, with its two critical end-points *F* and *G*, and its maximum pressure *E* [3]). The system water-methylethylketone furnishes an example of this even though we cannot quite reach the lower end-point in consequence of the appearance of the solid phase. So we have a system here for which simply by change of pressure one passes from a partially miscible system to a system with complete miscibility. So such a case, to find which many attempts have been made, appears really to occur. In how far other systems will belong to this, and if particularly the systems classed up to now in case I will appear to belong to II*b*, or possibly to a case I*a* with a plait-point line which has a line parallel to the *p*-axis as asymptote will have to be revealed by further experiment. In the same way further experiment will have to show whether systems may be found belonging to type II*b*, in which the maximum temperature *I* and the maximum pressure *E* can be reached.

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[1]) Loc. cit p. 243.

[2]) We avail ourselves of this opportunity to rectify a few inaccuracies in former tables. In the table annexed to p. 239 loc. cit, for methylalcohol + isopentane read: normal pentane. Idem in table VI, These Proc. XIII, p. 877. In the last table erroneously a L (lower mixing-point) is added to the system ethane + methylalcohol; this should be omitted, just as it is not found in the table of our first paper. Finally the said table VI shows an L? for the system ether and water. As the note of interrogation denotes, we think this lower mixing-point by no means proved. With our new apparatus we have already carried out a few experiments with the system water + ether; they all show that on increase of pressure and decrease of temperature the two phases will approach each other more and more; they point, indeed, in the direction of a lower mixing-point, but we have not succeeded as yet in definitely ascertaining whether or no this will be realisable on account of the appearance of the different ice modifications. We hope we shall be able to return to this subject later on.

We owe the different corrections mentioned in this note to Prof. KUENEN's great kindness, who drew our attention to the mistakes made.

[3]) Fig. 1 I c.

Summarizing we may state:

1. That we have given an experimental method to determine plaitpoints, and other phenomena which must be made directly visible, at high pressures to an amount of more than 3000 atm.

2. That we have demonstrated that the course of the theoretically predicted plaitpoint lines is in concordance with reality in the systems under investigation, albeit that the more intricate case of the splitting-up of a plait occurs more frequently, the less intricate case of simple retreat more rarely than was supposed.

Meteorology. — *"On the interdiurnal change of the air-temperature."* By Dr. J. P. VAN DER STOK.

(This communication will not be published in these Proceedings).

(April 24, 1913).

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING
of Saturday February 22, 1913.

President: Prof. H. A. LORENTZ.
Secretary: Prof. P. ZEEMAN.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 22 Februari 1913, Dl. XXI).

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Anatomy. — *"On the occurrence of a monkey-slit in man."* By Dr. C. T. van Valkenburg. (Communicated by Prof. **Winkler**).

(Communicated in the meeting of December 28, 1912.)

It has long been known that under some circumstances, in case of disturbances in the development of the central nervous system of man, a slit may occur on the surface of the occipital lobe vividly reminding of the so-called monkey-slit of anthropoides. I communicated an example of this fact in a former paper.[1] The slit then characterized as monkey-slit, answered to the requirement that at least part of its occipital boundary covered convolutions at the bottom of the slit connected with the parital lobe (operculation). Elliot Smith[2] has described the brains of many Egyptians in which he very often found (70 % of the hemispheres) a *sulcus simialis* sive *lunatus*. Brodmann[3] corroborated this view with the brain of three Javanese. On the other hand Zuckerkandl[4] thinks that the existence of a monkey-slit in man is by no means proved. As a proof he gives a reproduction of some hemispheres in his abovementioned essay. On these surfaces however — of course specially selected by Zuckerkandl — Elliot Smith would doubtlessly diagnosticate a monkey-slit.

How are these contradictory views to be reconciled. We read in Zuckerkandl's paper (l.c.): "Am menschlichen Gehirn soll nur "dann von einer Affenspalte die Rede sein, wenn an der Hemis-"phärenoberfläche beide Ränder der fraglichen Furche mit jenen der "Affenspalte am Affengehirn identisch sind. Trifft dies nicht zu, "liegt eine Furche vor, welche nur auf einer Seite (hinten) von einem "der Grensränder der Affenspalte abgeslossen ist, während der andere "(vordere) nicht mehr dem Gyr. angularis sondern einem Bestandteil "der Affenspaltengrube (Uebergangswindungen) angehört, dann hat "man es nicht mit der typischen Affenspalte zu tun."

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[1] Van Valkenburg, Surface and structure of the cortex of a microcephalic idiot. These Proc. XII p. 202.

[2] Elliot Smith, Studies on the morphology of the human brain. Records of the Egyptian Governmentschool of medicine. Cairo 1904.

Elliot Smith, The persistence in the human brain of certain features usually supposed to be distinctive of apes. Report of the British Assoc. for the advanc. of Science 1904, p. 715.

[3] Brodmann, Beiträge zur histologischen Lokalisation der Grosshirnrinde V. Journ. f. Psych. u. Neurol. Bd. VI. S. 296.

[4] Zuckerkandl, Ueber die Affenspalte und das Operculum occipit. des menschlichen Gehirns. Obersteiners Arbeiten Bd. XII, S. 207.

Zuckerkandl strongly emphasizes a difference between monkey-slit — i.e. the slit between the operculum occipitale and the parietal convolution lying frontally to the operculated transition-convolutions — and the monkey-slit sulcus — i.e. the sulcus lying on the bottom of the sulc. lunatus.

This difference must unconditionally be accepted, and to my knowledge this is done by the majority of authors (Bolk a.o.).

It is however another question whether this difference is really of such a nature that we should be compelled by it for ever to deny the homologisation between a monkey-slit and a very similar sulcus in man. For that similarity is even readily accepted by Zuckerkandl, as he admits the occurrence of "Affenspaltresten" in man. Elliot Smith is of opinion that the difference is nothing but a quibble of words. Evidently the matter hinges upon the question: what is in the monkey-slit-complex the cardinal point? We have then the choice between the *slit* — postulating the existence of bottom-convolutions and an operculum covering these — and the sulcus existing on the bottom of the slit, which if there are no bottom-convolutions to be operculated, looks like every other sulcus.

In lower monkeys (platyrrhines) and prosimii [1]) a sulcus is found that must doubtlessly be indicated as sulcus lunatus whilst bottom-convolutions, operculation, a proper "monkey-slit" [2]) may be absent.

This sulcus lies in the brains of these animals transversally — often not reaching the interhemispherical fissure — across part of the latero-dorsal surface of the lob. occipitalis. No other sulcus ends in it; it lies occipital from the sulcus parieto-occipitalis. In some platyrrhines (ateles) the sulc. interparietalis (which, as has been remarked, does not reach the sulc. lunatus) forms a *T*-shaped extremity, sometimes already indicated in some specimens of lemuridae. I refer those interested in this problem to the report that will be given by Dr. Ariens Kappers in 1913 at the International Congress of Medicine in London: Cerebral localization and the significance of sulci.

Ascending in the range of monkeys we find that the sulc. interparietalis in katarrhines has its distal termination in the s. lunatus. At the same time we find that, at the bottom of the latter, cortical convolutions are hidden; its occipital lip has grown an operculum.

The most developed katarrhines — the anthropoides — usually

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[1]) Ziehen, Ueber die Grosshirnfurchung der Halbaffen Arch. f. Psych. Bd 28 S. 898.

[2]) Kükenthal u. Ziehen, Untersuchungen über die Grosshirnfurchen der Primaten · Jenaische Zeitschr. für Naturwissensch. Bd. 29, S. 1.

For further literature vide Ariens Kappers (l. c.).

show the beginning of apparent return to lower relations, because part of the transition-convolutions (the first) has become superficial. It is however still separated by the sulc. interparietalis from the superficial part of the 2nd transition-convolution. A similar situation was to be found in the microcephalic idiot described by me in a former paper (l. c.). If now moreover the 2nd and 3rd transition-convolutions become superficial i.e. if they pass from the bottom of the monkey-slit to the surface of the lob. parietalis, then of the entire s. simialis-complex there remains only the bottom-sulcus which is then, with regard to its parietal lip, differently limited from what was the case with anthropoides, at least as regards the region of the 2nd and 3rd transition-convolution. This is however not always the case. Also where there is no question of great disturbances of development, as in the above-cited case of mikrocephalia, little hidden convolutions may be found (vide e. g. some drawings in ZUCKERKANDL's paper l. c.). Such brains connect the monkey-slit in a more limited sense — as it occurs in anthropoides — with the sulcus lunatus (as with ELLIOT SMITH we best call it) of man. About the frequency of the occurrence of this sulcus in Europeans I cannot fix a percentage on account of my limited material.

In 22 hemispheres of idiots of the Institute for Brain-research I find it 8 times. In the brain of normal individuals it likewise "often" occurs. ELLIOT SMITH fixed already the attention to the brain-photographs of RETZIUS. I could not decide with certainty whether, as it seems to be ELLIOT SMITH's view, there exists any preference in this respect for the left hemisphere.

Notwithstanding all these assertions it is necessary to fix as strongly as possible the diagnosis: sulcus lunatus. One cannot give a definition of it of *absolute* value, i. e. without involving in it the relation to neighbouring sulci. As conditions for accepting a sulcus lunatus I fixed in general the following relations and circumstances:

1. The sulcus in question lies somewhat crescentshaped (with its concavity caudad) or more transversal, not far from the pole of the occipital lobe;

2. In its lateral part terminates a sulcus, that is often connected with the first temporal sulcus (*sulcus praelunatus*);

3. More or less parallel to it, more towards the front, lies a

sulcus, into which the sulcus interparietalis terminates (sulc. occipitalis transversus);

4. The occipital extremity of the sulcus calcarinus falls (whether bent or not round the mantle-side) behind it, and sometimes extends between two sulci occipitales which are found there (they may be connected V-shaped).

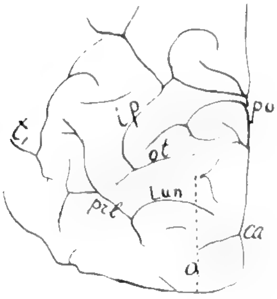

Fig. 1.

Occipital lobe of the idiot *D*, seen from behind. The dotted line indicates the direction of the section according to which fig. 4 has been drawn; for the shortenings vide text.

Fig. 1 represents an occipital lobe (of an idiot) seen from behind on which the above-mentioned desiderata have been most accomplished.

The principal requirements are fulfilled: the situation of the sulci occipitalis transversus (*o.t.*) and calcarinus (*c.a.*) resp. before and behind the sulcus lunatus (*Lun*) is typical. At the former the sulcus interparietalis (*i.p.*) terminates; the sulcus parieto-occipitalis (*po*) cuts frontally from it the medial mantle-side. An indication of a V-shape of the occipital sulci (*o*) between which the sulc. calcarinus points, is extant. The sulcus praelunatus (*prl.*) is distinct, but not immediately connected with the sulc. temporalis primus (t_1). All other hemispheres possessing the sulcus lunatus have a similar appearance. The greatest variation exists in the occipital sulci and the relations of the sulcus praelunatus. All our cases answer to the above-mentioned principal requirements, where a sulcus lunatus was admitted, with only one exception. In the latter case (it regards the cerebrum of an idiot, with a too little frontocaudal diameter; weight of the brain about 1000 grams) the cuneus is very narrow, because the sulcus calcarinus has a strongly dorsal direction. I refer to fig. 2. At the limitation of the second and posterior third part of the cuneus this sulcus splits T-shaped. The inferior branch terminates near the occipital pole, behind the sulcus lunatus, the dorsal branch reaches the medial mantle-side immediately behind the sulcus parieto-occipitalis; consequently not only far before the sulcus lutanus, but even before the sulcus occipitalis transversus. Vide fig. 3. I come to the conclusion that this branch must indeed be reckoned to the sulcus calcarinus, and is not a cuneus-sulcus

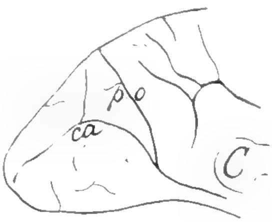

Fig. 2.

Left occipital lobe of the idiot *W*, seen from the medial side.

po = sulc. parieto-occipitalis
ca = sulc. calcarinus
C = corpus callosum (splenium).

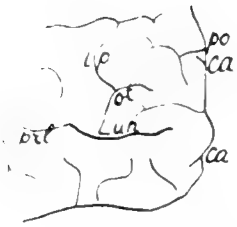

Fig. 3.
The same occipital lobe as fig. 2, seen from behind; shortenings as above.

terminating in the sulcus calcarinus from the fact, that its lips show as distinctly as the other part of the sulcus in question a beautiful stripe of VICQ D'AZYR. When using this argument we have introduced into our reasoning a new element of a microscopical, anatomical, and even, may be, of a physiological nature. Many anatomists indeed regard the region over which the above-mentiod stripe extends as the terminal region of the centripetal, geniculo-occipital radiation, the recipient optic cortical-field (Visuosensory: CAMPBELL, BOLTON, MOTT a.o.).

Apart from any physiological function and even from specific projection-combinations we may admit in man as irrefutable, that wheresoever the typical stria Vicq d'Azyr is found, we have to do with an area of a special character, which on account of its peculiar relations (in the greater majority of cases) to the limitations of the sulcus calcarinus, may be characterised as regio calcarina. Area striata (ELLIOT SMITH) area 17 (BRODMANN) and regio calcarina are consequently regarded in man as synonyms. My above mentioned conclusion that in reality the cuneus-sulcus terminating in the sulcus calcarinus must be regarded as a final branch of that sulcus seems consequently not to be a hazardous assertion.

As especially BRODMANN [1]) has taught us, the area striata (his area 17) extends in the monkey over the lateral surface of the lob occipitalis (the operculum occipitale) as far as the monkey-slit.

ELLIOT SMITH stated the same fact in his Egyptians, be it over a more narrow strip of the region concerned, and he uses this fact as one of the arguments for homologising his sulc. lunatus with the monkey-slit. This author conceives the connection between histologically-characterised areas and brain-sulci a little schematically: very regularly he admits and represents the latter as limits of the former [2]). Apart from the fact that after the investigations of BRODMANN, CAMPBELL a. o. his view cannot be maintained in this form, it postulates in the case discussed here a complete homology in the relation between the sulcus lunatus and the area striata in monkey and man. As appears from the phylogenesis of the sulci there is no complete parallelism between the evolution of the sulci and the relative migrations of the special cortical zones.

[1]) BRODMANN: Vergleichende Lokalisationslehre der Grosshirnrinde. Leipzig 1909.

[2]) ELLIOT SMITH: A new topographical survey of the human cerebral cortex. Journ. of Anat. and Physiol. Vol. 41.

ZIEHEN[1]) called already attention to the comparative slowness, with which in the range of development of mammals sulci change their places.

In the report that he intends to give (l.c.), ARIËNS KAPPERS comes on other grounds to the same but more developed conclusion: sulci are more conservative than the neighbouring cortical zónes.

Where we see in man the area striata extending as far as the sulcus lunatus — if the latter is extant — we may see in it a very welcome affirmation of the similarity between sulcus lunatus and monkey-slit, ascertained by other methods (morphologically). It can however not be a point of issue for proving a homology — in the way as ELLIOT SMITH regarded this fact.

As far as the extension of the area striata can be mapped out macroscopically (with the help of the magnifying glass, (ELLIOT SMITH's investigation was made in this way) the material of the Brain-Institute does not offer uniform indications. It seems that the area striata is not always dorsolaterally limited by the sulc. lunatus; this limitation is likewise not a sharp one in this sense, that sulcus and area must join each other without any intervening space (in this respect our material corresponds with BRODMANN's Javanese). The type of the cellamination offers the same evidence as that of the extension of VICQ D'AZYR's stripe. Fig. 4 gives a reproduction of the latter. It has been made after a section somewhat lateral from the place where in fig. 1 a dotted line has been drawn. The preparation consequently cuts the sulc. lunatus perpendicularly. The letters placed in the figure render a further description almost superfluous. I only draw attention to the slight depth of the sulc. lunatus, which is never found in anthropoids. In man (our material) this sulcus shows a very different depth; in this respect likewise it seems to show all the transitions between the anthropoid-like state and its total disappearance from the surface of the brain; its extremities (medial and lateral) are most undeep.

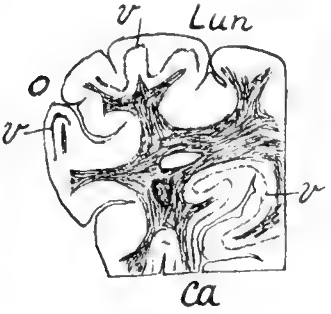

Fig. 4.

v = stria Vicq d'Azyr; other shortenings as above.

Sagittal section through the occipital lobe of the idiot *D.* (vide fig. 1).

It seems as if first the hidden convolutions, afterwards their bottom is brought to the periphery; the cortex is "smoothed".

The immediate connexion between area striata and sulc lunatus,

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[1]) ZIEHEN: Ein Beitrag zur Lehre von den Beziehungen zwischen Lage und Function im Bereich der motorischen Region der Grosshirnrinde, mit specieller Rücksicht auf das Rindenfeld des Orbicularis oculi. Arch. f. Physiologie 1899, S. 173.

shown by ELLIOT SMITH in his Egyptians — also distinctly visible in fig. 4 — needs not exist in the European who possesses this sulcus. But it is even impossible — at all events in the material I had to dispose of — in cases where a sulcus lunatus is extant always to ascertain a greater extension of the area striata on the lateral surface of the brain, than in cases where no vestige of the above mentioned sulcus is to be found. Of course there is no longer question of a limitation in the sense of SMITH; it is an illustration of the conservatism of sulci we spoke off above, even of one that is destined to disappear. [1])

I have asked myself if there was any connection between the existence of a sulcus lunatus on the lateral cortical surface and the extension of the area striata at the medial hemisphere-wall, in so far as the latter in general is connected with — is dependent upon — the direction and the modus of ramification of the sulcus calcarinus. No regularity at all could be ascertained in this respect. A sulcus lunatus can be found with all sorts of s. calcar. I gave already examples of two forms.

I can add as a third, extreme, form a case where sulcus calcarinus and sulcus parietooccipitalis are nowhere connected, where a superficial cuneo-limbic transition-convolution exists at the point of the cuneus, exactly as it is found — almost always — in anthropoids. The sulc. lunatus that was here very evident, showed *all* the above mentioned characteristics. A more or less "anthropoid" condition of the cuneus, caused by variations in the direction of the sulcus calcarinus does however, as it seems, not always hold connection with the existence of a sulcus lunatus.

In general the existence of a sulcus lunatus is by no means a *proof* of imperfect development of the brain in which it is found. In normal Europeans it is decidedly frequently met with, as ELLIOT SMITH concluded already from the drawings of others. The examples shown by me were taken from idiots, because I found in a comparatively little material such strong variations at the medial occipital surface, each time with distinct sulcus lunatus on the lateral one. It seems probable that defective development may often be the cause of these deviations in the direction of sulci and convolutions, but with regard to the many variations in normal brains it cannot be proved.

Whether and how — in a definite case — the existence of the sulcus lunatus is influenced by such a "defective development" is a phenomenon that lies completely beyond the field of our observation.

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[1]) In a case of Anophtalmos there existed a beautiful monkey-slit: the area striata at the medial brain-surface scarcely reached the occipital pole: calcarina extension normal.

Microbiology. — *"Metabolism of the nitrogen in Aspergillus niger."* By H. J. Waterman. (Communicated by Prof. M. W. Beijerinck).

(Communicated in the meeting of November 30, 1912).

In a previous communication [1] I described the circulation of the carbon in *Aspergillus niger.*

The changes which the plastic aequivalent or assimilation quotient of the carbon and the respiration- or carbonic acid aequivalent underwent in the course of time gave a clear view into the metabolism. In the beginning of the development a great plastic aequivalent was constantly found, which, however, lowered quickly, whilst the carbonic acid aequivalent rose considerably in the course of time.

The curve indicating the change of the two aequivalents with time could not be explained by an adsorption of nutrient substance.

The existence of an adsorption, that is to say, a change of concentration caused by molecular attraction of the components at the surface of a liquid formed by these components, gas, etc. and theoretically foretold by W. Gibbs and J. J. Thomson, has in many cases been experimentally confirmed. For such experiments it was desirable to artificially enlarge the surface, for example by formation of scum, in order to bring the phenomenon within the reach of the relatively rough methods of observation.

Animal and plant cells present a great surface in relation to their contents. So it might be possible experimentally to observe the adsorption by the disappearance of the food from the surrounding medium.

The above investigation, however, has proved that this is not the case and the following experiments confirmed this.

A living mould culture, some months old and washed out with distilled water, ca. 300 mgrs. dry and containing hardly any more glykogen, was during half an hour shaken with 50 cm^3 solution of 2 $^0/_0$ glucose, 0,15 $^0/_0$ ammoniumnitrate, 0,15 $^0/_0$ KH_2PO_4, and 0,06 $^0/_0$ magnesiumsulfate in tapwater. The mould layer, which had absorbed hardly any glucose from the solution, was then repeatedly washed out with distilled water at room temperature, boiled for ten minutes with distilled water, then filtered. The filtration did not reduce "Fehling", consequently contained no glucose.

If the concentration of the glucose in the mould were likewise

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[1] Folia microbiologica, Holländische Beiträge zur gesamten Mikrobiologie. Bd. 1 p. 422.

2 %, at least 6 mgrs. should have been found, a quantity which can with certainty be indicated by "Fehling".

This proves that there is no question of a considerable permanent adsorption at the outer surface of the protoplasm, but that it behaves more like a semi-permeable wall towards the glucose.

The same experiment was once more repeated, but this time with a 2 % glucose solution without anorganic substances, with shaking for two hours. Now, too, the mould proved to contain no glucose. A duplo-experiment gave only traces of glucose.

Hence the adsorption in *Aspergillus niger* is of no significance for the *accumulation* of nutrient substances.

Now it is a matter of course that the first stage of the accumulation is an adsorption, but it evidently escapes observation. The high plastic aequivalent in the beginning pointing to an extensive fixation of carbon-containing material, relates to a further stage of assimilation.

The food has then already passed into other compounds, *e.g.* into glykogen.

If the observations have ascertained that physiologic processes may be represented by an adsorption curve, this cannot be explained by accepting an adsorption in the first part of the process but it may be a consequence of what happens in a later stage.

Such an adsorption curve does not in general represent a simple process; it is more a combination of a whole series of successive physical and chemical phenomena.

In the study of the nitrogen results have been obtained corresponding to those found with the carbon.

It has namely been observed that also the nitrogen compounds used for the nutrition, are accumulated in the organism in a way not yet explained. First I convinced myself that the plastic aequivalent of the nitrogen at the end of the experiment is subject to only slight changes, as is shown in table I.

Compare for this nrs. 1 with 2 and 3, 4 with 5, 9 with 10, 11 with 12, 13 with 14. Secondly the quantity is independent of the nature of the source of carbon provided the weights of the mould be alike. For the levulose we find the same numbers as for the glucose. Lowering of temperature does not (nrs. 9 and 10) influence the rate of nitrogen of the mould, nor is it changed by addition of boric acid (nrs. 11 and 12).

Table II gives a view of the quantity of nitrogen fixed in the mould layer at various periods of development.

After 3 days the accumulation of nitrogen is of importance. Per

TABLE I. FIXATION OF NITROGEN BY ASPERGILLUS NIGER.

50 cm³. tapwater [1]), in which dissolved 0.15 % NH_4NO_3 [2]), 0.15 % KH_2PO_4, 0.06 % $MgSO_4$ (free from water) with the organic food given below. Temp. 33° C.

Nr.	Organ. food	Age of the mould	Carbon fixed in the mould (in mgrs.).	Particulars
1, 2, 3	2 gr. glucose	5 to 6 months	17.2; 17.3; 16.0	
4, 5	2 „ levulose	5 to 6 „	16.5; 18.6	
6	1 „ glucose	5 „	9.8	The culture liquid contained besides considerable quantities of ammonia
7	1 „ „	4 to 5 „	9.7	
8	1 „ „	4 „	10.1	
9, 10	1 „ „ [3])	4 „	9.1; 8.7	
11, 12	1 „ „ [4])	5 „	9.2; 9.2	
13, 14	1 „ levulose	5 to 6 „	10.–; 10.6	

1000 mgrs. of assimilated glucose, i.e. per 400 mgrs. carbon $\frac{100}{80}$. 19, 3 = 24, 1 mgrs. N is fixed after that time, that is 6 % N on the weight of mould. This value I will call *nitrogennumber*.

After 4 days the accumulation was fairly the same. The nitrogen number was decreased to 5. Nearly all the ammoniumnitrogen (ca. 13 mgrs.) was taken up by the organism, for with NESSLER's test the liquid gave but an insignificant reaction. The remaining 7 mgrs. are furnished by the nitratenitrogen

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[1]) An analysis of this water made in October last gave:

solid substance	461,3 mgr. p. L.	SO_4''	60,5 mgr. p. L.
org. „	69,7 „ „ „	Cl'	97,7 „ „ „
reduction power	3,5 mgr. O_2 p. L. (K Mn O_4)	NO_3'	traces
dissolved O_2	4,54 cM³ p. L.	NO_2'	absent
free CO_2	1,3 mgr. „ „	NH_4'	„
fixed CO_2	126,8 „ „ „	Silicic acid (SiO_2)	2,0 mgr. p. L.
Total CO_2	127,2 „ „ „	$Al_2O_3 + Fe_2O_3$	6,2 „ „ „
Temporary hardness (PFEIFER-WARTHA)	: 8,07°	Ca O	71,2 „ „ „
Total „ („)	: 9,43°	Mg O	30,1 „ „ „
Permanent „ („)	: 1,36°	Cu and Pb	absent
Mg „ („)	: 2,02°	Na_2O	120,2 „ „ „
Total „ (CLARK)	: 9,29°	„ from rest of combustion	128,9 „ „ „

[2]) With this corresponds somewhat more than 26 mgrs. nitrogen.

[3]) The temperature in these experiments was 25° C.

[4]) Addition of 5 mgrs. boric acid.

TABLE II. METABOLISM OF NITROGEN.

50 cm³ tapwater, in which dissolved 2 pCt. glucose (free from water), 0,15 pCt. ammoniumnitrate, 0,1 pCt. potassiumchloride, 0,05 pCt. crystallised fosforic acid, 0,1 pCt. crystallised magnesiumsulfate, 0,1 pCt. calciumnitrate (free from water). Temp. 34° C.

Nr.	Days after inoculation	Quantity of nitrogen fixed in the mould in mgrs.	Growth and spore formation [1].	Reaction of the culture liquid with	
				NESSLER.	Diphenylamin-sulfuricacid.
1	3	19.3	vigor., hardly any spores	slight	strong
2. 3. 4	4	20.3; 20.7; 19.6	„ , very few ,	„	„
5	5	17.5	„ , „ „ „	rather strong	„
6	7	11.8	„ , „ „	„ „	„
7, 8	9	9.9; 10.4	„ , rather many „	„ „	„
9	15	8.8	„ , „ „ „	„ „	„
10	18	10.6	„ , „ „ „	„ „	„
11	19	10	„ , „ „ „	„ „	„

Excepting nr. 1 where only 80 % of the glucose was used, all the glucose in the other culture tubes had been assimilated.

The dry weight obtained from them I have not determined in these experiments. For this my earlier investigations may be compared [2]).

Notwithstanding the quantity of fixed nitrogen had decreased on the 4th day from 6 to 5 % of the assimilated carbon, the absolute quantity was not lower. On the contrary, a slight increase was observed caused by the glucose still present after 3 days. The nitrogen excreted by the growing mould is assimilated again during the formation of new cells. When all the glucose had been used, which was already the case on the 4th day, nitrogen only was excreted. The consequence was a considerable lessening of the quantity fixed in the organism. After 5 days (nr. 5) only 17.5 mgrs. remained fixed. This was accompanied by a decrease of the nitrogennumber as graphically demonstrated (fig. 1.) (see p. 1051).

After 5 days it was already decreased to 4.4, after 7 days to 3, after 9 days to 2.5. Then it undergoes but insignificant changes.

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[1]) The use of very pure chemicals free from manganese causes the bad spore formation

[2]) Folia Microbiologica, Bd. 1 p. 122 and these Proceedings XV p. 753.

The metabolism of the nitrogen corresponds thus in both cases with that of the carbon, namely a considerable accumulation at first, which decreases very much in the course of time, finally to remain nearly unchanged.

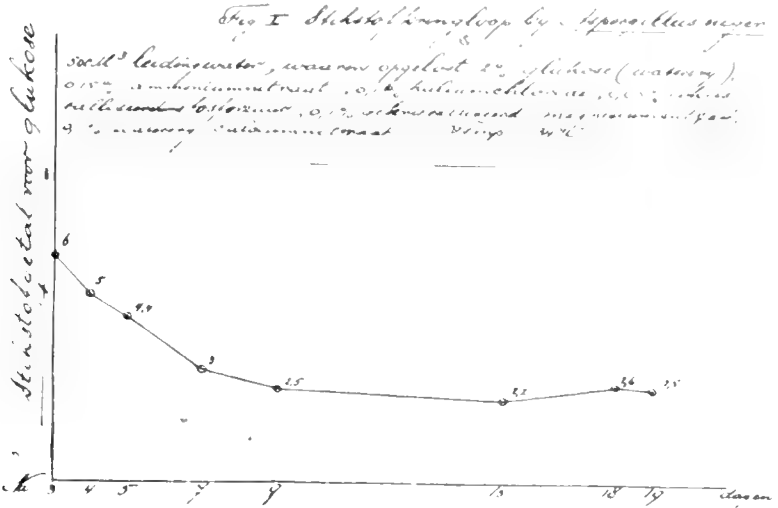

Fig. I. Metabolism of the nitrogen; 50 cm³ tapwater in which dissolved 2 % glucose (free from water), 0,15 % ammoniumnitrate, 0,1 % potassiumchloride, 0,05 % crystallised fosforic acid, 0,1 % magnesiumsulfate, 0,1 % calciumnitrate (free from water). Temp. 34° C.

Whereas carbonic acid is the form in which the carbon can leave the organism, the experiments in table II prove that the nitrogen is excreted as ammonium. The lowering of the nitrogennumber is parallel with a return of ammonium into the medium so that there is cause to consider, as before with the carbon, the course of the plastic aequivalent of the nitrogen and of the ammonium aequivalent in relation to time.

The decrease of the plastic aequivalent of the nitrogen is combined with an increase of the ammonium aequivalent. This view may, however, give rise to error as to the nitrogen, the ammonium being here a product of excretion, which *likewise* is mostly the form in which the nitrogen is given to the organism. By introducing the nitrogennumber this error is avoided. When excess of ammoniumnitrate is used it is chiefly the ammonium nitrogen which is assimilated, as proved before.

In a previous paper[1]) was shown that manganese does not change

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[1]) These Proceedings, XV p. 753.

T A B L E III. The conditions of the cultivation were the same as in table II.

Nr.	Particular.	Number of days after inoculation.	Nitrogen in the mould-layers in mgr.	Nitrogen-number.	Growth and spore-forming.
1	No manganese	After 3 days 1)	19.3	6.0	vigorous, *hardly any spores*
2	0.001 mgr. $MnCl_2$ 4 Aq.	„ 3 „ 2)	17.5	5.0	„ few spores
3, 4, 5, 6	No manganese	„ 4 „ 3)	19.6; 19.6; 20.7; 20.3	5.0	„ very few spores
7	0.001 mgr. $MnCl_2$ 4 Aq.	„ 4 „ 3)	18.5	4.6	„ rather many spores
8	0.01 „ „ „	„ 4 „ 3)	17.3	4.3	„ „ „ „
9	0.1 „ „ „	„ 4 „ 3)	17.0	4.2	„ „ „ „
10	0.001 Zincsulphate 7 Aq.	„ 4 „ 3)	20.2	5.0	„ very few spores
11, 12	No manganese and instead of KCl, RbCl	„ 4 „ 3)	18.6; 19.5	4.8	„ *hardly any spores*
13, 14	„	„ 6 „ 3)	18.4; 17.8	4.5	„ „ „ „
15, 16	„	„ 9 „ 3)	12.7; 12.2	3.1	„ rather many spores
17	„	„ 12 „ 3)	9.- ; 9.4	2.2; 2.3	„ „ „ „
18	No manganese	„ 18 „ 3)	10.6	2.6	„ „ „ „
19	No manganese, but instead of KCl, RbCl	„ 18 „ 3)	9.3	2.3	„ few spores
20	With manganese	„ 30 „ 3)	8.-	2.0	„ many spores
21	„ „	„ 35 „ 3)	8.2	2.0	„ „ „
22, 23, 24, 25	„ „	„ 40 „ 3)	8.3; 8.3; 8.4; 9. ; 9.	2.2	„ „ „

1) 80 pCt. of the glucose is assimilated.

2) 88 pCt. of the glucose is assimilated.

3) No glucose is remaining in the solution.

the nature of the metabolism of the carbon, but does modify its velocity and that substitution of rubidium to potassium neither changes that nature. This I have also found true for the nitrogen under the influence of the said metal, as is shown in table III.

Nr. 2, where manganese is added, has a lower nitrogennumber than 1, which is owing to the manganese. The nitrogennumbers of 7, 8, and 9, are lower than those of 3, 4, 5, and 6, where no manganese is added. The nitrogennumber of 10 is like that of 3, 4, 5, and 6. The addition of 0,001 mgr. zincsulfate ($ZnSO_4 . 7$ Aq. changes neither the metabolism of the nitrogen nor that of the carbon.[1]

That the replacing of potassium by rubidium has little influence on the metabolism of the nitrogen is proved by comparing nrs. 11 and 12 with 3, 4, 5, and 6, and 19 with 18, whose nitrogennumbers are nearly equal.

In the above described experiments the nitrogen in the liquid was of different nature, both in the form of ammonium and of nitrate. For that reason I repeated the experiment and used ammoniumchlorid as only source of nitrogen.

Various concentrations were also studied. The results are found in table IV.

From these experiments we may conclude that the nature of the metabolism with ammoniumchlorid is the same as with ammoniumnitrate. The nitrogennumber, high at first (6,1), descends rapidly; after 7 days it is already decreased to ± 2,5, then to remain nearly constant. Furthermore we see that excess of nitrogen does not change the metabolism. All the nitrogen excreted is found exclusively as ammonium, the sum of the nitrogen in the mould and of that present in the solution being constant. The losses of nitrogen which may partly be ascribed to errors in the analysis, are, as seen in the table, of little import, and partly repose on the evaporation of ammonia. Thus we see that in the till now examined cases *ammonia is a normal excretion product in the metabolism of Aspergillus niger.*

After Prof. Böeseken's advice I investigated if this is always the case; if also by nitrogen nutrition with KNO_3 ammonia is excreted.

The results of these experiments are found in table V. We see from them that also with KNO_3 as exclusive nitrogen food the nitrogen is accumulated in the organism, albeit less quickly than NH_4Cl or NH_4NO_3. The nitrogennumber lowers also here whilst ammonia comes into the culture liquid. There are hardly

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[1]) These Proceedings, XV p. 760.

TABLE IV. AMMONIUMCHLORID AS SOURCE OF NITROGEN.

A.

50 cm³ tapwater, in which dissolved:
0.2 pCt. NH_4Cl, corresponding with 26.2 mgr N.
0.15 pCt. KH_2PO_4
0.15 pCt. $Mg SO_4$, crystallised
2 pCt. glucose (free from water)

B.

50 cm³ tapwater, in which dissolved:
0.5 pCt. NH_4Cl, corresponding with 65.2 mgr. N.
0.15 pCt. KH_2PO_4
0.15 pCt. $Mg SO_4$, crystallised
2 pCt. glukose (free from water)

	A.						B.				
Nr.	Mgr N in the mould	Nitrogennumber	Mgr. N. as ammonia in solution.	Sum.	Assimilated glucose in pCt.	Number of days after inoculation	Mgr. N. in the mould	Nitrogennumber	Mgr. N. as ammonia in solution.	Sum	Assimilated glucose in pCt.
1	20.3		3.6	23.9	not determin.	3 days	19.9		44.5	64.3	not determin.
2	19.6	6.1	not determin.	—	79	3 "	23.5	6.2	not determin,	—	95
3	22.1		2.1	24.2	not determin.	4 "	21.4	—	38.9	60.3	not determin.
4	21.6	5.4	not determin.	—	98—99	4 "	21.7	5.6		—	97
5	16.2		5.6	21.8	not determin.	7 "	17.6		44.	61.6	not determin.
6	17.2	4.3	not determin.	—	100	7 "	17.4	4.3	not determin.	—	100
7	9.25	2.3	10.5	19.75	100	10 "	10.9	2.7	49.4	60.3	100
8	8.7	2.2	12.2	20.9	100	10 "	10.–	2.5	49.8	59.8	100
9	8.7	2.2	13.4	22.1	100	21 "	8.1	2.–	52.8	60.9	100

any losses of nitrogen, so, *Aspergillus niger* is able to reduce nitrate to ammonia.

Furthermore it is proved that the nitrogennumber of a mature mould layer with glucose or levulose as exclusive organic food for *Aspergillus niger*, independent of the source of nitrogen, amounts about to 2,0.

Notwithstanding a young mould culture sometimes contains 2 to 2½ times as much nitrogen as a corresponding old one, such a young, duly washed layer, when boiled with distilled water gave no trace of the above named anorganic salts which had been added to the medium as exclusive source of nitrogen. Here thus, too, the

TABLE V. KNO_3 AS NITROGEN NUTRITION.

50 cm^3 tapwater, in which dissolved 0,4 pCt. KNO_3 (28 mgr. N), 0,15 pCt. KH_2PO_4; 0,15 pCt. $MgSO_4$ (crystallised) and 2 pCt. glucose. Temp. = 34° C.

Nr.	Quantity of nitrogen in the mould	Quantity of nitrogen in solution as ammonia, in mgrs.	Number of days after inoculation	Growth and spore-forming.	Assimilated glucose in pCt.	Nitrogen-number
1	8.4	Solution gives no reaction with Nessler	3 days	vigorous, very few spores	47 pCt.	4.5
2	14	Solution gives no reaction with Nessler	4 "	vigorous, beginning spore-forming	80 "	4.4
3	12.7	Solution gives no reaction with Nessler	4 "	vigorous, rather many spores	75 "	4.2
4	14.8	Only extremely slight ammonia reaction	5 "	vigorous, rather many spores	97 "	
5	14.2	Only extremely slight ammonia reaction	5 "	vigorous, rather many spores	92 "	
6	9.9	Already rather much ammonia in the liquid	7 "	vigorous, many spores	100 "	2.5
7	10.2		7 "	" " "	" "	2.6
8	8.1	4.9	10 "	" " "	" "	2.0
9	11.8	1.3	10 "	" " "	" "	2.9
10	9.4	3.8	22 "	" " "	" "	2.3
11	9.2	3.5	22 "	" " "	" "	2.3
12	9.5	not determined	22 "	" " "	" "	2.4

excess of anorganic nitrogen compound attracted by the organism is very quickly converted into an unknown, nitrogen-containing intermediary product. Thus, here again the adsorption has no practical influence on the distribution of the nutrient substances between the medium and the mould.

These results which, as experiments have proved, hold also good for a few other examined organisms, show that in the literature the influence of the adsorption is often overrated[1].

In order to test the obtained views about the metabolism of the nitrogen the following experiments were made (table VI).

The quantities of added ammoniumnitrogen differ very much in the five series of experiments. In D there is just sufficient to satisfy the first wants 20.9 mgrs., in E was an excess of nitrogen, whilst in C, B and A there was a deficit of nitrogen relatively to the assimilated glucose. Still in B and C the additions were sufficient to satisfy the requirements of a mature mould layer.

In A this was not, however, the case and the quantity of nitrogen was even smaller than that fixed in an old mould culture containing little glykogen and obtained at the expense of 1000 mgrs. glucose. To this it must be ascribed that the assimilation of glucose is slackened. After 9 days 20 °/₀ is still unused. Fixation of nitrogen from the air could not be observed in this experiment, neither for A, nor for B or C, whilst yet these series of experiments might in particular come into consideration for an eventual fixation of atmospheric nitrogen in relation to the mentioned deficit in the nutrient solution. In the referring literature, however, are many statements tending to prove the contrary.

We further see that also the velocity of glucose assimilation in B is diminished although the general course of the process of nitrogen fixation remained the same: a high nitrogennumber at first which for all the series decreased with the time to 2 to 3.

The nitrogennumber of A, B, and C, and in slight degree also of D, was in the beginning bound to a certain limit determined by the added nitrogen and the mould.

Series A has a deficit of nitrogen with regard to the quantity of assimilable carbon; series E is characterised by a deficiency of carbon as to the quantity of fixed nitrogen.

We should still point to the association of the plastic aequivalent of the carbon and the nitrogennumber. If the former is high this is also the case with the latter and the reverse.

Summary.

1. The nitrogen fixed in the mature mould is proportional to the plastic aequivalent of the carbon independently of the nature of the carbon as well as of that of the nitrogen.

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[1] See also W. Reinders and D. Lely, These Proceedings, 1912, p. 482.

2. The nitrogennumber, by which is meant the nitrogen per 100 parts of weight of assimilated carbon lowers with time; for a mature mould it is ca. 2 (glucose or levulose as source of carbon).

3. The metabolism of the nitrogen has much resemblance to that of the carbon.

a. An accumulation of carbon is combined with a high nitrogennumber; inversely the mature mould has a low nitrogennumber.

b. The nature of the metabolism of the nitrogen does not change under the influence of many factors; neither is this the case with the carbon.

c. The velocity of the metabolism is subject to great changes.

d. The same factors that accelerate the metabolism of the carbon also further that of the nitrogen.

e. Substitution of rubidium for potassium is of little influence on the metabolism of the nitrogen.

4. The nature of the metabolism of the nitrogen is independent of the source of nitrogen. At first the nitrogennumber is high, then it decreases whilst the freed nitrogen returns into the nutrient solution as ammonia. This is proved for the cases when ammoniumnitrate, ammoniumchlorid, or potassiumnitrate is given as nitrogenfood. *Aspergillus niger,* thus, reduces nitrates to ammonia but not to free nitrogen. Only in the culture tubes with a deficiency of nitrogen as to the quantity of carbon, no ammonia can return into the solution as it is directly used for the production of new cells.

6. In the cases of a deficiency of nitrogen no fixation of atmospheric nitrogen could be observed.

Finally my hearty thanks to Professor Dr. J. Böeseken and Professor Dr. M. W. Beijerinck for their valuable help in this investigation.

Technical University, Organical-chemical Laboratory.

Delft, November 1912.

Microbiology. — "*Metabolism of the fosfor in Aspergillus niger*". By Dr. H. J. Waterman. (Communicated by Prof. Dr. M. W. Beijerinck).

(Communicated in the meeting of December 28, 1912).

In an earlier communication[1] I have shown that the metabolism of the nitrogen in this organism is analogous to that of the carbon[2]. These two elements are accumulated in the organism and are later partly excreted, the carbon as carbonic acid, the nitrogen as ammonia.

We find besides that an excess of these elements retards the spore-formation. For the carbon compare tables II*a*, II*b* and III (p. 451, 452, and 464 Folia microbiologica); for the nitrogen see table VI (Preceding paper).

I have further found that the fosfor behaves in the same manner as the above elements.

In the first place I ascertained that the rate of fosfor of an old mature culture of *Aspergillus niger* is constant, independent of the way in which it is obtained.

The mould layer was before the analysis washed with distilled water and after drying destroyed by strongly concentrated nitric acid in a closed tube. In the thus obtained solution the fosfor was determined after Finkener[3]) as ammonium fosfor molybdate $(NH_4)_3 PO_4 \, 12 \, MoO_3$. The results are found in Table I.

For shortness' sake I shall as for the nitrogen make use of the word "fosfornumber", which means the fosfor fixed in the mould per 100 parts of assimilated carbon. As in the experiments of table I all the glukose (1000 mgrs.) had been assimilated and this quantity corresponds with 400 mgrs. of carbon; the number of mgrs. of fosfor must thus be divided by 4 to find the fosfornumber.

As the table shows the fosfornumber is for an old mature mould-

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[1]) See the preceding paper.

[2]) Folia microbiologica (1912) Bd. I. p. 442.

[3]) The liquid containing ammoniumnitrate and the nitric acid is heated till the first bubbles appear, then precipitated with ammoniummolybdate under continuous stirring. The precipitate is then washed out with a solution containing ammonium-nitrate and nitric acid and dissolved in dilute ammonia. To the thus obtained clear solution is added an excess of ammoniumnitrate and a small quantity of ammoniummolybdate, after which it is again heated until the first bubbles appear; finally hot nitric acid is added under continuous stirring. The precipitate is dried in an air current to constant weight at 160° C. in a Gooch's crucible.

TABLE I.

Circumstances of cultivations: 50 cm^3. very pure distilled water, in which dissolved: 2% glucose and the anorganic substances mentioned below. Temp.: 33° C.

No.	Anorganic substances	Age	$(NH_4)_3PO_4$ $.12MoO_3$ (mgrs.)	Fosfor in mould (mgrs.)	Fosfor-number
	0,15% ammoniumnitrate				
1	0,05 „ fosforic acid (crystallised)	90 dagen	33,3	0,55	0,15
	0,1 „ magnesiumsulfate („)				
2	0,1 „ calciumnitrate (free fr. water)	„ „	32,9	0,55	0,15
	0.1 „ rubidiumchlorid				
	0,15 „ ammoniumnitrate				
	0,1 „ potassiumchloride				
	0,1 „ magnesiumsulfate (crystall.)				
3	0,05 „ calciumnitrate (free fr. water)	50 „	25,2	0,4	0,1
	0,05 „ ammoniumfosfate				
	0,05 „ fosforic acid (crystallised)				
	0,00001 mgr.: $MnCl_2 . 4Aq$				
4	As 3, but instead of 0,00001 mgr.: 0.0001 mgr. $MnCl_2 . 4Aq$	„ „	19,4	0,3	0,1
5	As 4, but instead of 0,0001 mgr.: 0,01 mgr. $MnCl_2 . 4Aq$	„ „	23,0	0,4	0,1
6	0,4 % potassiumnitrate 0,15 „ KH_2PO_4 0,15 „ magnesiumsulfate (crystall.) tapwater	30 „	66,8	1,1	0,25
7	0,15% KH_2PO_4 0,06 „ magn.sulf. (free from water) tapwater and 0,08% NH_4Cl	„ „	37,2	0,6	0,15
8	As 7, but instead of 0,08% NH_4Cl: 0,12% NH_4Cl	„ „	25,2	0,4	0,1
9		„ „	29	0,5	0,1
10	As 9, but instead of 0,12%: 0,32% NH_4Cl	„ „	28	0,45	0,1

layer rather constant so that in this respect, too, the fosfor corresponds quite with the carbon and nitrogen.

In the second place the action of various increasing fosfate concentrations on the metabolism of *Aspergillus niger* was studied. The results are found in table II. The fosfor was added as kaliumbifosfate to the nutrient liquid, whilst I ascertained by analysis that the rate of fosfor of this compound was indeed in accordance with the formula KH_2PO_4.

After one day already, growth was observed in all numbers, except in Nrs. 1 and 2. After two days it had considerably increased in Nrs 4—18, Nrs. 1 and 2 also showing a beginning of growth. After three days the growth of Nrs. 1 and 2 had not increased, as little in Nr. 3 where, however, more mycelium had been formed. The growth increased in the following Nrs. and was very strong in Nr. 8. This continued also after 7 and 14 days.

The retarding of the spore formation after 2 and 3 days is convincing in those experiments where much fosfor is added. After two days 3—6 had rather many spores. In 7 and 8 few had appeared whereas in the following Nrs. hardly any spores were seen. After 3 days 3—6 had many spores, 8 few, and the Nrs. with much fosfor very few. Only in Nrs 17 and 18 the spore-formation was considerable and about alike to that of Nr. 8. The same I have observed for the action of potassium, as before for the carbon and nitrogen, so that it seems of general significance. This may be explained thus: If an excess of the referring element, in this case fosfor, is present, the cells are continually overloaded with new food and with the therefrom arising intermediary products, by which the spore-formation is retarded. When the excess becomes very great it is possible that the process of the metabolism is so much accelerated that also the spore-formation is quickened. Probably such is the case in Nrs 17 and 18, where three days after inoculation more spores were produced than in Nrs. 9—16. After 7 days the differences in spore-formation are no more observable.

However, there are elements which in feeble concentrations counteract the spore-formation [1]) and then the limits will be quite different.

The quantity of mould is very small in Nrs. 1 and 2 where no fosfor was added, and amounts with increase of the fosfor; herewith the assimilation of glucose is parallel. After 4 days the solution in Nrs. 9, 10 and 11, no more contained fosfate, which after the same

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[1]) These Proceedings, November 1912.

TABLE II.

50 cm³. very pure distilled water, in which dissolved: 0,15 % ammonium nitrate, 0,1 % kaliumchlorid, 0,1 % magnesiumsulfate (crystall.) 0.05 % calciumnitrate (free from water), 0,00025 % $MnCl_2 . 4Aq.$, 2 % glucose (free from water).

Nr.	Added fosfor in mgrs.	after four days				after five days				after seven days				after sixteen days	
		Fosfor in mgrs.				Fosfor in mgrs.				Fosfor in mgrs.					
		in liquid as fosfate	in mould-material	Assimilated glucose	Fosfor-number	in liquid as fosfate	in mould-material	Assimilated glucose	Fosfor-number	in liquid as fosfate	in mould-material	Assimilated glucose	Fosfor-number	Assimilated glucose	Dry weight in mgrs.
1,2	0													± 10 %	
3	0,02													± 30 „	30
4, 5	0,22													more than 40 „	100 ; 106,5
6	0,44													55	150
7	0,66													83	259
8	0,88														
9	1,1	0	1,0	83 %	0,3										
10	1,55	0		79 „	0,5										
11	2,1	0		87 „	0,6										
12	3,2														
13, 14	4,2	fosfate still present	2,9	96 „	0,75										
15	10,5									8,7	1,6	100 %	0,4		
16	20,7						1,5	100 %	0,4						
17	104,														
18	207,														

time was still present in Nrs. 13 and 14. From these observations may be concluded that the mould had drawn to it all the fosfor in the three first experiments. As these quantities, especially that of Nr. 11, are considerably greater than those present in the old, mature mould layer (table I), it was indirectly proved that also the fosfor in the metabolism is accumulated in the organism in considerable quantity at the beginning of the development. This result was then in a direct way confirmed by analysis of the mould. So it was found for Nr. 9 that all the fosfor vanished from the solution was present in the organism (ca. 1 mgr.). For Nrs. 13 and 14 2.9 mgr were found in the mould, a quantity 7 tot 8 times as great as that in the old mould layer. The corresponding fosfor-number is **0.75**. This number may even be higher, as is seen from an experiment which may be mentioned here for comparison. In a five days old mould layer (culture liquid: 50 cm^3 distilled water, 0.15$^0/_0$ am. nitrate, 0.1$^0/_0$ KCl, 0.1$^0/_0$ $MgSO_4$ (crystall), 0.05$^0/_0$ Ca nitrate (free from water), 0.05$^0/_0$ fosforic acid (crystall), 2$^0/_0$ glucose), 3.9 mgrs. P was present. As all the glucose was then assimilated the fosfornumber was = **1.0**.

In opposition to what is found for the carbon and nitrogen this quantity of fosfor is loosely fixed in the organism. Ten minutes' boiling with water will do to dissolve considerable quantities. Of a mature mould layer, treated in the same way, no, or hardly any fosfor is dissolved; the same is the case with lecithine or phytine. As the mould grows older the superfluous fosfor, accumulated in the organism, returns into the solution as fosforic acid. This was already indicated by the fact that the fosfornumbers of mature cultures were very small (table I).

It was ascertained by direct analysis both of the mould and the culture liquid of N°. 15 after 7 days, and of the mould of N°. 16 after 5 days. For N°. 15 the sum of the fosfor in the mould and in the liquid present after 7 days is 8,7 + 1,6 = 10,3 mgrs. The totally added quantity was 10,5 mgrs., so that no loss of fosfor, in the form of hydrogenfosfid takes place.

By this study of the metabolism of the elements we obtain a better view of their signification than was hitherto obtained. We see that the quantities of the elements present in the mature mould, do not correspond with the quantities really active during the development. In the case of carbon the plastic aequivalent could in the course of time decrease to the half. For the nitrogen there was a threefold, for the fosfor I could point out a tenfold decrease. The quantities of the latter element required for the normal assimilation are much greater than is generally accepted, also as to the nitrogen, although in a less degree. When comparing the accumulation of the elements it thus seems, that during the metabolism this accumulation is greatest for those, which form a small permanent percentage of the constituents of the organism. So we see, that in the course of an experiment the same quantity of an element may be many times active in the metabolism, one cell taking up the products excreted by another cell.

Starting from this view the study of elements, such as manganese, which are already active in very dilute solutions, are interesting.

Meteorology. — "*A long range weather forecast for the East-monsoon in Java.*" By Dr. C. Braak. (Communicated by Dr. J. P. van der Stok.)

(Communicated in the meeting of November 30, 1912).

In a preceding communication [1]) it was deduced from a study of factors of correlation that in the Indian Archipelago, with the exception of the western part north of the equator, a connection is clearly perceptible between barometric pressure and rainfall. The nature of this connection appeared to depend upon the geographical position as well as upon the different seasons.

In the following an attempt will be made to show that by means of this connection it is possible to make a long range weather forecast.

For this purpose Java has been chosen, because a forecast is of greater value for this island than for any other part of the Archipelago on account of its intense cultivation. Moreover this research will be limited to the east monsoon, as the connection is less distinct in the west monsoon, and because a forecast for this season of abundant rainfall is of secondary importance.

It will be necessary to prove, that the changes of the barometer-readings from year to year succeed each other according to definite rules, so that they may be determined in advance. Further we must also prove that it is possible to ascertain with sufficient accuracy how the rainfall depends upon the barometric deviations.

With regard to the deviations of airpressure Java has an advantage over any other part of the world, because the variations of climate are determined by the variations of the barometric pressure in North Australia, which are characterised by an extraordinary regularity. No station outside North Australia can vie with it in this respect, not even Bombay of Cordova (Argentina) which stations

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[1]) These Proceedings 1912 p. 454.

were selected by LOCKYER as the representatives of both types of the barometric periodical oscillation of 3.5 years [1]) Moreover the amplitude in Australia is much greater than elsewhere.

The variations of the airpressure in North Australia from the normal value are shown in curve I of the plate, by means of the six-monthly deviations of the barometric pressure at Port-Darwin, marked monthly on the plate in such a way that, for instance, the deviation in the period January-June (in relation to the normal value in the same months) is drawn on the 1rst of April. Beginning with 1899 the base value has changed, apparently because something has been altered in the barometer or its position.

The curve shows some very regular series of waves, namely from 1878 till 1881, from 1885 till 1891, from 1896 till 1904. whereas in 1911 a new series seems to have begun. *The maxima and minima are characteristic of fixed seasons, they develop themselves namely in the first and last months of the year.*

Minima.	Maxima.
1 Dec. 1878	1 Febr. 1881
1 Oct. 1886	1 Sept. 1885
1 Febr. 1890	1 Jan. 1889
1 Febr. 1898	1 Oct. 1891
1 Sept. 1900	1 Nov. 1896
1 Febr. 1904	1 Febr. 1900
	1 Dec. 1902
	1 March 1912

It is further evident, that the time which elapses from minimum to maximum is one year, from maximum to minimum two years. The period is exactly 3 years.

The curve so closely resembles this schematic interpretation, that it may be represented by the schematic broken line IV of the plate. From 1878 it has been traced backward by means of the barometric observations made at Adelaïde. For simplicity's sake the maxima and minima have been drawn on the 1rst of January.

These regular periods are particularly adapted to forecast the airpressure a considerable time in advance. Disturbed periods are lying between them however, in which the curve makes the impression that there has been no development of the maximum for some years. The certainty with which the barometric variations may be predicted would decrease greatly, if the epochs at which these disturbed

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[1]) Solar Physics Committee. Monthly mean values of barometric pressure.

periods appear could not be predicted and one would always be uncertain whether the end of a regular series is near. Fortunately however these disturbances seem to be anything but irregular in their appearance, so that there exists a possibility of announcing them in advance. This may be seen from the comparison of the barometercurve I with the curve II, which represents WOLF's relative numbers of sunspots. *It is remarkable that the disturbances in the barometercurve coincide with the maxima of the sunspotcurve, whereas during the periods with small sunspot intensity the regular barometric wave is developed undisturbedly.*

It cannot be denied that the number of sunspot periods over which this comparison is possible, is but small, however there seems to be every reason to suppose that we have here to do with a real and not with an accidental connection. Indeed it is a matter of fact known already since long that there exists a connection between the number of sunspots and different meteorological phenomena, and the above mentioned result agrees with what has been found in earlier researches. At the close of this communication this connection will be still further considered.

One would be inclined to go back, beginning with the year 1876 and examine still more closely the connection between sunspots and disturbed barometerperiods by means of the observations made at other stations with longer records. For this purpose i.a. the stations Batavia, Adelaïde, Bombay, and Madras would be adapted. As however at these stations the oscillation itself is less regular, it is very difficult to distinguish what is disturbed by the sunspots and what is not, and the results would not be very convincing.

Now the question arises how the rainfall is affected with regard to the barometer oscillations. In answering this question the disturbed periods in which the connection is less distinct will be left out of account and only the regular waves will be considered. In curve V the rainfall deviations in West-Java (6 monthly means, calculated in the same manner as the deviations of curve I, accordingly reduced to one month) have been represented monthly; for the years 1875—1878 the curve is based on the Batavia observations only.

The curve shows clearly that the connection between rainfall and airpressure is different in the West- and the Eastmonsoon, it may serve to illustrate the numbers which are given below.

The investigation may be divided into three parts according to the schematic barometer curve.

1. The Eastmonsoons of the years in which the barometer is moving from maximum to minimum; these are years of transition.

2. The Eastmonsoons following the barometric minimum. The pressure remains below normal during the whole year.

3. The Eastmonsoons preceding the barometric maximum. The pressure is above normal during the whole year.

The first case is apparent in the years 1878, 1886, 1889, 1897, 1900, 1903, and 1912. The departures of the rainfall from its normal condition from June till November (the latter included)[1]), were in these years, averaged monthly, in millimeters.

	West-Java	East-Java
1878	—24 (*Batavia*)	*Not observed.*
1886	+ 1	+20
1889	+67	+50
1897	29	-30
1900	+34	+43
1903	+24	—15
1912	+ 2 (June-September)	—21 (June-September).

The second case is apparent in the years 1876, 1879, 1887, 1890, 1898, 1901, and 1904. The rainfall departures are in the same months as above averaged monthly:

	West-Java	East-Java
1876	+ 4 (*Batavia*)	*Not observed.*
1879	69	+79
1887	29	7
1890	52	44
1898	8	18
1901	15	18
1904	81	17

In the last case are the Eastmonsoons of 1877, 1880, 1885, 1888, 1891, 1896, 1899, 1902, and 1911.

The rainfall departures in the months June-November are:

	West-Java	East-Java
1877	— 74 (*Batavia*)	*Not observed.*
1880	+ 62	—23
1885	— 88	—53
1888	— 86	+ 2
1891	— 99	—60
1896	—102	—51
1899	— 12	—41
1902	—104	—57
1911	— 18	+ 7

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[1]) These are the months which have negative correlation between airpressure and rainfall as appears from the preceding communication.

In the years of transition mentioned sub 1°, evidently the rainfall is also in a state of transition: the signs of the departures are changing and have no fixed character.

On the contrary all Eastmonsoons mentioned sub 2° without exception have been too wet in West- as well as in East-Java, whereas of the Eastmonsoons mentioned sub 3°, out of 9 *cases* 8 *have been too dry in West-Java and out of* 8 *cases* 6 *too dry in East-Java.*

It cannot be denied that among the favourable cases there are some in which the departure is but small, but on the other hand it is a matter of fact that with 2 of the 3 unfavourable cases the departure also remains small. In these years the character of the monsoon has been indefinitely developed, or has been different in different parts of Java or, as occurred in 1911, the character was different during the different months. Certainly 1911 must be reckoned among the dry years, even though the heavy rainfall in June caused a positive departure in East-Java.

It must be remarked that to the numbers given for 1876—1878, as taken from the observations of only one station, but little value can be attached. It is however a well known fact that 1877 was a dry year over the whole of Java and that therefore the strong negative departure observed in Batavia has a general validity.

Above has been given a scheme of barometric changes and corresponding fluctuations of rainfall which may be applied to 23 years out of the 37 of the period 1876—1912. If we exclude the year 1876 for the above mentioned reason, this scheme gives for 15 years (mentioned sub 2 and 3) a definite answer to the question what was the sign of the rainfall departure in the Eastmonsoon in Java. With one exception in West-Java and two exceptions in East-Java this sign corresponds with reality.

On the principle upon which the scheme has been based it also would have been possible to forecast for these 15 *years the sign of the rainfall departure in West-Java* 14 *times, in East-Java* 13 *times, if we had considered that the term should be taken somewhat shorter at the beginning and at the end of a regular wave series e.g. half a year, whereas it might be taken longer between them, even* 1 *or* 2 *years.*

What may be concluded from the scheme for the near future about the rainfall in Java? The circumstances for a forecast may presently be called really favourable, because a new regular series of barometer waves has already made its appearance during the present sunspot minimum.

We have already passed the barometer maximum and the pressure is changing exactly in the direction indicated by the scheme, so that there is every reason to believe that the next minimum will appear at the expected time (namely about the 1rst of January 1913), while there is no indication in the course of the sunspot number that points to an early disturbance. Therefore also the appearance of the next barometric maximum about the 1rst of January 1915 is rather certain.

From this already now may be concluded, with certain reservations that must be admitted with every forecast, that most probably the Eastmonsoon in Java of 1913 *will deviate in the wet, and that of* 1914 *probably in the dry direction.*

Finally a remark may be made about the barometercurve itself. In the preceding communication the question was raised as to whether the barometerperiod of 3.5 years has a terrestrial or an extraterrestrial cause; as for the Port Darwin curve, (and to this one a considerable weight should be attached, because it is not only the most regular one, but it has also the greatest amplitude), I should like to call attention to the fact, that *the epoch of the maxima and minima seems to be entirely controlled by the terrestrial seasons.* This seems to me a new proof for its terrestrial origin. The cosmical influences instead of causing the barometric oscillations, seem to disturb them (namely during the sunspot maximum).

If the variations of climate (departures of airpressure, temperature and rainfall) of short period (BRÜCKNER's period and the longer ones excepted) are described as a combination of waves of terrestrial origin with a period of about 3 years, and a cosmical disturbance, which is acting during the sunspot maximum, it seems to me that a satisfactory explanation may be given of the influence, that (as a result of different researches) is attributed to the sunspots. By a combination such as described above the fact may be especially explained, that although in many cases a connection is found, it manifests itself at different epochs in a different way, as e.g. KÖPPEN has established for the temperature in the tropics.

The idea here given about the origin of barometric variation of 3 years is contrary, it is true, to the opinion of LOCKYER and BIGELOW, whose ideas are that it is controlled by the number of prominences. However the data on which this opinion is based are by no means convincing as a comparison between curves I and III may teach. In curve III we have put down the observations made at Rome and Catania about the number of prominences, which data have also been used by the two above mentioned investigators. Again the 6 monthly means of departure have been represented monthly in such a manner however that, following the example of Bigelow, for the elimination of the 11 year period the departures from the nearest 60 months (5 years) have been calculated and not those from the normal of the whole period.

Comparison teaches that in the beginning till 1891 the barometercurve shows indeed much conformity with the prominence curve; afterwards however every similarity has vanished and in the later years in which the prominences hardly show any variation, the barometeroscillation goes on with the same regularity as before. Therefore very likely the connection during the first years has been only accidental.

Welterreden, 10 October 1912.

Chemistry. — *"Dynamic researches concerning the reaction of* Friedel and Crafts." By S. C. J. Olivier and Prof. J. Böeseken. (Communicated by Prof. A. F. Holleman).

(Communicated in the meeting of December 28, 1912).

Dynamic researches have already been carried out with $AlCl_3$ or analogous substances as catalyst.

The first are those of A. Slator[1]), who investigated the action of chlorine on benzene in the presence of $SnCl_4$ and $FeCl_3$.

The absorption of the halogen dissolved in an excess of benzene was measured, and it was found that this proceeded according to the reaction scheme of the first order the constant being proportional to the amount of the catalyst.

We may conclude therefrom that the catalyst is constantly active; that its action is not sensibly altered by any of the reaction products.

Further we mention the research of B. D. Steele[2]), who has studied the ketone synthesis and the formation of phenyltolylmethane under the influence of $AlCl_3$ and FCl_3 where the progressive change of the reaction was determined from the amount of hydrogen chloride evolved.

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[1]) Proc. **19**, 135 (1903); Journ. Chem. Soc. **83**, 729 (1903); Zeits. phys. Ch. **45**, 513 (1903).

L. Bruner had carried out measurements as to the bromination of benzene, but as a catalyst iodine was used which is not directly comparable with $AlCl_3$; moreover it was not sufficiently taken into consideration that the bromine unites with the catalyst (see Dissertation S. C. J. Olivier).

Slator has also used iodine as catalyst. Although this research is very interesting as regards the benzene substitution, this part may be passed over for the reason stated.

[2]) Journ. Chem. Soc. **83**, 1470 (1903).

Although, in our opinion, this *modus operandi* (see Dissertation C. S. J. OLIVIER) cannot be expected to give accurate results it was rendered probable by him that, when in the ketone synthesis the proportion $AlCl_3 : C_6H_5COCl$ is smaller than (or at most only equal to) unity, the reaction was of the first order. With an excess of $AlCl_3$ a reaction of the second order would have to be assumed where the $AlCl_3$ would combine with the acid chloride as well as with the toluene.

The latter course of reaction would always have to be assumed with $FeCl_3$ as catalyst. The figures found by him for the synthesis of phenyltolylmethane differ so much that they do not admit of a safe conclusion.

Much more regular are the figures obtained by H. GOLDSCHMIDT and H. LARSEN [1]) in their research on the chlorination of nitrobenzene and the benzylation of anisole in the presence of substances such as $SnCl_4$ and $AlCl_3$.

They obtained the result that the reaction was of the first order and that the constant was directly proportional with the concentration of the catalyst.

As in the chlorination of benzene, the action of the catalyst appears not to be disturbed by the reaction products.

If we consider that $AlCl_3$ unites with the nitrobenzene as well as with the anisole to molecular compounds, and that these substances were always present in large excess, this result is not a matter of great surprise.

The catalyst is then greatly paralysed, which condition cannot be modified to any extent by the formation of chloronitrobenzene (benzylanisole, respectively) in small quantities in regard to the nitrobenzene (anisole, respectively).

That in the benzylation of anisole $AlCl_3$ is not very active is shown by the fact that this reaction could still be measured at 25° in a $N/_{10}$ solution of $AlCl_3$, although as a rule the hydrogen atoms of anisole are much more readily substituted than those of benzene.

The exceedingly slow chlorination of nitrobenzene at 50° may be due to the paralytic condition of the calalyst as well as to the lesser activity of the benzene hydrogen atoms.

From this survey as to what has been carried out in this direction it follows that a systematic research under various conditions was very much to be desired.

The only somewhat trustworthy results were obtained in the

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[1]) Zeitschr. phys. Ch. **48**, 424 (1904).

chlorination of benzene with $SnCl_4$ (SLATOR) and in the just mentioned research of GOLDSCHMIDT and LARSEN in which, however, neither the progressive change of the reaction nor the rôle of the catalyst has been much elucidated.

For this reason we have more closely studied the reaction between p-bromophenylsulphonechloride and benzene.

It was first our intention to carry this out in a neutral solvent for which carbon disuphide was chosen; it appeared, however, that the reaction then took quite another course [1]) so that we were compelled to choose the hydrocarbon itself as the solvent.

The p-bromosulphonchloride was prepared from bromobenzene by sulphonating this with fuming sulphuric acid, neutralising the mixture with lime and converting the calcium salt by means of sodium carbonate into the sodium salt; the sodium p-bromosulphonate thus obtained was converted by PCl_5 into the chloride. This was freed from $POCl_3$ with cold water and recrystallised from ether.

We had chosen the sulphonchloride as starting point because this is not decomposed by cold water, whereas it is rapidly decomposed on warming with aqueous silver nitrate, so that the unattacked sulphonchloride could be freed, by means of cold water, from the $AlCl_3$ and the HCl formed and afterwards be titrated with silver nitrate solution of known strength.

The benzene hydrocarbons were dried carefully over $AlCl_3$ and kept in stock with exclusion of moisture.

The measurements were carried out by making (with exclusion of light and moisture) a solution of definite quantities of sulphonchloride, aluminium chloride, and hydrocarbon; from time to time a definite volume of this solution was withdrawn and analysed.

For details we refer to the dissertation of Mr. OLIVIER which will appear shortly.

We reprint therefrom a few series of analyses.

The benzene required for this was treated before the reaction with $AlCl_3$ and distilled; a thiophene-free benzene which had not thus been dried and distilled exhibited a small initial value and a strong course of the constant.

From table I we see that the reaction between 1 mol. of $AlCl_3$ and 1 mol. of acid chloride is one of the first order; when, however, 80 °/₀ of the original quantity has been converted a serious retarda-

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[1]) It then proceeded according to the scheme: $Br\,C_6H_4SO_2Cl + AlCl_3 + C_6H_6 = Br\,C_6H_4SO_2AlCl_2 + C_6H_5Cl + HCl$.

TABLE I.

Action of $BrC_6H_4SO_2Cl$ (1 mol.) + $AlCl_3$ (1 mol.) on excess of benzene.
Concentration acid chloride = 0.1 n.; $T = 30°$.
$(a-x)$ — concentration acid chloride in grammols. after the time t in minutes
K_I = constant monomolecular reaction.
K_{II} = » bi » »

t	$(a-x)10^3$	K_I	K_{II}
0	86.1	—	—
120	75.3	0.00111	0.0139
240	66.4	0.00108	0.0144
360	59.2	0.00104	0.0146
480	50.6	0.00111	0.0170
720	39.2	0.00109	0.0193
1500	21.5	[0.00093]	—
4320	19.3	[0.00035]	—

TABLE II.

Action and concentration as above. Benzene not again dried.

t	$(a-x)10^3$	K_1
0	82.1	—
60	78.7	0.000698
210	71.8	0.000636
1320	50.6	0.000367

tion is noticed. We attribute this: 1st to the absorption of moisture during the manipulations, which exerts an influence particularly when the amount of the active catalyst has become small;
2nd to a slight paralysis caused by the reaction itself.

Influence of the temperature.

TABLE III.

As in table I, temperature = 40°

	$(a-x)10^3$	K_1
0	—	—
30	61.6	—
90	52.3	0.00273
165	43.1	0.00251

The proportion $\frac{K_{t+10}}{K_t} = \pm 2,5$, is therefore normal.

Influence of the concentration.

TABLE IV.

As in table I. Concentration of $AlCl_3$ as well as of $BrC_6H_4SO_2Cl$ = 0.2 n
(The expression $\frac{1}{2}(a-x)10^3$ indicates the percentages
of the acid chloride originally present.

	$\frac{1}{2}(a-x)10^3$	K_1
0	36.6	—
120	28 1	0.00220
300	19.6	0.00208
540	14.7	0.00169

The much more rapid progress of the reaction compared with that of the $N/10$ concentration was shown by the fact that after scarcely a quarter of an hour, which is the time required to obtain a homogeneous solution, more than 65 % of the original quantity had already been converted.

The constant for the $N/5$ concentration is twice that of the $N/10$ concentration.

We should conclude from this, that the entire course of the reaction can be represented by the reaction:

$$\frac{dx}{dt} = kC_{AlCl_3}(a-x)$$

that is to say, of a monomolecular reaction influenced catalytically, in which the velocity of the reaction is proportional to the amount of chloride present and to the quantity of the catalyst.

In that case, at a given concentration of the catalyst, a change of the initial concentration of the acid chloride should not cause any modification in the value of the constant.

If, however, we take an excess of acid chloride we obtain the following:

TABLE V.

Concentration $AlCl_3 = 0.1$ n.; acid chloride $= 0.15$ n.; $t = 30°$.

t	$^2/_3 \times (a-x)10^3$	K_1	K'_1
0	90.8	—	—
120	83.9	0.000656	0.00106
240	77.5	0.000662	0.00110
360	72.5	0.000617	0.00105

TABLE VI.

Concentration $AlCl_3 = 0.1$ n.; acid chloride $= 0.2$ n.; $t = 30°$.

t	$^1/_2 \times (a-x)10^3$	K_1	K'_1
0	89.7	—	—
185	82.0	0.00487	0.00117
370	76.6	0.00427	0.00108
585	70.9	0.00402	0.00110

Herein K_1 has been calculated as if all the acid chloride present is concerned in the reaction, hence in accordance with the above schema, whereas K'_1 has been calculated as if only the acid chloride which has formed a molecular compound with the $AlCl_3$, enters into reaction.

It is easy to see that, only on the latter supposition, we obtain a constant without course and which agrees with the constant obtained with equimolecular quantities of acidchloride-$AlCl_3$ (concentration $N/_{10}$).

The excess of acidchloride is therefore quite inactive; only that acidchloride which is combined with the aluminiumchloride is active.

Hence in connection with the preceding, applies the relation:

$$\frac{dx}{dt} = K \times C_{AlCl_3} \times C_{BrC_6H_4SO_2Cl.AlCl_3}$$

In solution of one of the active molecules, the velocity of reaction is therefore proportional to the quantity of the other molecule, in so far as this has united with the catalyst, as well as with the total quantity of the catalyst.

The part thereof which during the reaction passes to the sulphon:

$$AlCl_3BrC_6H_4SO_2Cl + C_6H_6 = HCl + BrC_6H_4SO_2C_6H_5AlCl_3$$

although not capable of rendering the acid chloride active must retain its catalystic activity in other respects.

We may explain this by assuming that $AlCl_3$ renders active the benzene, with which it forms *no* compound, *never mind whether the catalyst is united to the sulphonchloride or to the sulphon* [1]).

If the above relation is correct, the addition of an equivalent amount of sulphon to the catalyst before or during the reaction must either prevent or stop the same, because one of the necessary molecules cannot, or no longer, be rendered active.

From Table VIIa and b this appears really to be the case.

TABLE VII*a* and *b*.

a $AlCl_3$ = 0.1 n.; sulphonchloride = 0.1 n. sulphon = 0.1 n.		*b* As in *a*; the sulphon 0.1 n has been added after all had become homogeneous.	
t	$(a-x)10^3$	*t*	$(a-x)10^3$
0	99.2	0	83.6
180	99.3	155	83.9
500	99.8	435	83.6
		1200	85.5

If on the other hand our explanation is correct, an excess of $AlCl_3$, which cannot then be paralysed either by the sulphonchloride or by the sulphon, must exert a perceptibly stronger action. For we have assumed that the catalyst renders active the benzene also and it will do this undoubtedly better still when it is in looser combination; this is also confirmed by the experiment. (Table VIII).

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1) It is possible and even probable that the action of the $AlCl_3$ does undergo a *slight* change; the course of the constant (see table I) might be partly attributed to this.

TABLE VIII.

$AlCl_3 = 0.2$ n ; sulphonchloride $= 0.1$ n.

t	$(a-x)\,10^3$	K_1	
0	60.8	—	The $AlCl_3$ remained undissolved to a considerable extent.
45	38.0	0.0104	
105	17.3	0.0120	
240	3.4	0.0120	

When compared with table I, the reaction constant has become 10 times greater; also it is constant till the end. The lesser value at the commencement will, probably, have been caused by the fact that the benzene was not yet saturated with the catalyst which is but slightly soluble therein.

Hence, it must be observed that the relation given above only applies to partly paralysed $AlCl_3$; the free aluminiumchloride has a much more powerful action.

We can now go a step further. The above reaction may be imagined to take place in two phases:

$$\text{I}\quad BrC_6H_4SO_2Cl\,.\,AlCl_3 + C_6H_6 = BrC_6H_4SO_2ClAlCl_3C_6H_6$$

$$\text{II}\quad BrC_6H_4SO_2ClAlCl_3C_6H_6 = BrC_6H_4SO_2C_6H_5AlCl_3 + HCl$$

The first (I) represents the real catalytic reaction which shows us the formation of a ternary compound, called by one of us the dislocation.

[This dislocation applies here to the benzene because that of the other molecule in the formation of $BrC_6H_4SO_2Cl\,.\,AlCl_3$ has already taken place before the starting of the reaction. The arrows indicate that the benzene is rendered active by *all* the $AlCl_3$].

The second (II) is the elimination of the hydrogen chloride.

If now we supposed that I would proceed with infinite velocity in regard to II we should measure the reaction of decomposition of the ternary compound and the constant thereof could not be dependent on the concentration of the aluminium chloride. Only by assuming that I proceeds slowly in regard to II we obtain the course of the reaction as found by us [1]).

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[1]) Not the existence of a similar ternary compound is, therefore, essential because the course of the reaction shows that it breaks up, but the act of its formation called by one of us dislocation. (Also compare Dissertation H. J. PRINS Delft 1912 p. 12 and 54).

The research which is being continued in different directions in order to confirm the result obtained has elucidated the catalytic action of $AlCl_3$ thus far that it does *not* exert its action because it unites with one of the molecules, for the free $AlCl_3$ was much more active than the combined portion. The view already expressed many times by one of us that the catalytic action of aluminium chloride is based on an influence (called by him *dislocation*) which makes itself felt before the real compound is formed, has, therefore, been confirmed by this research.

In harmony therewith it appeared that there was measured an additive reaction of the acid chloride with benzene, the first rendered active only in so far as it is united to $AlCl_3$, the second rendered active by the total aluminium chloride present.

We have also carried out some measurements with benzene derivatives in order to get some knowledge as to the influence of the substituting group on the reaction velocity; there it was shown that the reaction with toluene using $N/_{10}$ acid chloride $AlCl_3$ at 30° proceeded so rapidly that the conversion had already practically taken place after the mass had become homogeneous; a constant could only be approximated. We give here also the reaction constants for benzene, chlorobenzene, bromobenzene and nitrobenzene at 30 and for a $N/_5$ concentration of the acidchloride-$AlCl_3$.

toluene for	0.1 n.	> 0.0064
benzene ,,	0.2 ,,	0.0021
bromobenzene ,,		0.00102
chlorobenzene ,,		0.00080
nitrobenzene ,,		0.00000

From this little survey we notice that in the reaction of Friedel and Crafts, another succession of the velocity influences is observed than in the nitration where, according to the researches of Holleman and his students, it is exactly opposed to this in the case of the methyl group and the chlorine atom. It may, however, be pointed out that our succession is based on measurements whereas the succession of the nitration is deduced from a comparison of the dirigent power of the groups on the entering nitro-group which, perhaps, has no direct connection with the velocity of nitration.

When carrying out the reaction of Friedel and Crafts it is desirable, according to this research, to have the catalyst in small excess when it forms an additional compound with one of the reacting molecules.

Delft—Wageningen, December 1912.

Chemistry. — "*On the behaviour of gels towards liquids and their vapours*". By Dr. L. K. Wolff and Dr. E. H. Büchner. (Communicated by Prof. A. F. Holleman)[1].

(Communicated in the meeting of December 28, 1912).

A paper by Mr. Bancroft[2], which came to our notice only a short time ago, induces us to publish the following account of an investigation, which we do not yet consider completed. It concerns a phenomenon, discovered by von Schroeder,[3] who found that gelatine, swelling in water vapour, behaved differently from gelatine, swelling in liquid water: in the first case it absorbs much less water than in the second. This phenomenon seems to contradict the second law of thermodynamics, which immediately leads to the principle, that, if a certain number of phases are in equilibrium, the equilibrium will not be disturbed, if one of the phases (in our case, the water) is taken away. Being convinced of the validity of the second law, and not satisfied by the given explanations, we started this research.

We can at once refute a seemingly obvious remark. It might be supposed, that the absorption of water vapour finally takes place so slowly, that the equilibrium would only be reached after a very long time, *i. e.* that we have a false equilibrium. The erroneousness of this suggestion is immediately proved by the fact, that gelatine, swollen in water, loses water, when brought into a space saturated with water vapour.

Von Schroeder found, that agar-agar showed the same phenomenon, though not so markedly, but he observed the reverse in the case of filter paper. As far as we know, no other experimental investigation of the subject has been published after von Schroeder's paper, though theoretical considerations have been given by Freundlich and Bancroft, which we will treat of later on.

We first repeated von Schroeder's experiments, concerning gelatine and agar; and we obtained the same results.

Both substances, when used in the proper concentration, can be quite easily dried with filter paper, which is an essential point, as it was suggested that mechanical adhering of water to the surface of the gelatine might serve as a means of explaining the phenomenon. When the plates grew mouldy or the growth of bacteria was noticed,

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[1] Although much work has been done, since the original paper was written (Dec. 1912), we prefer only to present the translation of the Dutch communication and to postpone the publication of our new results.

[2] J. physic. chemistry **16**, p. 395.

[3] Z. physik. Chemie **45**, p. 76.

the experiments were rejected. We used very pure gelatine (Nelson), the same as von Schroeder used. The agar too was very pure and freed as far as possible from foreign substances by continuously treating it with water. The substances were placed in desiccators in a room, which was as much as possible kept at temperature.

The data of an experiment on gelatine will be found in the following table; a solution of about 2°/₀ gelatine was solidified into a plate.

Weight of the fresh plate	1.797	Gr.
,, after 8 days in water vapour	0.056	,,
,, ,, 8 more days in vapour	0.056	,,
,, ,, 3 days in liquid	0.728	,,
,, ,, 11 ,, ,, vapour	0.039	,,
,, ,, 4 ,, ,, liquid	0.758	,,
,, ,, 8 ,, ,, vapour	0.043	,,
,, ,, 6 ,, ,, liquid	0.800	,,

Whereas gelatine in water vapour absorbs not yet half its weight, we see that it takes up more than twenty-five times its own weight in liquid water. The experiment was repeated with other plates and always with the same result. A similar proportion is found with agar-agar.

Weight of the freshly prepared plate	2.111	Gr.
,, after 8 days in vapour	0.032	,,
,, ,, 8 more days in vapour	0.037	,,
,, ,, 3 days in liquid	0.422	,,
,, ,, 11 ,, ,, vapour	0.033	,,
,, ,, 4 ,, ,, liquid	0.358	,,
,, ,, 8 ,, ,, vapour	0.040	,,
,, ,, 6 ,, ,, liquid	0.395	,,
,, ,, 22 ,, ,, vapour	0.035	,,

It will be observed that in our experiments agar shows the phenomenon much more distinctly than in von Schroeder's. This author also tried the experiment with filter paper; we however did not, because we found it impossible to free this material from the water adhering to the surface.

Then we investigated, whether other substances show the same phenomenon, and we found a very striking example in nitrocellulose. Celloïdin Schering was used, which is known to be very pure. This substance swells strongly at room temperature in 98 °/0 ethylalcohol, without being solved to any considerable degree; placed in saturated alcohol vapour at the same temperature, it loses a great part of the absorbed alcohol.

Celloïdin in ethylalcohol.

I.	II.
Weight of dry substance 0.774 Gr.	Weight of dry substance 0.561 Gr.
In *liquid*	In *vapour*
after 2 days 4.591 Gr.	after 2 days 0.806 Gr.
,, 5 ,, 5.440 ,,	,, 5 ,, 0.924 ,,
,, 7 ,, 5.430 ,,	,, 7 ,, 0.972 ,,
Composition of the gel 14.3 °/0 cell.	,, 12 ,, 1.073 ,,
Then in *vapour*	,, 14 ,, 1.060 ,,
after 2 days 5.139 Gr.	Composition: 52.9 °/0 celloïdin
,, 4 ,, 4.953 ,,	Then in *liquid*
,, 6 ,, 4.750 ,,	after 2 days 3.270 Gr.
,, 9 ,, 4.598 ,,	,, 5 ,, 3.388 ,,
,, 11 ,, 4.510 ,,	,, 7 ,, 3.391 ,,
,, 16 ,, 4.316 ,,	Composition: 16.5 °/0 cell.
,, 18 ,, 4.200 ,,	This quantity, now once more
,, 27 ,, 3.949 ,,	placed in saturated vapour,
,, 113 ,, 3.140 ,,	lost weight as in exper. I.

Weight in equilibrium, calculated from experiment II, 1.601 Gr.

It was noticed, that, when the swollen celloïdin, taken from the liquid and well dried off, was placed in the vapour, a few drops of alcohol were found after some days on the bottom of the weighing-bottle; these were removed before weighing.

Celloïdin also shows the phenomenon in methylalcohol; the absorption in liquid, as well as the loss in vapour are nearly equal to those in ethylalcohol. It was also found with rubber ("gummi elasticum" Ph. Ned. IV) in xylene and in chloroform. In these systems a difficulty presented itself viz. that the swollen rubber almost became liquid; we succeeded in separating it from the xylene or chloroform by centrifuging. Rubber is more soluble in these liquids than the other substances investigated are in water or alcohol, but that does not decrease the results of our experiments.

Laminaria and cornea of the ox show the phenomenon quite clearly in water; from the latter, though well dried after being taken out of the liquid, big drops were found on the bottom of the dish. The structure of these two substances, however, is so complicated, that we must allow for the possibility, that their behaviour may be explained in quite a different way.

Until now we have only treated colloïds; we thought it quite worth while to examine, if the phenomenon could also be found in crystalline bodies. A paper of FISCHER and BOBERTAG[1]) drew our attention to myricyl alcohol[2]), together with chloroform and amylalcohol. We are inclined to conclude, that this substance really shows the phenomenon, but the differences, which we found, are much smaller, and absolute certainty about the fact has not yet been obtained. The principal error in these experiments lies in the liquid adhering to the surface, and its influence will grow, according to the decrease of the total difference. Besides this substance we investigated stearic acid with acetic acid and anthracene with ethylalcohol; the differences in these systems are still smaller and the uncertainty therefore is still greater.[3])

All the above mentioned substances show the phenomenon more or less; a few others do not do so or at least they show differences, not exceeding the experimental errors; viz. silica jelly, (as could be seen from VAN BEMMELEN's investigations), coagulated albumen (serum-albumen, MERCK) and amongst the crystalline bodies stilbite; the latter absorbs only 3 % water in toto. We did not investigate the hydroxydes of the heavy metals, because we did not think it possible, to free them from the surface water. Therefore we do not wish to oppose ourselves to the researches made by FOOTE[4]) and RAKOWSKI[5]). A word must be said, however, concerning a remarkable observation of FOOTE, to which Mr. RAKOWSKI drew our attention. FOOTE found, that a crucible, containing pure water, placed in a well closed weighing bottle, on the bottom of which was some water, and which was pending in a thermostat, lost some weight. Now theoretically the water on the highest level must evaporate wholly, but, if we do not consider this fact, we notice, at all events,

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[1]) Jahresber. d. Schles. Ges. f. Vaterl. Kultur **86**, 36.

[2]) This substance was prepared for us of carnauba wax in Prof. HONDIUS BOLDINGH's laboratory; a crystallographic examination by Dr. B. G. ESCHER proved that it was wholly crystalline. We wish to express our hearty thanks to these gentlemen for their kindness.

[3]) Whether the phenomenon also appears in two normal, non miscible liquids, is a question, directly connected with the above. Experiments about this problem have been commenced.

[4]) J. Amer. Chem. Soc. **30**, 1388.

[5]) Zeitschr. für Chem und Industrie der Kolloïde. **11**, 22.

that the difference, which Foote speaks of (7 m.G.), is out of proportion to the differences, found by us (a hundred and more m.G.).

We now wish to proceed to consider the given explanations. In doing this the first question that suggests itself is, whether the examined substances are composed of one or of two phases. Since van Bemmelen and Hardy's investigations it is pretty generally assumed, that gels are systems of two phases. As to bodies like silica, we do not oppose this statement; but for gelatine, celloïdin and rubber, it does not seem to be at all certain. Let us examine the grounds, on which it is based:

1. the well-known "Umschlagpunkt" and the behaviour of silica jellies (van Bemmelen); agar, gelatine, celloïdin, and rubber do not show a similar behaviour.

2. the pressing experiments; these do not prove anything. In the same way, one can expel the water from a salt solution, by exposing it to a pressure that exceeds the osmotic one, in a pot with semipermeable walls. Under these circumstances some water is pressed out; but nobody will maintain this solution to be a system of two phases. In the case of agar the canvas, between which the agar is pressed, acts as a semipermeable membrane.

3. the analogy to mixtures of water, alcohol and gelatine, in which Hardy [1]) succeeded in observing the separation of small drops. Leaving the question, whether the drops appear just at the point of solidification, out of discussion, we are not allowed to apply results, obtained in a ternary system, to a binary one [2]).

4. the behaviour of gelatine and agar, which are soluble in water, when liquid, but insoluble, when solidified, whilst the solution generally solidifies as a whole. If one takes the hysteresis into account it does not seem impossible to explain this behaviour also in a system of only one phase.

5. the structures found by Bütschli. These however do not seem to be of much value, since they are on the limit of the power of the microscope and since they have to be called into existence by all sorts of artificial means. Moreover Zsigmondy and Bachmann [3]) have lately shown, by using the ultramicroscope, that both silica gel and gelatine are built up of much finer elements. It is doubtful though, if in this case we can speak of "phases". We too think it very likely, that molecular aggregates are formed in solutions of gelatine; but these are also to be observed (by means of the ultramicroscope)

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[1]) Z. phys. Chem. **33**, 326.

[2]) Bachmann, Z. Anorg. Chem. **73**, 125 expresses the same opinion.

[3]) Z. anorg. Chem. **71**, 356; **73**, 125.

in greatly diluted, non-solidifying solutions[1]), which, then, ought also to be considered as systems of two phases; a view, which to us seems to be without any foundation whatsoever.

6. the forming of a membrane in gels by opposite diffusion of salts that give a precipitate[2]). It is not clear to us, why these precipitates should only arise in the cavities of the gel.

Let us first of all examine BANCROFT's explanation, which is identical with the one, originally put forth by us, but which we have rejected for the reasons, we shall presently discuss. It assumes two phases in the gel — one with much, the other with little water — which are separated by curved surfaces. The equilibrium in the vapour decides the composition of the second phase; the water, which is taken by the gelatine up in the liquid, forms the first. According to our observations, the concentrated phase of agar would contain 50°/₀ agar, whilst 3 to 5 °/₀ would follow from HARDY's pressing experiments. So this does not agree exactly! If we try to obtain — as is necessary — a more detailed conception of the structure of the gel, we have to choose between an open and a closed cell structure. Assuming the former, one could only accept BANCROFT's hypothesis, if the surface tension of the diluted phase with regard to the concentrated one is as that of mercury with regard to glass. We have investigated, whether this is the case by covering glass capillaries on the inner surface with a thin layer of gelatine, agar, celloïdin or rubber. We found a behaviour as that of water-glass; only in the case of vapour-swollen or dry gelatine we observed a convex meniscus; gelatine, swollen in liquid, behaved as the other bodies. An open cell structure is, therefore, not consistent with BANCROFT's explanation. Another fact may be mentioned. which also speaks against this assumption; a plate of gelatine, dipped half way and vertically in water, only swells for the lower part, while the part above the water surface presents exactly as gelatine in equilibrium with vapour. For if there were an open cell structure, the canals should fill themselves by capillary action. Whether an open or a closed structure is obtained, will depend on the question, which phase separates first. If this is the most concentrated and consequently the most viscous one, an open structure will arise and the water will have a concave surface; if, on the contrary, the latter appears first, it will of course show a convex meniscus. If, therefore, we accept BANCROFT's explanation, we are obliged to suppose that the phase with much water separates first in all the systems that show the phenomenon; of course, this

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[1]) See especially BACHMANN, loc. cit.

[2]) BECHHOLD, Z. phys. Chem. **52**, 185.

is not impossible. In the case of silica and alumina jellies, where the concentrated phase separates, an open structure is to be expected. Since the surface tension will probably be similar to that of waterglass — the gel is completely moistened by water —, the gel will not show von SCHROEDER's phenomenon. In fact, we did not find it (nor did VAN BEMMELEN), in opposition to BANCROFT's declaration, that gelatine and aluminium gel are theoretically equivalent.

It is, therefore, possible to explain in this manner, why gelatine, swollen in water, loses water, when in a space saturated with vapour; we should even be able to calculate the size of the drops by the difference of the vapour pressures of the gelatine swollen in vapour and in water. VON SCHROEDER has tried to measure this difference by allowing gelatine to swell in salt solutions and by determining the concentration of the solution, in which the phenomenon no more appeared. He found this to be the case in a solution of sodium sulphate of a normality between 10^{-5} and 10^{-6}. This would give a difference in vapour pressure of ± 3.10^{-5} mm. of water, out of which the radius of the drops in the gel can be calculated to ± 9 mm.[1]), evidently an impossible result. In fact, we have, in repeating VON SCHROEDER's experiments, obtained different results: celloïdin, swollen in a solution of $3^{\circ}/_{0}$ sublimate in absolute alcohol, does show the phenomenon. We intend to try to determine the difference of the vapour pressures by a direct method. If, on the other hand, we suppose the diameter of the drops in gelatine to be 5 $\mu\mu$[2]), we calculate, that the vapour pressures must differ ± 100 mm. of water, which to us seems a rather high amount.

There is, however, a serious objection to be raised against this explanation. The gel, swollen in liquid, loses water in the vapour; in consequence of which either cavities, filled with air and vapour, are formed, or the gel shrinks, according to its losing water. Silica jelly shows the first alternative, as is proved by its opaqueness, appearing at a certain point; gelatine, agar, celloidin and rubber, however, remain quite clear, but their volume is diminished. *Now, if there are no cavities, we do not see, why they should be formed anew, when the gel is replaced in the liquid.* This objection, we think, entirely pulls down BANCROFT's theory.

As to VON SCHROEDER's remarks, we must observe, that they do not give an explanation in the proper sense of the word. VON SCHROEDER only wants to put an end to the controversy against the second law, by remarking, that the gel is taken from the liquid and

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[1]) According to the formula: $\Delta p = \dfrac{2\alpha\delta}{DR}$ (see Chwolson, Lehrb. d. Phys. III, 744), and assuming that the drops are bulbs.

[2]) 5 $\mu\mu$ is the diameter of the capillary canals in silica jelly, as put by Zsigmondy.

placed in the vapour very quickly and that the velocity of this process influences the work done. As BANCROFT says, this alleged explanation is not likely to satisfy anybody; moreover it can be refuted by arranging VON SCHROEDER's imaginary experiment in a slightly different manner. Pour upon the gelatine (in equilibrium with vapour) as much water, as can be totally absorbed, and place the whole in saturated vapour; it will now lose weight, till the vapour equilibrium is reached again. In this way the excess work, in VON SCHROEDER's opinion necessary for taking the gelatine quickly out of the liquid, is eliminated.

FREUNDLICH [1]) introduces special attracting forces of the surrounding liquid on the gel. As long as one does not enter into detail as to the nature of which these forces are, nor why they have so much influence especially with the gels, this explanation does not seem to be more than a circumscription of the facts, and we agree with BANCROFT, who declares it to be "neither very clear, nor very convincing".

We must acknowledge, however, that we ourselves are not able to give a better one. When looking for the directions, in which the solution might be sought, we find hysteresis, gravity, and capillary action. Hysteresis, of course, would do away with the possibility of a perpetuum mobile of the second kind; we should then have to assume, that every time slight changes are left in the gel, and that it would consequently be impossible to detect ad infinitum differences in water content, when the process of transferring the gel from liquid to vapour, and vice versa, is repeated. No fact, pointing in this direction, has however been found, neither by VON SCHROEDER nor by us; but it may be, that the process has not been repeated often enough; of course, this is not a more fundamental explanation either.

Concerning the influence of gravity, we wish to remark, that it might possibly explain the loss in the vapour, but never the gain in the liquid. Moreover, VON SCHROEDER made some experiments with regard to the influence of gravity, but with negative results. This would not, however, be a sufficient ground to deny the effect of gravity, since, as BANCROFT justly remarks, the effect might be too small for observation.

When, at last, we try to ascribe the phenomenon to the action of capillary forces, we do not make more progress than FREUNDLICH, though in this direction perhaps success will be most probable.

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[1]) Kapillarchemie, p. 494—497.

Microbiology. — "*Penetration of methyleneblue into living cells after desiccation*". By Prof. Dr. M. W. Beijerinck.

(Communicated in the meeting of December 28, 1912).

It is generally known that methyleneblue does not enter living yeastcells, when these are first soaked with water or swimming in a fermenting liquid, whilst it colours the dead cells intensely. It is even possible several days to cultivate yeast in wort, coloured dark blue with this pigment, without the cells being coloured in the least. On wortagar plates with methyleneblue, colourless colonies will develop. On these facts a method is based to ascertain in living yeast the number of dead cells, which gives very good results.

Meanwhile there is an exception to the rule that the cells, colouring blue are dead, and this exception will be more closely considered here.

At the examination of dried yeast, most cells of which take a dark blue colour with methyleneblue, whilst only a very small percentage remain colourless, the fermenting power often proves so great, that no other explanation can be given, but that the blue-colouring cells have for the greater part preserved that power. This is not unexpected, for it is well known that the alcoholic function is more permanent in dieing cells than the power of growth. Meanwhile, counting-experiments, whereby on one hand the number of cells colouring with methyleneblue was microscopically determined, on the other hand by plate culture, that of the cells growing out to colonies, showed that from certain dry yeast samples a much greater percentage of colonies developed, than the percentage of cells not colouring with methyleneblue. This fact was indeed unexpected and induced to a more minute observation.

First of all it was proved that the number of cells, colouring in a dilute solution of methyleneblue, depends on the way in which the solution is brought into contact with the cells. If this is done by introducing dry yeast into the solution, all the cells colour dark-blue and cannot be distinguished from the dead ones. In plate cultures, however, a greater or smaller number of colonies may be obtained from these cells, although all seem perfectly alike in their dark blue colour, and should be considered as dead by anyone ignorant of their origin. In favourable circumstances the number of colonies mounts even to 100 %, which is to say, that all the cells may colour blue and still grow out to colonies.

This is in particular obvious when the cells are beforehand coloured with methyleneblue, and the coloured material is used for sowing; it is easy then to recognise the blue cells on the plate and watch their germination under the microscope. The blue colour is then commonly seen to disappear before the formation of buds begins. But many of the later germinating cells remain blue and produce colourless daughter-cells. I never saw young cells taking the least trace of blue from the mother-cell.

But if the dried cells are beforehand allowed to swell up in wort or in water and if the soaked material is laid in the methyleneblue solution, which is the usual way to effect the colour reaction, the result is quite different. Then only part of the cells assume the colour and this part is the smaller as the cells have longer remained in the uncoloured solution. A certain percentage, however, continue to take up the colour without having lost their reproductive power, and it seems to be very difficult to soak these cells with water.

The simplest way to effect these experiments is by using dry yeast, quite free, or nearly so from dead cells. I obtained it by centrifugation of the small-celled variety of pressed yeast from strong fermentations, these being in their most active state.

To this end it was cultivated at 28° C. in nearly neutral wort, after 6 to 8 hours brought into the centrifuge, and then quickly transferred to filterpaper in a thin layer for desiccation.

The large-celled variety of pressed yeast is less resistant to drying. To compare the two varieties, of which the smallcelled is richer in protoplasm than the other, the yeast must very cautiously be dried, first at low temperature, e.g. 25° C., then at a higher one, e.g. 50° C. This precaution is not, however, necessary to render the blue-colouring of the dry living cells visible; to this end drying of common yeast at room temperature will do.

I have, however, also met with commercial dry yeast satisfying the requirement of containing hardly any dead cells at all, namely the "Konservierte Getreide Brennerei Hefe" of the yeast works of HELBING in Hamburg, which was sent directly from the manufactory. This preparation is delivered in solidly closed tins, but after some time it loses its power of growth and fermentation; its quality thus evidently depends on the length of time past since its fabrication. It seems that this loss corresponds to that of the germinative power of seeds, which depends on their state of humidity. I possess some more preparations from the same factory, that have hardly any fermentative power and contain no cells fit for reproduction, but they have not been directly got from the manufactory and are already some years old.

When using seed of *Brassica rapa*, soaked in solutions of 1 per

1000 or less of methyleneblue, the pigment penetrates through the seed coat into the germ, which partly colours blue. The germroot takes up the colour the earliest; then follows a triangular field on the outer of the two seedlobes, which lie folded up in the seed. The base of the triangle, which colours first and most intensely, lies at that margin of the cotyledo, which is turned towards the germroot.

Obviously the pigment has very quickly penetrated through the micropyle of the seed, and only later through the seed coat. With stronger methyleneblue solutions the experiments do not succeed much better, because then the pigment accumulates so much in the seed coat, that even water can only enter with difficulty. After 24 hours such seeds are but imperfectly swollen but, somewhat later, the germination takes place as well. The coloured germs swell at 30° C. so vigorously, that many soon burst out of the seed coat. When the partly blue germs, freed from the seed coat, germinate on filterpaper, they yield part of their pigment to it, but especially in the meristem of the germroot it continues to show for several days and disappears only at length, by the dilution which accompanies the growth. It is then easy to see how the part near the rootmeristem grows the most rapidly whilst the region of the roothairs grows no more at all.

That the pigment, without killing the cells, has penetrated into the inner part of the tissues, is not only shown by the germroots, but also by the coloured spots of the seedlobes, whose phloembundles even have taken up the colour.

Botany. — *"On Karyokinesis in Eunotia major Rabenh."*. By Prof. C. van Wisselingh. (Communicated by Prof. Moll).

(Communicated in the meeting of November 30, 1912).

Lauterborn's [1]) detailed investigation on Diatomaceae suddenly brought about in 1896 a complete change in our knowledge of the karyokinesis of these organisms. This investigator studied the process in Surirella calcarata, Nitzschia sigmoidea, Pleurosigma attenuatum, Pinnularia oblonga, and Pinnularia viridis. He came to the conclusion that the nuclei always divide karyokinetically. The karyokinesis here is not less complex than in higher plants. It shows an important deviation. For Lauterborn found that in all cases during karyoki-

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[1]) R. Lauterborn, Untersuchungen über Bau, Kernteilung und Bewegung der Diatomeen, 1896.

nesis a body appears, which plays an important part, namely the central spindle (Zentralspindel), a body which does not occur in higher plants, but is specially found in Diatomaceae. During karyokinesis the nucleolus and the nuclear membrane disappear. The network forms a skein (Knäuel) and by segmentation the chromosomes arise out of it. They are long and well-formed. In Nitzschia 16 appear and more in Surirella. In the middle the chromosomes form a ring round the central spindle. By division of this ring there arise two rings which separate from each other along the central spindle. Each of these rings consists of the halves of the chromosomes. The daughter nuclei develop from the rings.

Shortly after LAUTERBORN a paper was published by KLEBAHN [1]) on karyokinesis in Rhopalodia gibba (Ehrenb.) O. Müller. He describes the diaster stage and mentions the central spindle and the chromosomes which to the number of 5 or 6 are placed in a circle and are granular in shape.

Some years later KARSTEN [2]) described in detail the karyokinesis of Surirella saxonica. In general his results agree with those of LAUTERBORN; in one point however they disagree greatly, for KARSTEN found the chromosomes in Surirella calcarata and other Diatomaceae short and of irregular shape in complete contrast with the observations of LAUTERBORN.

In October 1903 I found an Eunotia in a ditch near Steenwijk. After further examination and consultation of the descriptions and drawings of the various species [3]), I assumed that the specimen found was Eunotia major Rabenh. In the healthy, although not plentiful, material I saw numerous stages of karyokinesis, and since this phenomenon had not yet been described in Eunotia, I determined to utilise this opportunity of studying it.

The living object was first investigated, and then material which had been fixed with FLEMMING's mixture. In order to study the karyokinetic figures better I treated the fixed material with a solution of chromic acid of 20°/₀. Various constituents of the cell-contents successively dissolve in it and finally there remains inside the siliceous skeleton of the cell-wall, when the cells contain no fatty oil, only the nuclear network, or what results from it. The prepa-

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[1]) H. KLEBAHN, Beiträge zur Kenntnis der Auxosporenbildung, I. Rhopalodia gibba (Ehrenb.) O. Müller, Pringsheim's Jahrb. f. wiss. Bot. Bd. 29, 1896, p. 595.

[2]) G. KARSTEN, Die Auxosporenbildung der Gattungen Cocconeïs, Surirella und Cymatopleura, Flora, 1900, Bd. 87. p. 253.

[3]) L. DIPPEL, Diatomeen der Rhein-Mainebene, 1905, p. 125.

VAN HEURCK, Traité des Diatomées, p. 298.

rations can easily be washed with water and stained, for example, with Brillantblau extra grünlich. The nuclear network, the nuclear plate or its halves which all fall over during the action of chromic acid are then stained a fine blue whilst the siliceous skeleton is not stained. I will not enlarge on the method followed. I have already earlier stated the advantages which it possesses and which must be borne in mind in its application [1]).

Like other Diatomaceae Eunotia major has but one nucleus, situated in the centre and surrounded by cytoplasm, which sends out strands in various directions. As seen from the side of the belt it shows an oval shape and seen laterally it is round. It is provided with a membrane and consequently shows a sharp outline. The nuclear network consists of grains which are united by threads of protoplasm. In the centre of the nucleus is the nucleolus. The latter dissolves in chromic acid more readily than the network. Special filamentous organs, such as occur in the nucleolus of Spirogyra, I have not been able to distinguish and to separate by the use of chromic acid in the case of Eunotia. The nucleolus agrees with that of the higher plants.

The cells in which karyokinesis is about to occur are broader than the others and possess four large flap-shaped chromatophores. When the cells are viewed from the side of the belt, the nucleus is seen in the midst of the four chromatophores, two of which lie in the epitheca and two in the hypotheca. When a cell has divided, two chromatophores lie in each daughter-cell. These change their shape and position. They become twice as long and place themselves opposite each other in the epitheca and the hypotheca. A constriction then occurs in the middle and finally each chromatophore has divided into two. This process, the division of the two chromatophores, therefore precedes the division of nucleus and cell.

The first phenomena of karyokinesis show agreement with those observed in other plants. The nuclear network becomes more and more roughly granular in appearance. In a number of places it conglomerates and forms lumps, which unite into larger masses which more or less resemble short threads. I have not been able to determine the number of these thicker parts in the network. They always remain united to each other by slender connections.

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[1]) Ueber den Nukleolus von Spirogyra. (Bot. Zeitung. Jahrg. 56. 1898. Abt. I. p. 199). — Ueber das Kerngerüst. (Bot. Zeitung. Jahrg. 57. 1899. Abt. I p. 155). — Ueber die Karyokinese bei Oedogonium. (Beih. z. Bot. Centralbl. Bd. XXIII. 1908. Abt. I. p. 138 ff.). — Ueber die Kernstructur und Kernteilung bei Closterium. (Beih. z. Bot. Centalbl. Bd. XXVII 1912. Abt. I. p. 414).

The thicker parts are comparable to chromosomes. Well-formed chromosomes, such as are met with elsewhere in the vegetable kingdom, do not occur in Eunotia. The nuclear wall dissolves and consequently the nucleus loses its sharp outline; the nucleolus also gradually disappears.

To this point karyokinesis in Eunotia presents nothing peculiar, but the further course of the process is wholly different from that in higher plants. In the centre of the mass of protoplasm in which the nucleus is found, the central spindle can soon be distinguished. It is a strand of protoplasm of which the outer ends are turned towards the two shells. At first I could distinguish the central spindle as a short rod embedded in the protoplasm, but in later stages of karyokinesis I observed it extending right across the whole mass of protoplasm; the two ends were seen to be club shaped and thickened. I was unable to study the origin of the central spindle, since the amount of material at my disposal was insufficient.

The nuclear network contracts around the central spindle, and in this way the ring shaped nuclear plate is formed in Eunotia. The latter divides into two halves which are likewise annular and separate from each other along the central spindle, until they are finally quite at the spindle ends. Together with this, there occurs division of the mass of protoplasm in which the nuclear plate lies. It divides into two parts, which send out strands of protoplasm in different directions just as did the whole mass and at first they are also connected with one another by strands of protoplasm. The whole figure very much resembles the diaster stage in higher plants, although I have never been able to distinguish a nuclear spindle. Meanwhile the primary division-wall has developed; it broadens out more and more and approaches the nuclear figure; the protoplasmic links between the halves of the nuclear plate and the central spindle are divided into two. The central spindle disappears. The daughter-nuclei are now very close against the division-wall, then separate again from each other, move into the neighbourhood of the epitheca and hypotheca and finally take up a position in the middle of the daughter-cells.

With the development of the annular halves of the nuclear plate into daughter-nuclei the same phenomena appear as in the formation of the nuclear plate from the resting nucleus, but in reverse order. The rings divide into lumps or short thread-shaped pieces which remain connected with each other by fine threads of protoplasm; the division proceeds to a point at which the nuclear network agrees again with that of the resting nucleus. In fully-developed nuclei I always saw one nucleolus and in less-developed ones often there were two. Probably also in Eunotia the nucleoli which appear in the daughter-nuclei gradually coalesce.

The primary division-wall, of which mention has been made, is a lamella easily soluble in dilute chromic acid. The siliceous shells are formed later. I have not found a centrosome in Eunotia.

Conclusions.

In Eunotia major Rabenh. the nucleus divides karyokinetically just as in other Diatomaceae, a fact established by LAUTERBORN and KARSTEN. In Eunotia major a central spindle (Zentralspindel) also occurs, a body which plays an important part in karyokinesis, as the above authors have also shown in other Diatomaceae. Well-developed chromosomes are not found in Eunotia major. The nuclear network forms short bodies of indefinite shape, which crowd round the central spindle and form an annular nuclear plate, which divides into two annular halves; these separate from each other along the central spindle and develop into daughter-cells.

With regard to the chromosomes, I may say that my results agree with those of KLEBAHN and KARSTEN, but not with those of LAUTERBORN. He found in Surirella calcarata and other Diatomaceae, in the mother-nucleus as well as in the daughter-nuclei, well developed long chromosomes, whose number could be ascertained (16 or more). KLEBAHN has not been able to see such chromosomes in Rhopalodia gibba nor KARSTEN in Surirella saxonica, but as I did in Eunotia major they found only a few short thick bodies of various shapes which could not be accurately described, and whose number was indeterminate. It must be remembered that the results which differ were obtained with different species.

Physiology. — *"On a shortening-reflex"*. By Prof. J. K. A. WERTHEIM SALOMONSON.

(Communicated in the meeting of December 28, 1912).

By the expression shortening reflex I propose to indicate the contraction of a muscle, the ends of which are passively brought nearer together. I shall try to prove this contraction to be a real reflex, though the primary shortening of the muscle may not be the direct cause.

We shall first consider what happens when any part of an extremity is moved passively, in which case one set of muscles is stretched, another group being shortened.

A living animal's muscles at rest are generally not entirely relaxed. A slight degree of elastic tension, called *tonus*, persists. Tonus is for the greater part caused and restrained by regulating impulses, originating from peripheral sensory and higher motor neurones. Also the cortex and the gangliongroups of the cerebrum, the labyrinth, the cerebellum control and influence the muscular tonus. Tonus varies under different circumstances, but it adapts itself automatically to the rate of stretching of the muscle. If the muscle be slowly stretched by a passive movement of the limb, its form changes. The muscle grows longer and thinner. But its tension does not change at the same rate. Only if the stretching be carried very far or happens within a very short space of time its elastic tension grows appreciably.

With a passive shortening of the muscle something analogous occurs. The length diminishes, the diameter increases but the tension adapts itself automatically to the new condition, and the muscle does not become slackened so far as to show folds or furrows.

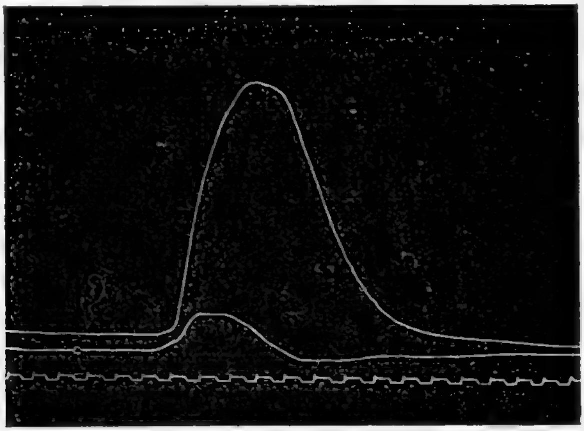
This adaptibility only persists as long as the muscle remains in contact with the intact nervous system. As soon as the muscle is freed from its nerve, its reflex-tonus disappears and it seems to behave simply as an elastic string, in which a definite tension corresponds to a definite length. The action of the nervous system seems to equalise the tension for different lengths and causes the resting-length of an innervated muscle to be a varying quantity.

If the passive shortening of a muscle is effected within a very short time *we sometimes observe a genuine contraction of the muscle* followed by the thickening caused by the reflextonus. This phenomenon I have called the shortening reflex.

If the foot be passively and somewhat forcibly extended (= dorsal flexion) we are sometimes able to see and feel a very short contraction of the m. tibialis anticus. After this contraction the tonus-thickening becomes visible. The contraction cannot be elicited in every healthy individual, and even where it is to be found, it is often rather difficult to obtain. We get it most easily in the tibialis anticus by extending the foot. In some cases I have also found it in other muscles, as in the flexors of the arm, the flexors of the leg after flexing the arm or the leg.

I have recorded the phenomenon with a special apparatus, constructed some 9 years ago for recording the foot-clonus. The difficulty was to rigidly attach a pair of MAREY's tambours to the bony parts of the leg, so as not to become displaced by the violent movements of the leg during the clonus. This difficulty was overcome by attaching a clamp to the upper part of the tibia and another to both malleoli, and connecting them by a very light hollow rod. To this rod the tambours were screwed with a pair of collars. With this arrangement which proved to be entirely satisfactory, I was able to record the thickening curve of any desired muscle of the leg and also the displacement of the foot with respect to the leg.

Fig. 1.



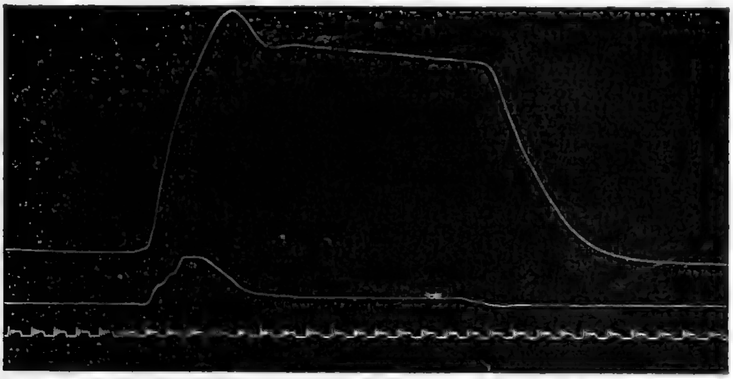
Shortening reflex in the tibialis anticus of a healthy man.
Upper curve: displacement of the foot.
Middle curve: thickening curve of tibialis anticus.
Lower curve: time marks of 0.1 second.

I reproduce a few records (fig. 1 and fig. 2) which were taken in this way. The upper line shows the movement of the foot; rising of the curve indicates dorsal flexion. The middle curve is a record of the thickening of the tibialis anticus. The time curve gives marks of 0,1 of a second.

Fig. 1 shows the tibialis contraction occurring with a short dorsal flexion of the foot. Fig. 2 gives the record of tibialis contraction caused by a rapid dorsal flexion of the foot, the foot being kept in dorsal flexion for nearly two seconds. In this last record we clearly see the initial tibialis twitch followed by the reflextonus-thickening.

From the records we soon gather the fact, that the tibialis response immediately follows the foot movement. By comparing a great many records we also find that the interval between the commencement of the foot-movement and the beginning of the tibialis-muscle-twitch is of a very short and yet extremely constant duration. If as the beginning of the footmovement be taken a point where the curve has risen about 1 millimetre, and a similar point on the tibialiscurve as the commencement of the muscle-twitch, the interval comes out as something between 0.028—0.032 second.

Fig. 2.



Shortening reflex in the tibialis anticus of a healthy man.
Upper curve: displacement of the foot.
Middle curve: thickening curve of tibialis anticus.
Lower curve: time marks of 0.1 second.

This fact points in the direction of a reflexphenomenon. If we had to deal with a voluntary contraction, the latent period would have been a great deal less constant. It is also a fact, that the interval between an external stimulus and the commencement of a voluntary movement is of the order of 0.12—0.15 second with a fairly experienced subject. Constancy of this latent period is only to be expected with the most experienced subjects or after a special training. The latency of sensory reflexes is much more constant, but it depends in most cases chiefly on the intensity of the stimulus. The highest constancy is shown only in the deep reflexes, in which the intensity of the stimulus does not seem to possess any influence on the latency. The latent period of the superficial reflexes is generally of the order of 0.07—0.09 of a second, whereas the deep reflexes show a latency of the order of 0.035 second. With these figures we have to take into account that the latency is measured from the commencement of the stimulus until the commencement of the muscular response as indicated by the *mechanical* record. If we had recorded the current of action we should have found lower figures.

In my experiments I was not able to get more exact or smaller figures for the latency. This was not due to the fact that I used a mechanically recording instrument, but only to the difficulty in determining the exact moment of the stimulus. The stimulus is applied during the passive movement of the foot. But we cannot tell the exact moment at which the stimulus is produced. Must the foot move with a certain velocity or must it travel over a certain distance? Perhaps both conditions are necessary. At least with a very slow movement of the foot we only obtain the tonus-thickening and with a very rapid movement over a short distance only, we sometimes fail and sometimes succeed in getting it. Therefore it is impossible to indicate the exact point in the record of the foot-movement which is to be considered as the beginning of the stimulus. If I take the first point in which both curves begin to rise from the zero-line, I find a latency from 0.038—0.045 of a second, with an average of 0.041 second. If we take a rise of 1 millimetre in both curves as the beginning of the stimulus and the response, we get an average of 0.029 second. Though the exact figure is doubtful, it is yet of interest to note that it agrees closely with the average latency found in the deep reflexes.

The duration of the muscular response has also to be considered. From direct observation and also from most of the records we come to the conclusion that we have before us a simple muscle-twitch, the duration of which is something between 0.2—0.5 second. Only in cases where the foot has been moved with great force, or has been kept in prolonged dorsal flexion, a muscular response of longer duration may be found. But in these cases the contraction shows a peculiarity, clearly visible in fig. 3, viz. a second contraction appearing before the first is finished. We shall consider this point later on.

As from our observations we see that: 1^{ly} the latent period is constant, 2^{dly} that the latency agrees with the latency observed in deep reflex, 3^{dly} that the contraction is generally a simple muscle-twitch, we may conclude that the phenomenon itself is a real reflex.

This being established we may ask where the reflexcentrum is situated, which is the reflexogene mechanism and which is the significance of the reflex.

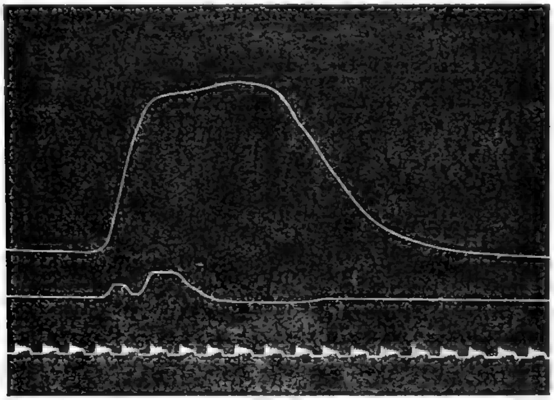
We may conclude from the latency that the reflexcentrum cannot be situated very high up in the central nervous system. I believe that another supposition as a medullary seat for the centrum need not be considered. The reflex has a close similarity to the deep reflexes and may probably be regarded as a third group of this kind, the other groups being formed by the tendonreflexes and the periostreflexes.

It is somewhat more difficult to understand the reflex-mechanism. We only know that the reflex is elicited by passive dorsal flexion of the foot. But then two things happen simultaneously : the extension-muscles of the foot are shortened and the triceps surae is stretched. Which of the two causes the reflex? I fail to see the possibility of choosing between the two on clinical grounds only. In the accident of a torn or cut Achillestendon, which is unlikely to occur in a healthy man, only a positive result would have any significance, as the reflex cannot invariably be elicited in healthy individuals. Some pathological arguments might perhaps be brought forward in support of the hypothesis, that the reflex is primarely caused not by the shortening of the muscle itself, but by the stretching of the antagonist.

As regards the significance of the reflex we may assume that it is the same as that of more elementary reflexes, viz, a means of protecting the organism against exogene stimuli. The obvious fact is that the contraction assists the automatic tonus-mechanism in attaining as soon as possible the necessary muscular tension corresponding to the changed attitude. Hence we conclude that the reflex is a protecting mechanism against a total want of control over the position of the foot, if the foot is passively moved.

I have already mentioned that in a few records a second contraction of the tibialis anticus appeared immediately after the first (fig. 3). This may be caused either by a voluntary or by an involuntary impulse. In my experiments I have tried to exclude as much as possible any voluntary movements by impressing upon the subjects

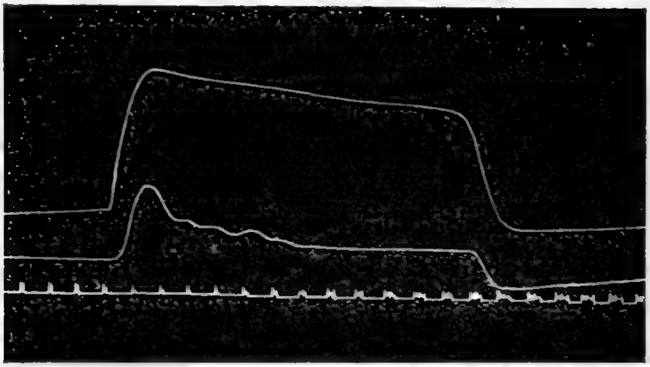
Fig. 3.



Shortening reflex of the healthy leg of a hemiplegic patient.

to keep their muscles relaxed, and to try not to make any movement. Judging from the curves, this request has been attended to, as the duration and form of the second contraction seem to exclude the possibility of a voluntary origin. I think I may assume that the second contraction was not caused by any intended or conscious impulse. But then we have two possibilities. Either the second contraction was also a reflex-response, but from a higher nervous level, or it might be the first from a strongly damped clonus. I am inclined to think, that in most cases the second contraction was caused by a reflex from a higher level, though I cannot prove it. But on the other hand I must also accept the other explanation. Amongst a series of curves taken from the "normal" leg of a hemiplegic patient, which often show the form of fig. 3, I found one single record

Fig. 4.

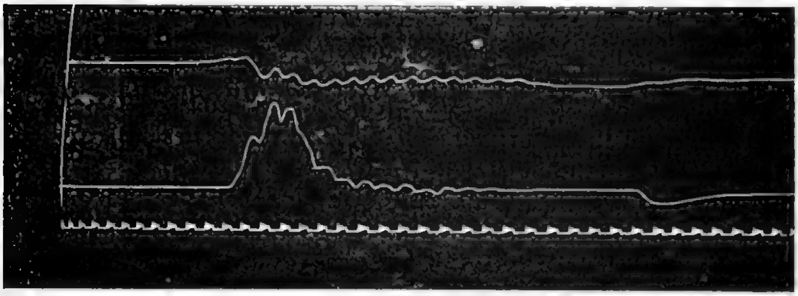


Curve from the same patient from whom fig. 3 was taken.

reproduced in fig. 4. Here we see that the tibialis contraction as soon as it is started, degenerates into a series of rhythmic, gradually ceasing clonic oscillations. In another patient suffering from a medullary disease, I obtained the record, shown in fig. 5. This record differs from the fig. 1—4 in as much as the upper curve does not represent the movement of the foot, but the thickening of the triceps surae. We immediately see, that the dorsal flexion of the foot starts the reflex and at the same time a series of clonic contractions in both the tibialis anticus and the triceps surae. These last contractions prove at least the possibility of the second tibialis contraction being the first of a strongly damped clonus.

As yet I have not considered the literature. There is some reason for this, as I have not been able to find in it any reference to a reflex such as has been described as appearing in healthy subjects. I have only found the well-known paradoxical contraction of

Fig. 5

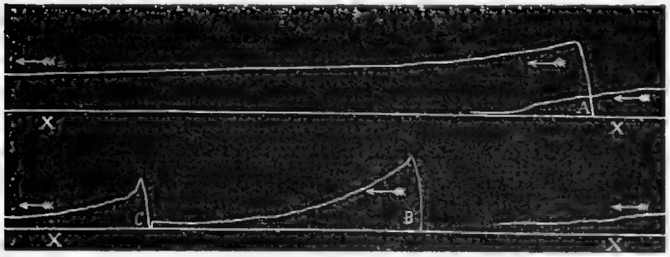


Shortening reflex in a case of arteriosclerotic medullary disease; clonic contractions in triceps (upper curve) and tibialis anticus (middle curve).

Westfahl (1880), which is a *tonic* contraction of the tibialis anticus appearing at dorsal flexion of the foot in some patients. It is of rather long duration, Westfahl observing a contraction of 27 minutes, Erlenmeijer of 45 minutes' duration. Charcot has seen the same contraction, also after massage of the calves and has taken graphic records, one of which, taken from his article in Brain (VIII p. 268) I reproduce here (fig. 6). From this curve and the explanatory text, also reproduced, we immediately see, that this contraction is not at all the same thing as the shortening reflex.

But there seems to be no doubt, that a relationship exists between

Fig. 6.



Same patient (April 12th). Tracing of contraction of the tibialis anticus obtained by massage of the muscles of the calf. — A, B, C, beginnings of three consecutive experiments. (In this and the last figure—much reduced in size—the length of XX represents one whole turn of the cylinder, viz. thirty minutes.)

the shortening reflex and the paradoxal contraction. I am inclined to suppose that the latter is the pathological form of the first.

The curves I have given as physiological were those taken in a patient with a severe trigeminus-neuralgia caused by periostitis alveolaris, who is now cured. His reflexes were not altered in the least.

The curves 3 and 4 were taken from the healthy side of a hemiplegic patient and are perhaps not to be considered as purely physiological. There is some reason to suppose, that hemiplegia may cause a heightening of the shortening reflex of the healthy extremity.

Amongst the pathological forms of the reflex we might perhaps include some forms of hysterical contracture and also some cases of crampi. But I intended to consider only the physiological aspects of the reflex.

Physics. — *"On the thermodynamical functions for mixtures of reacting components."* By Dr. L. S. Ornstein. (Communicated by Prof. H. A. Lorentz).

(Communicated in the meeting of November 30, 1912).

In his dissertation Dr. P. J. H. Hoenen has developed a theory of the thermodynamical functions for mixtures of reacting components [1]). Considerations closely connected to those of this dissertation are obtained if the statistical method of Gibbs is applied to the study of the equilibrium in chemical systems. I will show this in the following communication, and will restrict myself to the case that only one kind of reactions is possible in the mixture, the extension to other cases being possible without any difficulty.

In the following considerations I shall use a canonical ensemble of the modulus $\Theta\left(=\frac{R}{N}T\right)$ (R is the constant of Avogrado for the grammolecule, N the number of molecules present in this quantity of matter. We might as well use the micro-canonical ensembles; but for the calculations then being somewhat more complicated.

The molecules participating in the reaction are indicated by $\mu_1 \ldots \mu_\lambda \ldots \mu_k$ Then the reaction will be characterised by the stoechiometrical formula

$$\sum_1^k \nu_\lambda \mu_\lambda = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

the numbers ν_λ indicating the smallest numbers of molecules that

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[1]) Dissertation Leiden 1912, comp. also these proceedings XV p. 614.

can take part in the reaction. The r's are necessarily whole numbers, some of them must be negative.

We will imagine the molecules to be built up of atoms $a_1 \ldots a_\pi \ldots a_p$ in such a way that the chemical formula for the κ^{th} molecule is

$$\mu_\kappa = y_{\kappa 1} a_1 + \ldots y_{\kappa\pi} a_\pi + \ldots y_{\kappa p} a_p \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

the numbers $y_{\kappa\pi}$ being positive whole numbers or zero.

We will first treat the case that the system has so great a volume that the mutual action of the molecules may be neglected in the expression of the energy.

The state of the system can be characterised by the coordinates of the centres of gravity of the molecules and the corresponding moments of momentum and by a certain number of internal coordinates and moments of momentum. The expression giving the energy of each molecule consists in the kinetical energy of the centrum of inertia, a quadratic expression in the moments of momentum of this centrum, the coordinates of the centrum of inertia not playing a part. Further in the energy corresponding to the internal coordinates, which I shall represent by ε_κ. An element of the extension in phase corresponding to the internal coordinates of the κ^{th} molecules will be represented by $d\lambda_\kappa$. Be the mass of the molecules m_κ.

Be the total number of systems of the ensemble N, the statistical free energy Ψ.

We now want to know the number of systems (z'') in this ensemble, for which $n_1 \ldots n_\kappa \ldots n_k$ molecules of the different kinds are present in the volume V. That is to say those molecules produced by a completely specified combination of atoms, for which the internal coordinates and moments are situated in completely determined elements $d\lambda_1 \ldots d\lambda_\kappa \ldots d\lambda_k$. As for the situation of the molecules within the volume V, and the moments of momentum of the centres of gravity, we will not apply any restricting conditions [1]. We find for z''

$$z'' = N e^{\frac{\Psi}{\Theta}} \prod_1^k (2\pi m_\kappa \Theta)^{\frac{3}{2} n_\kappa} \left(e^{-\frac{\varepsilon_\kappa}{\Theta}} d\lambda_\kappa \right)^{n_\kappa} V^{n_\kappa} \quad . \quad . \quad . \quad (3)$$

The number of systems in which no restrictions are applied not even for the internal coordinates and moments is obtained by integrating over the $d\lambda_\kappa$'s with respect to all possible values.

We now put

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[1] Comp. for the case that one should want to specify for these quantities also, my diss. p. 39, where the case of non-reacting molecules is treated.

$$(2\pi m_\kappa \Theta)^{\frac{3}{2}} V \int e^{-\frac{\varepsilon_\kappa}{\Theta}} d\lambda_\kappa = I_\kappa \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

in which the integration must be extended over the above mentioned space. Now the number of the systems considered z' may be represented by

$$z' = N e^{\frac{\psi}{\Theta}} \prod_{1}^{k} I_\kappa^{n_\kappa} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Now we have to determine the number of systems in which the atoms are combined so as to give n_κ molecules of the κ^{th} kind, etc. We must bear in mind that the total number of atoms of each kind is fixed; so that when x_π is the number of atoms of the π^{th} kind, we have p equations of the form

$$n_1\, y_{1\pi} + \ldots n_\kappa\, y_{\kappa\pi} + \ldots \ldots n_k\, y_{k\pi} = x_\pi \quad . \quad . \quad . \quad . \quad (6)$$

Now, in order to get the number of combinations possible, we must in the first place consider that x_π atoms are to be combined into groups of $n_1 y_{1\pi} \ldots$ particles in

$$\frac{x_\pi!}{(n_1 y_{1\pi})! \ldots (n_\kappa y_{\kappa\pi})! \ldots (n_k y_{k\pi})!} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

different ways.

Further, that the number of different ways, in which $n_1 y_{1\pi}$ particles are to be combined into n_1 groups of $y_{1\pi}$ particles, is given by

$$\frac{(n_1\, y_{1\pi})!}{(y_{1\pi})_{n_1}\, n_1!\, (y_{1\pi}-1)!} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

In order finally to obtain the total number of cases possible, we still ought to consider in how many ways the n_1 groups of $y_{11} \ldots y_{1\pi} \ldots y_{1p}$ particles may be combined into molecules $a_1 y_{11} + \ldots a_\pi y_{1\pi} \ldots + a_p y_{1p}$. Suppose β_1 of the quantities $y_{1\pi}$ to differ from zero, then the wanted number of the combinations in question will be

$$(n_1!)^{\beta_1 - 1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

For the total number of combinations we find, bearing in mind that $(n_1!)^{\beta_1}$ etc. occurs in the denominator

$$\frac{x_1! \ldots x_\pi! \ldots x_p!}{n_1! \ldots n_\kappa! \ldots n_k! \,(y_{11} \ldots y_{1\pi} \ldots y_{1p})^{n_1} \ldots (y_{k1} \ldots y_{k\pi}\, y_{k\pi})^{n_k} (y_{11}-1)! \ldots (y_{kp}-1)!} \quad (10)$$

By uniting into a constant C the quantities not depending on n_κ, we get for the total number of systems, in which $n_\kappa \ldots$ molecules κ are present (z)

$$z = C\prod_{1}^{k}\frac{I_\nu^{n_\nu}}{n_\nu!\,(y_{\nu 1}\ldots y_{\nu\pi}\ldots y_{\nu p})^{n_\nu}} \quad . \quad . \quad (11)$$

(in which only those $y_{\nu\pi}$'s are to be taken into account that differ from zero). I will represent the factor $(y_{\nu 1}\ldots y_{\nu\pi}\ldots y_{\nu p})$ by s_ν.

Now in order to examine which of all systems is the most frequently occurring in the ensemble, which therefore is the system in equilibrium, we have to consider for which values of the n_ν, z or $\log z$, i. e.

$$\sum_{1}^{k} n_\nu\,(\log I_\nu - \log n_\nu + 1 - \log s_\nu) \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

is a maximum, ($n!$ being developed here according to the formula of STIRLING). The variations to which the numbers n_ν are submitted are $\alpha\nu_\nu$, in which α is a positive or negative whole number. The condition of equilibrium that is reached in this way is

$$\sum_{1}^{k} \nu_\nu\,(\log I_\nu - \log n_\nu - \log s_\nu) = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (12')$$

Introducing

$$I_\nu = (2\pi m_\nu \Theta)^{\frac{3}{2}}\, V\chi$$

for I_k, we get

$$\prod_{1}^{k} n_\nu^{\nu_\nu} = V^{\sum\limits_1^k \nu_\nu}\, T^{\frac{3}{2}\sum\limits_1^k \nu_\nu} \prod_{1}^{k}\left(\frac{2\pi m_\nu R}{N}\right)^{\frac{3}{2}\nu_\nu} \chi_\nu^{\nu_\nu} s_\nu^{-\nu_\nu} \quad . \quad . \quad (13)$$

As χ contains still terms that depend on T, this formula cannot yet be compared to that of Dr. HOENEN; however, in many regards it is already analogous to it. Now, applying the theorem that $\frac{R}{N}\log w$, (in which w is the probability of a state) is identical with the entropy, we find the entropy η of an arbitrarily chosen state to be given by

$$\eta = \frac{R}{N}\sum_{1}^{k} n_\nu\,\{\log I_\nu - \log n_\nu + 1 - \log s_\nu\} \quad . \quad . \quad . \quad . \quad (14)$$

This quantity therefore must agree with the entropy of a non-equilibrium state as defined by Dr. HOENEN. As appears from what is mentioned above, it possesses the quality of being a maximum in the state of equilibrium.

Now I will first use the result we obtained to calculate Ψ and through means of it the equation of state. Developing z with respect to α and summing up, we find for Ψ

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$$e^{-\frac{\Psi}{\Theta}} = C'' \prod_{1}^{k} \frac{I_{,}^{n_{,}}}{n_{,}^{n_{,}}(y_{,1} \dots y_{,p})^{n_{,}} e^{-n_{,}}} \quad \dots \dots \quad (15)$$

C'' is obtained from C', by dividing the total number of systems; $n_{,}$ denotes the value in the state of equilibrium.

Applying the relation

$$p = -\frac{\partial \Psi}{\partial V}$$

we find for the pressure

$$p = \frac{\Theta}{V} \sum_{1}^{k} n_{,} + + \Theta \sum_{1}^{k} (\log I_{,} - \log n_{,} - \log s_{,}) \frac{(n_{,} - n'_{,})}{dV},$$

where $n_{,}$ relates to the state of equilibrium of the volume V, $n'_{,}$ to that of the volume $V + dV$. These numbers always differ $\alpha r_{,}$, and so, taking into account the condition of equilibrium, we find

$$p = \frac{R\,T}{N\,V} \sum_{1}^{k} n_{,} \quad \dots \dots \dots \dots \quad (16)$$

In order to calculate the average energy we can apply the relation

$$\bar{\varepsilon} = \Psi - \Theta \frac{\partial \Psi}{\partial \Theta}$$

which gives, when the condition of equilibrium is taken into account

$$\bar{\varepsilon} = \sum_{1}^{k} n_{,} \left\{ \frac{3}{2} \frac{R}{N} T + \Theta^{2} \frac{\partial \log \chi_{,}}{\partial \Theta} \right\}.$$

Now, in many cases $\chi_{,}$ inasmuch as it depends on Θ, may be represented by $\Theta^{\gamma_{,}} q_{,}$ (q independent of Θ) or in other cases by a complicate function of Θ. So, in the first case,

$$\bar{\varepsilon} = \frac{R}{N} T \sum_{1}^{k} n_{,} \left(\frac{3}{2} + \gamma_{,} \right)$$

Putting the energy that is supplied when the numbers $n_{,}$ change with $r_{,}$, $c = \frac{R}{N} \Sigma\, r_{,} \left(\frac{3}{2} + \gamma_{,} \right)$, then we find that the condition of equilibrium (13) changes for this case into

$$\prod_{1}^{k} n_{,}^{r_{,}} = V^{\sum_{1}^{k} r_{,}}\, T^{\frac{N}{R}c} \prod_{1}^{k} \left\{ \left(\frac{2\pi\, m_{,} R}{N} \right)^{3/2} q_{,}\, s_{,} \right\}^{r_{,}} \quad \dots \quad (13^{a})$$

When we represent the energy of the molecules $\varepsilon_{,}$ by a constant $\alpha_{,}$ plus a function of the internal coordinates, then in the formula (13^{a}) the factor

$$e^{\sum_1^k \frac{a_\varkappa \nu_\varkappa N}{TR}}$$

still must be added. The formula obtained in this way agrees with that of p. 12 and 13 of the cited dissertation.

Just as in this dissertation p. 16, we can by comparing $dQ = d\varepsilon + pdv$ and $d\eta$ show that

$$d\eta > \frac{dQ}{T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

if we have to do with the changing into a state of non-equilibrium.

I will now consider what will become of our condition of equilibrium in the case we apply the theory of energy-quanta. Let us suppose we have the case of the molecules possessing 3 degrees of freedom of rotation, and $l_\varkappa$ vibratory degrees of freedom of the frequency $\tau_\varkappa$.

The value of $\chi_\varkappa$ can be given then. On account of the 3 rotations it contains a factor $\Theta^{3/2}$; further the integral is equal to a product of $l_\varkappa$ integrals of the form

$$\int e^{-\frac{\varepsilon_{t\lambda}}{\Theta}} d\lambda_{t\lambda}$$

relating to each of the vibrations. This integral has the value

$$\left(\frac{h\tau_\lambda}{1-e^{-\frac{h\tau_\lambda}{\Theta}}}\right)^{1)}$$

Introducing for each molecule the energy $a_\varkappa$ for the zero state and a constant originating from the integration with respect to the angular coordinates of the rotations, then the condition of equilibrium takes the form

$$\prod_1^k n_\varkappa^{\nu_\varkappa} = V^{\sum_1^k \nu_\varkappa} T^{3\sum_1^k \nu_\varkappa} \prod_1^k e^{-\frac{a_\varkappa \nu_\varkappa}{T}} S_\varkappa^{\nu_\varkappa} \prod_1^l \left(\frac{h\tau_\lambda}{1-e^{-\frac{h\tau_\lambda}{\Theta}}}\right)^{\nu_\varkappa} . \quad (18)$$

in which all constants relating to the molecules $\varkappa$ are contained in $S_\varkappa$. If the theory of quanta must be applied to some of the rotatory energies, then the exponent of T will be smaller.

As appears from the calculations of Dr. SCHEFFER[2]) the experi-

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[1]) The complications arising when equal frequencies occur are easily to be overcome. Comp. these proceedings 8 March 1912 p. 1103 and 1117.

[2]) These proceedings XIV. p. 743.

ments can more sufficiently be represented by applying the formula not of EINSTEIN, but of NERNST-LINDEMANN for the specific heat; the equation (18) leads for the specific heat to the formula of EINSTEIN. For solid matter BORN and VAN KARMAN have given a theory leading to a formula which seems to represent the experiments on s. h. as well as the formula of NERNST-LINDEMAN. They start from the conception that there cannot be attributed one definite frequency to the atoms of solid matter, but that, because of the coupling a great number of frequencies occur, which accumulate infinitely at one or more definite frequencies. The fact that the formula of NERNST is the more appropriate also for gases, makes it acceptable that also in gases, through the mutual influence of molecules, there cannot be spoken of a finite number of definite frequencies.

I may still observe, that for the given consideration the way in which the system at length comes into the most frequently occurring state, is of no importance. That it will get into it, may be regarded to be sure, as well from the point of view of statistical mechanics as from that of the theory of energy-quanta.

I will still consider now in what way we can, in liquid states, come to the condition of equilibrium. We must for a moment return to equation (3), then. There we could divide into parts relating to each of the molecules, the general integral which, according to the definition of GIBBS, denotes the number of systems of given state. However, in the case now considered we cannot proceed likewise, because of the mutual influence of the molecules. The number of systems of specified state is in general given by

$$N e^{\frac{\psi - \varepsilon}{\Theta}} dx_{11} \ldots dx_{n_\varkappa}\, m_1\, d\dot{x} \ldots m_\varkappa\, d\dot{x}_{n_\varkappa}\, d\lambda$$

where $x_{11} \ldots x_{n_\varkappa}$ represent the coordinates of the centres of gravity, n_{11} the velocities, and where $d\lambda$ relates to the internal coordinates and moments of all molecules. Now considering a system with $n_\varkappa$ molecules $\varkappa$, built up of specified atoms, and allowing all values for the coordinates of the centres of gravity, the total number of systems obtained in this way z'' may be represented by

$$N \prod_1^k (2\pi\, m_\varkappa\, \Theta)^{\frac{3}{2} \sum\limits_1^k n_\varkappa} \int e^{-\frac{\varepsilon'}{\Theta}} dx_1 \ldots d\lambda .$$

The value of the integral can always be represented by

$$V^{\sum\limits_1^k n_\varkappa} f(V\, n_1\, n_\varkappa \ldots n_k\, \Theta)$$

For a gas the function f takes the form of the function considered above. We will not consider the form more closely now. This being observed, it will be easy to point out the changes which (11), the formula that gives the number of systems, will undergo. We find

$$z = C f(V, n_1 \ldots n_\nu \ldots n_k, \Theta) \prod_1^k \frac{(2\pi\Theta m_\nu)^{\frac{3}{2}n_\nu} V^{n_\nu}}{n_\nu! \, (s_\nu)^{n_\nu}} \quad . \quad . \quad (19)$$

Asking again which is the most frequently occurring state, we find for the condition of equilibrium

$$\Sigma \nu_\nu \left(- \log n_\nu + \frac{3}{2} \log (2\pi\Theta m_\nu) + \log V - \log s_\nu + \frac{\partial \log f}{\partial n_\nu} \right) = 0. \quad . \quad (20)$$

For the statistical free energy we find

$$e^{-\frac{\Psi}{\Theta}} = \frac{C f(V n_1 \ldots n_\nu \ldots n_k, \Theta) \, V^{\sum\limits_1^k n_\nu} \, T^{\frac{3}{2}\sum\limits_1^k n_\nu}}{n_1^{n_1} e^{-n_1} \ldots n_\nu^{n_\nu} e^{-n_\nu} \, s_1^{n_1} \ldots s_\nu^{n_\nu}}$$

the numbers $n_1 \ldots n_\nu$ relating here to the maximal system.

Calculating the pressure from Ψ we find

$$p = \frac{RT}{NV} \sum_1^k n_\nu + \frac{RT}{N} \frac{\partial \log f}{\partial V}$$

where the terms again are zero on account of the condition of equilibrium. Like Prof. H. A. LORENTZ in his "Abhandlungen" also Dr. HOENEN uses the equation of state

$$p = \frac{R \, T}{N \, V} \sum_1^k n_\nu - q$$

(I put it in molecular form), the term q then denotes the deviation from the gas-laws, the q there used therefore agrees with our

$$q = \frac{RT}{N} \frac{\partial \log f}{\partial V}$$

$\log f$ may be given the form

$$\log f = - \frac{N}{RT} \int_V^\infty q \, dv + \vartheta$$

where ϑ is a function of temperature depending on the n_ν also. Introducing this into (20) then

$$\sum_1^k \nu_\nu \log n_\nu = \sum_1^k \nu_\nu \left(\frac{3}{2} \log (2\pi\Theta m_\nu) + \log V - \log s_\nu + \frac{\partial \vartheta}{\partial n} \right) - \frac{N}{RT} \sum_1^k \int_V^\infty \frac{\partial q}{\partial n_\nu} \nu_\nu \, dV.$$

Now if q is a function of the numbers n_1 the variation of q, if α varies with $d\alpha$, is because of dn_1 then being $\mathbf{r}_1 d\alpha$,

$$dq - \sum_1^k \frac{\partial q}{\partial n_1} \mathbf{r}_1 d\alpha.$$

So that this sum may be represented by $\frac{\partial q}{\partial \alpha}\, d\alpha$.

The condition of equilibrium thus changes into

$$\sum_1^l \mathbf{r}_1 \log n_1 = \sum_1^k \left\{ \left(\frac{3}{2} \log 2\pi\Theta m_1 \right) + \log V - \log s_1 + \frac{\partial \vartheta}{\partial n_1} \right\} \mathbf{r}_1 \quad \frac{N}{RT} \int_V^\infty \frac{\partial q}{\partial \alpha}\, dv.$$

Putting the zero-energy a_1 and introducing 3 vibrational freedoms then, when the remaining part of ϑ is represented by t, we get

$$\sum_1^k \mathbf{r}_1 \log n_1 = \sum_1^k \left\{ 3 \log T + \log V - \frac{a_1 N}{RT} - \log s_1 + \frac{\partial t}{\partial n_1} \right\} \mathbf{r}_1$$

$$- \frac{N}{RT} \int_v^\infty \frac{\partial q}{\partial \alpha}\, dv$$

the constant s_1 containing all quantities that do not depend on V and T. The quantity $\sum_1^k \mathbf{r}_1 \log s_1$ may also be substituted by a single constant.

Also in the case considered the quantity $\frac{R}{N} \log w$ can be defined for each state as entropy, and likewise we have for the supply of heat $\frac{dQ}{T} < d\eta$ for states of non-equilibrium and $= d\eta$ for states of equilibrium.

It may be regarded as an advantage of the statistical method, that it contains at the same time the thermodynamical consideration of Dr. HOENEN, and the kinetic result — the law of GULDBERG and WAAGE — that he is bound to introduce besides his thermodynamic considerations.

Groningen, November 1912.

Chemistry. — *"On velocities of reaction and equilibria."* By Dr. F. E. C. SCHEFFER. (Communicated by Prof. A. F. HOLLEMAN).

(Communicated in the meeting of January 25, 1913.)

1. In a previous paper in conjunction with Prof. KOHNSTAMM[1]), I discussed the relation between the velocity of reaction and the thermodynamic potentials of the substances participating in the reaction. It then appeared that the velocity of a reversible reaction may be given by the expression:

$$-\frac{dc}{dt}=C\left(e^{\frac{\mu_I-F}{RT}}-e^{\frac{\mu_{II}-F}{RT}}\right), \quad . \quad . \quad . \quad . \qquad (1)$$

in which μ_I represents the sum of the molecular thermodynamic potentials of the substances of the first member, μ_{II} the sum of the potentials of the substances of the second member of the reaction equation. The constant C accounts for the choice of the unities of concentration and time, and has therefore the same value for all reactions when the same unities are used. We have shown that the function F possesses the same value for both partial velocities, that it is independent of time and volume, and that it is equally in relation with both systems before and after the reaction. As further, quantities of energy and entropy must occur in the quantity F, we have tried to make clear that in general in case of chemical reactions "intermediate states" must be assumed, and we have pronounced the possibility that the energy and entropy of these transitional states are the only quantities dependent on the nature of the substances, which occur in the function F. By entropy we mean here the entropy "free from concentration"; we have namely shown in our cited paper that F is independent of the concentrations in case of gas reactions and reactions in dilute solutions; hence it can contain no terms originating from GIBBS's paradox. The value of the two partial velocities would therefore be determined according to this by the difference in energy and entropy (free from concentration) of the reacting substances and the transitional state. This in my opinion obvious assumption comes to this that both the difference of energy and the difference of entropy between the first and the second system must be split up into two parts; the first part then gives the differences of energy and entropy of the first system with

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[1]) These Proc. Jan. 1911. p. 789.

the transitional state, the other the differences of the second system with this transitional state.

As far as the values of energy are concerned such a solution was already proposed by VAN 'T HOFF in the Etudes de dynamique chimique and recently also TRAUTZ has tried an analogous splitting up of the values of energy, as we already mentioned in our previous paper. Though in his earlier papers on reaction velocities TRAUTZ considered a universally holding resolution possible, against which we thought we had to protest in the cited paper, TRAUTZ has introduced as possible ways different from reaction to reaction in his later papers, and with them different ways of splitting up, so that as far as the values of energy are concerned the difference between our considerations and those of TRAUTZ has partly disappeared. Yet also in this respect a difference continues to exist in our views, for TRAUTZ executes the splitting up of the energy at the absolute zero, and it seems more plausible to me to attribute the course of the reaction to the difference of energy at the reaction temperature. For the present it will certainly not be possible to obtain a definite decision of this question, as for the greater part the quantities occurring in the expressions for the velocity of reaction, have not yet been measured with sufficient accuracy, or sometimes are not even liable to direct measurement.

With regard to the splitting up of the entropy the difference between the mentioned views is still greater. Whereas TRAUTZ does not execute a splitting up of the entropy and introduces the absolute value of the entropy of the reacting system into the equation of velocity making use of the integration constants of the vapour pressure, an analogous splitting up seems necessary to us also for the entropy, especially when we adopt the views which BOLTZMANN has expressed on chemical actions in his Gastheory.

In the cited paper we have illustrated by the example of the chlorine-hydrogen equilibrium, how we think we have to imagine the transition states occurring there. If we adopt the standpoint of BOLTZMANN's theory, we must assume that the two hydrogen atoms in the hydrogen molecule are bound, in consequence of the fact that the "kritische Räume" of the two hydrogen atoms cover each other entirely or partially, and also those of the two chlorine atoms in the chlorine molecule. If we now inquire into the reaction between a chlorine and a hydrogen molecule, we must imagine that the two molecules get so close together that the four "kritische Räume" of the four atoms will entirely or partially coincide, so that the four atoms are in each others' sphere of action. After this transitional state a separation takes place of the "kritische Räume" of the hydrogen atoms and the chlorine atoms inter se, the dissimilar atoms remaining bound. Hence the energy quantity F must be the energy which prevails, when the four "kritische Räume" coincide, while the value of the entropy must take account of the volume of the coinciding Räume.

When we consider that the difference of energy between the reacting substances and the transitional state is no more to be calculated aprioristically than any other chemical change of energy, and that as yet we have no means at our disposal either, to predict the volumes of the "kritische Räume" by the aid of the properties of the substances, it is clear that we cannot test the above considerations except by examining whether we can assign plausible values of the energy and the entropy to the transitional states to get into harmony with the known material of facts. It is true that NERNST's theorem of heat, in the form as it is conceived by PLANCK, fixes the values of the entropy of solid substances at the absolute zero, so that the entropy constants of the gases are brought in relation with the integration constants of the vapour pressure, but even if one is convinced of the validity of the theorem of heat, yet the imperfect knowledge of the specific heats presents too great a difficulty up to now to calculate entropies a priori. With regard to the transitional states such a calculation is a fortiori impossible, as the facts known to us indicate that these transitional states greatly vary for different reactions, and are e. g. greatly influenced by catalysers.

When we now inquire into what the material of facts can teach us with regard to the transitional states, we will examine in the first place whether the energy in the transitional state is greater or smaller than in the initial or in the final state, or whether it perhaps lies between these two latter values. To answer this question I will (to keep the considerations as simple as possible), consider a reaction in a rarefied gas mixture that completely takes place in one direction. In this case the second partial velocity has a negligibly small value compared with the first. The velocity of the reaction is then represented by:

$$-\frac{dc}{dt} = Ce^{\frac{\mu_l - F}{RT}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If we now insert the value of μ_l for the dilute gas-mixture, which according to our preceding paper may be represented by:

$$\left.\begin{array}{l}\mu_l = \Sigma \nu_l \varepsilon_{0_l} - T\Sigma \nu_l \eta_{0_l} + \Sigma \nu_l \int c_{v_l} dT - T\Sigma \nu_l \int \frac{c_{v_l}}{T} dT + \\ \qquad + RT\Sigma \nu_l l n c_l + RT\Sigma \nu_l \end{array}\right\} \quad . \quad (3)$$

into equation 2, in which we write $\varepsilon_t - T\eta_t$ for F, where ε_t and η_t represent the above values of energy and entropy of the transitional states, and in which we separate the functions of concentration as separate factor, we get:

$$-\frac{dc}{dt} = Ce^{\frac{\Sigma r_I \varepsilon_{0_I} - T\Sigma r_I \eta_{0_I} + \Sigma r_I \int c_{v_I} dT - T\Sigma r_I \int \frac{c_{v_I}}{T} dT + RT\Sigma r_I - \varepsilon_t + T\eta_t}{RT}} \pi c_I \quad (4)$$

In this equation πc_I represents the recurring product of the concentrations of the reacting substances. The factor of πc_I is the so-called constant of velocity and is generally represented by the letter k. If we now determine the value of lnk and differentiate it with respect to T, we find:

$$\frac{dlnk}{dT} = -\frac{\Sigma r_I \varepsilon_{0_I} + \Sigma r_I \int c_{v_I} dT}{RT^2} + \frac{\varepsilon_t}{RT^2} - \frac{1}{RT}\left(\frac{d\varepsilon_t}{dT} - T\frac{d\eta_t}{dT}\right) \quad (5)$$

If now ε_t and η_t have the signification of energy and entropy (free from concentration) of the transitional state, the last term of the second member of equation 5 is zero; this is clear when we consider that $F = \varepsilon_t - T\eta_t$ can contain no functions of volume. Hence equation 5 reduces to

$$\frac{dlnk}{dT} = \frac{\varepsilon_t - \varepsilon_I}{RT^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

in which ε_I represents the energy of the first system at the temperature of reaction.

If we now return to the reversible (gas)-reaction, the relations

$$\frac{dlnk_1}{dT} = \frac{\varepsilon_t - \varepsilon_I}{RT^2} \text{ and } \frac{dlnk_2}{dT} = \frac{\varepsilon_t - \varepsilon_{II}}{RT^2} \quad . \quad . \quad . \quad . \quad (7)$$

will exist for the two partial velocities.

Hence the splitting up of the energy difference $\varepsilon_I - \varepsilon_{II}$ into two pieces $\varepsilon_I - \varepsilon_t$ and $\varepsilon_t - \varepsilon_{II}$ is very prominent. If we now consider that in general the velocity of chemical reactions increases with the temperature, it is clear that ε_t will be greater than ε_I and ε_{II}. The energy of the transitional states is therefore greater than the energies of the systems before and after the reaction. Accordingly this result necessarily leads us to the following conception: On coincidence of the "kritische Räume" of the reacting molecules gain of energy takes place, in other words there is work done against *repulsive* forces; the transitional state possesses therefore a *maximum* of potential energy.

As is known when molecules draw near to each other attraction takes place; this led us to expect in our previous paper that the transitional state would possess a *minimum* potential energy. As appears from the above consideration at such a distance that the "kritische Räume" invade each other, the repulsive forces outbalance the attractive forces and oppose therefore the invasion of the sphere of action.

A similar conclusion concerning the energy of the transitional states occurs already in TRAUTZ's first papers. He imagined that the transitional state consists of free atoms. It is then clear that this state contains more energy than the initial and the final state, since heat will be required for dissociation into atoms. That TRAUTZ makes this resolution take place at the absolute zero does not involve an essential modification. For this question is in close relation to the question whether it is allowed with regard to these transitional states to speak of specific heats, or what is the same thing of a mean value of energy at a certain temperature. And so far as is known the difference of temperature between the reaction temperature and the absolute zero generally causes no reversal of the sign of chemical heat-effects.

2. Before entering into a discussion of the energy and entropy values of the transitional states, I shall insert here some considerations on the energy and entropy differences between the systems before and after the reaction, referring to a paper on gas-equilibria that has appeared earlier in these Proceedings [1]. The algebraic sum of the entropies of the substances participating in a gas-reaction was represented in the cited paper by:

$$\Sigma nH = \Sigma nH_{\substack{T=1 \\ c=1}} + \Sigma n \int_1^T \frac{c_v}{T} dT - R \Sigma n \ln c \quad . \quad . \quad . \quad . \qquad (8)$$

If we join the first two terms of the second member of equation 8, and represent it by $\Sigma nH_{c=1}$ (the entropy free from concentration) this equation passes into:

$$\Sigma nH = \Sigma nH_{c=1} - R \Sigma n \ln c \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (9)$$

According to the cited paper the equilibrium condition for the gas mixture is:

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[1] These Proc. Dec. 1911. p. 743.

$$\Sigma n\mu = \Sigma nE - T\Sigma nH + \Sigma nRT = 0.$$

If in this we introduce the entropy free from concentration, this equation may be written as follows:

$$\Sigma nE - T\Sigma nH_{c=1} + RT\Sigma nlnc + \Sigma nRT = 0.$$

If we now express $\Sigma nlnc$ by lnK_c, in which therefore K_c represents the so-called equilibrium constant (in concentrations), then:

$$RTlnK_c = - \Sigma nE + T\Sigma nH_{c=1} - \Sigma nRT \quad . \quad . \quad . \quad (10)$$

Differentiating this equation with respect to T after division by RT, we easily find the well-known equation of VAN 'T HOFF:

$$\frac{dlnK_c}{dT} = \frac{\Sigma nE}{RT^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

If we now imagine ΣnE to be a very weak temperature function, which may be put practically constant over a limited temperature-range, equation 11 yields on integration:

$$lnK_c = -\frac{\Sigma nE}{RT} + C. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

On comparison of equation 12 with 10, it appears that on this supposition also the entropy free from concentration may be put independent of the temperature. This conclusion is moreover also clear when we consider that both the change of ΣnE and that of $\Sigma nH_{c=1}$ with the temperature is exclusively determined by the value of Σnc_v. If therefore really the value of Σnc_v in a certain range of temperature is negligibly small, the observations in this range may be represented by equation 12, in which two constants occur: $\frac{\Sigma nE}{R}$, the change of energy divided by the gas constant, and C, which contains the change of entropy and the gas constant.

And inversely when it appears that the constant of equilibrium as function of the temperature may be represented in an equation with two constants like 12, a measure will be found in the value of these constants for the change of energy and entropy during the reaction. If therefore in one graphical representation $RlnK_c$ is represented as function of $\frac{1}{T}$, and in another $TlnK_c$ as function of T, and if the observations in the first graphical representation give a straight line, this is also the case in the second. The inclination of the line in the first representation yields the energy value, that in the second the value of C in equation 12, so the entropy value, at least if the fact is taken into account that according to equation 10 C also contains the gas constant and Σn. If we now assume that the observations have been made with great accuracy, in general the curve in the first graphical representation will deviate from a straight line. If we now connect two points from this graphical representation, the slope of this straight line will indicate the value of energy which belongs to a temperature which lies between those of the two connected points. It will then be clear that if we wish to determine the energy value in a similar way, the found value will differ the less from that which corresponds to the two observation temperatures as $\Sigma n c_v$ is smaller. Hence the energy value will also be found with the greater relative accuracy as the energy value itself is greater, i.e. the energy found graphically will then proportionally differ only little from the energy values at the observation temperatures. If we now fill in the graphically found value in equation 12 and if we apply equation 12 to the two observation temperatures, a too great value for the energy difference will have been chosen for the one temperature, a too small value for the other. For a temperature between the two temperatures of observation the energy value is then chosen exactly right; hence the correct entropy value has therefore been yielded by equation 12 for this temperature. Therefore when equation 12 is used the found values of entropy will deviate somewhat from the real ones at the two temperatures of observation.

If we denote the two temperatures of observation by T_1 and T_2 and the temperature for which the graphically found value of the energy holds, by T_3, and if we imagine the value of energy found at T_3 and the corresponding entropy substituted in equation 10, we may question what deviation equation 10 gives us for the values of K_c at the temperatures T_1 and T_2. The error made in the energy when we apply equation 10 as T_1, amounts to $\int_{T_1}^{T_3}\frac{d\Sigma nE}{dT}\,dT$, that in the entropy-term amounts to $T_1\int_{T_1}^{T_3}\frac{d\Sigma nH_{v=1}}{dT}\,dT$. If we now consider that the energy and the entropy occur with opposite sign in the second member of equation 10 and that

$$\frac{d\Sigma nE}{dT}=T\,\frac{d\Sigma nH_{v=1}}{dT}\ ,$$

we see that these two errors cancel each other for the greater part in the second member of equation 10, and that therefore in spite of these approximations a pretty accurate value of K_c can be found. This fact explains why notwithstanding an appreciable value of the specific heats many gas equilibria can be accounted for by means of two constants, not only over a small temperature range, but sometimes even over a very large one, at least if the observations are not particularly accurate. The dissociation constant of the nitrogen tetroxide can e. g. be expressed by an equation of the form 12 (SCHREBER's equation), and also the dissociation equilibrium of carbonic acid, the errors of observation being comparatively large here, can be accounted for by equation 12 over a temperature range of hundreds of degrees.

These considerations teach us accordingly that observations of equilibrium constants with comparatively large energy and entropy values enable us to calculate them pretty accurately, but that generally no conclusion can be drawn about the influence of the temperature on energy and entropy, the errors of observation being generally too great for this. Thus the above formula of SCHREBER enables us to find a mean value for the heat of dissociation of the nitrogen tetroxide and for the "kritische Raum" of the NO_2-molecule [1]), but the influence of the temperature on either is not to be derived from the measurements of the equilibrium.

3. If we now return to the reaction velocities, we can also apply the considerations mentioned in the preceding paragraph here mutatis mutandis. Equation 6, which indicates the dependence of the velocity constant with the temperature, presents great analogy with VAN 'T HOFF's equation of equilibrium (equation 11). If $\varepsilon_l-\varepsilon_t$ is a very weak temperature function, equation 6 yields on integration:

$$l\,nk \qquad \frac{\varepsilon_l-\varepsilon_t}{RT} \qquad B \;.\;.\;.\;.\;.\;.\;.\;. \tag{13}$$

in which as appears from equation 4 B does not contain any constants depending on the nature of the substances, except the difference of entropy. So in this case too the difference of entropy between initial and transitional state is practically independent of the temperature. Here too we can therefore graphically represent $Rl\,nk$ as function of $\frac{1}{T}$, and determine the differences of energy between initial and transitional state. It seems therefore natural to examine whether the material of facts referring to the reaction velocities can be represented by equations of the form 13, where $\varepsilon_l-\varepsilon_t$ and B are considered as constants.

In his Etudes de dynamique chimique VAN 'T HOFF for the first time gave an expression for the dependence of the velocity con-

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[1]) BOLTZMANN. Gastheorie II. § 66.

stant on the temperature. Led by his relation of equilibrium (equation 11) he pronounced the supposition that for the velocity constant an equation would hold of the shape:

$$\frac{d\ln k}{dT} = \frac{A}{T^2} + B \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

This equation has been repeatedly put to the test in later times, generally, however, for reactions in dilute solutions. First of all the question suggests itself whether the considerations which have led us to equation 6, may also be applied to dilute solutions. Though the velocity of 6 for dilute solutions cannot be rigorously proved, an application also for these reactions does not seem open to serious objections. We have, namely, tested our original equation, by reactions in dilute solutions in the cited paper; it proved to be able to account for the course of reaction, and the reasons which led us to the assumption of transitional states, hold unchanged also for reactions in solution. Accordingly the shape of equation 6 leads us to expect that this will be generally valid. VAN 'T HOFF's equation (equation 11), moreover, holds also for equilibria in dilute solution, and it is therefore certainly natural to assume, that the splitting up of the value of energy will be essentially the same for all reactions.

Van 'T HOFF's equation is generally not applied in the form as it is given by 14, but in the form which arises when either A or B is put zero in 14. The expression which arises by the introduction of zero for B has been later defended by ARRHENIUS, and has appeared to be compatible with a great part of the material of facts. If, however, one puts B equal to zero in 14, really equation 13 is obtained by integration, and all the reaction-velocities which satisfy ARRHENIUS' expression, can therefore be represented with the aid of the two constants $\varepsilon_l - \varepsilon_t$ and B of equation 13. Reversely equation 13 furnishes us also with the possibility of pretty accurately calculating the differences of energy, at least if they are not too small; the absolute value of the difference of entropy, however, remains unknown, because B among others contains the unknown constant, which accounts for the unity of concentration and time. The above considerations, however, suggest that besides the difference of entropy B will not contain any constants dependent on the nature of the substances. In perfect analogy with the conclusion of § 2 we conclude also here that measurement of reaction velocities, at least if they have not been very accurately executed cannot decide whether the difference of energy and of entropy depends on the temperature.

I will apply the above considerations in my next paper to a series of experimental data from organic chemistry.

Chemistry. — *"On the velocity of substitutions in the benzene nucleus."* By Dr. F. E. C. Scheffer. (Communicated by Prof. A. F. Holleman).

(Communicated in the meeting of Jan. 25, 1913).

1. In the preceding paper the dependence of the velocity constant on the temperature was represented by the equations:

$$\frac{dlnk}{dT} = \frac{\varepsilon_l - \varepsilon}{RT^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and

$$lnk = \frac{\varepsilon - \varepsilon_l}{RT} - B \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and it was shown that the greater part of the experimental data allows the substitution of a constant value for $\varepsilon - \varepsilon_l$. According to the considerations of the preceding paper this value furnishes a pretty accurate measure for the energy difference between the reacting substances and the intermediate state during the reaction, at least if the velocities have been measured with sufficient accuracy, and the value of the energy difference is not too small.

In order to arrive at an opinion about the efficiency of these considerations and the equations 1 and 2 derived from them, I have tried to apply the latter to the experimental data. I have for this purpose tried to find those examples where we may expect the simplest behaviour, and in my opinion they are to be found in the department of organic chemistry.

If we imagine a reaction which is indicated by the equation of reaction $A + B = \ldots$ and if we determine the reaction velocities at different temperatures, the above mentioned energy value can be calculated. If we then replace the molecule A by another A', we can find the required quantity of energy also for the reaction of this molecule A' with B, and in this way obtain an insight into what influence a substitution of A' for A exercises on the differences of energy with the intermediate state.

Let us e. g. suppose that the molecule benzene is nitrated; we might then calculate from measurements of the nitration velocity at different temperatures what quantity of energy is required to force the nitric acid molecule into the sphere of action of one of the hydrogen atoms in the benzene nucleus. If we then replace the molecule benzene e. g. by chloric benzene, we can calculate the quantity of energy required for this reaction also by measurement of the nitration velocity, and obtain an insight in this way into what influence the chlorine atom in the benzene has on the required quantity of energy for the substitution. In this way a value can then be found which can quantitatively be expressed for that which is generally expressed by the intensity of the binding of the atoms which are liable to substitution.

Such calculations, however, cannot be carried out in the absence of the required material of facts. Determinations of velocity of substitutions as mentioned above have been hardly carried out as yet; though Prof. HOLLEMAN and his pupils have collected a considerable number of data on the relative velocity of the substitution of the different hydrogen atoms in the same aromatic molecule. All these measurements refer to simultaneous reactions, and it is just for this kind of reactions that the application of the above mentioned equations is very simple.

When we expose the molecule toluene to the action of nitric acid, three substitutions appear simultaneously. In the toluene three different kinds of hydrogen atoms liable to substitution occur, two on the ortho-, two on the meta, and one on the para-place with respect to the chlorine atom. So we have here three reactions proceeding simultaneously, each with a definite velocity constant. If we now want to apply the above equations we must first of all bear in mind that the velocity constant is determined by the energy and entropy difference required for the substitution, and that accordingly if these quantities were equal for the ortho-, meta-, and para-substitution, there would yet be formed twice as many ortho- and metadisubstitution products as paraproducts, because in a definite quantity of toluene there are twice as many ortho- and metahydrogen atoms liable to substitution, as para-hydrogen atoms. If therefore the velocity constants for ortho-, meta-, and para-substitution are represented by k_0, k_m, and k_p, the substitution velocities v_0, v_m and v_p are represented by the equations:

$$v_0 = 2k_0\, c_{\mathrm{C_6H_5Cl}}\, c_{\mathrm{HNO_2}}, \quad \ldots \ldots \quad (2a)$$

$$v_m = 2k_m\, c_{\mathrm{C_6H_5Cl}}\, c_{\mathrm{HNO_3}} \quad \ldots \ldots \quad (2b)$$

and

$$v_p = k_p\, c_{\mathrm{C_6H_5Cl}}\, c_{\mathrm{HNO_3}} \quad \ldots \ldots \quad (2c)$$

The ratio of the quantities ortho, meta-, and para-products, which are formed in the unity of time, therefore, amounts to $2k_0 : 2k_m : k_p$; hence it is independent of the time. If therefore the reaction is allowed to proceed regularly to its close, or if it is stopped at an arbitrary moment, the ratio of the obtained substitution products is at the same time the required ratio of the velocity constants[1]).

Not the velocity constants themselves, therefore, only their mutual ratio is to be derived from the measurements collected by Prof. HOLLEMAN.

If we now apply equations 1 and 2 to these examples, it appears that the application becomes so very simple in this case in consequence of the equality of the energy ε of the reacting substances for all the three reactions that take place simultaneously, and that therefore the difference in velocity of substitution at an ortho- and metaplace e.g. is different only in consequence of this that the quantity of energy (and entropy) to replace the ortho-hydrogen differs from the energy required to cause the substitution at the meta-place.

The objection that these reactions do not take place in dilute solution cannot be advanced against the application of the two equations, for in these substitutions a great excess (molecular) of the substituting substance is generally present. In nitrations e.g. the substance that is to be nitrated is added in drops to a large quantity of nitric acid, and the nitration is practically completed before the following drop is added.

Moreover I pointed out already in the preceding paper that the objection of higher concentrations cannot be serious, since it is self-evident that the splitting up of the energy values must always be carried out in essentially the same manner. It has, moreover, repeatedly appeared in these substitutions that different ratio of the reacting substances has no appreciable influence on the mutual ratio of the reaction products.

If we now represent the energy of the intermediate states for the three substitutions by ε_{t_o}, ε_{t_m}, and ε_{t_p}, then equation 1 gives:

$$\frac{d\ln\dfrac{k_o}{k_m}}{dT} = \frac{\varepsilon_{t_o} - \varepsilon_{t_m}}{RT^2} \quad \ldots\ldots\ldots \quad (3a)$$

$$\frac{d\ln\dfrac{k_o}{k_p}}{dT} = \frac{\varepsilon_{t_o} - \varepsilon_{t_p}}{RT^2} \quad \ldots\ldots\ldots \quad (3b)$$

$$\frac{d\ln\dfrac{k_m}{k_p}}{dT} = \frac{\varepsilon_{t_m} - \varepsilon_{t_p}}{RT^2} \quad \ldots\ldots\ldots \quad (3c)$$

Here the third equation is of course dependent on the two others.

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[1]) HOLLEMAN, Die direkte Einführung von Substituenten in den Benzolkern, p. 72. We also refer to this work for the experimental data occurring in this paper.

These equations enable us to calculate the differences of the required substitution energies from measurements of the velocity, at least for so far as they have been performed at different temperatures.

If we now also apply equation 2, we get:

$$ln \frac{k_0}{k_m} = \frac{\varepsilon_{t_m} - \varepsilon_{t_o}}{RT} + B_m - B_o \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4a)$$

$$ln \frac{k_0}{k_p} = \frac{\varepsilon_{t_p} - \varepsilon_{t_o}}{RT} + B_p - B_o \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4b)$$

$$ln \frac{k_m}{k_p} = \frac{\varepsilon_{t_p} - \varepsilon_{t_m}}{RT} + B_p - B_m \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4c)$$

With respect to the constants B from the equation 4 we know that each of them consists of the required entropy difference and of constants which do not depend on the nature of the reacting substances. These latter disappear therefore in equation 4, where always differences between two B-values occur, so that the value $B_m - B_o$ of equation $4a$ can be replaced by $\eta_{t_m} - \eta_{t_o}$, and just so for the other equations.

So we see that the difference of the substitution energies and entropies can be directly calculated for these reactions from the experimental determinations. The accuracy with which these calculations can be carried out, is of course determined by the value of the errors of observation.

When I applied equations 4 to the data, it soon appeared that the values for $\eta_{t_m} - \eta_{t_o}$ etc. in general possess small amounts, and sometimes differ very little from zero. I have therefore examined whether it is possible to account for the observations *only* by a difference of energy, hence by assuming that *the difference in substitution-entropy would be zero for the different hydrogen atoms.* Mathematically this comes to this that every substitution might be represented by the aid of *one* constant, which would then have the meaning of the difference in substitution-energy. On this hypothesis the equations 4 are transformed into:

$$ln \frac{k_0}{k_m} = \frac{\varepsilon_{t_m} - \varepsilon_{t_o}}{RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5a)$$

$$ln \frac{k_0}{k_p} = \frac{\varepsilon_{t_p} - \varepsilon_{t_o}}{RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5b)$$

$$ln \frac{k_m}{k_p} = \frac{\varepsilon_{t_p} - \varepsilon_{t_m}}{RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5c)$$

To show that the material of facts really admits of such a hypothesis, I subjoin the values which must be assigned to the differences of energy of the equation 5, expressed in calories.

Nitration of chlorobenzene.

$$\varepsilon_{t_o} - \varepsilon_{t_p} = 825$$

	$t = 0$		$t = -30$	
	found	cal.	found	cal.
ortho	30.1	30.4	26.9	26.6
para	69.9	69.6	73.1	73.4

Nitration of brombenzene.

$$\varepsilon_{t_o} - \varepsilon_{t_p} = 647$$

	$t = 0$		$t = -30$	
	found	cal.	found	cal.
ortho	37.7	37.7	34.4	34.3
para	62.3	62.3	65.6	65.7

Bromation of toluene.

$$\varepsilon_{t_o} - \varepsilon_{t_p} = 658$$

	$t = 25$		$t = 50$		$t = 75$	
	found	calc.	found	calc.	found	calc.
ortho	35.5	35.5	23.5	23.5	6.2	6.0
para	53.9	53.9	32.8	32.8	7.5	7.7

Nitration of benzoic acid.

$$\varepsilon_{t_o} - \varepsilon_{t_m} = 800$$

	$t = -30$		$t = 0$		$t = 30$	
	found	calc.	found	calc.	found	calc.
ortho	14.4	15.9	18.5	18.4	22.3	20.7
meta	85.0	83.5	80.2	80.3	76.5	78.1

Nitration of ethyl-benzoate.

$$\varepsilon_{t_o} - \varepsilon_{t_m} = 500$$

	$t = -40$		$t = 0$		$t = 30$	
	found	calc.	found	calc.	found	calc.
ortho	25.5	25.0	28.3	27.5	27.7	28.5
meta	73.2	73.7	68.4	69.2	66.4	65.6

Nitration of toluene.

$\varepsilon_o - \varepsilon_p = 135$; $\varepsilon_m - \varepsilon_o = 1490$

	$t = -30$		$t = 0$		$t = 30$		$t = 60$	
	found	calc.	found	calc.	found	calc.	found	calc.
para	39.3	38.7	38.1	37.6	36.8	36.6	35.3	35.7
ortho	57.2	58.6	58.0	58.6	58.8	58.5	59.6	58.2
meta	3.5	2.7	3.9	3.8	4.4	4.9	5.1	6.1

If we extend the investigation to the introduction of a third substituent in the twice substituted benzene, we get:

Nitration of m-chlor-benzoic acid. [1]

$\varepsilon_b - \varepsilon_a = 1290$

	$t = -30$		$t = 0$	
	found	calc.	found	calc.
a (1, 3, 6)	93	93.5	92	91.5
b (1, 3, 2)	7	6.5	8	8.5

Nitration of m-brom-benzoic acid.

$\varepsilon_b - \varepsilon_a = 1020$

	$t = -30$		$t = 0$	
	found	calc.	found	calc.
a (1, 3, 6)	89	89.2	87	86.8
b (1, 3, 2)	11	10.8	13	13.2

Nitration of m-dichlor-benzene.

$\varepsilon_b - \varepsilon_a = 1400$

	$t = -30$		$t = 0$	
	found	calc.	found	calc.
a (1, 3, 6)	97.4	97.3	96.2	96.4
b (1, 3, 2)	2.6	2.7	3.8	3.6

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[1] In these tables the place of carboxyle is indicated by 1.

Nitration of o-dichlor-benzene.

$$\varepsilon_b - \varepsilon_a = 1400$$

	$t = -30$		$t = 0$	
	found	calc.	found	calc.
a (1, 2, 4)	94.8	94.8	92.8	93.0
b (1, 2, 3)	5.2	5.2	7.2	7.0

Nitration of o-chlor-benzoic acid.

$$\varepsilon_b - \varepsilon_a = 890$$

	$t = -30$		$t = 0$	
	found	calc.	found	calc.
a (1, 2, 5)	86	86.4	84	83.8
b (1, 2, 3)	14	13.6	16	16.2

Nitration of o-brom-benzoic acid.

$$\varepsilon_b - \varepsilon_a = 760$$

	$t = -30$		$t = 0$	
	found	calc.	found	calc.
a (1, 2, 5)	82.9	82.9	80.3	80.3
b (1, 2, 3)	17.1	17.1	19.7	19.7

When we now pass in review the results of the above tables, it appears that the harmony between the found and the calculated values is very satisfactory in general. In the majority of the examples the deviations very certainly remain within the errors of observation. Only in the nitration of benzoic acid an appreciable deviation between the found values and the calculated ones occurs. This nitration, however, is according to Prof HOLLEMAN one of the first carried out examples, in which the "method of extraction" was applied, which was later replaced by more accurate analysis methods.

Probably the deviation remains within the errors of observation also here. This supposition seems not too hazardous when the results are considered which were obtained in the nitration of the methyl ester of benzoic acid, where very probably in the nitration an error occurs at 0°, which is greater than the above deviations. Prof. HOLLEMAN informed me that he too considered the agreement in the tables as very satisfactory.

The above test, therefore, really leads to the conclusion that the substitutions in the benzene nucleus can be satisfactorily accounted for up to now by one single constant, the difference of energy for substitution at the different places in the nucleus. If there were only one example known where the errors of observation were undoubtedly smaller than the deviation from the theoretically calculated value, the originally proposed hypothesis would have to be rejected; so it will have to appear from the continued investigation whether really all the examples without exception conform to the rule, for which no exceptions have been found as yet.

Equations 3 and 5 accordingly, account for the facts which are known up to now. If we now compare the two equations, we come to the following conclusion: The second members of the two equations have always opposed signs; if therefore in equation 5*a* $k_o < k_m$, i.e. if on substitution more meta- than orthoderivative is formed, then $\varepsilon_{m} - \varepsilon_{o}$ is negative.

It then follows from equation 3*a* that the value of $\frac{d \ln \frac{k_o}{k_m}}{dT}$ is positive. We can express this generally as follows:

The quantity of the product which is formed to a smaller degree, increases relatively on rise of temperature.

In this we should bear in mind that to decide whether a product is formed in a smaller quantity, it is necessary to divide the quantities formed by the value that indicates the number of equivalent places in the nucleus. Thus the nitration of toluene furnishes *seemingly* an exception, as *seemingly* the quantity of ortho is greater than the quantity of para-nitrotoluene. If however, it is borne in mind that in this substitution there are two ortho-places available to one para-place, and that therefore para and *not* ortho is the product that is formed in greater quantity, the stated rule appears to be valid also here.

As far as I am aware there are no exceptions to this rule either. Only the nitration of iodo-benzene does not follow it, as here the quantity of ortho-compound does not increase on rise of temperature, but decrease; this nitration is repeated in Prof. HOLLEMAN's laboratory, because the presence of dinitro-compounds may possibly give rise in this case to comparatively great errors in the analyses. In the case of another example that departs from the rule, the quantity of para-product in the nitration of benzoic acid and its methyl ester, the changes at varying temperature are so slight that the errors of observation may even have changed the qualitative conduct.

Moreover the above consideration establishes the already known practical rule that in general it is desirable for the preparation of pure substitution products to work at low temperature; for according to the stated rule higher temperature always promotes the formation of by-products.

When we examine what influence the above result exercises on our theoretical considerations, we arrive at the following conclusion:

When a hydrogen atom in the benzene nucleus is replaced by an atom or a group of atoms, an intermediate state makes its appearance, which is caused by exactly the same atoms for the substitutions at all available places in the benzene-nucleus. For instance in the case of a nitration the intermediate state is caused by the coincidence of the "kritische Räume" of the carbon atom of the nucleus at which the substitution takes place, of the hydrogen atom, and of the OH and NO_2 group of the nitric acid molecule, at least when in an analogous way as BOLTZMANN ascribes a "kritische Raum" to the NO_2 molecule, we do so for the groups in question. Then the above conclusion would involve that the volumes of the Räume which cover each other, do not differ, or only very little for the substitutions at the different places, but that the different velocity of substitution is caused by the fact that the more distant atoms influence in a different way the energy required for the different places.

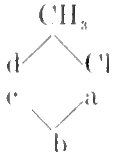
2. An entirely different question, which, however, can be brought in connection with what precedes, is the following: Is it possible when the quantity of the products, which are formed when a second substituent is introduced, is known, to calculate that of the substances which are formed when a third substituent is introduced? In other words is it possible to draw a conclusion from the energies required for the introduction of a second substituent, about the energy required for the introduction of a third? If e. g. we suppose that toluene is nitrated on one side, chlor benzene on the other, we know the relative quantity of the nitroproducts formed; if we now nitrate chlor toluene, it is the question whether the quantity

of the nitroproducts formed in the latter case is to be calculated from the former case. In the first place we should bear in mind that the energy of the substances we start from is different, and now it is true that this energy is cancelled in the determination of the relative quantities, yet the energy of the intermediate states may depend on this energy. To obtain an answer to the given questions we should therefore have to introduce a hypothesis concerning the energy quantities.

These hypotheses must necessarily be very arbitrary, as analogies with other phenomena are not yet known for them. One of the most plausible hypotheses would in my opinion be the following:

Let us denote the energy required for the substitution of the NO_2-group for the hydrogen atoms in the benzene molecule by ε_1. Then the energy for substitution of the hydrogen atoms in toluene and chlor benzene resp. may be represented by $\varepsilon_1 + \varepsilon_{o_1}$, $\varepsilon_1 + \varepsilon_{m_1}$, $\varepsilon_1 + \varepsilon_{p_1}$ resp. $\varepsilon_1 + \varepsilon_{o_2}$, $\varepsilon_1 + \varepsilon_{m_2}$ and $\varepsilon_1 + \varepsilon_{p_2}$.

If we now think a substitution carried out in the molecule orthochlortoluene, we might assume that the energies required for every substituable place must be added



For substitution at the place a, which is in an ortho-position with respect to chlorine and in metaposition with respect to CH_3, an energy quantity $\varepsilon_1 + \varepsilon_{m_1} + \varepsilon_{o_2}$ would then be required. Reasoning in an analogous way $\varepsilon_1 + \varepsilon_{p_1} + \varepsilon_{m_2}$ would be required for the place b.

Applying equation 5, we get:

$$ln \frac{k_b}{k_a} = \frac{\varepsilon_a - \varepsilon_b}{RT} = \frac{(\varepsilon_1 + \varepsilon_{m_1} + \varepsilon_{o_2}) - (\varepsilon_1 + \varepsilon_{p_1} + \varepsilon_{m_2})}{RT} =$$

$$= \frac{(\varepsilon_{m_1} - \varepsilon_{p_1}) - (\varepsilon_{m_2} - \varepsilon_{o_2})}{RT}.$$

When we now consider that the introduction of the second substituent requires:

$$ln \frac{k_{p_1}}{k_{m_1}} = \frac{\varepsilon_{m_1} - \varepsilon_{p_1}}{RT} \text{ and } ln \frac{k_{o_2}}{k_{m_2}} = \frac{\varepsilon_{m_2} - \varepsilon_{o_2}}{RT},$$

we find easily by combination of the three equations:

$$ln \frac{k_b}{k_a} = ln \frac{k_{p_1}}{k_{m_1}} - ln \frac{k_{o_2}}{k_{m_2}}$$

or

$$\frac{k_b}{k_a} = \frac{k_{p_1}\ k_{m_2}}{k_{m_1}\ k_{o_2}}.$$

This is the so-called rule of multiplication, which Prof. HOLLEMAN tried to apply for such calculations already before. This rule appeared to be in pretty close agreement with the observations for the nitration of the ortho-chlor and ortho-brom benzoic acids; in other cases, however, great deviations from the calculations are found.

Afterwards HUISINGA proposed a "rule of summation", but this too presents satisfactory agreement only in some cases. If we examine what relation would have to exist between the energy quantities required for substitution to arrive at a rule of summation, this relation appears to assume such an intricate form that it cannot be accounted for in my opinion from a theoretical point of view. A *general* rule for the calculation of substitution energies at the introduction of a third substituent from the values of energy which are required for the introduction of a second, seems to me impossible to find. It may, however, be possible to find a relation between analogous substitutions, and this relation might possibly be discovered by means of the energy values calculated above. Up to now I have however not made an attempt to do so, because the energy values on which the above tables are founded, can certainly still be modified in the units, and sometimes even in the tens; the extent of these modifications, namely, is in the closest relation with the errors of observation which may be allowed in the determinations.

Moreover I will finally point out that in this paper I only intend to show that the material of facts admits the assumption that the substitution entropies are identical for the different places in the nucleus. That this is really perfectly true has of course not been proved by the test; we can certainly also account for the data by means of equations with two constants (equation 4), in which the second constant in general possesses a small value. It appears in any case that in general the course of this type of reactions is chiefly determined by difference of energy, and the difference of entropy plays only a secondary part. As I showed at the end of § 1 our theoretical considerations about the mechanism of the chemical reactions may be brought into harmony with these results.

In conclusion I gladly express my cordial thanks to Prof. HOLLEMAN for supplying me with the information which I required for the foregoing investigation and for his interest in this work.

Physics. — "*A method for obtaining narrow absorption lines of metallic vapours for investigations in strong magnetic fields.*" By R. W. Wood and P. Zeeman. (Communicated by Prof. P. Zeeman).

(Communicated in the meeting of January 25, 1913)

In the summer of 1911 we intended to make together some observations concerning magnetic double refraction of metallic vapours.

The magnetic double refraction of some vapours was first discovered (and predicted) by Voigt, afterwards commented upon by Zeeman and Geest.

In the paper of the last named authors the interesting region between the components of the magnetically divided sodium lines was investigated and the results represented by drawings.

It seemed desirable to extend this investigation using very narrow lines, which can be maintained constant during a long time and to fix the result by photograms.

Our investigation never passed the preliminary stage and has become now superfluous by the paper of Voigt and Wagner which has since appeared.

During our preliminary observations we tested a great number of methods of obtaining narrow and constant absorption lines. It seems to present some interest to record one of our results.

The absorption lines of sodium were obtained beautifully narrow by using small glass tubes charged with a little metallic sodium, then sealed to the vacuum pump and evacuated. A tube some centimeters in length was placed vertically between the poles, the magnetic field being horizontal.

It is quite possible to use tubes of *an external width of some millimeters.* Of course much of the light of an arc lamp is reflected and diffused by the tube, but *enough remains to observe the inverse magnetic effect* with a large Rowland grating. The magnetic resolution of the narrow lines can be splendidly seen and photographed in a reasonable time.

The heating of the tube can be done by a flame, but preferently electrically.

Of course tubes with other volatile metals can be prepared in the same way [1]).

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[1]) The method has been since applied with success in an investigation by Mr. Woltjer in the Amsterdam laboratory; the results will be given separately.

Physics. "*The red lithium line*". By Prof. P. ZEEMAN.

Only those spectrum lines, which belong to pair series or to threefold series, are resolved by magnetic fields into complicated types, i. e. not into triplets. The cause of the complicated resolution is intimately connected with the presence in the spectrum of natural groups of two or three lines (series-doublet or series-triplet). It has nothing to do with the distribution of lines in series, for there exist connected series of lines, which are resolved into triplets by magnetic fields [1].

Recently [2] PASCHEN and BACK discovered that lines belonging to a very close seriés-triplet or series-doublet, influence each other in a very peculiar manner. Under the action of a sufficiently strong magnetic field we might expect to observe a superposition of the types of separation of the compounds, but contrary to expectation a normal triplet is seen.

Among the lines investigated by PASCHEN and BACK are also the lithium lines. Many physicists by analogy with the other alkali metals and their series expect that the lithium lines are very close pairs.

Sometimes the opinion has been expressed that the laws for the other alkali metals do not apply to lithium. This then might explain the result obtained by VOIGT [3] that the red lithium line (6708) contrary to PRESTON's rule is resolved by a magnetic field into a triplet, which is at least nearly normal. The measurements of BACK [4]) for four lithium lines prove that within the limits of the errors of observation the separation has the normal value.

It is therefore very interesting to know whether the lithium lines are really very narrow pairs or not. In the first case PASCHEN and BACK are right placing the lithium lines in parallel with the other doublets they investigate, but they also indicate 6708 Li as a "theoretische Doppellinie", because it has never been resolved.

I have been able to do this using the method given in the foregoing communication.

As glass is strongly attacked by heated lithium it is necessary to place a small iron or copper vessel inside the glass tube; the life of the tube is then at least increased.

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[1]) LOHMANN, Physik. Zeitschr. **9** p. 145, 1908; PASCHEN, Ann. d. Phys. **30**, 746, 1909, **35**, 864, 1911, ROYDS **30**, 1024, 1909.

[2]) PASCHEN u. BACK, Normale u. anomale ZEEMAN-effekte, Ann. d. Phys **39**, 897, 1912.

[3]) VOIGT, Physik. Zeitschr. **6**, 217, 1912.

[4]) Anhang BACK, l. c.

The observations were made in the second order spectrum of a large ROWLAND grating.

The red of the second order is superposed on the blue of the third order so that the line 6708 is seen in the absorption spectrum as a blue line. With small vapour density the line resolved into two components; this proves that the conclusion drawn from the analogy of the spectrum series of the alkali metals is true. That component of the double line which has the smaller wavelength seemed to be the most intense. The distance between the components could only be measured in a roundabout manner by means of a divided scale in the eye piece of the spectroscope. This measurement gave for the distance between the components about one fourth of an Ångström unit. From the empirical rule that in the case of the elements of the same family the frequency differences of the pairs are nearly proportional to the square of the atomic weights, it would follow that for lithium this distance ought to be $6 \times \frac{7}{23^2} = 0{,}6$ Ångström units. The observed distance is much smaller.

Physics. — "*Some remarks on the course of the variability of the quantity b of the equation of state.*" By Prof. J. D. VAN DER WAALS.

(Communicated in the meeting of January 25, 1913).

In my preceding communications I came to the conclusion that the differences which occur in the normal, not really associating, substances are to be ascribed to the different value of the quantity $\frac{b_g}{b_{lim}}$. As this quantity is greater, both f and s are greater, viz. $\frac{f-1}{3} = \frac{b_g}{b_{lim}}$ and $s = \frac{8}{3}\sqrt{\frac{b_g}{b_{lim}}}$. The deviation exhibited by the law of corresponding states, is also a consequence of the different course of the quantity b. Thus it becomes more and more clear that everything that can contribute to elucidate the cause of the difference in this course must be considered of the highest importance.

If the course of b is traced as function of v, a line is obtained which runs almost parallel to the v-axis with great value of v, and approaches asymptotically to a line parallel to the v-axis at a distance b_g from the latter. Not before $v = 2b_g$ does an appreciable difference begin to appear, and has the value of b descended to e.g. about

$0,96\, b_g$. On further decrease of the volume b descends more rapidly — and when also a line has been drawn which starts from the origin, so from $v=0$ at an angle of 45° to the v-axis, the continually descending b curve will meet this line at $b=b_{lim}$. If b_g and b_{lim} are given, this curve is determined. If b_g should have the same value, and if b_{lim} should be smaller, the curve lies lower throughout its course, and reversely if b_{lim} is greater, the whole b curve lies higher.

Of course if there did not exist a similar cause for the variability of b, we might imagine a more irregular course in the different b curves. But if such a cause is assumed, nobody will doubt of the truth of the above remarks. I have even thought I might suppose that there is a certain kind of correspondence possible in the course of the different b curves. The points of these curves which are of importance for the equation of state, run from $v=b_{lim}$ to $v=\infty$. At a value of $v=nb_{lim}$ (and n can have all values between 1 and ∞), b_g-b is smaller as b_g-b_{lim} is smaller. Now I deemed it probable that there would be proportionality between these two latter quantities, and that therefore the following character of these curves can be put, viz.

$$\frac{b_g-b}{b_g-b_{lim}}=f\left(\frac{v}{v_{lim}}\right),$$

and that this function of $\frac{v}{v_{lim}}$ is the same, entirely or almost entirely. When I considered the question what the meaning of this equation might be, the following thought occurred to me. Could possibly the quasi-association be the cause of this variability of b with the volume?

I treated this quasi-association in an address to the Academy in 1906, and later on in some communications in 1910, and I came then to the conclusion that it must be derived from the increase of tension of the saturate vapour in the neighbourhood of the critical temperature that at every temperature and in every volume a so-called homogeneous phase is not really homogeneous; but that dependent on the size of the volume and also on the temperature there are always aggregations of a comparatively large number of molecules which spread uniformly. In very large volume the number of these aggregations is vanishingly small and with small volume, and especially at low temperature this number increases greatly; so that at the limiting volume the number of free molecules has become vanishing small. If in each of these aggregations the value of b does not differ much from b_{lim} or perhaps coincides with it, the following value of

b might be derived. For that part of the substance that is in the state of free molecules the value of b is equal to b_q. If the fraction of the quantity of substance that is in the state of aggregation is put equal to x, and the fraction which is in the state of single molecules equal to $1 - x$, then $b = (1 - x)\, b_q + b_{lim}$ or

$$\frac{b_q - b}{b_q - b_{lim}} = x\,.$$

And if we compare this result with the equation the significance of which we tried to find, we see that $f\left(\frac{v}{v_{lim}}\right)$ is the function which determines the value of x in every volume, but we must at once add at any temperature. That b might also depend on T I have never denied; I have only denied that putting $b = f(T)$ would enable us to account for the course of the equation of state, but that chiefly the dependence of v is indispensable. So we should now have arrived at the relation:

$$\frac{b_q - b}{b_q - b_{lim}} = x = f\left(\frac{v}{v_{lim}}\,,\; T\right).$$

But I must not be detained too long by these considerations, for on further consideration I have had to reject the thought that quasi-association has influence in this way. For various reasons. First of all because at so great contraction of the volume the name of quasi-association would have to change into real association. Secondly because the generated heat would then have to be much more considerable — and further the course of association would also have to be different for almost complete association, to which I may possibly have occasion later on to draw the attention. This, however, obviates the necessity of making $\frac{b_q - b}{b_q - b_{lim}}$ dependent on T, and we return to the simpler equation:

$$\frac{b_q - b}{b_q - b_{lim}} = f\left(\frac{v}{v_{lim}}\right).$$

And though I am not yet able to give the theoretical form of this function, and though I cannot indicate a priori the constants occurring in it, I can apply a correction in the value of v_{lim}, which I gave in my least communication; and this has greatly weakened if not removed the objections I had to the assumption that the decrease of b with the volume is only an apparent explanation.

I have arrived at the value of $v_{lim} = b_{lim}$ by following the same train of reasoning as when I drew up the equation of state. For the only new thought about the influence of the dimensions of the molecule (Chapter VI) was this that the volume inside which the motion of the molecules takes place, must be considered as in reality smaller than it seems at first sight.

If in case the molecules should be material points, the consequence of the collisions is that they resist an external pressure $+\frac{RT}{v}$, the consequence of their own dimensions is that they resist a pressure $\frac{v}{v-b}$ times as great. And we cannot dispense with this consideration. We may introduce this thought immediately; and without having to speak of repulsive forces, write directly: $p+\frac{a}{v^2}=\frac{RT}{v-b}$, or if it is preferred first continue the course of the calculation with the aid of the theorem of the *virial* further than I have done. But finally to arrive at the true formula it is again necessary to follow the course taken by me. I showed this long ago. When I wanted to determine the value of this new quantity b, however, I soon perceived that this would be attended with great difficulties.

It was not so difficult to determine the value of b_g, and I could at once conclude that b_g is equal to 4 times the volume of the molecules. And it was also easy to see that b would have to decrease with the volume. Already the consideration that for infinitely large pressure the volume would have to be smaller than 4 times the volume of the molecules, and would have to depend on the grouping in that smallest volume, and that therefore b_{lim} would have to be $< b_g$, was sufficient for this. In reference to this I say what follows in Chapter VI (p. 52), after I had reduced the way to determine the quantity b to the abbreviation of the mean length of path, and had therefore put:

$$\frac{l-l_1}{l}=\frac{v}{v-4b_1}:$$

"but this formula cannot be applied up to the extreme limit of condensation of the substance", etc. as far as the word "verwachten".

It appears from the cited passage that I felt already then that the quantity b in a definite volume would have to be determined by the determination of the distance, at which during the impact the centre of the colliding molecule must remain from the central plane at right angles to the direction of motion, in consequence of the dimension of the two colliding molecules. This appears among others when I say that when $v < 4b_1$ not only the double-central shocks, but also the double tangent ones will not take place, and the factor 4 will not diminish so rapidly as might have been expected without taking this in consideration.

To make clear what I mean, imagine a molecule in motion to strike against another. On the supposition of spherical molecules draw a sphere which has its centre in the second molecule with a radius $= 2r$ (if r is the radius of a molecule). Then at the moment of the impact the centre of the colliding molecule must lie on that sphere with a radius twice as long as its own. Now imagine also through the second molecule a central plane at right angles to the direction of the relative motion, in which case the second molecule may be taken as stationary, then the mean abbreviation of the free length of path is the length of the mean distance at which the centre of the moving molecule lies from the said central plane. In very large volume the chance that the centre of the moving molecule strikes against a certain area of the sphere with $2r$ as radius is proportional to the extension of the projection of this area on the said central plane. It follows from this that the mean abbreviation of the free length of path is the mean ordinate of a half sphere with $4\pi r^3$ as basis, and so equal to $\frac{4r}{3}$. It is true that this is the abbreviation of the length of path for 2 molecules, but this is compensated by the fact that an abbreviation of the same value exists also at the beginning of the free length of path for the moving molecule.

If also in a small volume the chance to a collision with the sphere with $2r$ as radius could be determined, the way had been found to determine the value of b in every volume. For $v < 4b$ the double central impacts must be eliminated, but also the double tangent ones. And strictly speaking in every volume, however great, if not infinitely great, the chance to double central and double tangent impacts must have lessened. Here a course seems indicated to me which might possibly lead to the determination of the value of b for arbitrary volume. I do not know yet whether this will succeed, but at any rate it has appeared to me that this may serve to calculate b_{lim} and not only for spherical molecules. The latter is certainly not devoid of importance, as the case of really spherical molecules will only seldom occur.

Let me first demonstrate this for spherical molecules. In the extreme case when they are stationary, they lie piled up, as is the case with heaps of cannon balls, each resting on three others. Let us think the centres of these three molecules as forming the tops of the ground plane of a regular tetrahedron. For a volume infinitely little greater than the limiting volume the limiting direction of the motion of the 4^{th} molecule is that which is directed at right angles to the ground plane, and in case of collision the three molecules of the ground plane are struck at the same time. The sides of the tetrahedron have a length equal to $2r$, and the perpendicular from the top dropped on the ground-plane is equal to $2r\sqrt{\frac{2}{3}}$.

The abbreviation of the length of path in consequence of the dimensions of the molecules is equal to half $2r\sqrt{\frac{2}{3}}$, if one wants to make this comparable with the above found one of $\frac{4}{3}r$, because this value referred to the abbreviation at a collision of two molecules, whereas the now found abbreviation holds for a collision of 4 molecules. The number of times that $\frac{4}{3}r$ is greater than $r\sqrt{\frac{2}{3}}$, is the value of $\frac{b_g}{b_{lim}}$, or $\frac{b_g}{b_{lim}}$ is equal to

$$\frac{4}{3}\sqrt{\frac{3}{2}}=\sqrt{\frac{8}{3}}=1.633.$$

For spherical molecules, therefore, $\frac{f-1}{3}=1.633$ or f almost equal to 5,9 and $s=\frac{8}{3}\sqrt{1.633}$ or about 3,3. And then it would follow that these values $f=5{,}9$ and $s=3{,}3$ must be considered as the smallest possible values.

But I do not lay claim to perfect accuracy for these values. Doubts and objections may be raised against these results, which I cannot entirely remove. Hence the above is only proposed as an attempt to calculate b_{lim} for spherical molecules. The first objection is this — and at first sight this objection seems conclusive. The value of b_{lim} must be equal to v_{lim}. Is the thus calculated value of b_{lim} then the smallest volume in which stationary molecules can be contained? This is certainly not the case. The volume of n^3 stationary spheres placed together as closely as possible is equal to $4n^3r^3\sqrt{2}$ if n is very great, and accordingly $\sqrt{2}$ times smaller than if they should be placed so that every molecule would require a cube as volume with $2r$ as side. If this value must be the value represented by b_{lim},

$\frac{b_g}{b_{lim}} = \frac{4\frac{4}{3}\pi r^3}{4r^3\sqrt{2}} = \frac{2\pi\sqrt{2}}{3}$, and so in connection with the law given by me $f-1$ and s^2 would become much greater than the value given for them by experiment.

But the thus calculated value for stationary molecules is not what I have represented by b_{lim}; I should prefer to represent it by b_0. At the point where the b-curve meets the line which divides the angle between the v-axis and the b-axis into two equal parts, need not and cannot be the point in which b is equal to b_0. The b-curve does not cease to exist in this point; it passes on to smaller volume, or possibly follows the line $v=b$.

On closer consideration the b-curve appears to touch the line $v=b$ and at smaller volumes than that of the point of contact the value of v appears to be again larger than b.

In the same way as kinetical considerations were required for the determination of the value of b_g to show that b_g is equal to four times the volume of the molecules, and so equal to $4\frac{4}{3}\pi r^3 N$, b_{lim} cannot be found without the aid of kinetical considerations. And the attempt which I make to calculate the value of b_{lim}, follows the same train of reasoning as has been efficient for the determination of b_g. This train of reasoning is as follows. If the mean length of path for molecules without dimension is equal to $\frac{v}{N\,4\pi\,r^2}$, and if the abbreviation amounts to βr, then $\frac{v}{v-b} = \frac{v}{v-N\,4\pi\,r^2\,\beta r}$, or $b = \beta 4\pi r^3$.

For b_g is $\beta = \frac{3}{4}$, and if the above given calculation is correct, the value of $\beta = \sqrt{\frac{2}{3}}$ for b_{lim}. So that, if we also introduce a value $v_0 = b_0$, $\frac{v_{lim}}{v_0}$ amounts to $= 1{,}814$. If we assume a regular arrangement of the molecules in v_0 and v_{lim}, the distances of the centres are not equal to $2r$ in v_{lim}, but equal to $2r\sqrt[3]{1{,}814} = 1{,}22$ times $2r$.

But for moving molecules such a regular arrangement is perfectly improbable. For them no other rule is valid but this that within a certain small space of time in equal parts of the volume, if not in contact with the walls, the mean number of molecules is the same. But their arrangement in such an equal part of the volume is entirely arbitrary and always varying. A regular arrangement as would be the case for cubic distribution, when in every molecule, 3 directions could be pointed out at right angles to each other according to which they would be surrounded by 6 neighbouring molecules placed at equal distances, while in all the molecules these three directions and distances would be the same, is altogether inconceivable. This is a fortiori the case with the other mentioned regular arrangements, according to which it would be possible in every molecule to point out several directions inclosing angles of 60°, according to which they are surrounded by other molecules. This would only not be absurd for stationary molecules, and then v_0 is not equal to b_0, but $v_0 > b_0$. Now it might appear that the b_{lim} introduced by me would really have to be b_0. I introduced the b_{lim} when I discussed the ratio of the greatest liquid density to the critical density, and made use for this purpose of the rule of the rectilinear diameter. This greatest liquid density occurs for $T=0$, and would therefore seem to hold for stationary molecules. This, however, is only seemingly in my opinion. Below T equal e.g. to $\frac{1}{2}$ or $\frac{1}{3}$ T_k this rule cannot be verified, but apart from its approximative character this rule is extrapolated. It is then taken for granted that what we have observed over a wide range of temperature, will also hold outside these limits. And I too have assumed this in the determination of v_{lim}. All this refers to a volume in which moving molecules occur. And so, if we put $\frac{v_k}{v_{lim}} = 2(1+\gamma)$, the value b_{lim} in the relation of $\frac{v_k}{v_{lim}} = 2(1+\gamma) = r\frac{b_g}{b_{lim}}$ is also that which holds for moving molecules. If observations could also be made at $T=0$, the volumes which are smaller than that in which the curve touches the line $v=b$, could be realized. And I do not doubt at all that in the immediate neighbourhood of $T=0$ the rule of the rectilinear diameter would entirely fail.

Let us summarize the foregoing. There is only one point in which the b-curve has a point in which $v=b$. This takes place at a value of b which we have called b_{lim}, and in which, because $v=b$, the value of the pressure is infinitely great. In this point $\frac{db}{dv}=1$. Then in:

$$\frac{-\frac{dp}{dv}-\frac{2a}{v^3}}{p+\frac{a}{v^2}}=\frac{1-\frac{db}{dv}}{v-b},$$

because p and $-\frac{dp}{dv}$ = infinite, also

$$\frac{-\frac{dp}{dv}}{p} = \frac{0}{0} \quad \frac{\infty}{\infty}.$$

And the determination of v_{lim} and b_{lim} takes place as follows. In the formula yielded by kinetical considerations, viz.

$$\frac{v-b}{v} = \frac{v-4\pi r^2 \beta r}{v}$$

v_{lim} must be $= 4\pi r^2 \beta r$. And for the determination of v_{lim} the smallest value for β will have to be found. For collisions with 1 molecule at a time, $\beta = \frac{4}{3}$. For collisions with 2 molecules at the same time, so that at the impact 3 molecules are in contact, $\beta = \frac{2}{3}\sqrt{3}$. For collisions with 3 molecules at the same time, the value of β is equal to $\sqrt{\frac{2}{3}}$, as we saw above. And collisions with a greater number which are in contact at the same time, are excluded. So that now the value of $\frac{b_g}{b_{lim}} = \frac{4}{3}\sqrt{\frac{3}{2}} = \sqrt{\frac{8}{3}}$ for spherical molecules has been found back, but now on better grounds than above.

But this does not terminate the investigation into the value of b_{lim}. I have put the chance that in v_{lim} collisions with a single molecule or with 2 molecules might take place equal absolutely to 0. By putting $v_{lim} = 4\pi r^2 \beta r$ I have assumed the possibility that there is also a chance of collision for points the projection of which on the central plane at right angles to the direction of motion lies at the edge of this central plane, also still at this great density. A more complete investigation would probably yield a still somewhat lower value of β.

My principal aim was to draw attention to the difference in the value of b_0 and b_{lim}. I had been astonished myself at the comparatively small value of $\frac{b_g}{b_{lim}}$, whereas $\frac{b_g}{b_0}$ has such a large ratio. For spherical molecules the latter amounts to $\frac{4\pi}{3\sqrt{2}}$ or almost 3, whereas $\frac{b_g}{b_{lim}}$ may possibly come near to half 3. The relations at which I had arrived, viz. $\frac{f-1}{3} = \frac{b_g}{b_{lim}}$ and $s = \frac{8}{3}\sqrt{\frac{b_g}{b_{lim}}}$ would be altogether incorrect, if one should confuse b_{lim} and b_0. It is, however, very easy to see that the pressure equal to infinitely great *can* occur when $v = b$, but that this is not the case for $b = b_0$. Then for spherical molecules $\frac{v_0}{b_0} = \frac{3\sqrt{2}}{\pi}$. And so the final point of the b-curve does not lie in the line which divides the angle between the v and the b axes into two equal parts, but in the line which makes a much smaller angle with the v-axis, the tangent of which is about equal to $\frac{1}{\sqrt{2}}$ or about 0,74.

I have questioned myself whether I can account for the result at which I have arrived. Especially the existence of b_{lim} and the relation of this quantity to the existence of groups of molecutes which simultaneously, four at a time, collide, or at any rate are so close together that the space between them may be considered as zero. And though there are still numerous questions to which the answer cannot yet be given, and there is therefore reason to hesitate before publishing the foregoing, yet the considerations which result from this question have given me the courage which might else have failed me.

How large is the space allowed to the motion for molecules with dimension? The external volume must be diminished 1 by a volume at the wall. The centres of the molecules cannot reach the wall, but must remain at a distance $= r$. Hence if O is the area of the wall, a volume $= Or$ must be subtracted from the motion. 2. the centres cannot reach the surface of the molecules, but must remain at a distance $= r$. Then a volume $= O'r$ would have to be deducted, if O' is the area of the joint molecules, and so it would be the same thing if the molecules had a radius $= 2r$. But then if the molecule A collides with the molecule B, we have counted the space that is to be deducted, twice, both for A and for B. Of course the space to be deducted mentioned under 2 greatly preponderates on account of the great number of molecules.

But the occurrence of collisions is a reason for b_g to be diminished. If a molecule strikes against the wall o1 if a molecule approaches the wall so closely that there is no room for another to pass, two parts of the space inaccessible to the motion overlap, and hence the extent of the inaccessible space diminishes. This is also applicable for the collisions of the molecules inter se. If two molecules are so close together that a third cannot pass between, part of the space which is inaccessible to the 3rd molecule overlaps, and b is diminished. The greater the number of collisions, so the smaller the volume, the more b is diminished. Whether also the temperature has influence on this diminution of b has not yet been decided. In case of greater velocity there are indeed, more collisions, but we may also assume that they are of shorter duration. At the moment, however, I shall leave this point undecided. What I have said here about the cause of the diminution of b with smaller v is practically what I had assumed as cause already before when I assumed the so-called overlapping of the distance spheres as cause.

The formula then derived for $b = b_g - \alpha \frac{b_g}{v} + \beta \left(\frac{b_g}{v}\right)$ etc. was not satisfactory, and gave a far too rapid decrease with the calculated coefficients α and β. And the cause of this at least I think I shall have to attribute to the quasi association. If for a moment I disregard the motion, and think all the molecules to be distributed in pairs, every pair being in contact, the diminution in the value of b is $\frac{1}{2}$ N-times the overlapping of the space at the collision between these molecules. But if in the motion I again admit the arbitrary pretty regular distribution and if I assume the original space, the diminution in b would of course be much less, and would only hold for those that collide. So for every kind of collision either of 2 or 3 or 4 or perhaps of a greater number the chance that such a collision occurs in the given volume must be calculated, and this fraction must be multiplied by the parts of the spaces which overlap at every kind of collision.

In the formula $\frac{b_g - b}{b_g} = \alpha \frac{b_g}{v} + \beta \left(\frac{b_g}{v}\right)^2$ etc. $\frac{b_g}{v}$ represents the chance that 2 molecules come near enough to each other to bring about overlapping of the distance spheres; in the same way $\left(\frac{b_g}{v}\right)^2$ the chance that 3 distance spheres overlap etc. And multiplied by a certain coefficient this would also be the case in complete absence of any cause of association, so if there are no special reasons for the molecules to aggregate. The quantities α, β, are the pieces of the distance spheres that overlap. For b_g all the molecules without exception are counted, whether they are separate or whether they are part of an aggregation — and for the factor of α all the groups of 2 molecules, whether or no they appertain to a larger aggregation. But I have not yet calculated all this.

That with diminution of the volume the decrease of b will take place more and more rapidly may already be inferred from this that the number of every kind of collision or rather sufficient approach to each other, increases in a heightened degree, and at last if only the volume has become small enough, it may be assumed that overlapping of the distance spheres takes permanently place. For an arbitrary direction of motion we shall probably not have to go any higher than to a sufficient approach of 4 molecules, and this would justify the above given calculation of $v_{lim} = b_{lim}$. We should have calculated this point when with decrease of v, the decrease of b is equal to it. Then $\frac{db}{dv} = 1$. With values of $v < v_{lim}$ all the molecules are not yet in contact; then there are still motions possible in this space, e. g. flowing of the substance or vibratory motions. But the motion which we call heat, has become impossible. Not until v_0 is reached does every motion become impossible. The points of the b-curve, which I have continued as far as in b_0 above, have of course, no physical significance. The portion of the b-curve between $b_{lim} = b_0$ is then only to be considered as a parasitical branch. In the formula for the calculation of b this branch is probably also included. Accordingly I have entirely returned to the idea that the diminution of b is an apparent diminution of the volume of the molecules.

In these remarks I have touched upon several points which are of importance for the theoretical treatment of exceedingly condensed substances — without being able as yet to bring the investigation to a close. That I mention them already now is because I hope it may stimulate others to give their attention to it, and that they may try their strength to bring the investigation to a close. The determination of v_{lim} seems to me of special importance.

Summary of the results obtained in this and previous communications.

If it was rigorously valid the law of the corresponding states would have taught that all substances belonged to the same genus. This has proved not to be entirely complete. Experience teaches that from this point of view, there are differences. All the substances, indeed, belong to the same genus, but there are different species. If the quantities characteristic of a substance are called the quantities f, s, and r, they appear to differ. But these differences need not be considered as differences in 3 characteristic quantities, but they may be reduced to a single quantity. If this single quantity is called h, then $\frac{f-1}{1} = h$, $s = \frac{8}{3}\sqrt{h}$ and 2 is at least approximately equal to $\frac{3}{\sqrt{h}}$. When we try to find the significance of this characteristic quantity, it will be found, as was à priori to be expected in what was left out of account in the derivation of the law of corresponding states, viz. the variability of b. This variability of b differs for different substances, and depends on the form of the molecules or on the quasi-association, which indirectly influences the course of b. If we put b_g for the greatest value of b and b_{lim} for the smallest value which is of importance for the equation of state, the ratio $\frac{b_g}{b_{lim}}$ is different. This ratio however, oscillates comparatively little round the value 2.

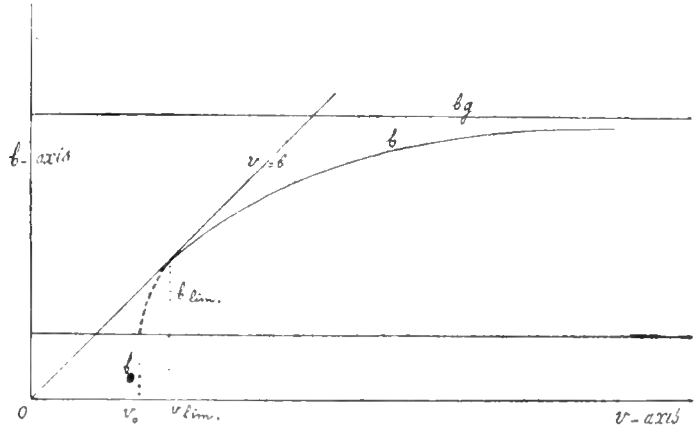

Fig. 1.

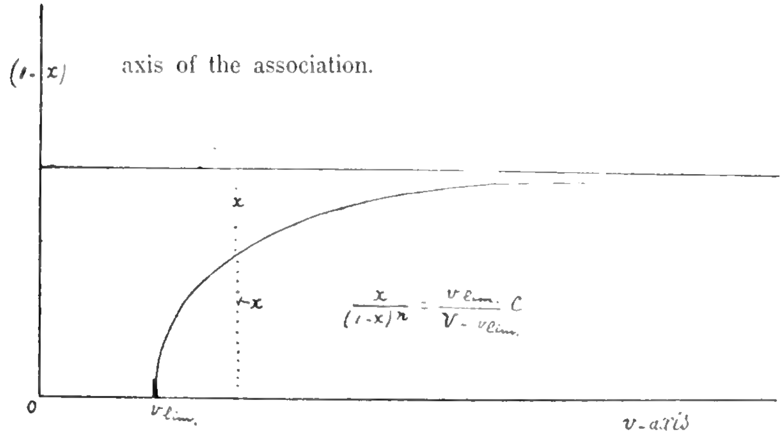

Fig. 2.

This ratio $h = \frac{b_g}{b_{lim}}$ determines, if I continue to speak of species, the species to which the substance belongs.

The value of b_{lim} is that value of b, for which v has the same value as b, and the pressure is therefore infinitely high. This value of $v_{lim} = b_{lim}$ is the smallest volume in which the substance can still be in thermal motion, but it is still appreciably greater than the joint volume, in which the molecules, when they were stationary, could be contained. The reduced equation of state which has the form

$$f\{\pi, \mathbf{v}, m\} = 0,$$

if b should be put constant, assumes the form:

$$f\left\{\pi, \frac{\mathbf{v}}{\sqrt{\frac{b_g}{b_{lim}}}}, m\right\} = 0,$$

when the variability of b is taken into account, with gradually increasing deviation, however, as the density approaches the limiting density.

The form of this latter function is:

$$\left\{\pi + 3\frac{\frac{b_g}{b_{lim}}}{\mathbf{v}^2}\right\}\left\{3\frac{\mathbf{v}}{\sqrt{\frac{b_g}{b_{lim}}}} - \frac{8}{rs}\frac{b}{b_g}\right\} = 8m.$$

The deviation gradually increasing with the density is caused by the variable term $\frac{b}{b_g}$. The influence of this deviation may be neglected for large values of $\mathbf{v}$. At the critical density the different values of $\frac{\mathbf{v}}{\sqrt{\frac{b_g}{b_{lim}}}}$ differ only a few percentages. At the limiting density the value of this latter quantity is equal to $\frac{1}{f-1}$. Now that f oscillates round 7, this greatest difference is after all perhaps less great than might be feared, but yet not negligible, and manifests itself in the different directions of the rectilinear diameter [1]).

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[1]) For more accurate and more definite views arrived at later I must refer to my "Weiteres zur Zustandsgleichung" Akademische Verlagsgesellschaft Leipzig, which will shortly appear.

Microbiology. — "*Oxidation of petroleum, paraffin, paraffinoil and benzine by microbes.*" By Dr. N. L. Söhngen. (Communicated by Prof. M. W. Beijerinck).

(Communicated in the meeting of January 25 1913).

In the following it is shown that the hydrocarbons[1]) of the paraffin series, which chemically are so difficult to decompose, are easily oxidised to carbonic acid and water under the action of microbic life.

Most of the fat-splitting moulds do not grow or only very poorly on paraffin. Rahn[2]) has described a white *Penicillium* which can use paraffin as source of carbon whilst, according to this experimenter, bacteria cannot grow on hydrocarbons.

But the latter statement is incorrect. Most of the bacteria which oxidise the hydrocarbons cannot decompose the fatty acids, which in their chemical composition differ little from the paraffins, but some species are also able to split fats by secretion of lipase.

Hence, the paraffin-oxidising bacteria can be classified in two groups: fat-splitting and non-fat-splitting.

To the former belong: *B. fluorescens liquefaciens*, *B. pyocyaneus*, *B. punctatus*, *B. fluorescens non liquefaciens*, *B. Stutzeri*, *B. lipolyticum* α, β, γ and δ, and the *Micrococcus paraffinae*, described below. To the second group belong some species of the genus *Mycobacterium*.[3])

Oxidation in crude cultures.

The oxidability of petroleum, paraffin, vaselin and benzine was ascertained as follows.

To 100 cm^3 of a culture liquid consisting of: tapwater 100, ammoniumchlorid 0.05, bikaliumfosfate 0,05, in Erlenmeyer flasks

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[1]) For these experiments were used: paraffin (Grübler), paraffinoil (Merck), vaseline, petroleum (American and Russian), and benzine Beside the common commercial petroleum I often used a more purified product obtained as follows. American petroleum was shaken with sulfuric acid D. 1,84, with repeated refreshing of the acid, then with potash solution; after this again treated with acid and once more with potash; it was then dried on sodium and distilled. The fraction 150°—250° (free from nitrogen) served after removing of a small quantity of sulfuric acid by potash solution as food for the microbes.

[2]) Rahn, Ein Paraffin zersetzender Schimmelpilz. Centralblatt für Bakt. 2 Abt. S. 382, 1906.

[3]) A. Weber, Ueber die Tuberkelbazillen ähnlichen Stäbchen und die Bazillen des Smegma's. Arbeiten aus dem kaiserlichen Gesundheitsamte 1903. Bd. 19. S. 251.
Neumann und Lehmann, Grundrisz der Bakteriologie. 5e Auflage 1912. S. 619.

of ± 450 cm³ capacity, was added about 1 °/₀ of one of the paraffins; this medium was inoculated with about a gram of garden soil and placed at 20°, 28° and 37° C.

Commonly after two days already growth of microbes is observed in the tubes at 28° and 37°; after about 7 days in those at 20°. The acceleration of the development is then very marked, so that the liquid becomes cloudy in consequence of the great number of microbes growing at the expense of the hydrocarbons. The growth in the cultures, transferred to a similar medium, is also very strong and the droplets of the hydrocarbons are enveloped by a thick slimy layer of microbes. In a short time the hydrocarbons, disappear entirely from the medium.

From the foregoing follows that petroleum, paraffin, paraffinoil, vaselin and benzine are oxidised by bacteria.

This explains the disappearance of the petroleum, daily brought at the surface of canals by motor boats and in other ways, and from the sewage water of the petroleum refineries.

Isolation of the bacteria.

The paraffin-oxidising bacteria were isolated by streaking the above described crude cultures on plates consisting of: washed agar 2 (or gelatin 10), bipotassiumfosfate 0,05, ammoniumchlorid 0,05, magnesiumsulfate 0,05, distilled water 100.

To this medium was added as source of carbon, petroleum in the form of vapour, from a small dish placed on the cover of the inverted culture box.

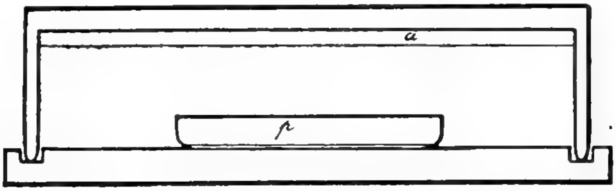

Fig. 1. Culture method on agar a with salts and petroleum as vapour from the dish *p*.

In this way only those bacteria which can oxidise petroleum vapour develop on the agar to colonies and are very easily isolated.

The growth of the microbes is vigorous, the bacteria assimilating, beside the vapour directly taken up, the petroleum condensed around the colonies and forming an iridescent layer on the agar.

On comparison of the velocity of growth of the various species, much difference between them is observed.

By direct sprinkling of soil, canal water, or other material on the plates, several species which do not accumulate in the described culture liquids, can be isolated. Moreover it is possible in this way to determine the number of paraffin-oxidising microbes in any material. So, in one gram of garden soil at Delft ± 50,000, in one cm^3. canalwater ± 8000 paraffin-oxidising microbes were found, which shows that they are very common.

It is clear that this method is also applicable to other volatile compounds.

For a nearer examination the cultures were sown, beside on the above plates, on broth gelatin and broth agar, and on media of other composition.

Accumulation of paraffin-oxidising species at various temperatures.

When the above media, consisting of tapwater, anorganic salts, and one of the hydro-carbons, are placed at temperatures between 15° and 25° C. and the transfers are also cultivated at these temperatures, *B. fluorescens liquefaciens, B. punctatus,* and other liquefying species are particularly obvious, but there likewise occur some fat splitting, non-liquefying bacteria and micrococci, which can all be distinguished on broth gelatin.

In the tubes placed at 26°—30° C. the number of liquefying bacteria is still very great, yet, non-liquefying species are more common than at lower temperatures. At the same time the non-fat-splitting group of the paraffin-oxidising species, the mycobacteria, begin to develop, but especially at 30°—37° C. they find their optimum. They are very striking by their morphological properties and pigment formation.

By this method white, brown, red, and red-brown species were isolated. At 37° C., with paraffin as carbon source, a fat-splitting micrococcus developed in almost pure state, which oxidised paraffins vigorously; it was called *Micrococcus paraffinae* and is in its properties, except in shape, similar to *B. lipolyticum* 1).

If instead of garden soil, sewage water is used for the infection, the growth of fluorescents and of *B. pyocyaneus* may become so intense,

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1) These Proceedings, 1911.

that the above mentioned species do not wel develop and often quite disappear.

At infection with pasteurised soil (5 minutes at 80° C.) no growth takes place, which shows that to the spore-forming bacteria no paraffin-oxidising species belong.

Under anaerobic conditions paraffins are not broken off by bacteria.

Description of the paraffin-oxidising mycobacteria.

These bacteria are immotile; in young cultures (8 hours on broth agar at 30° C.) they are rod-shaped, length 4 μ—10 μ, width 0.5 μ—1.5 μ, after division it often occurs that the two individuals are still joined in one point.

Very characteristic is the appearance of ramifications in these microbes, which remind of bacteroids such as are found in *B. radicicola.*

After some days' culture on broth agar or broth gelatin, these rod-shaped bacteria pass into *Streptococcus*-like organisms, the cells of this form having a diameter equal to the width of the rod form. The *Streptococcus*-form produces, on a new medium, first the rod form, which then again passes into that of the *Streptococcus.*

Spore formation does not occur; heating during 5 minutes at 65° is not resisted.

All species secrete some slime. The growth of the mycobacteria, which after their pigment-forming power on potatoes or on broth gelatin are distinguished in *Mycobacterium phlei* LEHMANN and NEUMANN, *M. lacticola* L. and N., *M. album*, and *M. rubrum*, varies very much on different media as is shown in the table below, where some of the results on growth and pigment formation are given.

On potato these microbes form most pigment ¹) and grow very well; likewise on broth-, malt-, und glucose gelatin. A very good medium is also broth gelatin or broth agar with 3 °/₀ glucose.

Besides on the above substances the fat-splitting bacteria and the *Mycobacteria* grow on humus compounds without these being decoloured. The best source of carbon is peptone, then follows asparagin, ammonium chlorid, and potassiumnitrate. Nitrate is reduced to nitrite; denitrification does not take place. In broth, with 3 °/₀ peptone, indol is not formed.

In broth with 3 °/₀ glucose, no fermentation is observed.

Tyrosin is not changed into melanin.

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¹) The pigment of *Mycobacterium rubrum* is probably carotine; it resists hydrochlorid (38 °/₀), potash solution, and ammonia, dissolves in chloroform and ether and is coloured dark blue by sulfuric acid of density 1,86.

GROWTH AND PIGMENT FORMATION BY *MYCOBACTERIUM* ON VARIOUS MEDIA.

		Broth gelatin	*Potato*	*Malt-gel.*	*Cane sugar gel.*	*Glucose gel.*	*Lactose gel.*	*Maltose gel.*	*Mannite gel.*	*Asparagin gel.*	*Calcium malate gel.*	*Calcium butyrate gel.*	*Calc. acetate gel.*	*Calc. formiate gel.*
Mycobacterium	album	white	whiterose	whiterose	white	white (acid)	white, very slight growth	—	white	white	white	as calc. malate gel. but slighter growth	white	—
	phleï	red-brown	red-brown	red-brown	—	orange (acid)	—	—	orange, bad growth yellow	orange-yellow	orange-yellow		red-brown	—
	lacticola	yellow	dark-yellow	yellow	yellow little growth	dark-yellow (acid)	—	—	yellow	yellow little growth	yellow		yellow	—
	rubrum	dark-red	dark-red	dark-red	—	dark-red no acid	—	—	—	red, little growth	red		red	—

Aesculin and indican are not decomposed.

Urea is only splitted by *Mycobacterium album*.

In feebly acid media the growth is inhibited; it is best in neutral or feebly alkaline solutions.

At the oxidation of paraffins, organic acids, probably fatty acids are formed as intermediary products; they are, however, only present in slight quantities and evidently are oxidised almost as quickly as produced. Acid formation from paraffin could, however, be shown with the help of washed agar plates to which a little congo red had been added, or in which some calciumfosfate was precipitated. In the former case blue fields appeared under the inoculation streaks, in the latter clear ones.

Velocity of the petroleum and paraffin oxidation.

The velocity with which *Mycobacterium album*, *M. rubrum*, *Micrococcus paraffinae*, and *B. fluorescens liquefaciens* oxidise petroleum, was ascertained by weighing the quantity of carbonic acid formed in a certain time. The diminution of the petroleum could not be directly stated as it always evaporates.

The quantity of the produced carbonic acid was ascertained as follows.

As culture vessel was used a one liter ERLENMEIJER flask provided with a ground glass stopper, bearing a vertical glass tube, reaching to near the bottom, and a side tube. It was filled with ± 200 cm^3 of a sterile culture liquid, consisting of distilled water, anorganic salts, and 2 cm^3. sterile petroleum.

The vertical glass tube was connected with a large U-tube filled with soda lime; the side tube was joined to an apparatus successively formed by U-tubes, filled with sulfuric acid, beads and paraffinoil (to keep back the petroleum vapour), calciumchlorid, potash solution to weigh the carbonic acid, and calciumchlorid for control, with a KÖRTING pump at the end. When the cock of the pump is opened a current of air, freed from carbonic acid, passes through the fluid and yields the dried carbonic acid, formed in the culture, to the potash tube.

During 24 hours are formed in the culture, if infected and placed at 28° C., Milligrs. carbonic acid by:

Mycobacterium album	55
Mycobacterium rubrum	41
M. paraffinae	34
B. fluorescens liquefaciëns	27
Crude culture	93

About a third part of the weight of the carbonic acid corresponds to the oxidised petroleum.

The velocity with which paraffin is oxidised by these bacteria was estimated by stating the diminution in weight, by the bacterial action, of two grams of paraffin, very minutely mixed with distilled water and anorganic salts, after a month's culture at 28° C.

The rest of the originally added paraffin was dissolved in petroleum-ether; of this solution a certain quantity was evaporated and the remaining quantity of the paraffin was weighed.

So it was found that during a month's culture was oxidised in mgrs. by:

Mycobacterium album	300
,, *rubrum*	330
Micrococcus paraffinae	180
B. fluorescens liquefaciëns	180
Crude culture	540

Summary.

1. Paraffins (petroleum, paraffin, benzine) can be used by certain species of microbes as source of carbon and energy, and are oxidised to carbonic acid and water. As intermediary products acid could be indicated.

The bacteria were obtained by means of the accumulation method, with the said substances as source of carbon.

2. The microbes active in this process belong to two groups.

a. Fat-splitting bacteria, very common in nature, as *B. fluorescens liquefaciens, B. pyocyaneus, B. punctatus, B. Stutzeri, B. lipolyticum, M. paraffinae.*

b. Non-fat-splitting bacteria belonging to the genus *Mycobacterium* likewise widely spread, of which the following were distinguished: *Mycobacterium album, M. phleï, M. lacticola,* and *M. rubrum.*

3. The paraffin-oxidising species decompose, on an average, 15 mG. petroleum and 8 mm. paraffin in 24 hours at 28° C. per 2 cm^2. surface of culture liquid.

Microbiological Laboratory of the
Technical University, Delft.

Physics. — *"The coefficient of diffusion for gases according to* O. E. MEYER." By Prof. J. P. KUENEN.

(Communicated in the meeting of January 25, 1913).

Among the various methods of deriving an expression for the coefficient of diffusion from the kinetic theory on the assumption that the molecules behave like elastic spheres there is one — that of O. E. MEYER [1]), — which leads to a result differing largely from the others and from observation, although the fundamental assumptions are essentially the same.

The deduction of MEYER's formula is shortly as follows [2]): a plane of unit area is considered at right angles to the gradient of concentration and therefore to the diffusion stream, and the numbers of molecules of each kind are calculated which cross the plane per second. It is assumed that the molecules have on the average had their last collision at a distance l (mean free path) from the point where they cross the plane and that their number in each direction is proportional to their density at the point where the last collision has taken place. The numbers in question of both kinds of molecules are found to be

$$a_1 = -\frac{1}{3} u_1 l_1 \frac{dn_1}{dx} \quad \text{and} \quad a_2 = -\frac{1}{3} u_2 l_2 \frac{dn_2}{dx},$$

where u is the mean molecular velocity, n the number of molecules in unit volume and x the direction of the diffusion stream; obviously $\frac{dn_1}{dx} = -\frac{dn_2}{dx}$; for l_1 and l_2, the mean free paths of the two kinds of molecules in the mixture, we have

$$l_1 = 1 : \left\{ \sqrt{2}\, n_1 \pi s_1^2 + n_2 \pi \sigma^2 \sqrt{\frac{m_1 + m_2}{m_2}} \right\}$$

and

$$l_2 = 1 : \left\{ \sqrt{2}\, n_2 \pi s_2^2 + n_1 \pi \sigma^2 \sqrt{\frac{m_1 + m_2}{m_1}} \right\};$$

where s is the diameter of the molecule and $\sigma = \frac{1}{2}(s_1 + s_2)$.

Owing to this double stream of molecules a total number $a_1 + a_2$ pass through the plane: this would in general represent a motion of the gas. As the gas considered as a whole is supposed to be at rest, the stream $a_1 + a_2$ will produce a pressure gradient by which a stream of the gas as a whole of the same amount in the opposite

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[1]) O. E. MEYER, Die kin. Theorie der Gase p. 252 seq. 1899.

[2]) e. g. L. BOLTZMANN, Kin. Theorie. I. p. 89 seq. 1896.

direction is generated. When this stream is superposed on the first. the numbers of molecules become $a_1 - \frac{n_1}{n}(a_1 + a_2)$ and $a_2 - \frac{n_2}{n}(a_1 + a_2)$ and the coefficient of diffusion D

$$D = \frac{1}{3n}(n_2 u_1 l_1 + n_1 u_2 l_2).$$

According to this formula D would vary strongly with the composition of the mixture, when m_1 and m_2 differ much. In order to show this we put successively $n_1 = 0$ and $n_2 = 0$ and find for the limiting values of D:

$$D\,(n_1 = 0) = \frac{1}{3}\,\frac{u_1}{n\pi\sigma^2}\sqrt{\frac{m_2}{m_1 + m_2}}$$

$$D\,(n_2 = 0) = \frac{1}{3}\,\frac{u_2}{n\pi\sigma^2}\sqrt{\frac{m_1}{m_1 + m_2}}$$

Using the relation $u_1^2 m_1 = u_2^2 m_2 = \frac{4}{\pi h}$, where h is the constant in MAXWELL's law of distribution, we can also write

$$D\,(n_1 = 0) = \frac{2}{3\pi n\sigma^2}\,\frac{1}{\sqrt{\pi h}}\sqrt{\frac{m_2}{m_1}\,\frac{1}{m_1 + m_2}}$$

$$D\,(n_2 = 0) = \frac{2}{3\pi n\sigma^2}\,\frac{1}{\sqrt{\pi h}}\sqrt{\frac{m_1}{m_2}\,\frac{1}{m_1 + m_2}}$$

The two values of D are to each other as $m_2 : m_1$ e. g. for carbon dioxide and hydrogen as $2 : 44$.

The experimental evidence ¹) is in favour of a coefficient which varies with n_1 and n_2, but only to a very small extent, so that a variation as given by MEYER's formula is out of the question.

The coefficient of diffusion according to STEFAN ²) is:

$$D = \frac{3}{16n\sigma^2}\,\frac{1}{\sqrt{\pi h}}\sqrt{\frac{m_1 + m_2}{m_1 m_2}},$$

therefore independent of the composition of the mixture, which agrees approximately with experiment. The same expression follows from MAXWELL's second theory when applied to elastic molecules; this was proved by LANGEVIN ³). The only simplifying supposition which

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¹) Compare A. LONIUS, Ann. d. Ph. (4) 29 p. 664. 1909

²) J. STEFAN, Wien. Sitz.ber. 65 p. 323. 1872

³) P. LANGEVIN, Ann. chim. phys. (8) 5 p. 245. 1905. MAXWELL himself had used the same method (Nature 8. p. 298. 1873): his result given without proof differs by the factor $^4/_3$ from that of LANGEVIN.

he had to make in order to carry out the required integrations was, that in ordinary slow diffusion MAXWELL's law of distribution may be taken as fulfilled. The want of rigour which this implies may perhaps account for the small difference between the formula and observation mentioned.

The question arises, what causes the great difference between MEYER's result and the others. GROSS[1]) criticised the superposition of the gas current on the diffusion current: he tried to improve the theory by leaving out the former and by taking $\frac{1}{2}(a_1+a_2)$ as the real diffusion stream; but this is certainly illegitimate, as the definition of D presupposes the gas to be at rest or the plane through which the diffusion stream is calculated to move with the gas.

LANGEVIN[2]) pointed out, that the dynamical action between the two kinds of molecules is lost sight of altogether in MEYER's method, but he failed to indicate, how to modify or supplement it in order to take this action into account. Neither does BOLTZMANN explain the striking contradiction between the two methods.

It is possible to remove this contradiction for the greater part by making use of the notion of *persistence* of molecular velocity which JEANS[3]) introduces into the kinetic theory and which also plays an important part in the theory of the Brownian movement. This quantity depends on the principle that, when a molecule collides with other molecules, it will after a collision on the average have retained a component of velocity in the original direction. JEANS has calculated what fraction of the original velocity this component is on the average: he calls this fraction the *persistence* ϑ and finds

$$\vartheta = \frac{1}{4} + \frac{1}{4\sqrt{2}} \, log\,(1+\sqrt{2}) = 0.406.$$

JEANS shows that the usual calculations in the kinetic theory of the various transport-phenomena of which diffusion is an example have to be corrected for this persistence. For the sake of simplicity it is assumed that a molecule describes the same distance l between successive collisions. Owing to persistence a molecule will on the average after describing a path l travel on in the same direction over distances successively of $l\vartheta$, $l\vartheta^2$ etc., therefore altogether describe a distance $l/(1-\vartheta)$ before its motion in the given direction is exhausted and similarly a molecule which reaches a plane from a distance l will not on the average have had a component 0 in the given

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[1]) G. GROSS. Wied. Ann. 40 p, 424 1890.

[2]) l.c.

[3]) J. H. JEANS. The dynamical theory of gases p. 236 sqq. 1904.

direction at that distance before it collided there, but at a distance $l/(1-\vartheta)$. We can also say, that the molecules which have had a collision at a distance $l/(1-\vartheta)$ succeed on the average in getting to the plane before their velocity in the given direction is reduced to 0. In the calculation of the numbers that cross the plane it was assumed that the velocities were evenly distributed in all directions at a distance l: as it now appears that this condition does not hold for a distance l but for the distance $l/(1-\vartheta)$, the correct result is obtained by replacing l by $l/(1-\vartheta)$ in the final formula.

In this manner JEANS corrects MEYER's formula [1]), but it is clear that by this means no improvement is effected, as D is multiplied by a constant factor and the anomalous dependence on n_1 and n_2 remains. An important point has however been overlooked by JEANS viz. that the persistence obtains a different value when one deals with a mixture of two kinds of molecules of different mass.

When the calculation of ϑ is carried out for a molecule m_1 amongst molecules m_2 one finds

$$\vartheta = \frac{m_1 + m_2 \left\{ -\frac{1}{2} + \frac{1}{2\sqrt{2}} \log(1+\sqrt{2}) \right\}}{m_1 + m_2} = \frac{m_1 - 0.188\, m_2}{m_1 + m_2}.$$

For $m_1 = m_2$ this expression reduces to the one given by JEANS. As a molecule m_1 collides not only with molecules m_2 but also with molecules of its own kind, the correct expression for the persistence is obtained by multiplying the average number of collisions of the latter kind by 0.406 and that of the former by the above fraction. In this manner the factor $1/(1-\vartheta)$ becomes

$$f_1 = 1 : \left\{ 1 - n_1 \pi s_1^2 \sqrt{2}\, l_1 \times 0.406 - n_2 \pi \sigma^2 \sqrt{\frac{m_1 + m_2}{m_2}}\, l_1 \frac{m_1 - 0.188 m_2}{m_1 + m_2} \right\}$$

for the molecules m_1 and

$$f_2 = 1 : \left\{ 1 - n_2 \pi s_2^2 \sqrt{2}\, l_2 \times 0.406 - n_1 \pi \sigma^2 \sqrt{\frac{m_1 + m_2}{m_1}}\, l_2 \frac{m_2 - 0.188 m_1}{m_1 + m_2} \right\}.$$

for the molecules m_2.

Repeating MEYER's argument we find for D

$$D = \frac{1}{3n} (n_2 u_1 l_1 f_1 + n_1 u_2 l_2 f_2).$$

If we now put $n = 0$, we obtain

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[1]) JEANS l.c. p. 273. Comp. M. v. SMOLUCHOWSKI, Bull. de l'Ac. d. Sc. de Cracovie 1906, p. 202.

$$D\,(n_1=0)=\frac{u_1}{3n\,\pi\sigma^2}\sqrt{\frac{m_2}{m_1+m_2}}\;\frac{1}{1-\dfrac{m_1-0.188\,m_2}{m_1+m_2}}=$$

$$=\frac{u_1}{3n\,\pi\sigma^2}\sqrt{\frac{m_1+m_2}{m_2}}\times\frac{1}{1.188}=\frac{2}{3\pi\,n\sigma^2}\,\frac{1}{1.188}\,\frac{1}{\sqrt{\pi h}}\sqrt{\frac{m_1+m_2}{m_1m_2}}.$$

The symmetry of this expression shows that exactly the same value holds for $n_2=0$. The form of D also agrees with Stefan's expression: the coefficients are in the relation of 1 : 1.05; therefore, considering the approximate character of the deduction, there is practically complete agreement.

For intermediate compositions the difference between the two expressions for D becomes material only when m_1 and m_2 are very different. This is probably due to the method of calculation which compels us to work with averages from the beginning. Moreover Jeans's method of calculating the persistence is not rigorous: it might perhaps be found possible by applying more rigorous methods to reduce the remaining difference between Meyer's corrected formula and the other one. As a matter of fact the object of this paper was not so much to deduce a correct formula, considering that the near accuracy of Langevin's method cannot well be doubted, as to remove the strong contradiction between the two results.

In conclusion it may be added, that the method which is indicated in this paper can immediately be used to deduce rational formulae for the viscosity and the conduction of heat for gas mixtures.

Mathematics. — *"On bilinear null-systems."* Communicated by Prof. Jan de Vries.

(Communicated in the meeting of January 25, 1913).

§ 1. In a *bilinear* null-system any point admits one *null-plane*, any plane one *null-point*. The lines incident with a point and its null-plane are called *null-rays*. If these lines form a linear complex, we have the generally known null-system, which is a special case of the correlation of two collocal spaces (null-system of Möbius). The null-rays of any other null-system (1,1) fill the entire space of rays; with R. Sturm we denote by γ the number indicating how many times any line is null-ray.

In the first we suppose $\gamma=1$ and we examine the null-systems which may be called *trilinear* and which can be represented by (1,1,1).

§ 2. If a plane q rotates around the line l its null-point F describes a conic $(l)^2$; for on account of $\gamma = 1$ there is one position of q for which F lies on l.

The null-points of the planes q passing through any point P lie on a quadratic surface $(P)^2$; evidently it contains P and on account of $\gamma = 1$ one point more on any line through P.

Evidently the null-plane of P touches $(P)^2$ in P and cuts it according to two lines g, g'. Any point F of one of these lines is null-point of a plane q passing through F and also through P. Therefore these lines are null-rays of ∞^1 pencils (F,q), i.e. *singular*.

So the singular lines of a (1,1,1) *form a congruence* (2,2).

All the other lines of $(P)^2$ are characterized by the fact that the null-planes of their points concur in P; otherwise: P is the vertex of the quadratic cone enveloped by these planes.

§ 3. Two surfaces $(P_1)^2$ and $(P_2)^2$ have in common the conic $(l)^2$ corresponding to the line $l = P_1P_2$. As any other common point S bears two and therefore ∞^1 null-planes, it is *singular*. The locus of this point S is a conic σ^2 meeting $(l)^2$ in two points.

The surfaces $(P)^2$ corresponding to the points P of l form a pencil; the surface passing through any point F is indicated by the point of intersection of l and the null-plane of F. The null-planes of any point S evidently form a pencil, the axis of which may be represented by s^*.

As σ^2 contains two points of $(l)^2$, the line l bears two null-planes the null-points of which lie on σ^2; therefore the locus of the axes s^* is a quadratic scroll or *regulus*.

According to the laws of duality there is a *quadratic cone* Σ_2 any tangent plane of which is *singular*, as it contains ∞^1 null-points lying on a line s_*; these lines generate a *second regulus*.

§ 4. We now consider three surfaces $(P)^2$. As any pencil of planes (s^*) admits a plane passing through a point P_3, the surface $(P_3)^2$ also contains σ^2. Amongst the points common to $(P_3)^2$ and the conic $(l_{12})^2$ we find in the first place the points of intersection of $(l_{12})^2$ and σ^2. One of the two remaining points common to $(P_3)^2$ and $(l_{12})^2$ is the null-point of the plane $P_1P_2P_3$, the other which may be denoted by T lies in three null-planes which do not pass through a line, on account of the arbitrary position of the points P; so T bears ∞^2 null-points, i.e. T is *principal point*.

Evidently all the surfaces $(P)^2$ form a *complex* with the *singular conic* σ^2 and the *principal point* T as common elements. This complex is *linear*, for through any triplet of points F_k passes the surface corresponding to the point of intersection of the null-planes $\varphi_1, \varphi_2, \varphi_3$.

The *vertex* of the *singular cone* Σ_2 bears ∞^1 *singular null-planes* σ not passing through a line; from this ensues that it coincides with the *principal point* T.

In an analogous way the *plane* τ of the *singular conic* σ^2 is *principal plane* of the null-system.

Let us consider the plane through T and one of the axes s^*; it has for null-point the singular point S lying on s^* but at the same time the principal point T; so it is singular and its null-points lie on the line $s_* = TS$. So the *regulus* s_* is a *cone* and consists of the *edges* of the cone projecting the singular conic σ^2 out of T.

Likewise the axes s^* form the *system of tangents* of a *conic* lying in the principal plane τ.

§ 5. The conics $(l)^2$ form a system ∞^4 admitting a representation on the lines of space. For through any two points F_1, F_2 one $(l)^2$ passes, which is completely determined by the line l common to the null-planes φ_1, φ_2.

The cones $[l]_2$ each of which is the envelope of the null-planes of the points of a line l also form a system ∞^4; any of these cones can be determined by means of two planes φ_1, φ_2 the null-points of which indicate then the line l.

If l lies in a singular null-plane σ, the conic $(l)^2$ breaks up into the line s_* bearing the null-points of σ and a second line l' which is bound to cut s_*; so the principal point T which also can figure as null-point of σ cannot lie outside s_*. So we find once more that the regulus (s_*) is a cone.

If l passes through the vertex of Σ_2 and bears therefore two singular planes, $(l)^2$ degenerates into two intersecting lines, the point of intersection coinciding evidently with the vertex of Σ_2; for the null-point of any other plane through l must coincide with that vertex.

§ 6. A special trilinear null-system is determined by the tangential planes of a pencil of quadratic surfaces Φ^2 touching each other along a conic σ^2, where the point of contact forms the null-point. ¹)

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¹) In the case of a general pencil with a twisted quartic as base we get a null-system (1, 3, 2), treated at some length by Dr. J. WOLFF ("Ueber ein Nullsystem quadratischer Flächen", Nieuw Archief voor Wiskunde 1911, vol. IX, page 85).

If the pencil is represented by

$$x_1^2 + x_2^2 + x_3^2 + \lambda x_4^2 = 0 \;^{1)}$$

the tangential plane in (y) has the equation

$$y_1x_1 + y_2x_2 + y_3x_3 + \lambda y_4x_4 = 0,$$

λ being determined by

$$y_1^2 + y_2^2 + y_3^2 + \lambda y_4^2 = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

So for its coordinates (η) we find

$$\eta_1 : y_1 = \eta_2 : y_2 = \eta_3 : y_3 = \eta_4 : \lambda y_4 , \quad . \quad . \quad . \quad (2)$$

or

$$\eta_1 : y_1y_4 = \eta_2 : y_2y_4 = \eta_3 : y_3y_4 = \eta_4 : -(y_1^2 + y_2^2 + y_3^2) \quad . \quad (3)$$

From (1) and (2) we deduce

$$\eta_1^2 + \eta_2^2 + \eta_3^2 + \frac{\eta_4^2}{\lambda} = 0,$$

i. e.

$$y_1 : \eta_1\eta_4 = y_2 : \eta_2\eta_4 = y_3 : \eta_3\eta_4 = y_4 : -(\eta_1^2 + \eta_2^2 + \eta_3^2) \quad . \quad (4)$$

So (4) shows that any plane has only one null-point.

If the null-plane (η) passes through the fixed point $P(z_k)$ we have $\Sigma z_k \eta_k = 0$, so the equation of $(P)^2$ is

$$z_1y_1y_4 + z_2y_2y_4 + z_3y_3y_4 = z_4(y_1^2 + y_2^2 + y_3^2) \quad . \quad . \quad . \quad (5)$$

The intersection of this surface with the surface belonging in the same way to the point $Q(w_k)$ breaks up into the singular conic

$$y_4^2 = 0, \qquad y_1^2 + y_2^2 + y_3^2 = 0$$

and a second conic lying in the plane

$$(z_1w_4 - z_4w_1)\,y_1 + (z_2w_4 - z_4w_2)\,y_2 + (z_3w_4 - z_4w_3)\,y_3 = 0.$$

The latter contains the null-points of the planes passing through PQ. From this ensues that γ is equal to one. [2])

All the surfaces $(P)^2$ pass through the principal point $y_1 = y_2 = y_3 = 0$. As could be expected, this point is the vertex of the quadratic cone touching all the surfaces of the pencil (Φ^2) along σ^2.

The null-planes (η) of the points (y) of the plane ζ envelope the quadratic surface

$$\zeta_1\eta_1\eta_4 + \zeta_2\eta_2\eta_4 + \zeta_3\eta_3\eta_4 = \zeta_4(\eta_1^2 + \eta_2^2 + \eta_3^2).$$

All these surfaces forming a system ∞^3 touching the plane $\eta_1 = \eta_2 = \eta_3 = 0$ $(x_4 = 0)$ and the quadratic cone with the equation $\eta_4 = 0$,

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[1]) Coefficients which might present themselves have been comprised into the definition of the coordinates.

[2]) This can also be found by considering the involution determined on PQ by the pencil (Φ^2); one of the coincidencies lies in the plane of the conic γ^2, the other is point of contact with one of the quadratic surfaces.

$\eta_1^2 + \eta_2^2 + \eta_3^2 = 0$, also represented by $x_1^2 + x_2^2 + x_3^2 = 0$. So we find once more that the plane of σ^2 is the principal plane and that the common enveloping cone of the surfaces Φ^2 touches all the singular null-planes.

By replacing σ^2 by the imaginary circle common to all the spheres, we find the metric null-system in which any plane has for null-point the foot of the normal out of the fixed point T.

We also find a trilinear null-system in the following way. Let σ^2 be any conic and T any point. We then consider as null-plane of any variable point Y the polar plane of TY with respect to the cone with Y as vertex and σ^2 as directrix.

By assuming O_4 in T and representing σ^2 by

$$x_1^2 + x_2^2 + x_3^2 = 0, \qquad x_4 = 0,$$

we find for the null-plane of X the equation

$$y_4 (y_1 x_1 + y_2 x_2 + y_3 x_3) = (y_1^2 + y_2^2 + y_3^2)\, x_4.$$

So the coordinates η_i of this plane satisfy

$$\eta_1 : y_1 y_4 = \eta_2 : y_2 y_4 = \eta_3 : y_3 y_4 = \eta_4 : -(y_1^2 + y_2^2 + y_3^2).$$

As these relations are identical to those of (3) this null-system is equal to the former.

§ 7. We now pass to *bilinear null-systems* where $\gamma = 2$.

Then the locus of the null-points of the planes of a pencil with axis l is a *twisted cubic curve* $(l)^3$ cutting l twice.

Analogously the null-planes of the points of a line l envelope a developable with index 3 (torse of the third class), i.e. they osculate a twisted cubic.

The locus of the null-points of the planes passing through a point P is a *cubic* surface $(P)^3$.

Two surfaces $(P)^3$ and $(Q)^3$ have the curve $(l)^3$ determined by the line $l = PQ$ in common. In general they admit as completing intersection a *twisted sextic* σ^6, cutting $(l)^3$ in *eight* points and forming the locus of the *singular null-points*, each of which bears a pencil of null-planes. (If these planes were to envelope a cone σ^6 has to be manifold curve on $(P)^3$ and this is impossible if we surmise that the intersection of $(P)^3$ and $(Q)^3$ breaks up into *two* parts only).

The axes s^* of the pencils of null-planes through the points S of σ^6 form a *scroll of order eight*; for the points of intersection of σ^6 and $(l)^3$ determine eight null-planes through l, each of which has a point S as null-point and contains therefore an axis s^*.

The surfaces $(P)^3$, $(Q)^3$ and $(R)^3$ have the singular curve σ^6 in common and moreover one point only, the null-point of the plane

PQR. For $(R)^3$ meets the curve $(l)^3$ belonging to $l = PQ$ in eight points on σ^6 and therefore in one point outside σ^6.

Evidently σ^6 is base curve of the linear complex of surfaces $(P)^3$

§ 8. A special null-system (1, 1, 2) can be obtained in the following manner. We start from two pairs of non intersecting lines a, a' and b, b'. We assign to any point F the plane φ of the two transversals t and u through F over a, a' and b, b'.

The hyperboloids (laa') and (lbb') admit a curve $(l)^3$ of which l is a chord as completing intersection. So we have indeed $\gamma = 2$. Also a, a', b, b' are chords of $(l)^3$.

Here the *singular curve* σ^6 is represented by the lines a, a', b, b' and their *quadrisecants* q, q'. So the figure of singularity has eight points in common with $(l)^3$.

For any point S of a the transversal u is determined while we can assume for t any ray of the pencil (Sa'). So the null-planes of S form a pencil with axis u. So the scroll (s^*) breaks up here into the four *reguli* with the director lines (a, b, b'), (a', b, b'), (b, a, a'), (b', a, a').

For any point of q the transversals t and u coincide and the same happens for any plane through q'. So the lines q, q' are not only loci of *singular points* but also envelopes of *singular planes*. As this is also the case with the lines a, a', b, b' the two dually related figures of singularity are united.

§ 9. For a line l intersecting a in A the locus $(l)^3$ breaks up into a conic $(l)^2$ and a line u containing the null-points of the singular plane (la); the conic lies in the plane (Aa') and passes through A, this point being the null-point of the plane connecting l with the transversal u_0 through A.

If l meets q, the curve $(l)^2$ degenerates in q and an $(l)^2$. The lines l determining conics $(l)^2$ form therefore *six special linear complexes*; so there are ∞^3 conics $(l)^2$.

If l meets both lines q and q' the hyperboloids (laa') and (lbb') intersect in l, q, q' and a fourth line l' meeting q, q' as l does. So the relation between l and l' is involutory; each of them contains the null-points of the planes passing through the other, the planes containing either q or q' discarded.

If l meets a and b, the curve $(l)^3$ breaks up into a line u in the plane (al), a line t in the plane (bl) and a line l' cutting t and u containing the null-points of the other planes through l.

If we assume for l a transversal t, the curve $(l)^3$ is represented by the lines u and u' of the planes (al), $(a'l)$ and by t itself. This line evidently contains the null-points of the remaining planes through t; therefore it is *singular*.

We derive from this that the surface $(P)^3$ contains the transversals t and u passing through P; so the null-plane of P is a threefold tangential plane. The third line of $(P)^3$ lying in that plane admits the property that the null-planes of its points envelop a cubic cone with P as vertex.

If a, a', b, b' form a skew quadrilateral each null-plane touches one of the quadratic surfaces of the pencil with those four lines as base. Then the surfaces $(P)^3$ have four nodes in common, the vertices of the tetrahedron with a, a', b, b', q, q' as edges.

§ 10 We still examine an *other null-system* (1,1,2) the singular curve of which degenerates.

Let us assume the conic σ^2 in the plane τ and a pair of non intersecting lines. Through F we draw the transversal t over a, a'; then the polar plane of t with respect to the cone $F(\sigma^2)$ may figure as null-plane of F.

Reversely, if the plane τ is cut by φ according to the line d and D is the pole of d with respect to σ^2, the transversal through D determines in φ the null-point F.

If φ rotates around l, the line d describes a pencil around the trace R of l as vertex and D describes a line of r. But then t describes a regulus with a, a', r as director lines, in projective correspondence with the pencil of planes (φ). Consequently the null-point F then describes a twisted cubic $(l)^3$ with l as chord. The two points common to (l) and $(l)^3$ lie on the regulus.

Each point A of the line a is *singular*. The transversal t describes a pencil in the plane (Aa'), its trace D with the plane τ describes a line e bearing the trace A'_0 of a'. So the polar line d rotates round a point E (pole of e); the null-plane of A describes therefore a pencil with axis AE.

If A describes the line a, the line e keeps passing through A'_0 and therefore E describes the polar line of A'_0. So the axes of the pencils of null-planes corresponding to the singular points A form a *regulus*. A second regulus contains the axes of the pencils corresponding to the singular points A' of a'.

The *conic* σ^2 too is *singular*. Any point S of it admits as null-planes all the planes touching σ^2 in S.

All the surfaces $(P)^3$ have in common the singular curve σ^2, the singular lines a, a' and also the line s through the traces A_0 and A_0' of a and a' with τ, containing two points S_1, S_2 of σ^2.

For any point of s the cone projecting σ^2 degenerates into the plane τ counted twice; so its null-plane is indefinite and this explains why s must lie on each surface $(P)^3$.

Indeed the plane τ is *principal plane*; for the null-plane of any point of τ lying neither on σ^2 nor on s coincides with τ as polar plane of a line t not situated in τ.

In connection with this result the cubic torse of the null-planes of the points lying on l always contains the plane τ, i.e. τ is common tangential plane of all the surfaces of class three enveloped by the null-planes of the points of a plane.

The trace d of a *singular* plane must be incident with the pole D, i.e. it must touch σ^2. In this case t is transversal of a, a', σ^2 and each of its points may figure as null-point. The locus of these transversals is a *quartic scroll* $[t]^4$ with a and a' as double director lines and the line s mentioned above as double generatrix.

The polar surface of any point P with respect to $[t]^4$ intersects σ^2 in six points; the planes touching $[t]^4$ in these points are *singular null-planes*. So these planes envelope a *torse of class six*.

§ 11. In the null-system considered in the preceding article the transversals t form a bilinear congruence. If we replace it by a congruence $(1, n)$ we get a null-system $(1, 1, n+1)$[1]. If the plane φ rotates once more around the line l, in which case its trace d describes a pencil in τ and the pole D a line r, then the ray t resting on r describes a scroll of order $n+1$. So the null-point of φ lies $(n+1)$ times on l $(\gamma = n+1)$ and describes a twisted curve $(l)^{n+2}$.

Let the congruence $(1,n)$ be determined by the director curve α^n and the director line a, which is to have $(n-1)$ points in common with α^n.

Each point of α^n is *singular* and bears a pencil of null-planes (see § 10). From a point of a the curve α^n is projected by a cone of order n with an $(n-1)$-fold edge a. To the trace of this cone, considered as locus of D corresponds a curve of class n, the envelope of the trace d of the null-plane φ. So each point A of a bears ∞^1 null-planes enveloping a cone of class n. So a is an n-fold line on the surface $(P)^{n+2}$.

Here also any point of the *singular conic* σ^2 bears a pencil of null-planes, the axis of which touches σ^2.

The intersection of two surfaces $(P)^{n+2}$ breaks up into a curve $(l)^{n+2}$, the curves α^n and σ^2, the line a (to be counted n^2-times) and

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[1] For $n = 0$ we get the null-system of § 6, for $n = 1$ that of § 10.

the n rays of the congruence lying in τ. As in § 10 the line s these n rays partake of the property that the null-plane of any of their points is indefinite.

The *singular null-planes* touch in the points of σ^2 the scroll $[t]^{2n+2}$ with σ^2, a^n, a as director lines and n double generatrices in τ. The polar plane of P cuts σ^2 in $2(2n+1)$ points each of which bears a singular null-plane; so the *singular null-planes* envelope a *torse* of *class* $(4n+2)$.

Evidently τ is once more *principal plane.*

The bisecants of a twisted cubic a^3 determine in an analogous way a *null-system* $(1, 1, 4)$. Here each point S of the singular curve a^3 is vertex of a quadratic cone enveloped by the null-planes of S.

Now two surfaces $(P)^5$ have in common the singular curve a^3, to be counted four times, the singular conic σ^2, a curve $(l)^5$ and finally the three chords of a^3 lying in τ.

§ 12. By the considerations of § 11 we have shown that bilinear null-systems with $\gamma > 2$ do exist.

Now we will prove that the locus of the singular points of a null-system $(1, 1, \gamma)$, with the condition $\gamma > 2$, *cannot be a single curve.*

Evidently the curve $(l)^{\gamma+1}$ containing the null-points of the planes through l is rational, l being a γ-fold secant. The null-points of the planes through P lie on a surface $(P)^{\gamma+1}$ touched in P by the null-plane of P.

The surfaces $(P)^{\gamma+1}$ and $(Q)^{\gamma+1}$ have a curve $(l)^{\gamma+1}$ in common. Now let us suppose that the completing intersection is a curve σ of order $\gamma(\gamma+1)$.

In order to determine the number of points common to (l) and σ we first determine the number H of transversals passing through any given point O and resting on (l) and σ.

For this number the known relation

$$m(\mu-1)(\nu-1) = 2h + H$$

holds, where μ, ν are the orders of both the surfaces, whilst m is the order of the first curve and h the number of its apparent double points.

Here we have $\mu = \nu = m = \gamma + 1$, $2h = \gamma(\gamma - 1)$, as (l) is rational. So we get $H = \gamma(\gamma^2 + 1)$.

The transversals under consideration are common edges of the cones projecting (l) and σ out of O; the remaining common edges pass through the points of intersection of both the curves.

For the number of these points we find therefore $\gamma(\gamma+1)^2 - \gamma(\gamma^2+1) = 2\gamma^2$.

Now the surface $(R)^{\gamma+1}$ has in common with (l) besides the $2\gamma^2$ points lying on σ and the null-points of the plane PQR still $\gamma(2-\gamma)$ more points and this is only possible for either $\gamma = 1$ or $\gamma = 2$.

So we may conclude that for $\gamma > 2$ the singular points must be arranged at least on *two* curves.

Mathematics. — *"On plane linear null-systems"*. By Prof. JAN DE VRIES.

(Communicated in the meeting of January 25, 1913).

§ 1. By a plane *null-system* (α, β) we understand a correlation between the points and lines of the plane in which to any point F correspond α null-rays f passing through it and to any ray f correspond β null-points situated on it.

We restrict ourselves to the case $\alpha = 1$ in which any point F bears only one null-ray (*linear null-system*) and represent by k the second characteristic number.

If the ray f rotates around a point P, its k null-points describe a curve of order $k+1$ passing through P and touching in P the null-ray of P; we denote that curve by $(P)^{k+1}$.

The curves $(P)^{k+1}$ and $(Q)^{k+1}$ have the k null-points of PQ in common; any of the remaining $(k+1)^2 - k$ points of intersection bears a ray through P and another ray through Q, therefore a pencil of null-rays; so these points are *singular*.

Therefore a *null-system* $(1, k)$ admits $k^2 + k + 1$ *singular points.*

The curves P^{k+1} form together a net with $k^2 + k + 1$ base points; through any pair of arbitrarily chosen points X, Y passes one curve determined by the point common to the two null-rays x, y.

A pencil of curves φ^n with n^2 base points determines a linear null-system, in which to any point F corresponds the tangent f in F to the curve passing through F. This pencil intersects an arbitrary line f in the groups of an involution of order n, admitting $2(n-1)$ double points, therefore $k = 2(n-1)$. This null-system admits $(4n^2 - 6n + 3)$ singular points. To these belong the n^2 base points, lying on ∞^1 tangents; the remaining ones must be nodes of curves φ^n. So we fall back on the known property of the pencil (φ_n) to contain $3(n-1)^2$ curves possessing a node.

§ 2. The *bilinear null-system* (1,1) has three singular points A, B, C. The line AB admits A and B as null-points and bears therefore ∞^1 null-points. So the sides a, b, c of triangle $A\,B\,C$ are *singular lines.*

If F describes any line l, the null-ray f envelops a conic touching a, b, c and l (the latter in its null-point).

The conic $(P)^2$ degenerates if P lies on a singular line. If we assume P on a the null-points of the other lines through P lie on the line PA.

Let f be a line cutting a, b, c in A', B', C' and F its null-point. If f rotates around A' the point F describes a line through A, and the cross ratio $(A'\,B'\,C'\,F)$ remains constant $= \delta$. If f rotates around B', the point F describes a line through B and $(A'B'C'F)$ is once more $= \delta$. So this cross ratio has the same value for all the rays and is characteristic of the null-system. Now, according to a known theorem, we have also $F\,(A\,B\,C\,f) = \delta$.

So any null-system (1,1) *consists of the pairs* $(F,\,f)$ *connected with each other with respect to the singular triangle* $A\,B\,C$ *by the relation* $F\,(A\,B\,C\,f) = const.$

In his "*Lehre von den geometrischen Verwandtschaften*" (vol IV, p. 461) M. R. Sturm proves that this construction furnishes a (1,1) but probably it has escaped him that we can get *any* (1,1) in this way.

A pencil of conics touching each other in two points A, B determine a (1,1) by its tangents. Then the singular points are A, B and the point C common to the common tangents in A and B.

If in any collineation with the coincidencies A, B, C the point F' corresponds to F, the line $f = FF'$ admits F as null-point in a bilineair null-system [1].

§ 3. From a given linear null-system $(F,\,f)$ we derive a new one $(F,\,f^*)$, if we replace f by the line f^* normal to it in F. In this construction f and f^* are harmonically related with respect to the absolute pair of points. By a *harmonic* transformation we will understand the transformation of a null-system in which f and f^* are harmonically separated by the tangents from F to a given curve φ^2 of class two.

For any point F of φ^2, the null-ray f passes into the tangent f^* of φ^2 in F; if f touches φ^2 in F_0 we may assume for f^* any line through F_0 and F_0 is a *singular point* of the new null-system

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[1] From $y_k = c_k\,x_k$, $\sum\limits_3 \xi_k\,x_k = 0$, $\sum\limits_3 \xi_k\,y_k = 0$ we deduce $\rho\xi_1 = (c_2 - c_3)\;x_2x_3$, etc.

i.e $\sigma\xi_1 x_1 = c_2 - c_3$, etc.

$(1, k^*)$. As any singular point of $(1, k)$ remains singular, k^* must surpass k.

In order to determine k^* we bear in mind that all the rays f, which pass into a definite ray f^* by means of the transformation considered, must pass through the pole P^* of f^* with respect to q^2. So the null-points of f^* lie on the curve $(P^*)^{k+1}$ corresponding to P^* in the null-system $(1, k)$.

So a $(1, k)$ *passes into a* $(1, k+1)$ *by the harmonic transformation.*

From these facts we can derive that $2(k+1)$ singular points of $(1, k+1)$ must lie on q^2. We can confirm this result as follows. Let G be the second point of intersection of q^2 with a ray f admitting a null-point F on q^2. Then the curve $(G)^{k+1}$ cuts q^2 in G and in $2k+1$ points F more. In any of the $2(k+1)$ coincidencies of the correspondence (F, G), the ray f touches q^2 and f^* can be taken arbitrarily through F; then F is singular.

By repeating the transformation (F, f^*) must pass reversely into the original null-system $(1, k)$. The null-points of f lie on the curve $(P)^{k+2}$ corresponding to the pole P of f in the null-system $(1, k+1)$. On this curve we also find the points of contact of q^2 with the tangents passing through P; these points are null-points of f in the special null-system $(0, 2)$ of the pencils the centres of which lie on φ^2. So the null-system $(1, k+1)$ is transformed into the combination of $(1, k)$ and a $(0, 2)$ admitting exclusively singular points (the points of q^2).

If a is a singular ray of a null-system $(1, k)$, harmonic transformation with respect to a pair of points lying on a generates once more a $(1, k)$. For in this case ¹) the pole P^* of a ray f^* lies on a, which implies that the locus $(P^*)^{k+1}$ breaks up into a and a curve cutting f^* in k null-points F^*.

§ 4. In the case of the null-system $(1, 2)$ the curves $(P)^3$ form a net with 7 base points. *Any net of cubic curves with 7 base points determines a null-system* $(1, 2)$, in which any line f admits as null-points two base points of a pencil belonging to the net. For the curves of the net generate on f a cubic involution of the second rank, the neutral pair of which belongs to ∞^1 triples, i. e. consists of two base points of a pencil.

The figure of singularity has no special characteristic, as we can choose the base points of the net arbitrarily. As soon as three singular

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¹) So the null-system $(1, 1)$ of the tangents of a pencil of conics in double contact passes by transformation with respect to the absolute pair of points into the null-system of the normals.

points are collinear, the line bearing them is singular, as it contains three and therefore ∞^1 null-points.

Though we can determine any (1, 2) by a net of cubic curves we do not judge it superfluous to point out some null-systems (1, 2) which can be obtained otherwise.

If the points F and F' correspond to each other in an involutory quadratic transformation (quadratic involution) they may be considered as null-points of the connecting line f. Then any line is cut by the conic into which it is transformed in its null-points. Then the figure of singularity contains the four points of coincidence and the three fundamental points and consists therefore in the vertices and the co-vertices of a complete quadrangle, the *six* sides of which are singular lines.

The same figure of singularity is found in the case of the null-system, where any line has for null-points its points of contact with two conics of a pencil.

Another null-system (1, 2) is determined by a pencil of cubic curves admitting three collinear points of inflexion B_1, B_2, B_3 with common tangents b_1, b_2, b_3. The cubic involution determined by the curves of this pencil on any line f has a threefold point on the threefold line $b_0 = B_1 B_2 B_3$; so f is touched by two cubic curves only. We generate a (1, 2) by considering their points of contact as the null-points of f. Three of the singular points coincide with the vertices of the triangle $b_1 b_2 b_3$, whilst B_1, B_2, B_3 are three others; the seventh is node of a non degenerating cubic curve. Evidently there are *four singular lines.*

By applying the harmonic transformation to a null-system (1, 1) with $ABC = abc$ as singular triangle in such a way that the conic q^2 touches a, b, c respectively in A', B', C' we get a null-system (1, 2) of which A, B, C, A', B', C' are singular points whilst the seventh can be found by a linear construction. Here a, b, c are *singular lines.*

§ 5. For any null-system $(1, k)$ the curves P^{k+1} form a net with the singular points as base points. Here any line f bears an involution of order $k+1$ and the second rank admitting a neutral group formed by the k null-points F. But for $k > 2$ the net is not more a general one; for this would cut any line in an involution with $\frac{1}{2}k(k-1)$ neutral pairs. Indeed a general net of curves q^{k+1} admits at most $\frac{1}{2}k(k+5)$ base points, whilst the curves $(P)^{k+1}$ pass through (k^2+k+1) fixed points and the latter number surpasses the former by $\frac{1}{2}(k-1)(k-2)$.

Evidently a null-system $(1, k)$ can be determined by the equations

$$\xi_1 x_1 + \xi_2 x_2 + \xi_3 x_3 = 0,$$
$$\xi_1 a_x^k + \xi_2 b_x^k + \xi_3 c_x^k = 0.$$

The null-points of the line (ξ) are its points of intersection with the curve indicated by the second equation.

For the curve $(P)^{k+1}$ corresponding to the point $P(y)$ we find, by means of the relation

$$\xi_1 y_1 + \xi_2 y_2 + \xi_3 y_3 = 0,$$

the equation

$$\begin{vmatrix} y_1 & y_2 & y_3 \\ x_1 & x_2 & x_3 \\ a_x^k & b_x^k & c_x^k \end{vmatrix} = 0.$$

So the singular points are determined by

$$\begin{Vmatrix} x_1 & x_2 & x_3 \\ a_x^k & b_x^k & c_x^k \end{Vmatrix} = 0.$$

By harmonic transformation with respect to the conic $a_\xi^2 = 0$ we find a null-system $(1, k+1)$, in which the line (η) indicated by $a_\xi a_\eta = 0$ corresponds to the point (x).

If we put for short

$$x_2 c_x^k - x_3 b_x^k = A_x^{k+1}, \quad x_3 a_x^k - x_1 c_x^k = B_x^{k+1}, \quad x_1 b_x^k - x_2 a_x^k = C_x^{k+1},$$

then we find

$$\xi_1 : \xi_2 : \xi_3 = A_x^{k+1} : B_x^{k+1} : C_x^{k+1},$$

i. e.

$$(a_{11}A + a_{12}B + a_{13}C)\eta_1 + (a_{12}A + a_{22}B + a_{23}C)\eta_2 + (a_{13}A + a_{23}B + a_{33}C)\eta_3 = 0,$$

and this equation determines with

$$x_1 \eta_1 + x_2 \eta_2 + x_3 \eta_3 = 0$$

the new null-system.

That it is impossible to deduce any arbitrary $(1, k+1)$ by harmonic transformation from null-systems $(1, k)$ can be shown already by remarking that the $2(k+1)$ new singular points furnished by this transformation lie on a conic, which does not happen generally for $k > 2$.

Botany. — *"The influence of temperature on phototropism in seedlings of Avena sativa."* By Miss M. S. DE VRIES. (Communicated by Prof. F. A. F. C. WENT).

(Communicated in the meeting of Jan. 25, 1913).

In connection with RUTGERS' [1]) investigation on the influence of temperature on the geotropic presentation-time in *Avena sativa* seedlings, I have undertaken experiments to find out how far temperature influences phototropism.

I had originally no intention of making a preliminary statement at this stage because some of the experiments are not yet complete, but after the publication of TORSTEN NYBERGH'S [2]) work on the same subject in which results wholly opposed to mine are given, it became desirable to make a communication now.

TORSTEN NYBERGH comes to the conclusion that temperature has no influence on the process of phototropical stimulation. According to him therefore the influence of temperature on phototropism may be represented graphically by a straight line. The results I have obtained at various temperatures can however be represented by a definite optimum-curve. Before I consider the results, I should like to say a few words about the method.

Seedlings of Avena sativa having a length of about 2.5 cm. were used. The boxes of seedlings were warmed for at least an hour beforehand in the thermostat used by RUTGERS at the temperature to be investigated; they were then exposed to light in the thermostat and then taken out of the apparatus. The seedlings always executed their curvature at 20° C. While the seedlings were in the thermostat, fresh air was drawn through it, moreover the dark room in which all the experiments took place was ventilated as much as possible. The warming of the thermostat was done by electric lamps; gas was not burnt in the dark room, so that the atmosphere was as pure as possible. The source of illumination was incandescent gas light, placed outside the room; the light entered through a frosted glassplate, when the diaphragm was open.

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[1]) A. A. L. RUTGERS: The influence of temperature in geotropism. Proceedings Royal Acad Amsterdam. Vol XIII, p. 476, 1910.

A. A. L. RUTGERS The influence of temperature on the geotropic presentation. time. Recueil des Trav. Botan. Néerlandais. Vol. IX, 1912.

[2]) TORSTEN NYBERGH. Studien über die Einwirkung der Temperatur auf die tropistische Reizbarkeit etiolierter Avena-Keimlinge. Berichte der deutschen Botan. Gesellschaft. Band 30. 1912.

The quantity of light-energy which at various temperatures was necessary to cause a definite degree of curvature was determined. As a standard a curvature of 2 mm. was always taken, that is to say, the apex of the coleoptile was bent 2 mm. out of the vertical.

To begin with, experiments were made at 20°C., since a quantity of light energy of 20 M. C. S. (metre-candle seconds) gave a curvature of 2 m.m. In order to find the quantity necessary for a curvature of 2 mm. a few boxes of seedlings were stimulated for a varying number of seconds, and it was ascertained after about 1½ hours how many seedling had curved. Boxes in which 50% of the seedlings showed a curvature of 2 mm. served as a standard. The product of duration of stimulus and intensity of light then gave the required quantity of luminar energy in M. C. S.

The experiments were performed at temperatures ranging from 0° to 40° C. No experiments were made above 40° C.; after one hour's preliminary warming at 40°, so prolonged an illumination was necessary and the curvatures which finally occurred, were so indistinct, that there was no question of determination after more prolonged warming. At 43° the seedlings died.

From 0° to 25° the observations were made at intervals of 5°; above 25° more frequent determinations were found to be necessary.

At each of the temperatures to be investigated there was first a warming of one hour's duration, afterwards of 2 hours, 4 hours, 6 hours etc., in order to see whether increased duration of preliminary warming had any effect.

The results of the experiments are collected in the table given below, in which in successive columns is given in M. C. S. the luminar energy necessary for a curvature of 2 mm., after 1 hour, 2 hours', 4 hours' warming, etc., corresponding to the temperature given in the first column.

It is clear from the table that the phototropic stimulation process is dependent on temperature and that at higher temperatures the time-factor is of a great influence.

From 0° to 25° the length of preliminary warming has no influence on the quantity of luminar energy. At 27.5° and 30° longer preliminary warming has a favourable influence; that is to say after a longer exposure to a higher temperature a smaller quantity of luminar energy causes the same curvature as a greater quantity after a shorter preliminary warming. The harmful influence of longer preliminary warming is first observable at 32.5° and this is the case also at 35°, 37° and at higher temperatures, in always increasing amount.

Temp.	1 hour	2 hrs.	4 hrs.	6 hrs.	12 hrs.	18 hrs.	24 hrs.	48 hrs.
— 2°	200	200						
0	160	160	160	160				
5	70	70	70	70				
10	52.5	52.5	52.5	52.5				
15	24.5	24.5	24.5	24.5		24.5		24.5
20	20	20	20	20		20		
25	9.5	9.5	9.5	9.5		9.5		
27.5	9.2	7.2	5.6	4.8	4	4	4	
30	8	6	4	3	2	2	2	2
31	8	8	8	8		8		
32.5	9.2	12	13.6	14.4		14.4		
35	10	15	20	22	25	26	26	26
37	40	64	80	88		92	92	
37.5	48	72	104	120		176	184	184
38	56	84	128	160		272	320	
39	120	176	240	280		400		
40	± 1600 [1]							

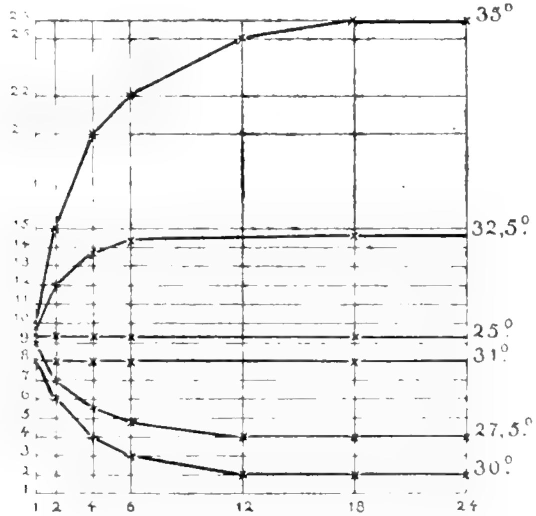

Fig. 1.

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[1] For the absolute correctness of this figure I cannot vouch on account of the difficulty mentioned on a previous page.

The favourable influence of longer preliminary warming at 27.5° and 30°, also the unfavourable influence of a longer exposure at 32.5° and 35° is represented graphically in figure 1 in which the abscissae show the duration of preliminary warming, and the ordinates the energy in M. C. S.

It is further clear from the figure that there is a transition point between the favourable and unfavourable influence; the amount of M. C. S. is here constant.

Figure 2 represents graphically the energy in M. C. S. which causes a curvature of 2 m.m., as a function of temperature. The abscissae represent temperature, and the ordinates luminar energy in M. C. S. As the drawing is much reduced the lines representing longer preliminary warming are omitted for the sake of clearness; only the line for one hour's warming has been drawn.

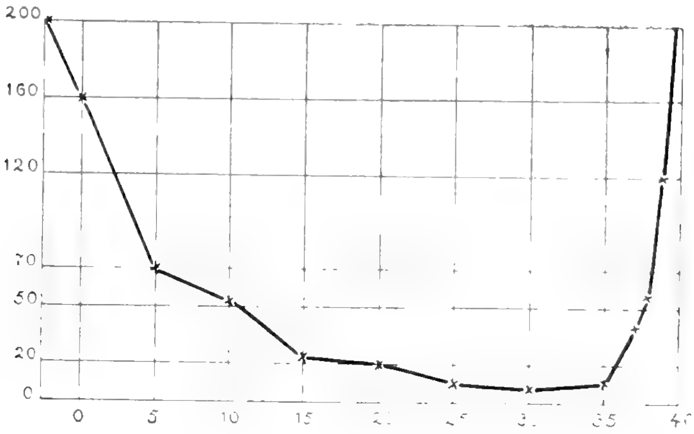

Fig. 2.

Evidently we are here concerned with an optimum-curve. The optimum is at 30°.

Finally there is the question whether VAN 'T HOFF's rule applies to phototropism. The energy in M. C. S. decreases to the optimum because perception takes place more rapidly. To determine the temperature-coefficients, the ratios of the quantities of luminar energy must not be taken, but the ratios of their reciprocal values, as was done by RUTGERS[1]) for geotropism. For this reason $\frac{K_{10}}{K_{20}}$ etc. is taken, and not $\frac{K_{20}}{K_{10}}$ etc.

The following temperature-coefficients are then found:

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[1]) A. A. L. RUTGERS. Proceedings Royal Acad. Amsterdam, Vol. XIII.

$$\frac{K_0}{K_{10}} = 3. \qquad \frac{K_{15}}{K_{25}} = 2.6.$$

$$\frac{K_5}{K_{15}} = 2\ 8. \qquad \frac{K_{20}}{K_{30}} = 2.5.$$

$$\frac{K_{10}}{K_{20}} = 2.6. \qquad \frac{K_{25}}{K_{35}} = 0.95.$$

The quotients appear to remain constant up to 30° and after that decrease markedly, in agreement with what is observed in other vital processes. I refer to the paper of COHEN STUART [1]) for this point.

Does the observed influence of temperature only affect perception or is the time of curvature (reaction-time) also influenced by temperature? The reaction took place at 20° C in all the experiments. Of course it is conceivable that there is an after-effect of the preliminary warming at the temperature investigated. The times of curvature (reaction-times) amounted to:

At	0° C.	120	minutes	
,,	5° ,,	90	,,	
,,	10° ,,	90	,,	
,,	15° ,,	90	,,	
,,	20° ,,	90	,,	
,,	25° ,,	85	,,	
,,	30° ,,	85	,,	
,,	35° ,,	90	,,	after 1 to 12 hours' previous warming after longer warming 120′
,,	37° ,,	90	,,	after long warming 120′
,,	38° ,,	± 100	,,	after long warming 120′
,,	39° ,,	120	,,	
,,	40° ,,	$2^1/_2$ to 3 hours.		

By time of curvature (reaction-time) there is here meant the time which elapses till 50% of the plants are curved. The reaction-time is therefore fairly constant except at 0° and at the high temperatures. It seems clear from the tables, that, if there is any influence of the temperature at which the plant was warmed beforehand, on the reaction, this is found exclusively at 0°, 39° and 40° and, when the previous warming is of very great duration also at 35°, 37° and 38°. It may therefore be considered probable that the influence of temperature specially acted on perception.

I hope later to give further theoretical considerations and a review of the literature in a fuller communication.

Utrecht, January 1913. *University Botanical Laboratory.*

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[1]) C. P. COHEN STUART. "A study of temperature-coefficients and VAN 'T HOFF'S rule". Proceedings Royal Acad. Amsterdam; Vol. XIV. p. 1159, 1912.

Physics. — *"On the law of the partition of energy."* By J. D. VAN DER WAALS Jr. (Communicated by Prof. J. D. VAN DER WAALS).

(Communicated in the meeting of January 25, 1913).

§ 1. *Introduction.*

The law of equipartition of energy must hold for the kinetic energy of all systems whose equations of motion[1] can be represented in the form of the equations of HAMILTON. This is shown in statistical mechanics.

Experiment shows that this law is not fulfilled. This has first clearly appeared from the fact, that the kinetic energy of monatomic and diatomic gases, as it may be derived from the value of c_v, accounts for only 3 and 5 degrees of freedom respectively, whereas the molecules of these gases have undoubtedly more degrees of freedom, which appears i.a. from the light which they can emit.

Later the observations of NERNST and his disciples have shown, that the c_v of solids decreases indefinitely when we approach to the temperature $T=0$ (absolute) which is also in contradiction with the equipartition law.

Finally we usually deduce from the equipartition law that the partition of the energy over the different wavelengths in the normal spectrum must be as it is indicated by the spectral formula of RAYLEIGH. In this case also experiment shows that the consequences of the equipartition law are not fulfilled in nature.

It appears from the above considerations that we are obliged to assume, *that the equations of motion of the real systems cannot have the form of the equations of* HAMILTON. The following considerations are to be considered as an attempt to find a way, which may lead to the deduction of the form of the equations of motion of the real systems occurring in nature. In this attempt I will assume that the partition of energy in the normal spectrum is accurately represented by the spectral equation of PLANCK; so I will try to indicate a way which may lead to the drawing up of equations of motion from which the equation of PLANCK can be derived. In consequence of the mathematical difficulties, however, I have not succeeded in finding those equations of motion themselves.

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[1]) With "equations of motion" I mean the equations which are required to reduce the time derivatives of the independent variables by which the condition of a system is determined from the values which these variables have at a given ime, independent whether or no these changes refer to motions in the strict sense.

It seems natural to assume, that these equations when they shall have been found, will be able to account for the different above-mentioned deviations from the law of equipartition of energy. In fact these deviations are closely connected with one another. If e.g. the energy of visible lightvibrations at 100° is imperceptibly small compared with that of infra-red rays, we cannot wonder that the vibrations of electrons which are in equilibrium with those light vibrations have an energy very small compared with that of vibrations of greater period. The thermal motion of the molecules may here probably be considered as a vibration of rather large period, although it is not a simple harmonic vibration. At a higher temperature the small wavelengths become more predominant in the spectrum. It is therefore to be expected that also the vibrations of the electrons of short period, which at a low temperature are devoid of energy, at a higher temperature will obtain a measurable amount of energy, so that the specific heat with constant volume will increase with the temperature.

The physicists occupied with these problems have noticed this connection between the normal spectrum and the specific heats from the beginning. JEANS[1]) e.g. has applied his theory, which originally was meant to be an explanation of the c_v of gases, to explain the properties of the normal spectrum; and it is not astonishing that vice versa the theory of PLANCK for the normal spectrum was soon used for the explanation of the specific heats.

The method in which we start from a theory for the normal spectrum and deduce from it the value of c_v seems to have advantages over the opposite way. For we have in the spectral formula of PLANCK a relation which agrees well with the observations and which moreover is independent of the special nature of the walls. I will therefore follow this method.

§ 2. *The centra of radiation.*

We may make the following two assumptions concerning the way in which the partition of energy of the normal spectrum is brought about.

1st. We may assume that every vibrator considered separately has the property to transform radiation of an arbitrary partition of energy into the partition of energy of the normal spectrum.

2nd. We may assume that this property only belongs to groups

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[1]) J. H JEANS, Proc. Royal. Soc. of London **67**, p. 236, anno 1900.
Phil. Mag. (6) **2**, p. 421 and 638, anno 1901.
Proc. Phys. Soc. of London **17**, p. 754, anno 1901, etc.

of vibrators, when their vibration is influenced by their interaction (collisions).

I shall start from the first supposition. In the first place because it is simpler. But it seems to me also to be more plausible. For we cannot doubt that the equations of motion are not linear. A vibrator therefore, when set into vibration by a perfectly homogeneous ray of light, will not execute perfectly harmonic vibrations. The radiation, emitted by it will therefore contain vibrations of other period than the incident ray. If therefore it is inclosed in a space with perfectly reflecting walls it will change the partition of energy of radiation which is also inclosed in that space. If now the spectrum which originates in this manner was not the normal spectrum (because this latter was only brought about by a great many interacting vibrators) it would be astonishing, that even the most rarified gases, in which relatively only a few collisions occur, always give rise to the normal spectrum, and not to a spectrum whose partition of energy lies between the normal spectrum and that of one vibrator.

I will therefore imagine one single vibrator. If its motion was determined by the equation:

$$m\frac{d^2x}{dt^2}+fx-g\frac{d^3x}{dt^3}=e\mathfrak{E}\ . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which the coefficients m, f, g, e were constants, then it would necessarily give rise to a partition of energy agreeing with the spectral formula of RAYLEIGH [1]).

Therefore we shall assume from the outset that the equation (1) is not satisfied. The vibrator will then not be able to execute perfectly harmonic vibrations, but its vibrations, when analysed in a series of FOURIER, will consist of several, in general of an infinite number of harmonic vibrations. This seems not to agree with the fact, that undisturbed vibrating vibrators as they occur in gases, emit very sharp spectral lines. We must, however, bear in mind, apart from the fact that no element exists whose spectrum consists in *one* single line, — that according to the electron-theory the mass is not *perfectly* constant and the light of a vibrator therefore not *perfectly monochromatic*. It is true that light of a period T, differing from the fundamental period T_0 of a vibrator, often occurs only to an imperceptibly small amount in its radiation. But it cannot be totally wanting. Now it is well known that the intensity of radiation of a certain period in the normal spectrum does not depend upon the emission alone, but upon the ratio between emis-

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[1]) Comp. H. A. LORENTZ, Nuovo Cimento V, 16. Anno 1908.

sion and absorption, so that a certain wavelength may be represented in the spectrum to its normal amount, even if the emissive power of the walls be imperceptibly small for that wavelength, provided the absorption have a corresponding, small value. The small value of the emissive power has no influence on the final partition. It only occasions that radiation of other energy-partition will only very slowly be transformed into the normal partition.

So we shall assume that the centra of radiation are vibrators whose equations of motion are for the present unknown. These equations cannot have rigorously the form (1), but they need differ only very little from it.

§ 3. *The independent variables. The ensemble.*

We will imagine an ensemble each system of which consists of a parallelopipedic space inclosed in perfectly reflecting walls and containing one vibrator, whose centre has a fixed position in that space. We will assume that the motion of that vibrator is determined by *one* coordinate.

The choice of the independent variables requires a certain circumspection. The aether namely represents an infinite number of degrees of freedom, each of which can therefore possess an infinitely small amount of energy. The vibrator on the other hand possesses a finite amount of energy. It seems, however, difficult to deal with an ensemble in which one variable possesses on an average infinite times as much energy as the other variables. Therefore I will choose the variables as follows: If a monochromatic ray of light passes a vibrator the latter will be set into vibration. After a certain time this vibration will have become stationary. Now I will determine by *one* coordinate the amplitude of the ray and the stationary vibration of the vibrator caused by it.

Besides this I will assume that the vibrator has a "proper" coordinate. Now if this proper coordinate, and also its time derivative are zero, this does not mean that the vibrator stands still in its position of equilibrium. It does mean that the motion of the vibrator consists exclusively of the stationary vibration, which it assumes through the influence of the radiation to which it is subjected. If the proper coordinate is not zero, then the vibrator has a motion which does not agree with the absorbed vibration. So it is possible to assume, that in a radiation field which is in equilibrium (i. e. in which the energy partition is that of the normal spectrum) the proper coordinate of the vibrator has always an infinitely small amount of energy (in the same way as the separate coordinates which determine the condition of the aether), and that yet the vibrator vibrates with a finite energy the amount of which agrees with that calculated for it by PLANCK [1]).

We can divide the electromagnetic field into two parts: 1st The electrostatic field which agrees with the momentary position of the electron, 2nd A field consisting of the really existing electric and magnetic forces diminished by those static forces. In agreement with the above we assume, that the position of the electron and therefore also the 2nd field is determined by the first. As for this latter field we have:

$$Div\,\mathfrak{E} = 0 \qquad \text{and} \qquad Div\,\mathfrak{H} = 0\,,$$

we can represent it as follows, if for simplicity's sake we assume, that the space in which it is inclosed is a cube with a side equal to unity:

$$\left.\begin{aligned}
\mathfrak{E}_x &= \Sigma\,(q\alpha + q'\alpha')\cos 2\pi\,ux\,\sin 2\pi\,vy\,\sin 2\pi\,wz\\
\mathfrak{E}_y &= \Sigma\,(q\beta + q'\beta')\sin 2\pi\,ux\,\cos 2\pi\,vy\,\sin 2\pi\,wz\\
\mathfrak{E}_z &= \Sigma\,(q\gamma + q'\gamma')\sin 2\pi\,ux\,\sin 2\pi\,vy\,\cos 2\pi\,wz\\
\mathfrak{H}_x &= \Sigma\,(p'\alpha + p\alpha')\sin 2\pi\,ux\,\cos 2\pi\,vy\,\cos 2\pi\,wz\\
\mathfrak{H}_y &= \Sigma\,(p'\beta + p\beta')\cos 2\pi\,ux\,\sin 2\pi\,vy\,\cos 2\pi\,wz\\
\mathfrak{H}_z &= \Sigma\,(p'\gamma + p\gamma')\cos 2\pi\,ux\,\cos 2\pi\,vy\,\sin 2\pi\,wz
\end{aligned}\right\} \quad .\;.\;.\;. \quad (2)$$

In the summation we must take for $2u$, $2v$, and $2w$ all positive integers; $\sqrt{u^2+v^2+w^2}$ represents the number of waves in 1 cm. and $2\pi c\sqrt{u^2+v^2+w^2} = \nu$ the number of vibrations in 2π seconds. The quantities α, β, γ and α', β', γ' are the direction coefficients of two directions which are mutually perpendicular, and also perpendicular to the direction determined by $\dfrac{u}{\sqrt{u^2+v^2+w^2}}, \dfrac{v}{\sqrt{u^2+v^2+w^2}}, \dfrac{w}{\sqrt{u^2+v^2+w^2}}$.

The quantities q, q' and p, p' are the independent variables. One of these variables corresponding to a certain set of values u, v, w will be represented by q_{uvw} or p_{uvw}. It can be proved that the variables

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[1] Comp. i. a. MAX PLANCK. Acht Vorlesungen über theoretische Physik. p. 84. In fact our suppositions quite agree with what PLANCK does, when he treats his vibrators as resonators and assumes that their energy is perfectly determined by the radiation field, to which they are subjected. In that case it is however not allowed to equate the entropy of the system to the sum of the amount of entropy of the radiating energy, and that of the vibrator. For the motion of the vibration is perfectly determined by the radiation; the vibrations of the vibrator and of the radiation are therefore coherent and their united entropy is no more equal to the sum of their separate amounts of entropy as this is the case with the entropy of two coherent rays of radiation. (Comp. M. LAUE, Ann. d. Phys. **20** p. 365. 1906; **23** p. 1 and p. 795. 1907 etc.).

p may be considered to be the momenta corresponding to the coordinates q. As however we must assume that the equations of Hamilton do not apply, this observation is of no consequence for the equations of motion of the system.

Now if no vibrator occurred in the space, every partition of energy would remain unchanged, and there would be no occasion to speak of an equilibrium partition. If a vibrator occurred which had the property to be able to transform radiation of every wavelength into every other wavelength and whose motion was determined by the equations of Hamilton, then the energy partition would approach to that indicated by the formula of Rayleigh. In this case we might represent the condition of the system by means of an ensemble for which the probability of phase would be represented by [1]:

$$P = e^{\frac{\psi - \frac{1}{16}\Sigma q^2 - \frac{1}{16}\Sigma p^2}{\theta}} \quad \ldots \ldots \ldots \quad (3)$$

where ψ and θ are constants and $\frac{1}{16}\Sigma q^2 + \frac{1}{16}\Sigma p^2$ is the energy of the system, the summation being extended over all quantities q and p, also over those provided with accents.

Properly speaking this expression for the energy is incomplete. In the first place the energy of the proper coordinate of the vibrator has been neglected, but moreover we have neglected the energy of the vibrator, which it has in consequence of its forced vibrations. If we imagine the volume sufficiently large these approximations will meet with no serious objections. More risky is another simplification which I will introduce; I will namely represent an element of extension-in-phase [2]) by $H\,dp dq$ and here also I will neglect the proper coordinate (or coordinates if the electron has more degrees of freedom). I think I may suppose that this simplification also will not affect our conclusions greatly. Perhaps it is even perfectly justified. It is namely possible that we must assume, that the motion of the vibrator is entirely determined by the electromagnetic field, and that therefore there is no reason to introduce a "proper" coordinate.

As the spectral formula of Rayleigh is not satisfied by the experiments, the formula (3) cannot give the right expression for the probability of phase. I shall therefore put:

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[1]) Comp. Gibbs. Elementary principles in statistical mechanics p. 16.

[2]) Comp. Gibbs, l.c. p. 6.

$$P = e^{\frac{\psi - \frac{1}{16}\Sigma q^2 - \frac{1}{16}\Sigma p^2}{\theta}} \varphi\,(q\ldots p). \quad . \quad . \quad . \quad . \quad (4)$$

If it is possible to find such a form for the function φ (which represents a function of all variables q and p) that the following formula is satisfied:

$$\frac{\int \frac{1}{16} q^2 e^{\frac{\psi - \frac{1}{16}\Sigma q^2 - \frac{1}{16}\Sigma p^2}{\theta}} \varphi\,(q\ldots p)\, \Pi dq dp}{\int e^{\frac{\psi - \frac{1}{16}\Sigma q^2 - \frac{1}{16}\Sigma p^2}{\theta}} \varphi\,(q\ldots p)\, \Pi dq dp} = \frac{\theta}{2} \frac{\frac{h\nu}{\theta}}{e^{\frac{h\nu}{\theta}} - 1} \quad (5)$$

then the average energy in the ensemble for every degree of freedom has the value which is indicated for it by the spectral formula of **Planck**. The function of φ must of course have such a form that an equation of the form (5) is satisfied for every variable, not only for the q's, but also for the p's. The function φ may moreover contain the frequencies ν, but it must be independent of θ, for else the equations of motion of the system would depend on θ, whereas the conception "equation of motion" involves, that they are perfectly determined by the condition of the system at a given instant (the q's and p's and constants), and that they do not contain a quantity as θ, which is not characteristic of the individual system, but of the ensemble. If the condition that φ must be independent of θ did not exist, then it would be easy to find several solutions for the integral equations (5). *With* this condition it seems to offer rather great difficulties [1]).

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[1]) The integral equation can in general be brought into the following form:

$$\int e^{\frac{-\frac{1}{16}\Sigma q^2 - \frac{1}{16}\Sigma p^2}{\theta}} \varphi\,(q\ldots p) \left\{ \frac{q^2}{8} - \frac{\nu h}{e^{\frac{\nu h}{\theta}} - 1} \right\} \Pi dq dp = 0.$$

It is possible that φ may be split up into a product of functions $f(q, \nu)$ each of which contains only one variable and the number of vibrations belonging to it. In this case the equation for the determination of $f(q, \nu)$ may be written:

Yet I have thought it useful to draw attention to this equation as its solution would be an important step on the way which leads to the drawing up of a system of dynamics from which not the spectral formula of RAYLEIGH, but that of PLANCK would follow.

In this system of dynamics the equations of motion can of course not be brought into the form of HAMILTON. Instead of the law of conservation of density in phase, which follows from this form of the equations of motion, another relation can be derived, which is found as follows. In order that the state is stationary, it is of course required that the probability of phase for a point with constant coordinates is constant. If we indicate the time derivative for such a point with $\frac{\partial}{\partial t}$, then we have in the case of equilibrium:

$$0=\frac{\partial P}{\partial t}=-\Sigma\left(\frac{\partial P\dot{q}}{\partial q}+\frac{\partial P\dot{p}}{\partial p}\right)$$

or

$$P\Sigma\left(\frac{\partial\dot{q}}{\partial q}+\frac{\partial\dot{p}}{\partial p}\right)=-\Sigma\left(\frac{\partial P}{\partial q}\dot{q}+\frac{\partial P}{\partial p}\dot{p}\right).$$

It follows from the form of P that we may also write:

$$\frac{1}{\varphi}\Sigma\left(\frac{\partial\varphi}{\partial q}\dot{q}+\frac{\partial\varphi}{\partial p}\dot{p}\right)=-\Sigma\left(\frac{\partial\dot{q}}{\partial q}+\frac{\partial\dot{p}}{\partial p}\right)\quad\ldots\ldots\quad(6)$$

When the function φ is found by solution of the equation (5), then (6) is a relation which the equations of motion must satisfy. It has for the modified mechanics the same significance as the thesis of LIOUVILLE has for classical mechanics.

§ 4. *The equations of motion of the electrons.*

Though the vibrator does not figure explicitly in equation (6), the values of $\dot{q}$ and $\dot{p}$ occurring in it are determined by the properties of the vibrator. For the motion of the electron we can deduce the following equations. We start from the expression for the electrical force of which the X-component can be represented by:

$$\int_{-\infty}^{\infty}e^{-\frac{1}{16}\frac{q^2}{\theta}}f(qr)\,dq=\frac{4\sqrt{\pi hr}}{\sqrt{1-e^{-\frac{rh}{\theta}}}}.$$

In the original Dutch paper there is an error in these two formulae and in equation (5), which I have corrected in the English translation.

$$\mathfrak{E}_x = \Sigma\,(q\alpha + q'\alpha')\cos 2\pi\,ux \sin 2\pi\,vy \sin 2\pi\,wz + m\,\frac{x}{4\pi r^3}$$

m denoting the electrical moment of the vibrator.

From this expression follows:

$$\frac{d\mathfrak{E}_x}{dt} = c\left(\frac{\partial \mathfrak{H}_z}{\partial y} - \frac{\partial \mathfrak{H}_y}{\partial z}\right) - \varrho\mathfrak{v}_x = \Sigma\,(\dot q\alpha + \dot q'\alpha')\cos 2\pi\,ux \sin 2\pi\,vy \sin 2\pi\,wz + \frac{x}{4\pi r^3}\frac{dm}{dt}$$

and in connection with (2) and with equations of the form $r\alpha' = c\,(v\gamma - w\beta)$:

$$\Sigma\{(\dot q + rp)\,\alpha + (\dot q' + rp')\,\alpha'\}\cos 2\pi\,ux \sin 2\pi\,vy \sin 2\pi\,wz =$$

$$= -\varrho\mathfrak{v}_x - \frac{x}{4\pi r^3}\frac{dm}{dt} \quad . \quad . \quad . \quad (7)$$

The divergence of the vector in the lefthand member of this equation is zero, and so also that of the vector in the righthand member. We can therefore represent it by:

$$\Sigma\,(\sigma\alpha + \sigma'\alpha')\cos 2\pi\,ux \sin 2\pi\,vy \sin 2\pi\,wz.$$

Equation (7) being satisfied identically in x, y and z, we have

$$\dot q + rp = \sigma \qquad \dot q' + rp' = \sigma' \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Differentiating these equations respectively with regard to q and q' we get:

$$\frac{\partial \dot q}{\partial q} = \frac{\partial \sigma}{\partial q} \qquad \frac{\partial \dot q'}{\partial q'} = \frac{\partial \sigma'}{\partial q'} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

If we treat the expressions for the components of $\mathfrak{H}$ in the equations (2) in the same way, we find:

$$\dot p - rq = 0 \qquad \dot p' - rq' = 0 \quad . \quad . \quad . \quad . \quad . \quad (8a)$$

and

$$\frac{\partial \dot p}{\partial p} = 0 \qquad \frac{\partial \dot p'}{\partial p'} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9a)$$

and therefore:

$$-\Sigma\left(\frac{\partial \dot q}{\partial q} + \frac{\partial \dot p}{\partial p}\right) = \frac{1}{\varphi}\,\Sigma\left(\frac{\partial \varphi}{\partial q}\dot q + \frac{\partial \varphi}{\partial p}\dot p\right) = -\Sigma\,\frac{\partial \sigma}{\partial q}$$

When φ is known, we can substitute in (10) the values for $\dot q$ and $\dot p$ from (8) and (8a) and so we get a relation which the coefficients σ as functions of q and p must satisfy. The value of the σ's on the other hand depends upon the value of ϱ as a function of x, y, and z and upon the velocities $\left(\mathfrak{v}_x\ \frac{dm}{dt} \text{ in equation (7)}\right)$ which

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the electron assumes under influence of the field determined by q and p.

§ 5. *Conclusions.* In the above considerations I have tried to show that it is possible to account for the partition of energy in the normal spectrum with the aid of differential equations, which admit of a continuous emission and absorption of energy, and that it is therefore not necessary for the explanation of the normal spectrum to have recourse to the supposition of quanta, either of energy or of "action". For this explanation it is necessary to draw up a system of mechanics, in which a relation of the form (6) takes the place of the equation of LIOUVILLE in "classical" mechanics. In order to determine this equation further knowledge of the function q would be required, which function can be found by solution of the integral equation (5). I have however not succeeded in this solution.

If such an explanation with the aid of continuous equations is possible for the partition of energy in the spectrum, then this will also be the case for the variation of the specific heat with the temperature, which follows from this energy partition.

Chemistry. — "*Hexatriene* 1, 3, 5." By Prof. P. VAN ROMBURGH.

(Communicated in the Meeting of February 22, 1913).

In previous communications, published in this Proceedings [1]), an account was given of the results of an investigation carried out jointly with Mr. VAN DORSSEN and which had led to the preparation of the above hydrocarbon. Owing to the departure of Mr. VAN DORSSEN the continuation of the study of hexatriene has experienced considerable delay. Since then, however, a fairly considerable quantity of this substance has been prepared and kept in sealed bottles. As hexatriene — as might be expected from its analogy with other unsaturated compounds (and what also proved to be the case)-exhibited a tendency towards polymerisation particularly on warming, I have submitted the contents of the bottles which had been kept for five years, to investigation.

On distillation fully 50 °/₀ passed over below 80°: the residue in the flask was then distilled in vacuo. At ± 100° about 30 °/₀ passed over whilst in the flask was left behind a colourless, very viscous mass which dissolves in benzene. From this solution it is again precipitated by acetone or alcohol. If the residue is heated more strongly,

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[1]) Nov. and Dec. 1905; June 1906.

there remains a colourless, transparent, gelatinous product which swells in contact with benzene, but does not dissolve therein.

The liquid boiling at about 100° in vacuo, when distilled at the ordinary pressure passes over at ± 215° with formation, however, of products with a higher boiling point. After fractional distillation in vacuo the bulk was obtained as a perfectly colourless liquid which is more viscous than hexatriene (b.p. 99°.5 at 16 mm. pressure).

The elementary analysis (found: C 89.43, H 10.1; calculated C 89.91, H 10.09) and the vapour density determination (according to HOFMANN: found 5.5; calculated 5.5) led to the formula $C_{12}H_{16}$, so that the substance is to be considered as a dimer of hexatriene.

$$D.^{11} = 0{,}880 \qquad n_D^{11} = 1.51951$$

$$MR = 55.2 \quad \text{Calculated for } C_{12}H_{16} \overline{|}_{4} \; 53.54^{1)}$$

The density is considerably higher than that of hexatriene (0.7498 at 13°) whereas the exaltation of the molecular refraction is much smaller. This is particularly striking when we compare the spec. exaltations.

$$\text{For hexatriene } E\Sigma_D = 3.125$$

$$\text{For the dimer } E\Sigma_D = 1.037$$

The dimer of hexatriene readily forms an additive compound with one mol. of bromine; on further addition much hydrogen bromide is eliminated. It is rapidly oxidised by a solution of potassium permanganate. The investigation thereof is being continued.

The method by which hexatriene was formerly obtained (interaction of formic acid on s. divinylglycol) did not exclude the possibility that it might be contaminated with hydrogenated derivatives thereof and hence it was thought desirable to try other means and get it in a pure condition by regeneration from crystalline derivatives. Mr. MULLER who for a considerable time has been engaged on the study of hexatriene has succeeded in regenerating the hydrocarbon from the beautifully crystallised dibromo additive compound. By treating hexatriene with sulphur dioxide he has also obtained a solid product, the investigation of which is not yet concluded and from which the hydrocarbon may be prepared also.

It was further to be expected that hexatriene would also be formed by dehydration of the hexadiene 1.5-ol 4, which alcohol might be obtained by reduction of the divinylethylene oxide recently descri-

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1) Here it has been assumed that with elimination of two double bonds, a ring has been formed, as suggested by the high density.

bed by Mr. LE HEUX [1]). The yield of the alcohol from the oxide, already so difficult to prepare, was, however, so small that the application of this method was out of the question.

Jointly with Mr. VAN DORSSEN, I endeavoured some time ago to prepare this alcohol according to the method applied by **FERD. TIEMANN** and R. SCHMIDT [2]) in the preparation of homolinalool where they allowed a mixture of allyl iodide and methylheptenone to act on granulated zinc. With acraldehyde and allyl iodide we did not get a successful reaction. Nor did we succeed in obtaining the desired alcohol by the interaction of these substances in ethereal solution on "activated" zinc (GLADSTONE and TRIBE), whilst in an experiment with 70 grams of zinc filings, 60 grams of allyl iodide and 60 grams of acraldehyde only a slight action took place, so that we refrained from further experiments.

Mr. LE HEUX has tried, in vain however, to obtain the desired alcohol by means of allyl bromide, acraldehyde and magnesium.

The favourable result obtained by Dr. C. J. ENKLAAR [3]) when applying the method of FOURNIER [4]) to crotonaldehyde for the preparation of the heptadiene 2.6-ol 4. induced Mr. LE HEUX to allow (according to FOURNIER's directions) allyl bromide, zinc turnings and absolute ether to act on acraldehyde with the object of obtaining the alcohol in larger quantities. With a yield of 30°/₀ of the theoretical quantity, the hexadiene 1.5-ol 4 was now obtained as a liquid boiling at 132°.2 — 132°.4 under 769 m.m. pressure. The elementary analysis and the vapour density determination confirmed the formula $C_6H_{10}O$.

$$D_4^{10.5} = 0.8698 \qquad n_D^{10.5} = 1.45231$$

$$MR = 30.44 \qquad \text{calculated } 30.498$$

The odour of the alcohol reminds of that of allyl alcohol but it does not produce the irritating after effect, however.

With acetic anhydride and a drop of sulphuric acid the acetate is formed as a liquid boiling at 151°.2 — 152°.7.

Phosphorous tribromide yields the bromide (bp. 59°—63° at 35 mm. pressure) which very readily absorbs 1 mol. of bromine; a further addition of bromine acts but very slowly without, however, yielding hydrogen bromide.

From this alcohol Mr. MULLER has obtained a hydrocarbon, by the

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[1]) Proc. April 1912.

[2]) B. **29**, 691 (1896).

[3]) Chem. Weekbl. **10**, 60 (1912).

[4]) Bull. Soc. Ch [3] **11**, 124 (1894).

action of potassium hydrogen sulphate as well as of phthalic anhydride, which, judging from provisional experiments consists of hexatriene.

In consequence of the fact noticed by Dr. C. J. ENKLAAR (loc. cit.) that the homologue of hexatriene which he prepared can be obtained in a crystalline condition by strong cooling, Mr. MULLER has cooled a freshly prepared and carefully fractioned specimen of hexatriene in a mixture of solid carbon dioxide and alcohol and obtained it also in the crystalline form [1]), so that this fact may be utilised for the purification of this hydrocarbon.

Finally it may be mentioned here that Mr. LE HEUX, by reduction of the chloroacetine of *s.* divinylglycol with a copper-zinc couple in ethereal solution with addition of hydrochloric acid, obtained a liquid boiling at 77°—81° which on strong cooling became crystalline and consists very probably of hexatriene 1, 3, 5. At any rate it yields with bromine a dibromide identical with the dibromide from the said hydrocarbon.

Utrecht. *Org. Chem. Lab. Univ.*

Physics. — "*On Einstein's theory of the stationary gravitation field.*" By Prof. P. EHRENFEST. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of Febr. 22, 1913).

§ 1. Let a "laboratory" L with the observers in it have some accelerated motion with regard to a system of coordinates x, y, z, which is not accelerated. Let it e.g. move parallel to the z-axis with some positive acceleration or other. Then the observers will find that all the inert masses which are at rest with regard to the laboratory, exert a pressure on the bodies which are in contact with their bottom side. There are two ways for these observers to explain this pressure: *a.* "Our laboratory has an acceleration upwards, hence all inert masses press on the bodies under them." *b.* "Our laboratory is at rest. A field of force acts in it, which pulls the masses down."

Observations on the course of the rays of light seem to make it possible to decide experimentally between the suppositions *a* and *b*: with regard to the system of coordinates x, y, z the light travels rectilinearly. Hence with regard to an accelerated laboratory *curvilinearly.* By means of this curvilinear propagation of the rays of light the observers might therefore ascertain that their laboratory has an accelerated motion.

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[1]) Preparations which have been kept for some time and then contain polymerides do not solidify even at this low temperature.

The possibility of such an experimental decision disappears immediately when also in a stationary laboratory, in which there is a field of force, the rays of light are admitted to have a corresponding curvature.

The "hypothesis of equivalence" on which EINSTEIN bases his attempt at a theory of gravitation [1]), really requires such a curvature of the rays of light in a field of attraction.

The hypothesis of equivalence, namely, demands that a laboratory *L'*, which *rests in a field of attraction,* is equivalent with respect to *all* physical phenomena with a laboratory *L without gravitation, but accelerated."*

It is therefore required that the observers which are in *L*, cannot ascertain in any way by experiments, whether their laboratory has an accelerated motion, or whether it is at rest (in a corresponding field of attraction). So we are here concerned in the first place with an attempt to extend the theory of relativity of the case of *uniform* motion of a laboratory to that of non-*uniform* motion.

The physical significance of EINSTEIN's hypothesis of equivalence would, however, chiefly lie in this that it requires a certain functional relation between the field of attraction and other physical quantities (e.g. the velocity of light).

When working out the hypothesis somewhat more closely, EINSTEIN is confronted by certain difficulties. These led him to pronounce the supposition [2]) that the theory of equivalence would possibly only be valid for infinitely small regions of space and time, and not for finite ones.

EINSTEIN confined himself here to a mere supposition, as the said difficulties only presented themselves in the consideration of the dynamic phenomena in the laboratory *L'*, and he had to do there with derivations from so great a number of suppositions, that it becomes difficult to see, *where* the difficulties arise from: the hypothesis of equivalence, or one of the other more special suppositions (as e.g. concerning the dynamic actions of rigid kinematic connections).

The following considerations try to throw light on this question. They show that similar difficulties already occur in those phenomena which are the most elementary in EINSTEIN's theory: in the propagation of rays of light in a statical field of attraction.

The principal result is: *All the statical fields of attraction with the exception of a very particular class, are in contradiction with Einstein's hypothesis of equivalence. Already the statical field of*

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[1]) Ann. d. Phys. Bd. **35** (1211) p. 898; Bd. **38** (1912) p. 355 and 443.

[2]) Ann. d. Phys. Bd. **38** (1912) p. 452—456.

attraction brought about by several centres of attraction which are stationary with respect to each other, is not compatible with the hypothesis of equivalence.

§ 2. Let, therefore a laboratory L' be given, in which there is a statical field of attraction. With EINSTEIN we suppose that the rays of light propagate in it curvilinearly in some way or other, but so that the following conditions are satisfied:

When *once* a ray of light may have passed through the points $A, B, \ldots F, G$ of the laboratory L' [1]), then

[**A**] this way $A, B, \ldots F, G$ must *always* be possible for the light (*"Constancy of the ways of light"*),

[**B**] the *reversed* way $G, F, \ldots B, A$ must also be always possible (*"reversibility of the ways of light"*).

The hypothesis of equivalence now compares this laboratory L' resting in the field of attraction with a laboratory L which is free from gravitation, but has a corresponding acceleration instead. *How must the points of this laboratory in which there is no gravitation move, so that the observers in it shall observe constancy and reversibility of the ways of light in the sense of the hypothesis of equivalence?*

§ 3. For the sake of simplicity we confine ourselves to a two-dimensional laboratory L. As fundamental system of coordinates, with respect to which L moves in an accelerated way may serve the system of coordinates x, y, which has no acceleration, and the time t measured in it. With respect to this system which is without gravitation, the rays of light move in straight lines and with constant velocity 1. In the corresponding x, y, t-world-space of MINKOWSKI every optical signal travelling in this way is represented by a straight line forming an angle of 45° with the t-axis. Such a line in the x, y, t-space is called *"a line of light"*. The motion of the different points $A, B, \ldots F, G$ of the moving laboratory L is represented by the same number of (curved) world lines $a, b \ldots f, g$.

When the observers in the laboratory L state that they have succeeded in making an optical signal S_1 pass through the points $A, B, \ldots F, G$ of their laboratory this means that the corresponding line of light s_1 intersects the world lines $a, b, \ldots f, g$ of these points of the laboratory.

According to condition [**A**] of § 2 the observers in the laboratory L must in this case be able to send light signals $S_2, S_3 \ldots$ through

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[1]) These points may be imagined e.g. as apertures in the walls of the laboratory.

the points $A, B, \ldots F, G$ of the laboratory at other moments as many times as they like. Geometrical representation in the x, y, t-space: The world-lines $a, b, \ldots f, g$ are intersected by all the ∞^1 lines of light $s_1, s_2 \ldots$; they all lie on the ruled surface formed by the ∞^1 light lines.

In agreement with condition [**B**] of § 2 the observers of the laboratory L must then moreover as often as they like be able to send optical signals $S'_1, S'_2, \ldots$ in *opposite* direction $G, F, \ldots B, A$. In the x, y, t-space again ∞^1 light lines $s'_1, s'_2, \ldots$ correspond with this, which all intersect the world lines $a, b, \ldots f, g$. Hence the world lines $a, b, \ldots g, h$ all lie on a surface covered by two systems each of ∞^1 light lines. If we then bear in mind that the light lines all make an angle of 45° C. with the t-axis, it is easy to see that such a surface must necessarily be an equilateral hyperboloid of revolution with the axis of revolution // to the t-axis; i.e. the equation of this surface has the form:

$$A(x^2+y^2-t^2)+Bx+Cy+Dt+E=0 \quad . \quad . \quad . \quad . \quad (1)$$

In particular the case may also present itself that $A=0$, i.e. that the hyperboloid degenerates into a plane.

Such hyperboloids will be briefly called "*light-hyperboloids*". Accordingly the world lines $a, b, \ldots f, g$ of the points $A, B, \ldots F, G$ of the laboratory L lie on a common "light hyperboloid" H_{ab}.

Now the observers might just as well have sent a light signal instead of from A to B, from A to any other point B' of the laboratory. In exactly the same way we see then that also the two world lines a and b' must lie on a common light hyperboloid $H_{ab'}$. Let the equation of this be:

$$A'(x^2+y^2-t^2)+B'x+C'y+D't+E'=0 \quad . \quad . \quad . \quad . \quad (2)$$

So the world line a lies at the same time on two different light-hyperboloids H_{ab} and $H_{ab'}$; it is the section of both, and this is necessarily a plane section. (Multiply equation (1) by A' and equation (2) by A, and subtract). If we now bear in mind that the point A of the laboratory must never have a greater velocity than that of light, of all the plane sections of a light-hyperboloid only two types deserve consideration: hyperbolas the two branches of which run from $t=-\infty$ to $t=+\infty$, and as limiting case the light lines of the hyperboloid. (In other words the sections with planes which **1** cut the gorge circle of the hyperboloid, and **2** make an angle of $\leq 45°$ with the t-axis. As besides, the case may occur that the light hyperboloids which pass through the world line a, degenerate to planes, the world line a may also be a straight line, making an angle with the t-axis, which is smaller than 45°.

A, however, was an arbitrary point of the laboratory L. So we have proved the following:

"If the observers in a moving laboratory L, which is without gravitation are to observe constancy and reversibility of the ways of light, it is necessary that the "world-lines" of the points of the laboratory are a system of ∞^2 branches of hyperbolas, or else straight lines in the x, y, t-space."

Without a new supposition, only in consequence of the circumstance that through every pair of these world-lines — e.g. p and q — can always be brought a light hyperboloid H_{pq} [1], it can further be proved: that the ∞^2 world line hyperbolas lie in ∞^1 *surfaces*, which pass fanlike through a straight line Γ of the x, y, t-space; they cut Γ in two real or conjugated imaginary points Ω_I and Ω_{II} (which may also coincide). In this way dependent on the situation of the points Ω_I and Ω_{II} ∞^6 fields of world lines originate, which are of a very particular nature. [2])

§ 4. The frequency of the static fields of attraction caused by n centres which are stationary with respect to each other, is already greater than ∞^6 for $n > 3$. But the "hypothesis of equivalence", cannot be satisfied in any other case than in that of the very special fields of attraction, which correspond to the ∞^6 fields of acceleration of the preceding §.

REMARK.

Up to now we have only used the constancy of the *form* of the rays of light. Moreover in every point of the laboratory L' the *velocity* of the light must also be independent of the time. In order to introduce this condition, the measurement of time in L' would have to be taken into account in the considerations, which renders them more intricate.

Possibly the class of fields for which the hypothesis of equivalence is admissible, might then be still further limited.

The field of hyperbolas which in the x, y, t-space represents BORN's "motion of hyperbolas" of a two-dimensional laboratory, is contained in the ∞^6 fields of hyperbolas of § 4 as a special case.

Moreover it satisfies (with suitable measurement of time in L') the condition that the velocity of the light is independent of time.

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[1]) Formed by the lines of light of the signals, which may be sent from P to Q, and from Q to P.

[2]) A proof for these theses and a classification of the above mentioned ∞^6 fields of world lines is found in a paper by Mr. CH. H. VAN OS, which will shortly appear.

Astronomy. — *"The variability of the Pole-star."* By Dr. A. PANNEKOEK. (Communicated by Prof. E. F. VAN DE SANDE BAKHUYZEN).

(Communicated in the meeting of January 25, 1913).

A slight variability of α Ursae minoris has already several times been suspected by different observers (SEIDEL, SCHMIDT). When in 1889 and 1890 I executed a great number of observations (estimates with the naked-eye after ARGELANDER's method) for the determination of the brightness of the stars of the 2nd and 3rd magnitudes, such great differences showed in some of these stars, that they were being observed as regularly and as often as possible in the following years with a view to probable variability. Among these stars was also the Pole-star[1]). In 1890 I found that the period was about 4 days; each time 2 days after a great intensity came a faint one and the reverse. I did not succeed, however, in finding an accurate value for the period. From the observations in December 1890 I found two maxima on Dec. 7.0 and Dec. 29.8 (in reality they occurred on Dec. 6.6 and Dec. 30.4), which yielded a probable period of 3.8 days; this however did not agree with the observations of that winter.

After all it must indeed have been hopeless to derive the elements of the variation from these observations only. As the mean error of an estimate amounted to 0.7 of the whole amplitude, as appeared later on, it might even happen that a maximum and a minimum seemed to have changed places owing to errors of observations. Moreover the remembrance of the results of previous days may spoil an observation. If on one particular day the star has, perhaps wrongly, been estimated very faint, one expects to see it very bright two days afterwards, and this may influence the estimate. On the other hand the small number of observations in a given interval of time, say a month, owing to bad weather, did not allow to counteract the uncertainty of the separate estimates, by uniting a great number into a normal place. I have long continued the observations of this star, up to 1899, in order to have material for a closer investigation, in case the variability should be proved and the period should be accurately known.

In 1898 CAMPBELL discovered that the radial velocity of this star is variable and hence that it is a spectrocopic double star with a

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[1]) The other stars in which I consider variability to be probable, although I cannot prove it with certainty owing to the smallness of the amplitude, are ζ Tauri (period of a few days), 40 Lyncis (26 days) and π Herculis (14 months); the latter two are of a red colour.

period of 3.968 days. Lack of time, because of my work at the observatory, prevented me from immediately reducing my observations by means of this value for the period and so testing the variability. The probability that α Ursae minoris was indeed a short-period-variable of the type of δ Cephei grew stronger, when I found in 1906 [1]) that it showed the same peculiarity in its spectrum as those stars (c-character after Miss Maury) and has, as all stars of short period of this type, an extraordinary slight density. In a footnote attention was already drawn to these moments of probability.

Starting from the consideration, that for all these short-period-variables the photographic amplitude is much larger than the visual one, Hertzsprung at Potsdam has thereupon (in 1910 and 1911) taken a great number of photographs (418 plates in 50 nights) of Polaris, and from this settled with absolute certainty a variability with an amplitude of 0.17 magnitude [2]). For the epoch of maximum light he found J. D. 2418985.86 ± 0.08 Greenwich M. T. Subsequently J. Stebbins has executed a number of photometric measurements with his exceedingly sensitive selenium-method in 1911—12; these also clearly show a variability with a visual amplitude of 0.07 magnitude [3]). The epoch of greatest brighness as found by him, viz. J. D. 2418985.94 Gr. M. T. agrees very well with Hertzsprung's result.

I have also reduced my observations of 1890—1900 with the aid of the periodic time $3^d.9681$, as spectrographically found. In the second half of each year I used for comparison the stars of Perseus and Andromeda, in the first half those of Ursa major. Thus the observations form two mutually independent series, partially overlapping in wintertime. For the 1st series α Persei = 6.3, β Andromedae = 3.8, γ Andromedae = 3.1, and exceptionally α Arietis = 5.4 and α Andromedae = 2.3 were used as a scale of comparison-stars; for the 2nd series served ε Ursae maj. = 2.4, η Ursae maj. = 0.0, and, exceptionally, α Ursae maj. = 4.0. The observations were not corrected for atmospheric extinction, since this influence disappears in the mean of many observations and at the most can make the mean error seem too great. Taking all together, from 1890 up to 1899 259 comparisons with the Perseus-Andromeda-stars were available and 251 comparisons with those of Ursa major. With the aid of the periodic time 3.968 all epochs of observation were reduced to

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[1]) See A. Pannekoek. The luminosity of stars of different type of spectrum. Proceedings Acad. Amsterdam **9**, 1906, p. 134.

[2]) Astronomische Nachrichten 4518 (Bd. 189, 89).

[3]) Astronomische Nachrichten 4596 (Bd. 192, S. 189).

one single period, viz. Aug. 3—7 1894, and subsequently united into normal places. These normal places are the following:

First series			Obs.—Calc.
Aug. 3.12	3.72	(18)	+ 0.03
3.42	3.94	(16)	+ 11
3.73	4.11	(21)	+ 08
3.96	3.91	(17)	— 29
4.22	3.94	(20)	— 42
4.54	4.68	(17)	+ 18
4.76	4.86	(16)	+ 33
4.94	4.76	(16)	+ 24
5.18	4.11	(17)	— 34
5.52	4.45	(14)	+ 19
5.76	4.11	(20)	+ 02
5.94	3.67	(18)	— 29
6.23	3.67	(16)	— 11
6.46	3.78	(14)	+ 10
6.73	3.79	(19)	+ 16

Second series			Obs.—Calc.
Aug. 3.21	0.59	(18)	— 0.03
3.48	0.68	(16)	— 08
3.65	0.59	(13)	— 28
3.92	1.13	(18)	+ 07
4.25	1.39	(20)	+ 10
4.46	1.40	(22)	00
4.65	1.69	(24)	+ 22
4.94	1.55	(14)	+ 05
5.22	1.20	(17)	— 23
5.46	1.27	(18)	— 03
5.72	1.02	(20)	— 11
6.22	0.74	(19)	— 04
6.48	0.86	(16)	+ 22
6.86	0.67	(16)	+ 11

Both series show, as does the graphic representation, with unmistakable certainty a periodical variation of the brightness to an amount of about one scale-unit with a maximum on 4.8 August. The calculation of a sine-formula resulted in (zero epoch 3.0 August):

1st series $4.08 + 0.45 \sin(q - 72°0)$ Maximum 4.79 Aug. $\pm 0^d.13$

2nd series $1.03 + 0.47 \sin(q - 78°9)$ Maximum 4.86 Aug. $\pm 0^d.09$

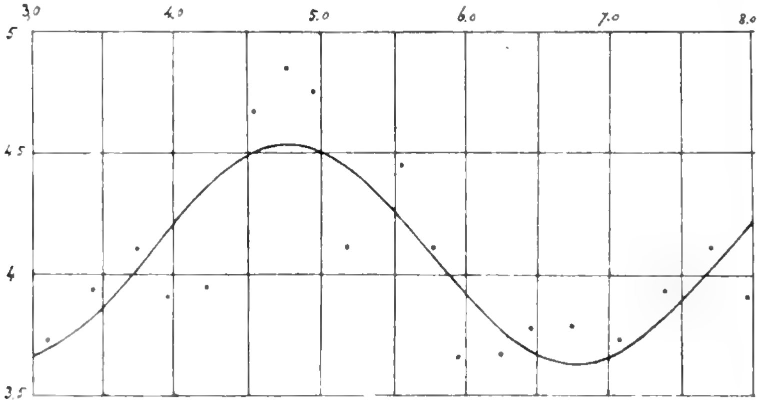

Fig. 1.

The remaining deviations Obs.-Calc. have been placed in the last column. They yield for the mean error of a normal place

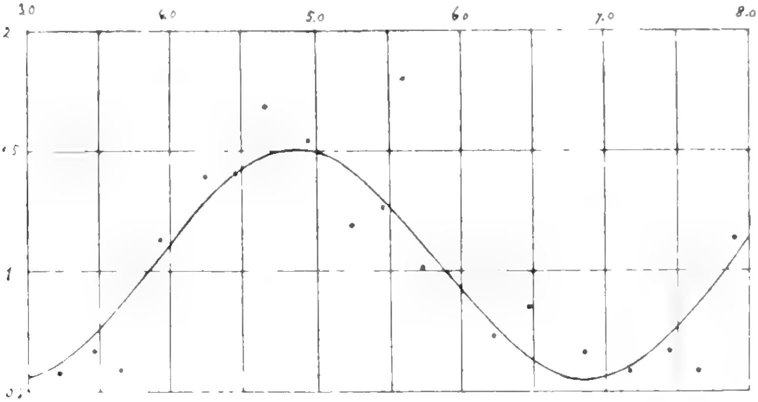

Fig. 2.

according to the mean of the two series, 0.21 (if we adopt this same value for both series, then each maximum has a mean error of $0^d.11$), from which we find 0.84 as mean error of one observation, while 0.7 had been found from the differences between the separate results and the adopted normal places. The deviations of the normal places from the sinusoid, it is true, show a systematic character, in the sense that the maximum is very sharp, the minimum very flat, hence that a term with $2q$ is indicated, the positive maximum of which falls together with the maximum of the principal term. Since, however, nothing of this kind is to be observed in the light-curves of HERTZSPRUNG and STEBBINS, no further attention has been paid to this phenomenon. Thus my observations yield as epoch of the maximum, after reduction to Greenwich-time:

$$1894 \text{ Aug. } 4.81 \text{ Gr. M.T.} = \text{J.D. } 2413045.81 \pm 0^d.08.$$

The interval between my normal-epoch and that of HERTZSPRUNG J. D. 2418985.86 is 5940.05 days = 1497 periods of 3.9680 days.

In order to reduce the brightness of maximum and minimum to the same photometric scale, the catalogues of Potsdam and Harvard were used. For the reduction of the magnitudes given there to the homogeneous scale that has been derived and adopted in my dissertation "Untersuchungen über den Lichtwechsel Algols" (p. 146—158) first a correction was added to the values of Harvard **44**, in order to reduce them to Harvard **14**. This was derived from the differences between the two catalogues, calculated by MÜLLER and KEMPF and communicated in their "Generalkatalog der photometrischen Durchmusterung" 1), Einleitung S. XXIII. For our purpose they were given the following form:

$$H.\,44 - H.\,14 = -\,0.01 + a\,(c - 4.0)$$

in which c is the colour-number according to Osthoff and a a function of the magnitude, varying linearly with the difference between the apparent brightness of the star in the two photometers, calculated in the manner as has been indicated on p. XXIV of the same introduction (for magnitude 1.0, 2.0, 3.0 we have $a = +\,0.062$, $+\,0.054$, $+\,0.042$). Subsequently to these magnitudes, reduced to H. **14** and to the magnitudes of H. **14** itself, the correction for colour was added, which has been found in my dissertation p. 158. There is also to be found the correction varying with the magnitude which has to be added to the results with Photometer C II, in order to reduce them to the same system 2). All stars used by me have been observed in Potsdam also with Photometer C III. As they have no excessive apparent brightness in this instrument and hence no variation with the brightness is to be expected in this case, a constant correction $-\,0^{m}.23$ was added to the results with C III.

For the employed comparison-stars, supplemented with a few other stars, continuing the scale further to the fainter side, we give successively: the colour according to Osthoff, (derived in the manner as indicated in my dissertation p. 168), next the magnitudes of Harvard **14**, Harvard **44**, Potsdam C II and C III, all corrected in the way already mentioned, subsequently the adopted simple mean value from these four and then the brightness in the employed scale of comparison-stars.

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1) Publicationen Potsdam **17**.

2) Müller and Kempf have not corrected the results obtained with C II, because they could not discover a systematic difference between C I and C II (Einleitung S. XIV). Since, however, for the comparison of these instruments they could only avail themselves of stars between magnitudes 3.5 and 5.5, this does not clash with my result that a correction is needed for the brighter stars up to the 2nd magnitude, which of course can only be found by comparison with another catalogue. While the comparisons employed by Müller and Kempf can teach nothing about the absence of systematic errors for these bright stars, the fact that increasing negative corrections are needed for C I above magnitude 4.8, and for photometer D above magnitude 6.1 (Einleitung S. XII), renders it exceedingly probable that similar corrections are needed for C II above magnitude 3.5, such as I derived in my dissertation. The final values of the Potsdam "General Catalog" are therefore likely to be systematically erroneous above the 3rd magnitude. For this reason I have not been able to use simply the Potsdam system for the magnitudes of the comparison-stars, as would have been a matter of course for fainter stars. By using the Potsdam system I should have found the amplitude too small.

Star	Colour	H 14	H 44	P.C II	P.C III	Mean	Scale	Calc.
α Persei	3.4	1.94	1.88	1.87	1.95	1.91	6.3	1.92
α Arietis	5.4	2.03	2.10		1.96	2.03	5.4	2.02
β Andromedae	6.2	2.20	2.05	2.04	2.11	2.10	3.8	2.14
γ Andromedae	5.2	2.13	2.19	2.09	2.14	2.14	3.1	2.16
α Andromedae	1.8	2.09	2.22	2.21	2.17	2.17	2.3	2.15
γ Cassiopeiae	2.1	2.32	2.35	2.24	2.23	2.28	0.8	2.25
β Cassiopeiae	2.9	2.43	2.50	2.36	2.33	2.41	—1.7	2.43
α Ursae maj.	4.9	1.96	1.88	1.79	1.77	1.85	4.0	1.86
ε Ursae maj.	1.8	1.86	1.89	1.98	1.84	1.89	2.4	1.89
η Ursae maj.	1.4	2.03	2.03	1.98	2.05	2.02	0.0	2.03
ζ Ursae maj.	2.1	(2.40)	2.29	2.18	2.12	2.20	3.6	2.25
α Coronae	1.8	2.39	2.38	2.32	2.39	2.37	—4.8	2.32
ε Bootis	4.8	2.55	2.57	2.37	2.52	2.50	—5.7	2.43
β Ursae maj.	1.7	2.63	2.71	2.41	2.42	2.54	—8.9	2.56
γ Ursae maj.	1.8	2.59	2.66	2.54	2.39	2.55	—9.7	2.61

The relations between the scale-values n and the magnitudes m are represented by the following formulae (3.7 is the colour-number of α Ursae minoris):

1st series $m = 2.335 - 0.065\, n + 0.020\, (c - 3.7)$.
2nd series $m = 2.07 \quad - 0.059\, n + 0.020\, (c - 3.7)$.

The magnitudes of the stars calculated after these formulae are given in the last column of the preceding table. With the aid of the same relations the sine-formulae for the brightness of α Ursae minoris, become expressed in magnitudes:

1st series $2^m07 - 0^m029\, \sin\, (\varphi - 72°0)$
2nd series $2^m01 - 0^m028\, \sin\, (\varphi - 78°9)$.

So the amplitude of the variation of light amounts to 0^m057, while we find as mean error of an observation based on the deviations of the separate observations 0.043 and on the deviations of the normal places from the formulae 0.051.

II.

Among the older material that may serve for the examination ot the variability of Polaris, we must in the first place consider the observations executed by G. Müller in 1878—81 at Potsdam for the determination of the atmospheric extinction and published in Vol. III of the Potsdam "Publicationen". As these observations consist in measurements of the differences in brightness between Polaris and 5 other stars observed in very different zenithdistances, they yield abundant material for the determination of the variability of Polaris

For this purpose I have examined the deviations of these differences from their mean value, remaining after correction for mean extinction, which are to be found in Müller's Table IV, last column but one (p. 261—265). Excluded were all observations in which the zenithdistance exceeded 60° and all those indicated as uncertain by the observer. The others were arranged according to the phase, counted from 1879 December 12.0 + $n \times 3^{d}968$. The unit of these deviations is that of the third decimal place of the logarithm of the proportion star: Polaris, i. e. 0.0025 magnitude. In order to give the positive sign to the maximum light, the signs must be reversed. In the following table are given the normal places formed from these deviations reversed in sign and reduced to magnitudes; the number of observations on which each normal deviation depends has been added in brackets.

Epoch	Deviation	O—C	Epoch	Deviation	O—C
Dec. 12.02	$+0^{m}022$ (25)	$+0^{m}001$	Dec. 14.11	$-0^{m}028$ (24)	$-0^{m}012$
12.34	+ 030 (18)	000	14.50	— 009 (20)	+ 015
12.64	+ 047 (23)	+ 014	14.81	— 009 (23)	+ 013
12.92	+ 008 (20)	— 021	15.05	— 021 (25)	— 004
13.21	+ 028 (18)	+ 008	15.20	— 048 (19)	— 036
13.63	+ 006 (20)	+ 003	15.34	+ 017 (24)	+ 022
13.84	— 010 (17)	— 004	15.69	+ 008 (29)	— 001

Here also the variability of Polaris appears with unmistakable clearness and it may be expressed by the following sine-formula:

$$\text{Deviation} = + 0^{m}004 + 0^{m}028 \, sin \, (q + 35^{\circ})$$

Maximum Dec. 12.61 = 1879 Dec. 12.57 ± 0.14 M. T. Greenwich

The last column of the table contains the differences Obs.—Calc. The mean error of a mean value from about 22 observations is $0^{n}016$, hence the mean error of one observation $0^{m}077$.

The immense number of photometric measurements made at the Harvard Observatory, in which Polaris has been used as comparison-star, have already been condensed into normal values by PICKERING[1]. Calculating the time of maximum light also from the mean deviations given by him, by means of a sine-formula, we obtain:

$$\text{Deviation} = +0^m02 + 0^m039 \, sin \, (q + 254°)$$

Phase	Deviation		O.—C.	Phase	Deviation		O.—C
0^d2	$+0^m01$	(120	$+0^m047$	2^d2	$+0^m03$	(123)	-0^m011
0 .6	06	(197)	— 031	2 .6	+ 03	(179)	— 002
1 .0	— 02	(152)	— 012	3 .0	00	(168)	012
1 .4	— 01	(126)	025	3 .4	03	(169)	— 018
1 .8	+ 09	(126)	+ 056	3 .8	— 02	(150)	+ 011

The last column again contains the differences Obs. Calc. The mean error of a normal deviation is 0^m033. As a positive sign here means a greater brightness of Polaris, the maximum-light occurs at the phase $2^d.16 \pm 0^d.24$. The zero epoch of the phase is at J. D. 2400000 + 3.9683 E; for $E = 2073$ this becomes J.D. 2408226.29, so that the normal epoch of maximum becomes

J. D. 2408228.45 ± 0.24.

III.

Putting together the hitherto obtained results for the light-variation of α Ursae minoris and comparing them with the formula for the maxima given by HERTZSPRUNG:

J. D. 241 8985.86 + 3.9681 E

we find the following table:

Year	E.	*Observed* 24	*O—C*	*Amplitude*	*Observer*
1879	— 2845	07696.57 ± 0.14	-0^d05	0^m056 vis.	MÜLLER
1881	— 2711	08228.45 ± 0.24	+ 0.11	0 .078 vis.	HARVARD
1894	— 1497	13045.81 ± 0.08	+ 0.20	0 .057 vis.	PANNEKOEK
1910	0	18985.86 ± 0.08	0.00	0 .171 ph.	HERTZSPRUNG
1911	(+ 100)	18985.94 ± 0.09	+ 0.08	0 .078 sel.	STEBBINS

Attempting to correct with these data HERTZSPRUNG's formula, we find (adopting as weights 2, 1, 4, 4, 4) as correction:

$$+0^d.07 \, (\pm 0^d.06) - 0.00001 \, (\pm 0.00004) \, E$$

Thus for the length of the period the exact value adopted by HERTZSPRUNG is found. The most probable formula for the maximum-epoch of α Ursae minoris now becomes:

$$\text{J. D. } 241\,8985.93 \, (\pm 0.06) + 3.96809 \, (\pm 0.00004) \, E.$$

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[1] Harvard Circular Nr. 174, Astronomische Nachrichten 4597 (Bd. 192, S. 219).

Chemistry. — *"Equilibria in ternary systems"* IV. By Prof. F. A. H. SCHREINEMAKERS.

(Communicated in the meeting of January 25, 1913).

We consider a liquid L, saturated with the solid substance F and in equilibrium with the vapour G. We allow this liquid to proceed along a straight line which passes through the point F.

If we call dn the quantity of solid substance F that dissolves in the unit of quantity of the liquid, we get:

$$dx = (\alpha - x)\, dn \qquad dy = (\beta - y)\, dn$$

If we substitute these values in (6) (II) and (7) (II)[1]) we have:

$$-M \,.\, dn = AdP - BdT \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$-N \,.\, dn = CdP - DdT \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where for the sake of brevity:

$$M = (x - \alpha)^2 r + 2(x - \alpha)(y - \beta)s + (y - \beta)^2 t$$

$$N = (x_1 - x)(x - \alpha)r + \{(x - \alpha)(y_1 - y) + (x_1 - x)(y - \beta)\}s + (y_1 - y)(y - \beta)$$

From this follows:

$$dP = \frac{DM - BN}{BC - AD} \,.\, dn = \frac{DM - BN}{BC - AD} \,.\, \frac{dx}{\alpha - x} \quad . \quad . \quad . \quad . \quad (3)$$

$$dT = \frac{CM - AN}{BC - AD}\, dn = \frac{CM - AN}{BC - AD} \,.\, \frac{dx}{\alpha - x} \quad . \quad . \quad . \quad . \quad (4)$$

$$\frac{dP}{dT} = \frac{DM - BN}{CM - AN} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

As in the previous communication, we assume the very probable case that $BC - AD$ is positive.

If now we call $x = \alpha$ and $y = \beta$ then $M = 0$, $N = 0$ and $\frac{M}{\alpha - x} = 0$, but $\frac{N}{\alpha - x}$ does not become 0 as a rule. If we call $tg\varphi = \frac{y - \beta}{x - \alpha}$ we get:

$$dP = \frac{B[(x_1 - \alpha)r + (y_1 - \beta)s + \{(x_1 - \alpha)s + (y_1 - \beta)t\}\, tg\varphi\,]}{BC - AD}\, dx \quad . \quad (6)$$

and for dT a same form with this difference that in the numerator B has been replaced by A.

To perceive the significance of this we take fig. 1 in which the closed curves indicate the boiling point lines of the solutions saturated with F. The exphased ones, as has been stated previously, have

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[1]) The figures (I), (II), and (III) refer to the former communications.

shifted to that side of F where the vapour region is situated. On increase of pressure, the boiling point line disappears finally in the point M, the correlated vapour line in the point M_1. The point D indicates the vapour which can be in equilibrium with the solid substance F and the liquid F, therefore the vapour which forms at the minimum melting point of the compound F. The line XFY is the tangent in F at the boiling point line passing through F. We have already noticed previously that the lines DFE and XY are conjugated diagonals of the indicatrix in F at the liquidum side of the ζ-plane.

We now lay down through F an arbitrary line ZZ_1 and let a liquid proceed along this line: as according to (6) dP and dT have a definite value differing from *nil* it follows that in this point neither the pressure nor the temperature is at a maximum or a minimum.

If, however, we choose the line in such a manner that

$$(x_1-\alpha)r + (y_1-\beta)s + \{(x_1-\alpha)s + (y_1-\beta)t\}\, tg\,\varphi = 0 \quad . \quad . \quad (7)$$

then dP as well as dT is *nil.* From 13 (1) it follows that (7) is satisfied when the line drawn through F comes into contact in F with the boiling point line passing through this point, therefore when the liquid proceeds along the straight line XFY.

If now we introduce a line element $d\varrho$ positive in the direction away from F and negative in the direction towards F, and if we let φ change from 0° to 360° we have $dx = \cos\varphi \,.\, d\varrho$ so that (6) is converted into:

$$dP = \frac{B[\{(x_1-\alpha)r + (y_1-\beta)s\}\cos\varphi + \{(x_1-\alpha)s + (y_1-\beta)t\}\sin\varphi]}{BC-AD}\, d\varrho. \quad (8)$$

The factor

$$\{(x_1-\alpha)r + (y_1-\beta)s\}\cos\varphi + \{(x_1-\alpha)s + (y_1-\beta)t\}\sin\varphi \quad . \quad . \quad (9)$$

in the point F is *nil* towards X as well as towards Y; in all other directions it differs from *nil.* If to φ is given such a value that the line passes through the point D we notice that the factor (9) is positive. Hence, in the point F the value of (9) is positive in the direction towards D and negative in the direction towards E.

We may now easily deduce that (9) is positive if, starting from F, we move towards that side of the line XFY where the point D is situated; and that (9) is negative when we move from F towards the other side of the line XFY. These positive or negative values are, however, very small if the direction almost coincides with FX or FY so that at some distance a reversal of the sign may perhaps take place. $B = H - \eta_1$ being positive it follows from (8) that the pressure when starting from F increases towards that side of the line XFY where the point D is situated and decreases when starting from F towards the other side of the line XFY.

Hence, if a liquid proceeds along the line FD or FM_1 or FZ the vapour pressure increases starting from F; if it proceeds along the line FZ_1 or FG or FE the vapour pressure decreases from F. Only in the direction of F towards X or towards Y the vapour pressure remains at first unchanged.

It will be easily perceived that these considerations are in harmony with fig. 1. For the closed curves drawn in fig. 1 are the boiling point lines of the solutions saturated with F; each curve, therefore, applies to a definite constant pressure. As the pressure becomes higher, these curves draw nearer to M to finally disappear in this point. Of course, it may happen also that on increase of pressure a curve moves away entirely or partially from M to again draw nearer to M at a further increase of pressure. In the point F this, however, is not the case; we have already demonstrated that the part of the boiling point line passing through F situated in the vicinity of F moves on increase of pressure towards M, and on reduction of pressure away from M.

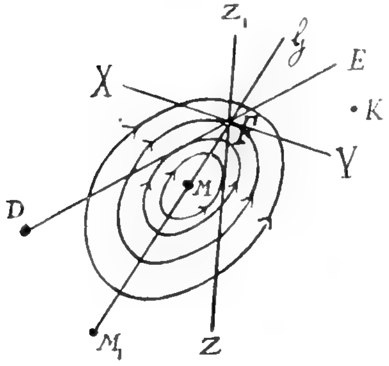

Fig. 1.

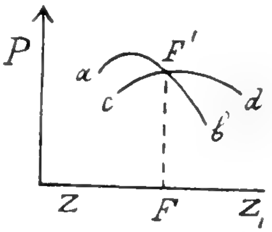

Fig. 2.

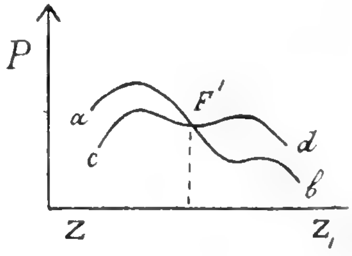

Fig. 3.

In fig. 2 the line ZFZ_1 represents the same line of fig. 1; the part FZ lies, therefore, at the same side of XFY where the point D is situated; the part FZ_1 lies, therefore, at the other side. Perpendicularly on the line ZZ_1 we place the pressure axis, hence the vapour pressures of the liquids saturated with F of the line ZFZ_1. As according to our previous considerations the pressure increases from F towards Z and decreases towards Z_1 the vapour pressure curve in F' must have a direction like curve $aF'b$. As the line FZ comes into contact with one of the exphased boiling point lines, the pressure in this point is a maximum; on the curve $aF'b$ of fig. 2 a maximum vapour pressure must, therefore, occur somewhere between a and F'.

If, however, the line ZFZ_1 of fig. 1 is turned in such a manner that it keeps on passing continually through F, the curve $aF'b$ of fig. 2 will change its form although it will of course, also keep on passing through F'. From our previous considerations it follows at once that the direction of the tangent in F' and the position of the point with maximum vapour pressure changes. If ZFZ_1 coincides with XFY we obtain in fig. 2 a curve $cF'd$ with a horizontal tangent in F'.

We have assumed in fig. 1 that the boiling point line passing through F is curved in the point F in the direction towards D; in our previous communication (II) we have noticed, however, that, in the vicinity of F it may be curved in some other direction also. It may then present a form such as curve aFb of fig. 2 (II) in which, however, we must imagine the arrows to point in the opposite direction. We have deduced this form while assuming that the vapour contains one of the three components only. Although in this case, the appearance of such a form is not very likely, the possibility thereof is greater when the vapour contains the three components and when, for instance, in the system LG a maximum temperature occurs. We now imagine through point F of fig. 1 and also at somewhat higher and lower pressures, boiling point lines of this form. Lines proceeding from F towards that side of XFY where the point D is situated will then each again come into contact with a boiling point line, so that a pressure maximum must occur. Lines which proceed from F towards the other side of XFY either do not come into contact with a boiling point line at all, or else they meet two of these, so that there occurs one point with a maximum and one with a minimum vapour pressure. The latter case will occur on lines in the vicinity of FX and FY.

On turning the line ZFZ_1 of fig. 1 we will, therefore, have vapour pressure curves like $aF'b$ of fig. 2, further like $aF'b$ of fig. 3, and if ZFZ_1 coincides with XFY of fig. 1, a vapour pressure curve $cF'd$ of fig. 3.

In order to investigate the change in temperature in the point F on the lines passing through this point we take the formula corresponding with (8):

$$dT = \frac{A[\{(x_1-\alpha)r+(y_1-\beta)s\}\cos\varphi+\{(x_1-\alpha)s+(y_1-\beta)t\}\sin\varphi}{BC-AD}\,d\varphi \,. \quad (10)$$

in which $A = V - v$ therefore positive or negative.

From this it follows that dT will be *nil* when (9) is *nil*, therefore when the line drawn through F coincides with the tangent XFY in F at the boiling point line passing through this point, or what amounts to the same thing, at the saturation line under its own vapour pressure. We now distinguish two cases.

$V > v$. The saturation lines under their own vapour pressure are now situated as in fig. 14 (I); we now imagine, in this figure, the tangent drawn on to the saturation line under its own pressure, passing through F. As in fig. 1 we will call this XFY. The point corresponding with the point D of fig. 1 is, of course, situated in fig 14 (I) on the vapour line correlated to the saturation line under its own vapour pressure which passes through the point F. Hence it is situated, as in fig. 1 to the left of the line YFX.

If now we move in fig. 14 (I) from F towards that side of the line XFY where the point D is situated, then, as follows from (10), the temperature increases starting from F; when moving towards the other side of the line XFY the temperature decreases from F.

After the previous considerations in regard to Fig. 1 it is evident that this agrees with fig. 14 (I). If in this figure we imagine a line drawn from F towards that side of XFY where the point D is situated this will come into contact with one of the exphased saturation lines under their own vapour pressure. As each of these curves belongs to a definite constant temperature differing, of course, from curve to curve, the temperature in this point of contact is a maximum one. If now in fig. 2 we imagine the pressure axis to be replaced by the temperature axis we again obtain a curve like $aF''b$ with a maximum temperature between a and F''. If in fig. 14 (I) we turn the line passing through F until it coincides with XFY, the curve $aF''b$ of fig. 2 is transformed to curve $cF''d$ of this figure.

Should the case occur that in F the saturation line under its own vapour pressure becomes curved away from D, we obtain curves as in fig. 3 in which we must again imagine the pressure axis to be replaced by the temperature axis.

$V < v$. The saturation lines under their own vapour pressure are no longer situated as in fig. 14 (I); we may, however, easily imagine them from this figure if we suppose the point F to lie on the line MM_1 between M and M_1. From a consideration of this figure it then follows that, starting from F, the temperature decreases towards that side of the line XFY where the point D is situated and increases towards the other side of this line. At the side turned away from the point D of the line XFY is now also found the temperature maximum. This is also in agreement with (10). $A = V - v$ now being negative it follows that for positive values of (9) and of $d\varphi$, dT from (10) is now negative; this means that the pressure decreases from F towards that side of the line XFY where the point D is situated.

We now take $\frac{dP}{dT}$ from (5) and write this in the form:

$$\frac{dP}{dT} = \frac{B - RD}{A - RC} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

In this:

$$R = \frac{M}{N} = \frac{\{(x-\alpha)r + (y-\beta)s\}\cos\varphi + \{(x-\alpha)s + (y-\beta)t\}\sin\varphi}{\{(x_1-x)r + (y_1-y)s\}\cos\varphi + \{x_1-x)s + (y_1-y)t\}\sin\varphi} \quad . \quad (11a)$$

For $x = \alpha$ and $y = \beta$, $R = 0$ unless φ is chosen in such a manner that the denominator also becomes 0; this is the case, when starting from F in fig. 1, one moves along FX or FY. We will first assume that this is not the case.

If one moves from F towards that side of XFY where the point D is situated R will be positive; when moving from F towards the other side R will be negative. We now let a liquid saturated with solid F proceed along the line ZFZ_1; from (11) it now follows that in the point F

$$\frac{dP}{dT} = \frac{B}{A} = \frac{H - \eta}{V - v} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

$V > v$. In the PT-diagram of fig. 4 aK represents the sublimation.

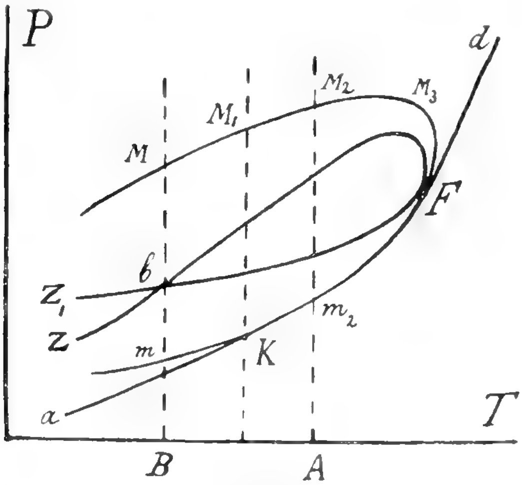

Fig. 4.

KF the three-phase and *Fd* the melting point curve of the compound *F*; these three curves are therefore the same as the homogeneous curves of fig. 3 (III). The direction of the melting point curve *Fd* (fig. 4) is determined by:

$$\frac{dP}{dT}=\frac{H-\eta}{V-v}$$

From (12) it follows that, in point *F* of fig. 4, the *PT*-curve ZFZ_1 must come into contact with the melting point line *Fd*. The further course of this *PT*-curve in the vicinity of the point *F* may be traced in the following manner:

We proceed in fig. 1 from *F* towards Z_1, *R* thus becoming negative. From (11) it now follows that $\frac{dP}{dT}$ remains positive so that the curve must be situated like curve FZ_1 of fig. 4.

If, in fig. 4 we move from *F* towards *Z*, *R* becomes positive. *A* being small, the denominator of (11) will soon become *nil* so that curve *FZ* of fig. 4 must have a vertical tangent in the vicinity of the point *F*. If in fig. 1 we move further from *F* towards *Z*, then $\frac{dP}{dT}$ from (11) will become negative first, and *nil* afterwards, so that curve *FZ* of fig. 4 must have a horizontal tangent. As $\frac{dP}{dT}$ afterwards becomes positive, curve *FZ* is bound to fall at a decreasing temperature.

Proceeding from point *Z* we find on curve ZFZ_1 first a pressure- and then a temperature maximum, further a point of contact with the melting point line *Fd* of the compound *F* at the minimum melting point of the compound and finally a receding branch FZ_1. All this reminds of the *P*, *T*-curves deduced by VAN DER WAALS for solid + liquid + gas in binary systems.

To some differences, for instance that the *P*, *T*-curves mentioned here do not meet the sublimation line of *F* in the maximum sublimation point, I will refer later.

In fig. 4 it has been assumed that curve ZFZ_1 exhibits a double point *b*, namely a point of intersection of the branches *FZ* and FZ_1. In order to perceive the possibility of a similar double point we take a circumphased boiling point line (fig. 1). On this occurs a point with a maximum and another with a minimum temperature. These points divide the boiling point line into two branches and in such a manner that to each point of the one branch appertains a definite point of the other branch, namely in that sense that both points indicate solutions of the same temperature and the same vapour pressure, and saturated with F.

Of all straight lines which unite two such correlated points of the two branches one is sure to pass through the point F. If now, we allow the line ZFZ_1 of fig. 1 to coincide with the above mentioned connecting line, we then find two solutions situated at different sides of F, which have the same temperature and the same vapour pressure. The branches FZ and FZ_1 of fig. 4 then must intersect each other at that temperature and pressure.

$V < v$. The melting point line Fd of fig. 4 now proceeds from the point F towards lower temperatures and higher pressures; the point F of curve ZFZ_1 now gets situated between the point with a maximum temperature and that with a maximum vapour pressure.

To each of the solutions of the line ZFZ_1 of fig. 1 saturated with solid F, appertains of course a definite vapour; the points representing these vapours form a curve which we will call the vapour line conjugated with the line ZFZ_1. It is evident that this vapour curve conjugated with ZFZ_1 must pass through the point D of fig. 1. If the line ZFZ_1 is turned, the conjugated vapour curve will also alter its position and form, but still pass through the point D. In fig. 5, the vapour curve conjugated with ZFZ_1 is represented by the dotted curve ($fca\ De$).

In fig. 5 it is assumed that the straight line ZFZ_1 and its conjugated vapour curve intersect each other in a; that such a point of intersection can appear is easy to understand. On each of the boiling point lines of fig. 1 occurs a point where the temperature along this curve is a maximum and another point where it is a minimum. If now we take the vapour phase appertaining to a similar solution, this with the liquid and the point F, will lie on a straight line. We now draw, through a similar liquid b with a maximum or minimum temperature, the line ZFZ_1 (fig. 5); the vapour a which is in equilibrium with this liquid b is then also situated on the line ZFZ so that the vapour curve fe must intersect the line ZFZ_1 in a. With each liquid of the line bZ_1 is now in equilibrium a vapour of curve ae, such as liquid d with vapour e, liquid F with vapour D, liquid b with vapour a. With each liquid of line baZ a vapour of curve

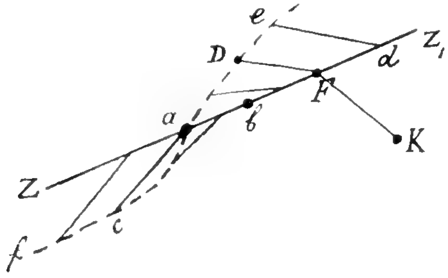

Fig. 5.

aef is in equilibrium. If *e* represents the vapour in equilibrium with the liquid *a*, a vapour between *a* and *e* will be in equilibrium with a liquid between *a* and *b*. If each liquid is united with the vapour with which it is in equilibrium, these conjugation lines not only occupy the strip eaZ_1 and faZ but also a part situated between *ba* and curve *ea* outside this field.

We have taken the point of intersection *a* of ZFZ_1 and the curve *fe* between *F* and *Z*; it is evident that it may also be situated at the other side of *F*.

We now imagine drawn in fig. 5 a set of straight lines passing through *F* and for each one its conjugated vapour curve; these latter all pass through the point *D*. Among these there is one that also passes through the point *F*. At the maximum sublimation point of the compound *F* the vapour in equilibrium with solid *F* has the composition *F* and the liquid which then, of course, is present in an infinitely small quantity only, a composition *K* (fig. 5). We can observe this also by other means. We imagine then in fig. 1, besides the boiling point lines of the solutions saturated with *F*, also drawn their appertaining vapour lines; one of these passes through the point *F* so that at a definite *P* and *T* a vapour exists of the same composition as *F* which can be in equilibrium with solid *F* and a liquid. This liquid is represented by the point *K* of the boiling point line of the pressure *P*, appertaining to the vapour point *F*. In fig. 1 and 5 this point is represented by *K*. Hence, the equilibrium solid *F* + vapour *F* + liquid *K* occurs; we are therefore, at the upper sublimation point of the compound *F*, therefore, in the point *K* of the sublimation line *aK* of fig. 4.

If now in fig. 5 we turn the line ZFZ_1, until it passes through the point *K*, its conjugated vapour curve will pass through the points *D* and *F*.

We have noticed above that the straight line ZFZ_1, and its conjugated vapour line can have a point of intersection *a* (fig. 5). As in this case the vapour *a*, the liquid *b* and the solid substance *F* are situated on a straight line, it follows from (11) that:

$$\frac{dP}{dT}=\frac{(x_1-x)\,B-(x-\alpha)\,D}{(x_1-x)\,A-(x-\alpha)\,C}=\frac{(x_1-\alpha)\,H+(\alpha-x)\,H_1+(x-x_1)\,\eta}{(x_1-\alpha)\,V+(\alpha-x)\,V_1+(x-x_1)\,v} \qquad (13)$$

so that the same relation applies as if the three phases belong to a binary system.

If, on one of the straight lines ZFZ_1, the points *a* and *b* of fig. 5 coincide, the solid substance *F* is in equilibrium with a liquid and a vapour which both have the same composition. This is the case if in the ternary system liquid + vapour, a singular point occurs and when the saturation curve of F passes through this point. As in this case $x = x_1$ and $y = y_1$ it follows from (11), as R becomes infinitely large, that:

$$\frac{dP}{dT} = \frac{D}{C} = \frac{H_1 - H}{V_1 - V} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

We have noticed above that if the straight line ZFZ_1 passes through point K of fig. 5, its conjugated vapour curve must pass through D and F and that with the liquid K a vapour F is in equilibrium. Hence, we have for the point K $x_1 = \alpha$ and $y_1 = \beta$. As R now becomes -1 it follows from (11) that:

$$\frac{dP}{dT} = \frac{B + D}{A + C} = \frac{H_1 - \eta}{V_1 - v} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

The above formula also determines the sublimation line $a\,K$ of the compound F (fig. 4) If, in fig. 5 the straight line ZFZ_1 passes through the point K, the corresponding P,T.-curve in fig. 4 must meet the sublimation curve aK in the point K. We now give in fig. 1 different positions to the straight line ZFZ_1; to each position appertains a definite P, T-curve in fig. 4 so that we can draw in this figure an infinite number of P, T-curves. From our previous considerations it now follows that *all* these (I will refer later to a single exception) meet the melting point line Fd of the compound F in the point F and that *one* only meets the sublimationcurve $a\,K$ in the point K. The latter takes place when the straight line ZFZ_1, in fig. 1 passes through the point K.. All other P, T-curves in fig. 4. proceed above the point K, or in other words: at the upper sublimation temperature T_k, of the compound F the vapour pressure of each system: solid F + liquid + vapour is greater than the vapour pressure of the solid substance F.

Different P, T-curves, besides coming into contact in F with the melting point curve Fd will also meet the three-phase line FK. Although all this is evident from what has been said previously, we will still consider a few of these points in another manner.

On warming the solid compound F, this, as mentioned previously, proceeds along the sublimation curve $a\,K$ of fig. 4 until the upper sublimation point K is attained; then the equilibrium: solid F + liquid + vapour is formed which proceeds along the three-phase line $K\,F$ of fig. 4 until the melting point line Fd has been obtained.

We have already noticed previously that the liquid and vapour continually alter their composition therewith and we may now ask what curves they proceed along in fig. 1.

At the temperature T_K of fig. 4, therefore at the upper sublimation point of the compound F, the vapour has the composition F and the liquid which can be in equilibrium with that vapour the composition K of fig. 1. At the temperature T_F of fig. 4, therefore at the minimum melting point, the vapour has the composition D and the liquid the composition F of fig. 1. Whereas the compound F proceeds in the P,T-diagram of fig. 4 along the three-phase line FK the liquid in fig. 1 proceeds along a curve from K towards F and the vapour along a curve from F towards D; we will call these curves the curves KF and FD.

We now imagine drawn in fig. 1 some more boiling point lines of the solutions saturated with F among which also those passing through the point K; on each of these a maximum and a minimum temperature occurs. The curve KF now intersects each of the boiling point lines situated between K and F in the point with the maximum temperature, or in other words the curve KF is the geometrical place of the points with a maximum temperature on the boiling point lines situated between K and F.

The liquid and vapour of the three-phase line KF of fig. 4 being formed from the solid substance F, the three points F, L, and G in fig. 1 must always lie on a straight line.

This means that the temperature along the boiling point line of such a liquid is a maximum or a minimum one.

From a consideration of fig. 1 it follows that here the temperature in this case is a maximum, from which follows at once what has been said above as to the course of the curve KF.

In the same manner we find that the curve FD also intersects each of the vapour lines conjugated with the boiling point lines in the point with the maximum temperature.

In fig. 1 we might also have drawn instead of the boiling point lines the saturation lines of F under their own vapour pressure. We then should have found that the curve KF intersects each of these lines in the point with the minimum vapour pressure.

We now turn the line ZFZ_1 of fig. 1 until it intersects the curve KF of this figure; the corresponding P,T-curve in fig. 4 must then meet the three-phase curve FK in a point. For in the point of intersection of the line ZFZ_1 and the curve KF in fig. 1 the pressure and temperature for both curves is namely the same; as, however, the curve KF passes through the points with maximum temperature of the boiling point lines in fig. 1 and as this is not the case with the line ZFZ_1 a higher temperature (the pressure being equal) is found on curve KF than on the line ZFZ_1. The P,T-curve of the line

ZFZ_1 therefore comes into contact with the three-phase line KF of fig. 4 and is situated further above and to the left of this three-phase line.

In order to deduce something more from the P,T-curves, we take a temperature T_B lower than the minimum melting point of the compound F. The saturation line of F under its own vapour pressure has at this temperature T_B a form as in fig. 7 (I) or 11 (I); the minimum vapour pressure in the point m of this saturation line under its own pressure we call P_m, the maximum pressure P_M. Of all the equilibria of F + liquid + gas appearing at the temperature T_B, the highest vapour pressure is, therefore, P_M and the lowest P_m. If, in fig. 4, we represent both pressures by the points M and m, one P,T-curve passes through the point M and one through the point m, whereas all the others must intersect the perpendicular line placed in B between M and m. One obtains the P,T-curve passing at T_B through the point M when the moving line ZFZ_1 of fig. 1 coincides with the line FM, and the one passing through the point m when the line ZFZ_1 coincides with the line F_m of fig. 7 (I) or 11 (I). In fig. 4 two P,T-curves must pass through each point between M and m. For if we choose a pressure P between P_M and P_m we notice from fig. 7 (I) and 11 (I) that at the temperature T_B two different systems: solid F + liquid + gas have a vapour pressure P, from which it follows at once, that in fig. 4 two P,T-curves must pass through each point between M and m.

If on the curve $Mamb$ of fig. 7 (I) or 11 (I) we imagine two points of equal pressure connected by a straight line, we notice that there must be a definite pressure P_b at which this conjugation line passes through the point F. If now, the straight line ZFZ of fig. 1 passes through this conjugation line, the corresponding P,T-curve at the temperature T_B and the pressure P_b must exhibit a double point. This curve is represented in fig. 4 by $ZbFbZ_1$. All the other P,T-curves as a rule intersect the line Mm in two points of which one is situated above and the other below the point b.

If the temperature T_B is changed, then in fig. 7 (I) or 11 (I) the saturation line under its own vapour pressure changes its position and form, while P_M, P_m and P_b also change. The points M, m and b in fig. 4 then proceed along a curve; the curve through which the points M and m go, is represented by $MM_1M_2M_3Fm_2Km$; we will call this curve the boundary curve of the system: solid F + liquid + gas.

The equilibrium between solid F, liquid, and gas is determined by (6) II and 7 (II). To the point M and m also applies the relation:

$$\frac{x-\alpha}{x_1-x} = \frac{y-\beta}{y_1-y}.$$

From this follows for the boundary curve:

$$\frac{dP}{dT}=\frac{(x_1-x)B-(x-\alpha)D}{(x_1-x)A-(x-\alpha)C}$$

so that this boundary curve must come into contact with the sublimation line of the compound in the maximum sublimation point K and with the melting line in the minimum melting point F. Further it is evident that the three-phase line KF of the compound F is a part of the boundary curve.

Hence, all the P,T-curves in fig. 4 are situated in the region encompassed by the boundary curve; through each point of this region pass two P,T-curves and through each point of the boundary line passes a P,T-curve which meets this boundary line in that point.

The boundary curve itself is, therefore, no P,T-curve in that sense that it corresponds with a straight line passing through F; this, however, is the case if only one of the three components of F occurs in the vapour.

The double point b passes in fig. 4 through a curve terminating in the point F. When the saturation curves under their own vapour pressure possess, in the vicinity of the minimum melting point T_F, a form as in fig. 12 (I) no double point of a P,T-curve appears above T_F. The double point curve in fig. 4 then proceeds from F towards lower temperatures.

If, however, the saturation line at T_F under its own vapour pressure has a form such as the curve aFb in fig. 2 (II) the double points are still possible above T_F and at each temperature more than one may appear.

From (11a) it appears that R can become nil only for $x=\alpha$ and $y=\beta$, therefore, in the point F. R, however, may become infinitely great and change its sign in other points of the component triangle. This will be the case when the denominator becomes 0, hence:

$$\{(x_1-x)\,r+(y_1-y)\,s\}\cos q+\{(x_1-x)\,s+(y_1-y)\,t\}\sin q=0\ . \quad (16)$$

Let us call the solution for which this is the case, the solution q; (16) then means that the line Fq comes into contact in q with the liquidum line passing through the point q, of the heterogeneous region $L+G$. We may express this also as follows: R becomes infinitely great when the conjugation lines liquid-solid and liquid-gas are conjugated diagonals of the indicatrix in the liquidum point. As $R=\infty$, (11) is converted into:

$$\frac{dP}{dT} = \frac{D}{C} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

in which D and C have another value than in (14).

Equation (16) is, of course, also satisfied $x = x_1$ and $y = y_1$, hence by a singular point of the system liquid + gas. In this case, D and C and consequently $\frac{dP}{dT}$ obtain the same value as in (14). We now imagine also the P,T-curve of the singular point drawn in fig. 4; we may then easily demonstrate that $\frac{dP}{dT}$ is determined for this curve by (14).

If now, on one of the straight lines ZFZ_1 of fig. 1 a singular point occurs, so that in the equilibrium of solid F + liquid + vapour the two latter ones have the same composition, its P,T-curve must meet the P,T-curve of the singular point in fig. 4.

Such a case occurs when at a definite P and T a singular point appears or disappears on the saturation line of F, so that the saturation line and the correlated vapour line meet each other in that point.

With the aid of the previous formulae we might be able to investigate more accurately the course of the P,T-lines if we expressed the quantities r, s, t etc. by means of the equation of state of VAN DER WAALS, in which a and b must then be considered as functions of x and y.

(*To be continued*).

Chemistry. — "*Equilibria in ternary systems.*" V. By Prof. F. A. H. SCHREINEMAKERS.

(Communicated in the meeting of February 22, 1913).

In the previous communication we have disregarded the case when the straight line ZFZ_1 of fig. 1 (IV) coincides with the line XFY of this figure. If a liquid moves from the point F of this figure towards X or towards Y then, as follows from (11^a) (IV) both the numerator and denominator of R are $= 0$.

The value of $\frac{dP}{dT}$ from (11) (IV) then becomes indefinite so that we will consider this case separately. In order to simplify the calculations we again limit ourselves to the case when the vapour contains one component only so that we may put x_1 and $y_1 = 0$.

Our conditions of equilibrium are given in this case by (18) (II) (19) (II). We now write these:

$$\left.\begin{array}{l} x\dfrac{\partial Z}{\partial x}+y\dfrac{\partial Z}{\partial y}-Z+Z_1=0 \\[2ex] (x-\alpha)\dfrac{\partial Z}{\partial x}+(y-\beta)\dfrac{\partial Z}{\partial y}-Z+\zeta=0 \end{array}\right| \quad . \quad . \quad . \quad . \quad (1)$$

If we develop these with regard to x, y, P and T and call $x=\alpha$ and $y=\beta$ we find, if we keep to the same notation as in communication (II):

$$a\,dx+b\,dy+\tfrac{1}{2}c\,dx^2+d\,dx\,dy+\tfrac{1}{2}e\,dy^2+\ldots.$$
$$=-C\,dP+D\,dT+\ldots. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$
$$\tfrac{1}{2}r\,dx^2+s\,dx\,dy+\tfrac{1}{2}t\,dy^2+\ldots=A\,dP-B\,dT+\ldots \quad . \quad . \quad (3)$$

In equation (3) are wanting the terms $dx\,dP$, $dy\,dP$, $dx\,dT$ and $dy\,dT$. A, B, C and D have herein the same significance as in communication II; therein, however we must now call $x=\alpha$, $y=\beta$, $x_1=0$ and $y_1=0$.

We now allow the liquid, saturated with F and in equilibrium with vapour, to proceed along the line ZFZ_1 in fig. 1 (IV). For this we call $dy=tg\,\varphi\,.\,dx$; from (2) and (3) now follows:

$$(a+b\,tg\,\varphi)\,dx+\tfrac{1}{2}(c+2d\,tg\,\varphi+e\,tg^2\varphi)\,dx^2+\ldots.$$
$$=-C\,dP+D\,dT+\ldots. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$
$$\tfrac{1}{2}(r+2s\,tg\,\varphi+t\,tg^2\varphi)\,dx^2+\ldots=A\,dP-B\,dT+\ldots. \quad . \quad (5)$$

We now allow the straight line ZFZ_1 in fig. 1 (IV) to coincide with the line XFY of this figure. As XFY is the tangent in the point F at the liquidum line of the heterogeneous region passing through F, this is determined by:

$$(\alpha r+\beta s)\,dx+(\alpha s+\beta t)\,dy=a\,dx+b\,dy=0.$$

Hence, if in fig. 1 (IV) the line ZFZ_1 coincides with the line XFY, $a+b\,tg\,\varphi=0$.

If we substitute this value of $tg\,\varphi$ in (4) and (5) we get:

$$-\frac{1}{2b^2}\,Q\,.\,dx^2+\ldots=-C\,dP+D\,dT+\ldots \quad . \quad . \quad . \quad (6)$$

$$\frac{1}{2b^2}\,S\,.\,dx^2+\ldots=A\,dP-B\,dT+\ldots \quad . \quad . \quad . \quad . \quad (7)$$

In this Q and S have the same value as in communication (II), namely:

$$Q=2abd-a^2e-b^2c$$

$$S=a^2t+b^2r-2abs=(rt-s^2)(\alpha^2r+2\alpha\beta s+\beta^2t)$$

At first, we may limit ourselves to terms recorded in (6) and (7); from this we find:

$$\frac{dP}{dT} = \frac{B}{A} \cdot \frac{Q - \mu S}{Q - \lambda S} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

in which μ and λ have the same significance as in communication (II), namely

$$\lambda = \frac{C}{A} \text{ and } \mu = \frac{D}{B}$$

and further:

$$dP = \frac{B}{2b^2} \cdot \frac{Q - \mu S}{BC - AD}\, dx^2 \quad dT = \frac{A}{2b^2} \cdot \frac{Q - \lambda S}{BC - AD} \cdot dx^2 \quad . \quad . \quad (9)$$

wherein, as in the previous occasion, we take $BC - AD > 0$.

Let us first take a P,x-diagram such as in fig. 2 (IV) and 3 (IV). As $B = H - \eta_1$ is always positive, dP has the same sign as $Q - \mu S$. In communication (II) we have seen that $Q - \mu S$ is negative when the boiling point line, of the solutions saturated with F passing through F is curved in the point F towards O. The point O here represents the component occurring in the vapour. The boiling point line then has a form like the curve aFb in fig. 1 (II). dP now being negative, the P,x-curve must have a form like $cF'd$ in fig. 2 (IV).

If the boiling point line of the solutions saturated with F is curved in the point F away from the point O so that it presents a form like curve aFb in fig. 2 (II), $Q - \mu S$ will be positive. From the value of dP from (9) it now follows that the P,x-curve must have a form like curve $cF'd$ of fig. 3 (IV).

In order to find the T,x-curve in the vicinity of the point F we must distinguish two cases.

$V > v$ or $A > 0$. If $Q - \lambda S$ is negative, the saturation curve of F under its own vapour pressure is curved in the vicinity of F towards O and, therefore, has a form like curve aFb in fig. 1 (II); dT is now negative and the T,x-curve has a form like curve $cF'd$ in fig. 2 (IV). If $Q - \lambda S$ is positive the saturation line of F under its own vapour pressure will have a form like aFb in fig. 2 (II); dT from (9) is now positive and the T,x-curve has a form like $cF'd$ in fig. 3 (IV).

$V < v$ or $A < 0$. If $Q - \lambda S$ is negative the saturation curve of F under its own vapour pressure will have a form like curve aFb in fig. 4 (II); dT from (9) is now positive and the T,x-curve, has consequently a form like curve $cF'd$ in fig. 3 (IV). If $Q - \lambda S$ is positive the saturation curve of F under its own vapour pressure will have a form like curve aFb in fig. 3 (II); dT from (9) is now negative so that the T,x-curve has a form like curve $cF'd$ of fig. 2 (IV).

From the value of $\frac{dP}{dT}$ from (8) it follows that this is not equal to $\frac{B}{A}$; the P,T-curve corresponding with the straight line XFY of fig. 1 (IV) will, therefore, not meet, in fig. 4 (IV), the melting point line Fd in F. Whereas, as we have stated previously, all the P,T-curves in fig. 4 (IV) meet the melting point line of F in the point F this is no longer the case when the straight line ZFZ_1 in fig. 1 (IV) coincides with XFY.

In order to determine this P,T-curve in the vicinity of F more closely we eliminate dx^2 from (6) and (7); we then get:

$$a_1\, dx^3 + \ldots = (AQ - CS)\, dP - (BQ - DS)\, dT + b_1\, dx dP + c_1\, dx dT + \ldots \quad (10)$$

In this equation, as dP and dT are according to (9) of the order dx^2, $dxdP$, and $dxdT$ are of the order dx^3; the terms omitted are all of the order dx^4 and higher. We now substitute in (10) the value of dx which we can deduce from (7) namely:

$$dx + \ldots = a_2 \sqrt{AdP - BdT} + \ldots \quad (11)$$

so that (10) is converted into

$$a_3\, (AdP - BdT)^{3/2} = (AQ - CS)\, dP - (BQ - DS)\, dT +$$
$$+ a_2\, (Adp - BdT)^{1/2}\, (b_1\, dP + c_1\, dT) \quad (12)$$

in which the terms omitted are of an order higher than dx^3. For (12) we write:

$$(AQ - CS)\, dP - (BQ - DS)\, dT = (b_2\, dP + c_2\, dT)\, (A\, dP - B\, dT)^{1/2} \quad (13)$$

or:

$$(a_4\, Y - b_4\, X)^2 = (b_2\, Y + c_2\, X)^2\, (AY - BX) \quad (14)$$

In order to investigate (14) we take a straight line $a_4\, Y - b_4\, X = \delta$, in which δ is infinitely small so that this line is situated parallel to, and in the immediate vicinity of, the tangent in the point F. Its points of intersection with (14) are given by:

$$a_4\, Y - b_4\, X = \delta \quad \text{and} \quad (b_2\, Y + c_2\, X)^2\, (AY - BX) = \delta^2.$$

This is satisfied by;

$$Y = a_5 \,.\, \delta^{2/3} \quad \text{and} \quad X = b_5\ \delta^{2/3} \quad (15)$$

hence: $a_4 a_5 - b_4 b_5 = 0$ and $(b_2 a_5 + c_2 b_5)^2\, (Aa_5 - Bb_5) = 1$

or:

$$\frac{b_5^{\,3}}{a_1^{\,3}}\, (Ab_4 - Ba_4)\, (b_2 b_4 + c_2 a_4)^2 = 1 \quad (16)$$

$$\frac{a_5^{\,3}}{b_1^{\,3}}\, (Ab_4 - Ba_4)\, (b_2 b_4 + c_2 a_4)^2 = 1 \quad (17)$$

As X and Y do not change their sign when δ does so, it follows that the P,T-curve has in point F a cusp so that we find at both sides of the tangent in F a branch of this curve. Now $a_4 = A(Q-\lambda S$ $b_4 = B(Q-\mu S)$

$$Ab_4 - Ba_4 = (BC - AD)\,S$$

so that $Ab_4 - Ba_4$ is positive. From (16) and (17) it now follows that b_5 and $A(Q-\lambda S)$ have the same sign, and the same applies to a_5 and $B(Q-\mu S)$.

In connection with (15) follows:

dT of X has the same sign as $A(Q-\lambda S)$ . . (18)

dP ,, Y ,, ,, ,, ,, ,, $B(Q-\mu S)$ . . (19)

what agrees with (9).

We will now consider some cases.

$V > v$ hence $A > 0$ and $\lambda > 0$; $Q - \lambda S < 0$; $Q - \mu S < 0$. From

$$\frac{dP}{dT} = \frac{A}{B} \cdot \frac{Q-\mu S}{Q-\lambda S} = \frac{A}{B}\left[1 + \frac{(\lambda-\mu)S}{Q-\lambda S}\right] \quad . \quad . \quad . \quad . \quad (20)$$

it follows that $\frac{dP}{dT}$ is smaller than $\frac{B}{A}$. (From our assumption $BC - AD > 0$ follows namely $\lambda - \mu > 0$). If in fig. 1 the line d_1Fd represents the tangent at the point F of the not drawn melting point line, the P,T-curve XFY will, in its turning point F, have a tangent like the dotted line in fig. 1 passing through F. From (18) and (19) and also from (9) it follows that dP and dT are negative, so that the curve XFY in fig. 1 must proceed from F towards lower temperatures and pressures. The latter may be found also by other means. For this we take the minimum melting point of the compound F, therefore the temperature T_F of fig. 1; as $Q - \lambda S < 0$, the saturation line of F under its own vapour pressure has at this temperature a form like curve aFb in fig. 1 (II) in which we must also imagine the tangent XFY to be drawn. As this tangent has only one point in common with the saturation curve, namely the point of contact F, a vertical line passing in fig. 1 through the point F may intersect the curve XFY in the point F only.

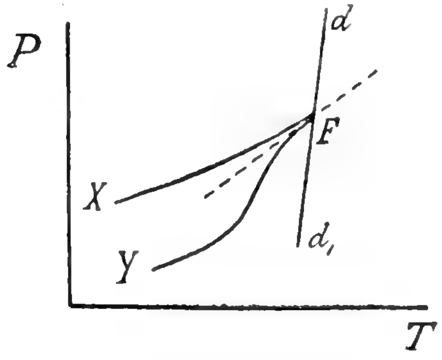

Fig. 1.

We now take a temperature T' somewhat lower than T_F; if now in fig. 1 (II) we also imagine to be drawn the saturation line under its own vapour pressure of this temperature T'', we notice that this intersects the line XFY in two points. In fig. 1, therefore, a vertical line corresponding with the temperature T'' must intersect the curve XFY in two points.

If we take a temperature T''' somewhat higher than T_F we find that the vertical line corresponding with this temperature does not intersect the curve XFY in fig. 1.

We now take the boiling point line of the compound F of the pressure P_F, that of a somewhat lower pressure P'' and that of a somewhat higher pressure P'''. As $Q - \mu S < 0$ it follows that that of the pressure P_F has a form like curve aFb of fig. 1 (II) in which, however, we must imagine the arrows to point in the opposite direction. From a consideration of these boiling point lines it follows that in fig. 1 curve XFY is intersected by a horizontal line corresponding with the pressure P_F in F only, and in two points by a horizontal line corresponding with the somewhat lower pressure P'.

$$V > v \text{ therefore } A > 0 \text{ and } \lambda > 0;\ Q - \lambda S < 0;\ Q - \mu S > 0.$$

From (8) it follows that $\frac{dP}{dT}$ is negative, from (9) and also from (18) and (19) that dT is negative and dP positive. In fig. 2 d_1Fd again represents the tangent at the point F of the not drawn melting point line; the dotted line passing through the point F is the tangent in the cusp F of curve XFY.

The fact that the curve XFY proceeds from F towards lower temperatures and higher pressures may be deduced also in the following manner. From a consideration of the saturation lines under their own vapour pressure of the temperature T_F, the somewhat lower temperature T'', and the somewhat higher temperature T''', it follows that curve XFY in fig. 2 is intersected by the vertical line corresponding with the temperature T_F in F only and in two points by the vertical line corresponding with the somewhat lower temperature T'.

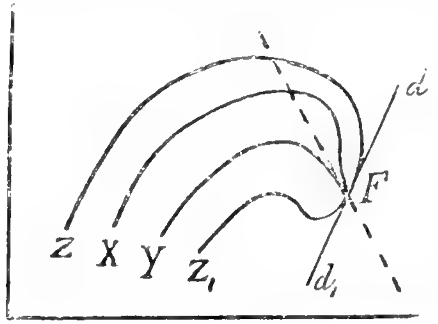

Fig. 2.

As $Q - \mu S > 0$, the boiling point line of the solutions saturated with F has, at the pressure P_F a form like curve aFb of fig. 2 (II) in which, however, the arrows must be imagined to point in the opposite direction. If we imagine in this figure the tangent XFY, we notice that the latter, besides the point of contact F, has another two points of intersection in common with curve aFb, which both appertain to a lower temperature than T_F. The horizontal line in fig. 2 corresponding with the pressure P_F must therefore intersect the curve XFY, besides in F, also in two other points to the left of point F; the one point of intersection must lie on the branch XF, the other on the branch YF.

If now we take the boiling point line of a somewhat lower pressure P', this will be intersected in fig. 2 (II) in two points by the line XFY. Hence, the horizontal line in fig. 2 corresponding with this pressure P' must intersect curve XFY in two points.

The boiling point line of a somewhat higher pressure P'' is intersected by the line XFY in four points, of which two lie on the part XF and two on the part YF of this line. The horizontal line corresponding with this pressure P'' in fig. 2 intersects therefore each of the branches XF and YF in two points.

If in fig. 2 (II) we take a straight line ZFZ_1 whose direction differs but little from the tangent XFY this will intersect the boiling point line of the pressure P_F not only in F but also in three other points namely two on FZ_1 and another on FZ. The horizontal line in fig. 2 corresponding with the pressure P_F, therefore, intersects the curve ZFZ_1 in F and further the branch ZF in one and the branch Z_1F in two points. Hence, on branch Z_1F must occur a point with a maximum and another with a minimum vapour pressure

$V > v$ therefore $A > 0$ and $\lambda > 0$; $Q - \lambda S > 0$; $Q - \mu S > 0$.

From (20) follows: $\frac{dP}{dT}$ positive and greater than $\frac{B}{A}$; from (9) and also from (18) and (19) follows dP and dT positive. The curve XFY must therefore have a form as drawn in fig. 3 wherein d_1Fd again represents the tangent in the point F at the omitted melting point line; the dotted line passing through F represents the tangent in the cusp F at curve XFY.

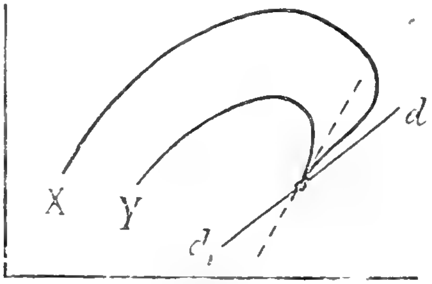

Fig. 3.

The fact that curve XFY in fig. 3 must proceed from F towards higher temperatures and pressures is again evident from a consideration of the saturation line of the temperature T_F under its own vapour pressure, and of the boiling point line of the solutions saturated with F of the pressure P_F. For both curves have in this case a form like in fig. 2 II) so that the tangent XFY besides meeting the curve aFb in the point F, also intersects this in two other points. In harmony with fig. 3 we find that the vertical line corresponding with the temperature T_F must intersect the curve XYF in two points above F, and the horizontal line corresponding with the pressure P_F must intersect this curve in two points at the left of F.

From a consideration of the straight lines whose direction differs but little from the tangent XFY it follows that their P,T-curves in fig. 3 must exhibit on the one branch proceeding from F, a point with a maximum temperature and one with a maximum pressure, and on the other branch, besides two similar points, also one with a minimum temperature and a minimum pressure.

The deduction and further consideration of the other cases I must leave to the reader.

We can also determine the course of the saturation lines under their own vapour pressure and of the boiling point lines of the solutions saturated with solid matter, which has been discussed in the previous communications, in a different manner.

For the stability requires that if we convert a system, at a constant temperature, into another having a smaller volume the pressure must increase; if converted into one with a greater volume the pressure must decrease.

We may also perceive this in the following manner. At the pressure P exists the system S which is converted at the pressure $P+dP$ into the system S'. We represent the ζ of the system S, at the pressures P and $P+dP$ by ζ_P and ζ_{P+dP}, that of the system S' by ζ'_P and ζ'_{P+dP}.

As at the pressure P the system S is the stable one, it follows that $\zeta_P < \zeta'_P$.

As at the pressure $P+dP$ S' is the stable one it follows that $\zeta'_{P+dP} < \zeta_{P+dP}$. If we represent the volumes of S and S' at the pressure P by V and V' the latter condition can also be expressed by:

$$\zeta'_P + V'dP < \zeta_P + VdP.$$

From this now follows in connection with the first condition:

$$V'dP < VdP$$

hence, $V' < V$ if dP is positive and $V' > V$ if dP is negative.

The volume V'' of the system S', is, at the pressure $P+dP$, like $V' + \frac{dV'}{dP}dP$, in which $\frac{dV'}{dP}$ is negative; from this now follows:

$V'' < V$ if dP is positive and $V'' > V$ if dP is negative.

Hence, if we compare two systems S and S' which are converted into each other, at a constant temperature, by a small alteration in pressure, it follows from the foregoing that:

If S exists at a higher pressure than S', the volume of S is smaller, if S exists at a lower pressure than S', the volume of S is greater than that of S'. And reversally:

if S has a smaller volume than S' it exists at a higher, if it has a greater volume than S' it exists at a lower pressure than S'.

We may express this also a follows:

a system S is converted by increase in pressure into a system with a smaller and on reduction in pressure into a system with a greater volume. And reversally:

if a system S is converted into another with a smaller volume, the pressure must increase, and if converted into one with a greater volume the pressure must decrease. We may then compare the volumina of the two systems either both under their own pressure or both under the pressure of the system S, or both under the pressure of the system S'.

It is evident that a similar consideration applies to two systems S and S' which, at a constant pressure, are converted into each other by a small change in temperature. For the case in question, the equilibrium: solid + liquid + gas we may also deduce the above rules in a different manner. For this, we take at the temperature T and the pressure P a complex consisting of n quantities $F + m$ quantities $L, + q$ quantities G. We now allow a reaction to take place between these phases at a constant T and P wherein: $(n + dn)$ quantity $F + (m + dm)$ quantity $L' + (q + dq)$ quantity G' is formed and in which L' and G' differ but infinitesimally from L and G.

The increase in volume Δ in this reaction is then determined by:

$$vdn + Vdm + V_1dq + m\frac{\partial V}{\partial x}dx + m\frac{\partial V}{\partial y}dy + q\frac{\partial V_1}{\partial x_1}dx_1 + q\frac{\partial V_1}{\partial y_1}dy_1.$$

As the total quantity of each of the three components remains unchanged in this reaction we have:

$$\alpha dn + xdm + x_1dq + mdx + qdx_2 = 0$$
$$\beta dn + ydm + y_1dq + mdy + qdy_1 = 0$$
$$dn + dm + dq = 0.$$

After elimination of dn, dm, and dq we find:

$$m\{(y_1-\beta)A + (\beta-y)(A+C)\}dx - m\{(x_1-\alpha)A + (\alpha-x)(A+C)\}dy$$
$$-q\{(y-\beta)A_1 + (\beta-y)(A_1+C_1)\}dx_1 + q\{(x-\alpha)A + (\alpha-x_1)(A_1+C_1)\}dy_1$$
$$=\{(x_1-\alpha)(y-\beta) - (x-\alpha)(y_1-\beta)\}\Delta$$

which for the sake of brevity we write:

$$mA_ydx - mA_xdy - qA_{y_1}dx_1 + qA_{x_1}dy_1 = E\,.\,\Delta$$

We will choose the new system $F+L'+G'$ in such a manner that it is in equilibrium at the temperature T and the pressure $P+dP$. Then, as follows from our previous communications, dx, dy, dx_1 and dy_1 are determined by:

$$[(x-\alpha)\,r+(y-\beta)\,s]\,dx+[(x-\alpha)\,s+(y-\beta)\,t]\,dy=AdP$$

$$[(x_1-\alpha)\,r+(y_1-\beta)\,s]\,dx+[(x_1-\alpha)\,s+(y_1-\beta)\,t]\,dy=(A+C)\,dP$$

and two corresponding equations which determine dx_1 and dy_1.

From this we find:

$$E\,(rt-s^2)\,dx=-(sA_x+tA_y)\,dP \qquad E\,(rt-s^2)\,dy=(rA_x+sA_y)\,dP$$

$$E\,(r_1t_1-s_1{}^2)\,dx_1=(s_1A_{x_1}+t_1A_{y_1})\,dP \quad E\,(r_1t_1-s_1{}^2)\,dy_1=-(r_1A_{x_1}+s_1A_{y_1})dP.$$

After substitution we find:

$$m\,\frac{rA^2{}_x+2sA_xA_y+tA^2{}_y}{rt-s^2}+q\,\frac{r_1A^2{}_{x_1}+2s_1A_{x_1}A_{y_1}+t_1A^2{}_{y_1}}{r_1t_1-s_1{}^2}=-E^2\,\frac{\Delta}{dP}$$

so that Δ and dP must have the opposite sign.

In the above relation Δ represents the change in volume if both systems are compared at the same pressure P; if, when the new system is taken at the pressure $P+dP$, the change in volume is represented by Δ', we get:

$$\Delta'=\Delta+\frac{dV_t}{dP}\,.\,dP$$

in which V_t represents the total volume of the new system at the pressure P. From this follows that Δ' and Δ have always the same sign and Δ' and dP always the opposite one.

Let us now consider the system $F+L+G$ at a constant temperature, namely the saturation line of F under its own vapour pressure and its conjugated vapour line. These are respresented in fig. 7 (I), 11 (I), 12 (I) and 13 (I) by the curves $Mamb$ and $M_1a_1m_1b_1$.

We now take the system $S=F+L+G$ which is stable at the pressure P and the system $S'=F+L'+G'$ which is stable at the pressure P'. If now the volume of S' is smaller than that of S, P' will be greater than P; if the volume of S' is greater than that of S, P' will be smaller.

Reversally, if P' is greater than P the volume of S' is smaller than that of S; if P' is smaller than P the volume of S' will be greater.

All this applies, as we have noticed previously, if S and S' can be converted into each other and when P and P' differ but little.

We now omit from the system S the vapour so that we retain $F+L$ only. We now can distinguish two chief cases, depending on whether a phase reaction is possible, or impossible, between the three phases of the system $F+L+G$.

A. No phase reaction is possible. The three phases form the apexes of a three phase triangle such as, for instance, Faa_1, in fig. 4 (I). We may further distinguish three other cases, namely

1. $F + L$ is converted by a change of pressure in the one direction into $F + L' + G'$ and by a change of pressure in the other direction, into $F + L''$. Hence on change of pressure in the one direction vapour is formed, but not when in the other direction.

2. $F + L$ is converted by a change of pressure in the one direction into $F + L' + G'$, and by a change of pressure in the other direction into $F + L'' + G''$. Hence, vapour is formed on increase as well as on decrease of pressure.

3. $F + L$ is converted by a change of pressure in the one direction into $F + L'$ and by a change in the other direction into $F + L''$. Hence, no vapour is formed either on increase or on reduction of pressure. The case cited in 1 is the one generally occurring; those mentioned in 2 and 3 only occur exceptionally.

B. A phase reaction is possible. The three phases are now represented by three points situated on a straight line. The system $F + L$ can then be converted by a change in volume unaccompanied by a change of pressure, into the system $F + L + G$. So long as these three phases are adjacent, neither the pressure nor the composition of liquid or vapour is altered by a change in volume: all that happens is a reaction between the three phases. As regards this reaction, we can now distinguish three cases:

1. $F \rightleftarrows L + G$.

In the graphic representation, the point F is situated between the points L and G. On a change in volume in the one direction solid matter is deposited; when in the other direction this disappears.

2. $F + L \rightleftarrows G$.

In the graphic representation the point G is now situated between the points F and L. On change in volume in the one direction, gas is formed; when a change takes place in the other direction the gas disappears.

3. $F + G \rightleftarrows L$.

In the graphic representation the point L is now situated between the points F and G. On change in volume in the one direction, liquid is formed, when in the other direction this disappears. If, in one of the reactions sub *A* and *B* vapour is formed, the volume will as a rule become larger and if vapour disappears it will become smaller. The reverse, however, may also occur as will be perceived in the following manner. In order to convert $F + L$ into $F + L' + G'$ we first of all form from L a little of the vapour G'; the liquid L

is hereby converted into a somewhat different liquid L''. Now, so as to convert L'' into L' either solid F must dissolve in L'' or crystallise from the same. If now this solution or crystallisation of F is accompanied by a great decrease in volume, this may exceed the increase of volume occurring in the generation of the vapour; the system $F+L$ is then converted with decrease in volume into $F+L'+G'$.

Such a conversion may be particularly expected in points of the saturation line under its own vapour pressure which are adjacent to the point F. The liquid then differs but little in composition from the solid substance F so that in order to slightly alter the composition of the liquid large quantities of solid substance must either dissolve or else crystallise out. Moreover, if in this case the solid substance F melts with increase in volume, the latter will increase on addition of F and decrease on the separation of the same. If F melts with decrease in volume, the volume will decrease on addition of F and increase when this substance is deposited.

Hence, in the case of points of the saturation line of F under its own vapour pressure situated in the vicinity of F, the system $F+L$ can be converted with decrease in volume into $F+L'+G'$:

1. if in that conversion solid matter separates and if this melts with increase of volume ($V > v$).

2. if in that conversion solid matter dissolves and if this melts with decrease of volume ($V < v$).

We may now apply the above considerations in different ways. If, for instance, we take the change in volume along the saturation line under its own vapour pressure as known, we may determine the change in pressure; if the value of the latter is known we may determine the change in volume. We now merely wish to demonstrate that these views support our previous considerations. We first take the case when all the points of the saturation line under its own vapour pressure are removed comparatively far from the point F, so that the two-phase complex $F+L$ is converted with increase in volume into the three-phase equilibrium $F+L'+G'$.

We represent the equilibrium $F+L+G$ by the three-phase triangle Faa_1 of fig. 3 (1) or 4 (1); the two-phase complex $F+L$ is then represented by a point of the line Fa.

As, according to our assumption the system $F+L$ which exists at the pressure P, is converted with increase in volume into the three-phase equilibrium $F+L'+G'$ existing at the pressure P', the new pressure P' must be smaller than P.

From a consideration of fig. 3 (1) or 4 (1) it follows at once that the new liquid L' must be situated in such a way that the new conjugation line FL' is situated at the other side of Fa than the point a_1. From all this it follows that, on reduction in pressure, the conjugation line solid-liquid turns away from the vapour point, and that on increase in pressure it turns towards the same.

We notice at once that this is in conformity with the change in pressure along the saturation line under its own vapour pressure in fig. 7 (I) and 11 (I).

For if we allow the conjugation line solid-liquid to turn away from m towards M or along maM or along mbM, it always turns towards the vapour point while the pressure increases. We now take the case when the saturation line of F under its own vapour pressure is situated, in part, adjacent to the point F. We now distinguish two cases depending on whether the substance F melts with increase or decrease in volume.

$V > v$. The substance melts with increase in volume. For these points of the saturation line under its own vapour pressure which are removed far from the point F, $F+L$ will be converted into $F+L'+G'$ with increase of volume; for points in the vicinity of F, $F+L$ may pass into $F+L'+G'$ with decrease in volume, provided that, as stated above, much solid matter is deposited in this conversion.

We have already seen above in what direction the conjugation line solid-liquid turns when $F+L$ is converted with increase in volume into $F+L'+G'$; we may now readily deduce that this conjugation line will turn in the opposite direction if that conversion takes place with decrease in volume. Hence, we find the following: we take from the three-phase equilibrium $F+L+G$ the two-phase complex $F+L$; if $F+L$ is converted into $F+L'+G'$ with increase of volume the conjugation line solid-liquid on reduction of pressure turns away from the vapour point; at an increased pressure it turns towards the vapour point.

If $F+L$ is converted into $F+L'+G'$ with decrease in volume the conjugation line solid-liquid turns in the opposite direction.

Let us now consider the saturation line of fig. 12 (I) under its own vapour pressure of which a part is adjacent to the point F and which, as we have seen before, applies to the case when the substance F expands on melting ($V > v$). We draw through F two tangents at this curve Mm; we will call these points of contact R and R'.

As seen from the figure, the conjugation line solid-liquid now moves, on increase in pressure, on the branch RMR' towards the vapour point; on the branch RmR', however, it moves away from the vapour point. In connection with the above, it now follows that the conversion of $F+L$ into $F+L'+G'$ is accompanied on the branch RMR' with an increase and on branch RmR' with a decrease in volume.

In the points of contact themselves where both branches amalgamate, the case sub A 3 now occurs. Let us take the two-phase complex $F +$ liquid R. We now see that, on increase as well as on reduction in pressure, the conjugation line F-liquid R gets outside the new three-phase triangle so that no vapour can be formed.

Let us now see what happens in a similar point of contact R if the pressure changes but infinitesimally. At this infinitesimal change of pressure, the liquid then moves at an infinitesimal rate along the tangent FR either towards or away from F. The only thing what happens is that in the liquid a little F is dissolved, or else crystallised from the same, without any vapour being formed.

If now a substance F melts with increase in volume and, therefore, in this case also dissolves with increase in volume, it will crystallise out on increase in pressure and get dissolved on reduction of the same. This also is in harmony with the change in pressure along the saturation line under its own vapour pressure in the point R of fig. 12 (I): on elevation of the pressure the liquid moves, starting from R, from the point F; this signifies that solid matter is being deposited. On reduction of pressure the liquid moves from R towards the point F; this means that solid matter is being dissolved.

The fact that in a point of contact R no vapour takes part in the reaction may be also demonstrated in the following manner. We again take at the pressure P a system S consisting of:

$$n \text{ quantities } F + m \text{ quantities } L + q \text{ quantities } G\,;$$

at the pressure $P + dP$ is formed thereof the system S' consisting of:

$$(n+dn) \text{ quantities } F + (m+dm) \text{ quantities } L' + (q+dq) \text{ quantities } G'$$

From the three relations already employed for this and which indicate that the quantity of each of the three components remains the same in this conversion we can deduce:

$$\begin{aligned}
Edn &= -\, m \{(y_1-y)dx - (x_1-x)dy\} - q \{(y_1-y)dx_1 - (x_1-x)dy_1\}\\
Edq &= \, m \{(\beta-y)dx - (\alpha-x)dy\} + q \{(\beta-y)dx_1 - (\alpha-x)dy_1\}\\
Edm &= \, m \{(y_1-\beta)dx - (x_1-\alpha)dy\} + q \{(y_1-\beta)dx_1 - (x_1-\alpha)dy_1\}
\end{aligned}$$

in which all the letters have again the same meaning as before.

If now we proceed at the pressure P from the system $F + L$ we must call $q = 0$; we then obtain:

$$\begin{aligned}
Edn &= -\, m \{(y_1-y)dx - (x_1-x)dy\}\\
Edq &= \, m \{(\beta-y)dx - (\alpha-x)dy\}\\
Edm &= \, m \{(y_1-\beta)dx - (x_1-\alpha)dy\}.
\end{aligned}$$

Hence, as a rule dn, dm and dq are not 0; if, however, we can draw through the point x, y of the saturation curve under its own vapour pressure a tangent passing through the point F we find:

$$\frac{dy}{dx} = \frac{\beta - y}{\alpha - x}$$

hence $dq = 0$, whereas dn and dm differ from *nil*. It means that no vapour takes part in the reaction so that the system $F + L$ is converted into another system $F + L'$ devoid of vapour.

We have noticed previously that the saturation line of the substance F under its own vapour pressure which passes through the point F can have a form like the curve Fab of fig. 2 (II). At a somewhat lower temperature this curve still possesses about this form but it becomes circumphased. In fig. 4 a part of this curve has been drawn. So long as the point F is situated sufficiently close to this curve we can draw through F four tangents at this curve with the points of contact R, R', X and X'. Let us now imagine in fig. 4 the saturation line under its own vapour pressure to be shifted further towards the left and also its correlated vapour line to be drawn.

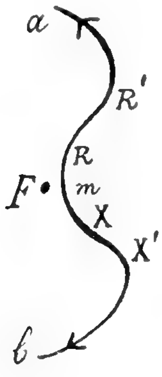

Fig. 4.

We now allow a conjugation line solid-liquid to turn from m in such a direction that the pressure increases. Let us now proceed from m towards a. On the branch mR, the conjugation line F-liquid turns towards the vapour point, from R to R' away from the vapour point and from R' to a and further on it again turns towards the vapour point. The same applies to the branch $mXX'b$ on which, in the points X and X', the direction of the rotation of the conjugation line gets reversed. The conversion of $F + L$ into $F + L' + G'$ then takes place on branch mR and mX (and mX) with increase in volume, on branch RR' (and XX') with decrease in volume and on branch $R'a$ (and $X'b$) again with increase in volume. In the point of contact R now appears the case sub A 2 and in the point of contact R' the case cited sub A 3. Let us take for instance the two-phase complex $F +$ liquid R. We now notice that on increase as well as on decrease in pressure the conjugation line F-liquid R gets situated within the new three-phase triangle so that $F +$ liquid R is converted into $F + L' + G'$.

On an infinitesimal change in pressure, nothing takes place in the points R and R' but a solution, or a crystallisation of solid matter. As F melts with increase in volume and in this case also dissolve with increase in volume, crystallisation will occur at an increased and solution at a reduced pressure. This is, moreover, in conformity with the change in pressure in the points R and R' along the saturation line under its own vapour pressure.

The same considerations as the above-cited may be also applied to the case when the substance F melts with decrease in volume.

(To be continued).

Chemistry. — *"The dynamic Allotropy of sulphur."* (Fifth communication.)[1] By Dr. H. R. KRUYT. (Communicated by Prof. P. VAN ROMBURGH.)

(Communicated in the meeting of January 25, 1913).

As point 5 of the résumé of my third paper on the above subject I wrote in 1909:

"Es wurden neue Untersuchungen über den Einfluss des S_{μ} auf den Umwandlungspunt $S_{rh} \rightleftarrows S_{mon}$ in Aussicht gestellt".

In connection therewith I wrote[2] in July 1911:

"Dr. VAN KLOOSTER of Groningen has this year started that investigation and although the provisional result is only of a qualitative character as yet it may be taken for granted . . . ."

Nevertheless, Messrs. SMITS and DE LEEUW published, in these Proceedings (XIV, p. 461), an investigation concerning this question.

In the Zeitschr. f. Electrochemie[3] I communicated, in connection with some other questions regarding sulphur, that the above investigation had been continued and brought to a close, also to what conclusions it had led and that a detailed communication would soon appear: recently it appeared as the fourth communication in this series.

Meanwhile, Dr. DE LEEUW (Proc. XV p. 584) has contradicted the above cited conclusions and condemned the still unpublished investigations in advance.

Although I should have every reason not to take any notice of that paper, two reasons in particular have induced me to repeat and extend

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[1] For the previous communications see Zeitschr. f. physik. Chem. viz. I: **64**, 513 (1908); II: **65**, 486 (1909); III: **67**, 321 (1909) and IV; **81**, 726 (1913).

[2] Chem. Weekbl. **8**, 643 (1911).

[3] Z. f. Elektrochemie **18**, 581 (1912).

the investigations of Dr. DE LEEUW and to communicate here the results. First of all, the criticism did not concern my work only, but also that of Messrs. VAN KLOOSTER and SMIT who carried this out at my request and whose work I wish to defend and in the second place, owing to a paper by Messrs. KOHNSTAMM and ORNSTEIN [1]), the question as to the change of the transition point of sulphur has been introduced into the discussion of the heat theorem of NERNST. Looking at the eminent importance of the problem whether the facts confirm, or do not confirm the conclusions from the heat theorem, each experimental fact supporting the theorem must be as much as possible elucidated.

Therefore, I will discuss the said treatise of DE LEEUW, but only in so far as required by the considerations just mentioned.

I have first of all verified whether the result of DE LEEUW's experiment is correct namely, that a dilatometer, which contains a sulphur mixture rich in S_μ, after it has been placed for some hours in a thermostat at 70°—80° C., exhibits a rise of the liquid in the capillary which is followed by a fall. This indeed proved to be the case. This verification appeared to me necessary because the statements in DE LEEUW's table only contain observations of changes which sometimes amount to only $1^1/_2$ mm. and seldom more than 2 mm. For no one who has experience with the dilatometer these observations will have any definite value. And although the fact first investigated proved correct, the conclusions arrived at by DE LEEUW are not proof against a more elaborate investigation.

The rise observed is attributed in all the treatises cited to the change in volume in the conversion $S_{rh} \rightarrow S_{mon}$, because the conversions $S_{mon} \rightarrow S_{rh}$, $S_\mu \rightarrow S_{rh}$ and $S_\mu \rightarrow S_{mon}$ take place with contraction of volume. Owing to the reaction $S_\mu \rightarrow S_\lambda$ taking place meanwhile, the S_μ concentration is attained at which the conversion $S_{rh} \rightarrow S_{mon}$ at the temperature of experiment ceases; hence the rise in the capillary ceases also and a fall is exhibited there as a consequence of the still proceeding reaction $S_\mu \rightarrow S_\lambda$. On elevation of the temperature the phenomenon ought to repeat itself each time. Such are the views of Dr. DE LEEUW. In fig. 1 the thin line with the arrows indicates the changes of condition which the sulphur in the dilatometer ought to pass through.

In my experiments, however, it appeared that the behaviour of the dilatometer is absolutely contrary to the expectations raised by this diagram.

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[1]) These Proceedings XIV p. 802.

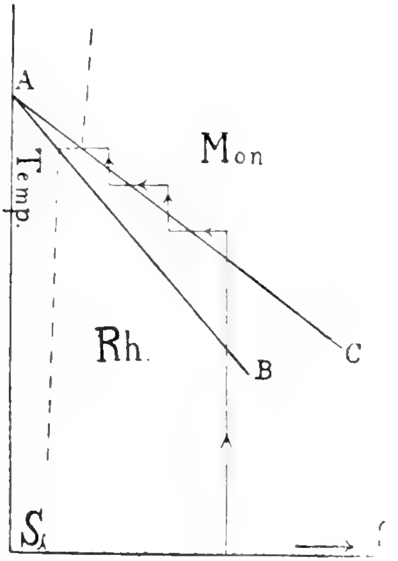

Fig. 1.

Owing to the peculiar method followed by Dr. DE LEEUW to observe for a few minutes only whether the dilatometer exhibits a rise or a fall, one gets from his communication the impression as if each time, with the different (rising) experiment-temperatures, a similar phenomenon repeats itself. Now, such is by no means the case. Only once or twice, the said maximum occurs. I have observed repeatedly *that it then returned no more.* The slight increase, or decrease observed by him at the subsequent temperatures have no significance, moreover, such trifling values never have a definite meaning; the dilatometer is not an instrument of precision not even when the best acting thermostat is used.

In order to obtain really trustworthy results the experiments should be so arranged that the reaction studied exhibits a suitable rise or fall; this should then surely exceed a few m.m.

Below are given some of my investigations.

As, for these experiments, glacial acetic acid is a much more appropriate liquid than turpentine-carbon disulphide (see communication IV), these experiments have been carried out with that liquid. The thermostat has been described in communication (III). The sulphur was treated exactly as directed by Dr. DE LEEUW.

Table I contains the result of a series of experiments represented graphically in fig. 2. We notice that, when we wish to attribute the great rises at 76°.2 and 83°.0 to conversions according to the scheme of fig. 1 it becomes inexplicable why at the temperatures 86°.7 and 91°,9 the phenomenon does not appear, but returns at 97°.8. Moreover, the conversion at the latter temperature exhibits the plain character of a conversion above the transition temperature. From this series I already gained the impression that the maximum occurring at 76°.2 and 83°.0 has nothing to do with the conversion $S_{rh.} \rightleftarrows S_{mon}$.

One might imagine that, during the time corresponding with the falling branches in A and B fig. 2, so much S_λ has been regenerated that at the subsequent rises of the temperature one does not arrive any longer above the line AC in fig. 1. True, that difficulty

TABLE I.

A. *Temperature* 76°.2.

Day	Hour	Dilatometer
M.	9.55 a.m.	placed
	12.03 p.m.	533
	1.00	560
	2.18	583
	4.07	607
	7.24	645
	9.14	635
Tu.	9.29 a.m.	585
	1.52 p.m.	580

B. *Temperature* 83°.0.

Day	Hour	Dilatometer
Tu.	2.15 p.m.	attained
	3.37	517
	4.53	558
	10.20	694
	10.50	701
W.	9.25 a.m.	741
	12.12 p.m.	731
	4.28	727
Th.	9.44 a.m.	677

C. *Temperature* 86°.7.

Day	Hour	Dilatometer
Th.	10.00 a.m.	attained
	11.00	482
	12.04 p.m.	477
	3.37	467
F.	9.25 a.m.	439

D. *Temperature* 91°.9.

Day	Hour	Dilatometer
F.	10.25 a.m.	attained
	11.00	483
	12.00	480
	3.00 p.m.	482
	5.05	481
Sat.	9.48 a.m.	474

E. *Temperature* 97°.8.

Day	Hour	Dilatometer
Sat.	10.25 a.m.	attained
	11.25	438
	12.15 p.m.	548
	3.40	>1000

then applies *a fortiori* to DE LEEUW's experiments where the dilatometer liquid does not obstruct that conversion which certainly was the case in our experiment.

In order to avoid this objection anyhow, I proceeded, in a subsequent experiment, to the higher temperature so soon as the maximum had been attained. The result is shown in a series which in addition teaches other things as well (Table II).

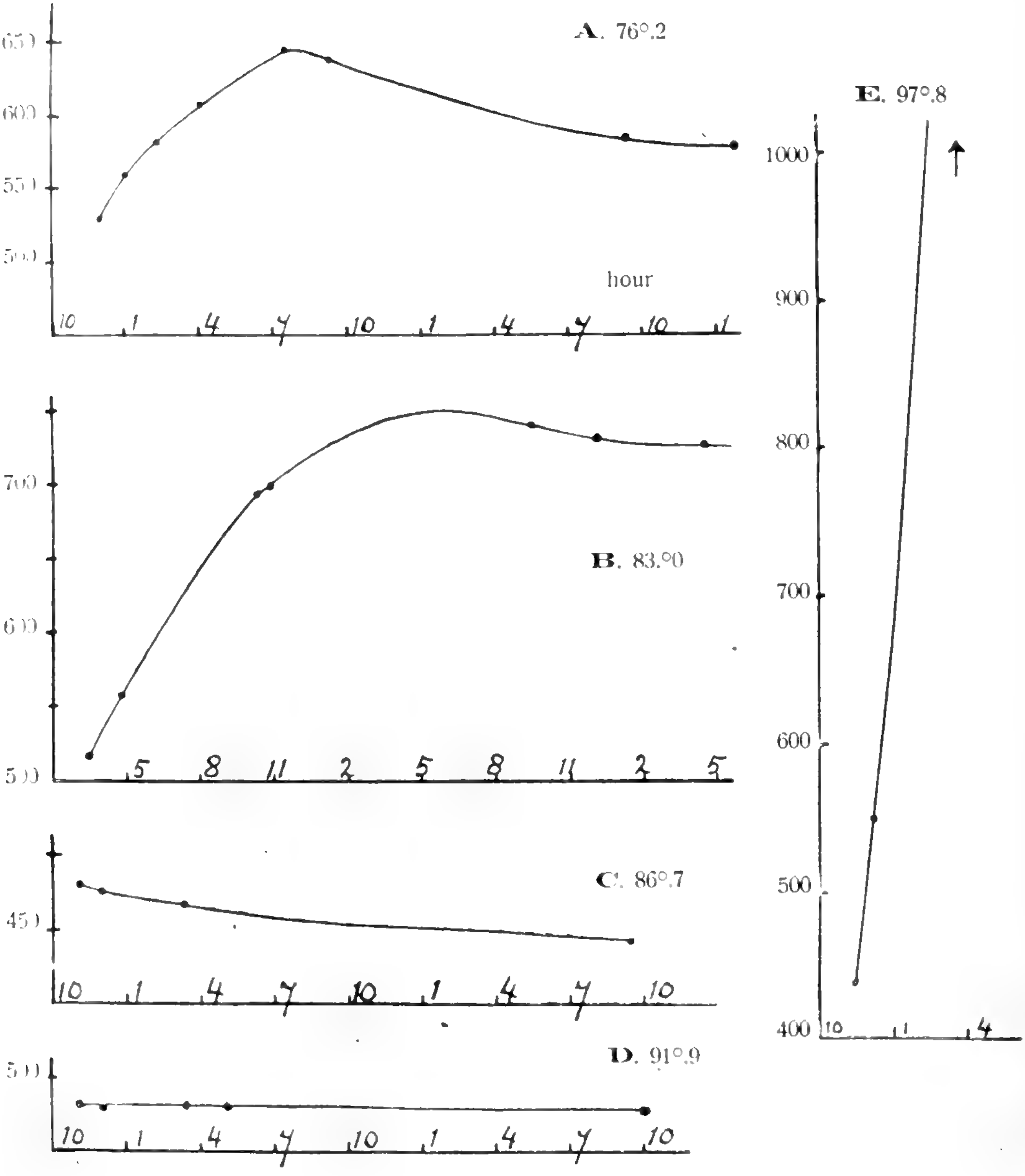

Fig. 2.

This table gives us two minor results and two highly important ones. The first is that in Table II A a previous fall in the dilatometer occurs. Hence, the total behaviour on introduction is: a rise and a fall — a rise and a fall. This first rise and fall finds its explanation in the REGNAULT effect and has been predicted and discussed in my fourth communication p. 736. The negative catalysis of the acetic acid

TABLE II.

A. *Temperature* 75°.3.

Day	Hour	Dilatometer
M.	11.05 a.m.	placed
	11.33	476
	12.02 p.m.	465
	12.14	458
	1.22	465
	3.07	525
	5.15	625
	8.24	636
	8.45	628
	9.04	624

B. *Temperature* 84°.8.

Day	Hour	Dilatometer
M.	9.45 p.m.	attained
	10.01	439
	10.30	439
Tu.	9.31 a.m.	406

C. *Temperature* 93°.0.

Day	Hour	Dilatometer
Tu.	10.04 a.m.	attained
	10.24	745
	3.34 p.m.	745
	5.05	748
	10.10	748
W.	9.34 a.m.	740

D. *Temperature* 94°.2.

Day	Hour	Dilatometer
W.	10.37 a.m.	attained
	11.17	464
	12.14 p.m.	464
	2.14	460
	3.00	458

E. *Temperature* 95°.2.

Day	Hour	Dilatometer
W.	3.10 p.m.	attained
	3.22	510
	3.45	510
	4.18	511
	6.21	510

F. Been during the night at 95°.9. No change.

G. *Temperature* 97°.2.

Day	Hour	Dilatometer
Th.	9.30 a.m.	attained
	10.06	629
	11.17	631
	1.50 p.m.	630

H. *Temperature* 98°.6.

Day	Hour	Dilatometer
Th.	2.05 p.m.	attained
	2.15	692
	2.45	693
	3.22	767
	3.48	870

J. *Temperature* 96°.4.

Day	Hour	Dilatometer
Th.	5.00 p.m.	757
F.	9.25 a.m.	> 1000
	10.54	756 1)
	11.18	778

K. *Temperature* 95°.8.

Day	Hour	Dilatometer
F.	11.45 a.m.	753
	12.04 p.m.	752
	1.10	753

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[1] After the position had been regulated with a sweeping capillary.

causes the rising branch to maintain itself here so much longer than in the experiment described previously. We may, meanwhile, conclude that notwithstanding the acetic acid present, S_{μ} present in large concentration, rapidly reverts to S_{λ}, a conclusion that had already been drawn in my fourth communication; for the explanation of the experiments it is not to be neglected because it is thus shown that the S_{μ} concentration has already considerably receded at the moment that the rise observed by DE LEEUW commenced. Secondly, the rise in this experiment appeared to occur only once, and not to repeat itself either at 84°.8 or at 93°.0.

Much more important are the following conclusions: The rise has no connection with the conversion $S_{rh} \rightleftarrows S_{mon}$. If, at the lower temperatures, monoclinic sulphur had formed it would have been impossible to realise a retardation of the said conversion above the highest transition temperature. The tables II G and H, however, clearly prove the possibility thereof. Even at 98°.6, 40 minutes after this temperature had been attained, the conversion had yet to start; once started it was, of course, very evident, also still at a temperature of 96°.4 (Table II J) whereas when *unintroduced* it had not appeared at 96°.2 (Table II G).

The fourth conclusion is derived from Table II K, namely, that at 95°.8, the reaction $S_{rh} \rightleftarrows S_{mon}$ stops in the presence of some percent of S_{μ}, just as was shown by the investigations communicated in my fourth paper, again in conflict with the communications criticised here.

If one should opine that the phenomena are fundamentally different owing to the use of acetic acid as dilatometer liquid, it may be communicated here that I have also carried out the experiments with turpentine-carbon disulphide. There it appeared, as might have been expected, that the first maximum appears in a less pronounced manner and also that, on using that liquid, subsequent risings at higher temperatures do not take place; in fact no fundamental difference occurs.

The above investigations had therefore demonstrated that the explanation of the dilatometer behaviour at temperatures of 70°—80° by the conversion $S_{rh} \leftrightarrows S_{mon}$ failed utterly. Also as regards the conversion $S_{\mu} \rightarrow S_{\lambda}$, I had my doubts as to whether this sufficiently explains the fall after the maximum has been attained. This was corroborated by the following experiment. Sulphur was heated to boiling in a dilatometer vessel, gaseous ammonia was passed for a few minutes, then it was chilled and not until after three days acetic acid was introduced.

Table III represents the progressive change with this dilatometer.

TABLE III.

Day	Hour	Temp.	Dilatometer
16 Nov.	11.30 a.m.	86.6	placed
	11.51	86.6	451
	12.14 p.m.	86.4	462
	1.41	86.3	470
	3.18	86.4	469
	6.35	86.4	459
18 Nov.	9.24 a.m.	86.6	386
	4.17 p.m.	86.3	364
19 Nov.	9.32 a.m.	86.6	352
20 Nov.	9.24	86.5	328
21 Nov.	10.30	86.5	328

A quite similarly treated sulphur mass was analysed (also three days after its preparation) and contained 0.6 $^0/_0$ of S_μ.

Although this experiment has been carried out with a not irreproachably acting thermostat the result cannot be open to doubt. After a small rise a great fall takes place, whereas according to the theory opposed the essential conditions are wanting; hence this experiment also shows that the fact stated by Messrs. SMITS and DE LEEUW is absolutely unexplained by their interpretation, and that here quite new explanatory principles must be found. As to the question in what direction these should be looked for, I will not go into this although my research indicated some possible explanations; Dr. DE LEEUW seems to occupy himself with it just now and I feel compelled not to communicate any investigations of which it is known to me that they relate to a subject on which somebody else is engaged.

The above investigation has, therefore, led to the conclusion:

a. that the change in volume of strongly supercooled sulphur, in the temperature range of 70°—95°, is different from that observed by Dr. DE LEEUW;

b. that the phenomena occurring have no connection with the conversion $S_{rh} \rightleftarrows S_{mon}$;

c. that the conclusions from my previous papers remain unaffected (are confirmed), for instance that the transition point is elevated by added S_{μ}.

Utrecht, January 1913. VAN 'T HOFF-*Laboratory*.

(May 30, 1913).

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday March 22 and Friday April 25, 1913.

President: Prof. H. A. LORENTZ.
Secretary: Prof. P. ZEEMAN.

Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 22 Maart en Vrijdag 25 April 1913, Dl. XXI).

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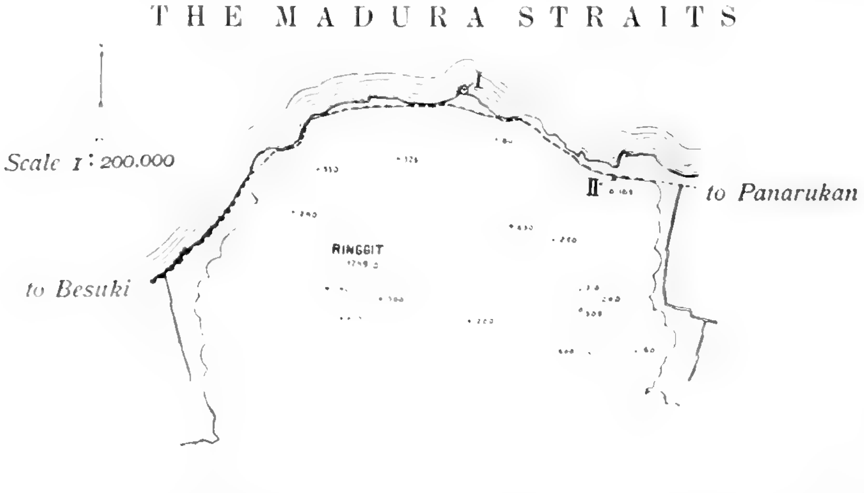
Geology. — *"Leucite-rocks of the Ringgit (East-Java) and their contact-metamorphosis".* By H. A. Brouwer. (Communicated by Prof. Molengraaff).

(Communicated in the meeting of December 28, 1913).

The following pages will afford new proofs of the intermediary place which the contact-metamorphosis of the basic leucite-rocks occupies between that of the trachytic and the basaltic rock.

The Gunnong Ringgit (a corruption of the Madurese word renggik=saw-shaped) forms a steep mountain-range with five pointed tops on the northeoast of Java between Besuki and Panarukan; according to Verbeek [1]) the whole mountain-range with the old craterwall of the Gunong Besar south of it consists of lava-cakes and loose blocks of leucite-rocks. During a trip to Madura I visited the north-foot of the Ringgit; along the great postal-road at the northfoot lava is in several places found in situ. Near the 15th milestone from Besuki, we see to the North of the road in the flat country one hillock consisting of leucite-lava forming a cape projecting into the sea (marked I on the annexed map). The rock is a leucitite with phenocrysts of biotite which are much resorbed



whilst it is characterized by a great number of enclosures, measuring from a few centimeters to a few decimeters, and consisting, as far as they have been examined, of a reddish andesite. It is in these enclosures that the contact metamorphosis of the leucitites can be studied.

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[1]) R. D. M. Verbeek en R. Fennema. Java en Madoera I. page 71.

Contact metamorphism caused by effusive rocks is eo ipso insignificant, both on account of the low temperature at which the metamorphism takes place, and on account of the escape of the pneumatolytic gases during the eruption. It can however be studied in the enclosures of older rocks on which the magma whilst still under pressure, could react in the same way as if it were a deep-seated rock. LACROIX[1]) had divided the effusive rocks into two groups, according to the character of their contact metamorphosis: the basaltic and the trachytic rocks, differing from each other in either containing or not containing orthoclase and acid plagioclase. The metamorphosis caused by rocks of the former group is chiefly restricted to the influence of heat confined to a narrow contactzone, whereas the rocks of the latter group, in consequence of their greater viscosity during the effusion, and in consequence of the pneumatolytic gases dissolved in these viscous magmas, are in less intimate contact with the inclosures, but, impregnating these inclosures by pneumatolytic substances can cause intensive chemical changes, which are not restricted to the contactzone, but can affect the entire enclosure.

The leucitite containing the enclosures which will be now described, shows besides many phenocrysts of augite, numerous strongly resorbed phenocrysts of biotite. Macroscopically we see both the minerals the augite of a green, the biotite of a brownish red colour contrasting against a greyish-black or brownish-red ground-mass.

The augitephenocrysts are under the microscope colourless or greenish; traverse-twins occur, and also twins according to (100) sometimes with polysynthetic lamels. Greenish and colourless portions alternate without regularity or in zones in the same crystal; sometimes there is a green core surrounded by an uncoloured margin; occasionally one sees a green band between a colourless core and a marginal zone, both of which extinguish simultaneously, but not together with the green transition-zone. Similar zones with varying optical properties occur likewise without observable differences of colour. As a rule the augite is poor in enclosures, only a few little prisms of apatite and flakes of biotite are enclosed.

The biotitecrystals are for the greater part strongly resorbed; some are entirely altered into a black ore which can be proved to represent altered biotite by comparison with crystals, in which still remains of the strongly pleochroitic biotite can be distinguished dimly between the specks of the ore. There is likewise a younger generation of biotite, just as has been described by me from a mica-

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[1]) A. LACROIX. Etude sur le Métamorphisme de contact des roches volcaniques. Mémoires présentés par divers Savants à l'Académie des Sciences. Tome XXXI. 1894.

leucite basalt of East-Borneo, discovered by Prof. **Molengraaff**[1]). This last-mentioned biotite is not resorbed, and is often deposited in the rock of the Ringgit round the older resorbed crystals, however with different optical orientation of the optical groundmass. These little brownish-red crystals which also occur dispersed through the rock, and as a rule do not show any definite shape, enclose particles of the groundmass. The groundmass consists of leucite, augite and ore. Sometimes the leucite attains somewhat larger dimensions than the majority of the crystals of the groundmass, without forming real phenocrysts, the augites are column-shaped and colourless or light-green, the ore is plentiful in the rock.

Macroscopically one sees already locally in little cavities neogenic minerals of very small dimensions, many of which show the shapes of crystals of leucite or sodalite, or also of feldspar. Under the microscope one sees in these little cavities isotropic crystals, together with neogenic feldspar and sometimes some biotite, whilst the dark background against which the prisms of augite set off between crossed nicols, is often interrupted by anisotropic portions, which for some distance have the same optical orientation, and poicilitically surround the particles of the groundmass. These anisotropic portions sometimes consist of kalifeldspar, twinned according to the Carlsbad-law; polysynthethic twins have not been observed, but the zonal structure which is often distinguishable, points also to the presence of plagioclases. These minerals have been formed after the crystallisation of the groundmass of the rock and point to pneumatolytic elements in the magma, which have been set free after the final crystallisation; consequently they are no normal constituents but products of the autopneumatolysis in the rock. Locally they may occur in considerable quantities.

The enclosures of this leucite are coloured light-red or brownish, and contain little phenocrysts of plagioclase where they have not been altered into a hypo- or cryptocrystalline groundmass.

In some of the enclosures examined the plagioclases show microscopically a well developed zonal structure, in others they are only slightly so, or sometimes not at all. Major twins according to the Carlsbad-law of the polysynthetically twinned feldspars occur. The basicity of the feldspars sometimes decreases regularly from the centre to the margin, in which case transitions were observed from labrador or bytownite to oligoclase or andesine, but alternations of

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[1]) H. A. Brouwer. On micaleucite basalt from Eastern-Borneo. These Proceedings, June 26, 1909 p. 148.

more basic and more acid lamellae are very frequent, and sometimes are found repeated several times in one and the same crystal.

Phenocrysts of the dark minerals are not met with as such, but sometimes we find specks consisting of opaque secondary minerals proving by their shape that such phenocrysts may originally have been present. The groundmass is likewise strongly weathered and contains laths of plagioclase, flakes of chlorite and opaque products of disintegration of the ore which is not found in large quantity; moreover often an isotropic substance is found in large quantities, which is considered as glass; in this case the rock must be called an andesite.

Metamorphosis.

The metamorphosis of the enclosures examined encludes in the first place the alterations caused by the magma itself, appearing only at the immediate contact, and consisting, at the utmost, of remelting and recrystallisation after chemical exchange; in the second place the alterations caused by imbibition of volatile substances which penetrate well into the interior of the enclosures. From this the intermediary place becomes apparent, which this contactmetamorphosis occupies between that of the basaltic and that of the trachytic rocks. Especially the intensity of the pneumatolytic influences varies greatly in the different enclosures; sometimes the chemical exchanges in the contactzone can be explained without pneumatolysis. In the examined rocks it is most frequently the case that in part of the enclosures a porous structure has been developed even to a great distance from the contact, whilst in the cavities neogenic minerals have been formed showing great analogy to the autopneumatolytic minerals of the enclosing leucitite, whilst in the contact zone the combined effect of remelting and pneumatolysis can be observed. The formation of a gold-yellow aegirine-augite is characteristic.

As an example may serve an enclosure of a few centimeters in diameter in which to a great distance from the contact a neogenic yellow pyroxene is formed in very small columns, sometimes accumulating locally and then accompanied by an isotropic mineral with low index of refraction and by neogenic feldspar. The angles of extinction of this yellow pyroxene point to aegirine-augites of varying composition. The ore is strongly disintegrated, here and there a reddish substance has been formed pointing to an oxydation to haematite. A small quantity of the yellow pyroxene is also found in the phenocrysts of plagioclase. The transition-zone with the leucitites is characterised by the occurrence of a very great number of little columns of gold-coloured aegirine-augite and of a few larger crystals with yellow margin which are mixed with feldspar, consisting partly of kalifeldspar, partly of plagioclase.

In this transition-zone we find only a very little quantity of ore, whereas the larger augite crystals with yellow margin have after all originated from phenocrysts of the leucitite. Very near to the contact we find the original plagioclases of the enclosure as an opaque central portion in the neogenic feldspars; whereas at a short distance the original plagioclases have been conserved as such, and the neogenic minerals have been crystallized in small cavities of the rock. The appearance of the ore points to chemical interchanging of elements between the lava and enclosures; the gold colour and the modified optical properties of the augite and likewise the crystallization of neogenic minerals to a great distance from the contactzone of the enclosure which has become partly porous, indicate the influence of pneumatolytic gases. Leucite-tephrites of the Somma metamorphosed by fumaroles show very similar modifications.

That in the contact-zone really melting has taken place is in suchlike enclosures often proved by the fact, that the transition-zone penetrates tongue-shaped into the magma which has been crystallized as leucitite. Macroscopically the line of demarcation between the transition-zone which is only a few millimeters wide, and the leucitite can often easily be followed by the rapidly decreasing of the percentage of ore, and by the colour which for this reason becomes lighter.

Among the smaller enclosures there are numerous ones, which have entirely been altered into a very porous rock, have obtained a yellowish colour, and contain besides the colourless neogenic minerals and the yellow pyroxene also a few crystals of haematite which macroscopically are perceptible as little black specks.

In a larger enclosure with a diameter of about 20 centimeters the transition-zone was hardly brighter in colour than the leucitite, and this fact appeared to be accompanied by a much more gradual diminution of the percentage of ore. Moreover the augite shows no change of colour, and neither do we find the gold-yellow augite in the enclosure at some distance from the contact, notwithstanding the porous structure and the crystallization of pneumatolytic minerals. In the transition-zone little, but likewise much larger crystals of neogenic kalifeldspar and zonular plagioclase can be observed, enclosing the ore and the little columns and larger crystals of unmodified augite. In this contact-zone again borders of neogenic feldspar appear around the opaque plagioclases of the enclosure.

The metamorphoses described above, which are connected by all sorts of transitions show great resemblance to those found in blocks of leucite-tephrite of the Fosso di Caucherone (Vesuvius)[1]) which have been altered by the action of fumaroles. The microlithes and phenocrysts of augite have become yellow, and the extinction-angles agree with those of an aegirine-augite, sometimes with those of aegirine. Haematite is abundant with the exclusion of magnetite. The biotite and amphibole show modifications of colour.

In the "sperone" of Latium, likewise a metamorphic rock which by transitions is connected with a normal black leucitite, the normal green augite has been altered into a gold-coloured one, whose angle $c:\mathfrak{c}$ varies between 65° and 85° whilst likewise the original magnetite has more or less completely disappeared. Moreover there is often formed a yellow melanite[2]).

Finally a green-yellow aegirine-augite occurs in varieties of the shonkinite of the Katzenbuckel (Odenwald) which has been modified by pneumatolytic processes[3]). The iron-ore has here been altered into pseudobrookite, the feldspars are more or less zeolitised. Analyses made by LATTERMANN indicate that in the rock modified by pneumatolysis, the percentage of Fe_2O_3 had increased from 5,86°/₀ to 8,51°/₀, whilst in the variety with yellow augite the FeO of 3,23°/₀ which had been found in the original rock, had entirely disappeared. Likewise in the analyses of sperone the Fe_2O_3 [4]) dominates strongly over the FeO; evidently the metamorphosing agencies had an oxydizing influence. The modification of the optical properties of the gold-coloured pyroxene tends to prove that the Na_2O percentage has also been increased, which could not be concluded from the different analyses.

In connection with what has been said a second locality of rocks with gold-coloured pyroxene may be mentioned (II of the annexed map) situated directly South of the road from Panarukan to Besuki at mile-post 18. At the northern foot of a bare hill a porous light-grey rock that microscopically proves to be rich in gold-coloured pyroxene, appears between rocks of dark-grey biotite-leucite-tephrite.

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[1]) A. LACROIX. Etude minéralogique des produits silicatés de l'éruption du Vésuve (avril 1906). Nouv. Archives du Muséum. 4e Série. Tome IX, 1907, pp. 73, 94.

[2]) A. LACROIX, l. c. p. 95.

[3]) W. FREUDENBERG. Geologie und Petrographie des Katzenbuckels. Mitt. Groszh. Badische Geol. Landesanstalt V. I. Teil, 1906, p. 81.

[4]) V. SABATINI. I Vulcani dell' Italia centrale. I. Vulcano laziale. Mem. Carta geol. d'Italia, X, 1900, pp. 150, 163.

In the dark-grey leucite-tephrite one sees, macroscopically, phenocrysts of plagioclase and dark minerals few millimeters in diameter, the former contrasting little against the groundmass. Under the microscope it appears that the plagioclases have a well marked zonal structure, the augite crystals are light-green and often include numerous specks of ore. The little phenocrysts of biotite are sometimes strongly resorbed; the angle of the optical axes is very small, the pleochroism is strong from brown-black to light-yellow. The groundmass is composed of plagioclase with zonal structure, leucite (and some nepheline), green augite, a little biotite and much iron-ore. The latter mineral often obtains somewhat larger dimensions, without forming real phenocrysts. The leucite has likewise somewhat larger dimensions than the majority of the crystals in the groundmass.

The porous light-grey rocks with gold-coloured pyroxene show numerous phenocrysts of white plagioclase (some as long as 0.75 c.m., but usually smaller) and smaller phenocrysts of the dark minerals in a groundmass which is either dense or micro-crystalline; in the cavities neogenic minerals have been formed. Under the microscope we see porphyric crystals of strongly zonal plagioclase and gold-coloured or partly still green pyroxene, in a groundmass of strongly zonal plagioclase, gold-coloured pyroxene iron-ore, an isotropic, sometimes light-brownish substance, and a few little columns of apatite. Further a few rather large broad prisms hexagonal in cross section of an optically negative mineral with one optical axis, with a high refraction index, have been observed, which are slightly pleochroitical with $\varepsilon > 0$; they are almost colourless or tinged very lightly brownish, and include sometimes particles of a black or vermilion-red substance. A cleavage parallel with the axis of the prisms is indistinctly developed. In case originally some leucite has been present in this rock, the mineral is now altered into pseudomorphoses, on account of its feeble resistance against pneumatolytic agents.

Without entering into details about the metamorphosic and preneogenic minerals found in these rocks, it can be mentioned that the aegirine-augites belong to different chemical combinations; we observed e. g. in sections parallel to (010) made across columns twinned according to (100), symmetrical extinctions of 14°, whilst several lath-shaped sections extinguish with angles of 20° to 30°; very small angles of extinction were equally observed. Black iron-ore, blue-black in reflected light, is found in great abundance in the rock, sometimes it surrounds as a border the aegirine-augites, which likewise can include the ore in great quantity.

Moreover one sees elongated sections consisting entirely of black ore, around which a mixture of ore and prisms of gold-coloured aegirine-augite columns is formed.

The metamorphoses described above by which gold-coloured pyroxenes with the optical properties of aegirine-augites are formed, appear to be connected with pneumatolytic processes in magmas rich in alkali.

Finally it may be mentioned here, that to the South of the road Panarukan Besuki, quite near to mile-post 13, a loose piece of a leucitite was found with phenocrysts of leucites as large as 4 m.m., which certainly had come down from the northern slope of the Ringgit and consequently may be expected there in greater quantities; hitherto such types of rocks were not recorded from the Ringgit-mountain.

Mathematics. — "*Expansion of a function in series of* ABEL's *functions* $\varphi_n(x)$". By Prof. W. KAPTEYN.

(Communicated in the meeting of February 22, 1913).

1. In the Oeuvres complètes of ABEL[1]) may be found the following expansion

$$\frac{1}{1-r}\, e^{-\frac{xr}{1-r}} = \sum_{0}^{\infty} \varphi_n(x) r^n$$

where

$$\varphi_n(x) = 1 - C_1^n x + C_2^n \frac{x^2}{2!} - \ldots . + (-1)^n \frac{x^n}{n!},$$

C_p^n representing the binomial coefficients.

These polynomia form the object of the dissertation of Dr. A. A. NIJLAND (Utrecht 1896) and have been treated afterwards by E. LE ROY in his memoir "Sur les séries divergentes" (Annales de Toulouse 1899).

In this paper I wish to examine when a given function of a real variable may be expanded in a series of this form

$$f(x) = a_0 + a_1\varphi_1(x) + a_2\varphi_2(x) + \ldots \ldots \qquad (1)$$

2. In this article we collect those properties of the polynomia $\varphi_n(x)$ which we want for our investigation and which we take from NIJLAND's dissertation.

In the first place we have the important relations

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[1]) Oeuvres Complètes II p. 284.

$$\left.\begin{aligned}\int_0^\infty e^{-x}\varphi_m(x)\varphi_n(x)dx &= 0 \ \ (m \neq n)\\ \int_0^\infty e^{-x}\varphi_n^2(x)dx &= 1\end{aligned}\right\} \quad . \ . \ . \ . \ . \ . \quad (2)$$

In the second place $\varphi_n(x)$ satisfies the differential equation

$$x\varphi_n''(x) + (1-x)\varphi_n(x) + n\varphi_n(x) = 0$$

which also may be written

$$\frac{d}{dx}\left[xe^{-x}\varphi_n'(x)\right] + ne^{-x}\varphi_n(x) = 0 \, . \quad . \ . \ . \ . \ . \ . \quad (3)$$

In the third place we have the following properties, which may be easily obtained

$$\varphi_n(x) = \varphi_n'(x) - \varphi'_{n+1}(x) \quad . \ . \ . \ . \ . \ . \ . \ . \quad (4)$$

$$\frac{x}{n}\varphi_n'(x) = \varphi_n(x) - \varphi_{n-1}(x) \quad . \ . \ . \ . \ . \ . \ . \quad (5)$$

$$(n+1)\,\varphi_{n+1}(x) - (2n+1-x)\varphi_n(x) + n\varphi_{n-1}(x) = 0 \, . \quad . \ . \quad (6)$$

$$\begin{aligned}\int_0^\infty e^{-x}x^n\varphi_m(x)dx &= (-1)^m\, C_m^n\, n!\,(m \leq n)\\ &= 0 \qquad\qquad\qquad (m > n)\end{aligned} \quad . \ . \ . \ . \quad (7)$$

3. If the expansion (1) is possible, the coefficients a_n may be expressed by means of the equations (2)

$$a_n = \int_0^\infty e^{-\alpha}f(\alpha)\varphi_n(\alpha)d\alpha.$$

With these values the second member of (1) reduces to

$$S = \sum_0^\infty \varphi_n(x)\int_0^\infty e^{-\alpha}f(\alpha)\varphi_n(\alpha)d\alpha. \quad . \ . \ . \ . \ . \ . \quad (8)$$

In order to determine this sum we introduce $\varphi_n(x)$ in the form of a definite integral. This definite integral, which has been given by LE ROY, may be found in the following way.

Denoting by $J_0(t)$ the Besselian function of order zero, MACLAURIN's expansion gives easily

$$e^x J_0(2\sqrt{\alpha x}) = \sum_0^\infty \frac{x^m}{m!}\varphi_m(\alpha) \, . \quad . \ . \ . \ . \ . \ . \quad (9)$$

Hence, multiplying both members by $\dfrac{e^{-\alpha}\alpha^n d\alpha}{n!}$ and integrating between the limits 0 and ∞

$$\frac{e^x}{n!}\int_0^\infty e^{-\alpha}\alpha^n J_0(2\sqrt{\alpha x})d\alpha = \frac{1}{n!}\sum_0^\infty \frac{x^m}{m!}\int_0^\infty e^{-\alpha}\alpha^n \varphi_m(\alpha)d\alpha$$

where the second member may be reduced by means of (7) to

$$\sum_0^n (-1)^m C_m^n \frac{x^m}{m!} = \varphi_n(x).$$

Therefore we have

$$\varphi_n(x) = \frac{e^x}{n!}\int_0^\infty e^{-\alpha}\alpha^n J_0(2\sqrt{\alpha x})\,d\alpha \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

and

$$S = \sum_0^\infty \frac{\varphi_n(x)}{n!}\int_0^\infty f(\alpha)\,d\alpha\int_0^\infty e^{-\beta}\beta^n J_0(2\sqrt{\alpha\beta})\,d\beta\,\cdot$$

Now, from the equation (9) we obtain

$$\sum_0^\infty \frac{\beta^n\varphi_n(x)}{n!} = e^\beta J_0(2\sqrt{\beta x})$$

thus

$$S = \int_0^\infty f(\alpha)\,d\alpha\int_0^\infty J_0(2\sqrt{\alpha\beta})\,J_0(2\sqrt{\beta x})\,d\beta.$$

or, putting β^2 instead of β

$$S = 2\int_0^\infty f(\alpha)\,d\alpha\int_0^\infty J_0(2\beta\sqrt{\alpha})\,J_0(2\beta\sqrt{x})\,\beta\,d\beta \quad . \quad . \quad . \quad (11)$$

3. This double integral may be determined by a theorem of HANKEL (Math. Ann. Bd. 8 p. 481), who proved that

$$\int_0^\infty \gamma\,\varphi(\gamma)\,d\gamma\int_0^\infty J_0(\beta\gamma)\,J_0(\beta\xi)\,\beta\,d\beta = \varphi(\xi)$$

where ξ represents a positive value and $\varphi(\xi)$ a function which satisfies the conditions of DIRICHLET for all values between 0 and ∞. Putting

$$\gamma = 2\sqrt{\alpha}, \qquad \xi = 2\sqrt{x}, \qquad \varphi(2\sqrt{x}) = f(x)$$

this theorem gives immediately

$$S = 2\int_0^\infty f(\alpha)\,d\alpha\int_0^\infty J_0(2\beta\sqrt{\alpha})\,J_0(2\beta\sqrt{x})\,\beta\,d\beta = f(x) \quad . \quad . \quad (12)$$

Thus we have established the result, that every function $f(x)$ which satisfies the conditions of DIRICHLET for all values between 0 and ∞ may be expanded in a series of the form

$$f(x) = a_0 + a_1 \varphi_1(x) + a_2 \varphi_2(x) + \dots \qquad 0 \leqq x < \infty \quad . \quad (1)$$

where

$$a_n = \int_0^\infty e^{-\alpha} f(\alpha) \varphi_n(\alpha)\, d\alpha$$

It is to be remarked that the values $f(c+0)$ and $f(c-0)$ being different, the second member reduces to $\frac{1}{2}[f(c+0) + f(c+0)]$.

4. We now proceed to give two interesting examples of this expansion and to show the value of this expansion for the problem of the momenta.

As a first example suppose it is required to express $f(x) = \dfrac{1}{1+x}$ in a series of ABEL's functions $\varphi_n(x)$.

Evidently this function satisfies the conditions of DIRICHLET from $x = 0$ to $x = \infty$, thus

$$\frac{1}{1+x} = a_0 + a_1 \varphi_1(x) + a_2 \varphi_2(x) + \dots$$

where

$$a_n = \int_0^\infty \frac{e^{-\alpha} \varphi_n(\alpha)\, d\alpha}{1+\alpha} .$$

Now the following relation holds between successive functions φ:

$$(n+1)\varphi_{n+1}(\alpha) = (2n+1-\alpha)\varphi_n(\alpha) - n\varphi_{n-1}(\alpha) \quad . \quad . \quad (6)$$

Multiplying this by $\dfrac{e^{-\alpha}}{1+\alpha} d\alpha$, and integrating between 0 and ∞ we obtain

$$(n+1) a_{n+1} = (2n+1) a_n - n a_{n-1} - \int_0^\infty \frac{\alpha e^{-\alpha}}{1+\alpha} \varphi_n(\alpha)\, d\alpha \cdot$$

But, as

$$\frac{\alpha}{1+\alpha} = 1 - \frac{1}{1+\alpha}$$

we have

$$\int_0^\infty \frac{\alpha e^{-\alpha}}{1+\alpha} \varphi_n(\alpha)\, d\alpha = \int_0^\infty e^{-\alpha} \varphi_n(\alpha)\, d\alpha - a_n$$

where the latter integral, which may be written

$$\int_0^\infty e^{-\alpha}\, \varphi_0(\alpha)\, \varphi_n(\alpha)\, d\alpha$$

vanishes according to (2) if $n > 0$.

Therefore three successive coefficients of this expansion are related in the following way

$$(n+1)\, a_{n+1} = 2\,(n+1)\, a_n - n\, a_{n-1}\ (n > 0)$$

so that all the coefficients may be expressed in a_0 and a_1.

Now

$$\varphi_1(\alpha) = 1 - \alpha$$

hence

$$a_1 = \int_0^\infty \frac{e^{-\alpha}(1-\alpha)}{1+\alpha}\, d\alpha = \int_0^\infty \frac{e^{-\alpha}[2-(1+\alpha)]}{1+\alpha}\, d\alpha = 2a_0 - 1$$

which proves that all the coefficients are dependent on the first

$$a_0 = \int_0^\infty \frac{e^{-\alpha} d\alpha}{1+\alpha} = -\, e\, l\, i\left(\frac{1}{e}\right) = 0{,}596347\ldots$$

These coefficients may also be obtained in another way.

From Abel's expansion

$$\frac{1}{1-v}\, e^{-\frac{1}{1-v}} = \sum_0^\infty \varphi_n(x)\, v^n$$

which holds where

$$mod\ v < 1$$

we see, by putting

$$t = \frac{v}{1-v}$$

that

$$e^{-xt} = \frac{1}{1+t} + \frac{t}{(1+t)^2}\, \varphi_1(x) + \frac{t^2}{(1+t)^3}\, \varphi_2(x) + \ldots$$

if

$$mod\, \frac{t}{1+t} < 1\,.$$

Multiplying this equation by $e^{-t}\, dt$ and integrating between the limits 0 and ∞, we obtain

$$\frac{1}{1+x} = a_0 + a_1\, \varphi_1(x) + a_2\, \varphi_2(x) + \ldots$$

where

$$a_n = \int_0^\infty e^{-t} \frac{t^n}{(1+t)^{n+1}}\, dt \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

Comparing this result, with the former, we obtain the interesting formula

$$\int_0^\infty e^{-t} \frac{t^n}{(1+t)^{n+1}}\, dt = \int_0^\infty \frac{e^{-t}\varphi_n(t)}{1+t}\, dt \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

which is evident if we put $n=0$.

From (13) we see also that

$$\sum_0^\infty a_n = \int_0^\infty e^{-t} \frac{1}{1+t} \sum_0^\infty \left(\frac{1}{1+t}\right)^n dt = \int_0^\infty e^{-t}\, dt = 1\,,$$

which shows, that the expansion

$$\frac{1}{1+x} = \sum_0^\infty a_n\, \varphi_n(x)$$

holds for $x=0$.

5. As a second example we will expand a discontinuous function. Supposing $f(x)=1$ from $x=0$ to $x=1$ and $f(x)=0$ for $x>1$ we have

$$f(x) = a_0 + a_1\,\varphi_1(x) + a_2\,\varphi_2(x) + \ldots$$

where

$$a_n = \int_0^1 e^{-\alpha}\, \varphi_n(\alpha)\, d\alpha\,.$$

This coefficient may be determined in the following way. From the differential equation

$$\frac{d}{dx}\left[x\, e^{-x}\, \varphi_n'(x)\right] + n\, e^{-x}\, \varphi_n(x) = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

it appears that

$$x\, e^{-x}\, \varphi_n'(x) + n \int_0^x e^{-x}\, \varphi_n(x)\, dx = 0$$

therefore, putting $x=1$, we have

$$a_n = -\frac{1}{ne}\,\varphi_n'(1) \qquad (n>0)$$

or, according to (5)

$$a_n = \frac{1}{e}\left[\varphi_{n-1}(1) - \varphi_n(1)\right] \qquad (n>0)$$

The two first coefficients may be obtained directly, for

$$a_0 = \int_0^1 e^{-\alpha} \, d\alpha = 1 - \frac{1}{e}$$

and

$$a_1 = \frac{1}{e} \left[\varphi_0 (1) - \varphi_1 (1) \right] = \frac{1}{e} \, .$$

The remaining coefficients are dependent on these. For putting $x = 1$ in the recurrent relation

$$(n + 1) \varphi_{n+1} (x) - (2n + 1 - x) \varphi_n (x) + n \varphi_{n+1} (x) = 0 \quad . \quad (6)$$

we get

$$(n + 1) \varphi_{n+1} (1) - 2n \varphi_n (1) + n \varphi_{n-1} (1) = 0$$

and, changing n into $n + 1$

$$(n + 2) \varphi_{n+1} (1) - 2 (n + 1) \varphi_{n+1} (1) + (n + 1) \varphi_n (1) = 0 \, .$$

thus, subtracting the former from the latter equation

$$(n + 2) a_{n+2} - (2n + 1) a_{n+1} + n a_n = 0 \, .$$

6. The expansion holding for the value $x = 0$, we must have

$$\sum_0^\infty a_n = 1$$

and remarking that $x = 1$ is a point of discontinuity

$$\sum_0^\infty a_n \varphi_n (1) = \tfrac{1}{2} \, .$$

To prove these equations directly we may remark that

$$\sum_1^n a_p = \frac{1}{e} \sum_1^n \left[\varphi_{p-1} (1) - \varphi_p (1) \right] = \frac{1}{e} \left[1 - \varphi_n (1) \right]$$

so

$$\sum_1^\infty a_p = \frac{1}{e} - \frac{1}{e} \operatorname*{Lim}_{n=\infty} \varphi_n (1) \, .$$

Now, the number n being very large, we have

$$\varphi_n (x) = 1 - nx + \frac{n^2 x^2}{(2\,!)^2} - \frac{n^3 x^3}{(3\,!)^3} + \,..\, = J_0 (\sqrt{nx})$$

and

$$\operatorname*{Lim}_{n=a} \varphi_n (x) = \operatorname*{Lim}_{n=\infty} J_0 (\sqrt{nx}) = \operatorname*{Lim}_{n=\infty} \sqrt{\frac{2}{\pi \sqrt{nx}}} \cos \left(\sqrt{nx} - \frac{\pi}{4} \right) = 0$$

therefore

$$\sum_1^\infty a_p = \frac{1}{e}$$

and finally

$$a_0 + \sum_1^\infty a_p = 1 - \frac{1}{e} + \frac{1}{e} = 1 .$$

The second equation may be obtained as follows.

From the differential equation

$$\frac{d}{dx}[xe^{-x}\varphi_p'(x)] + pe^{-x}\varphi_p(x) = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

we may conclude

$$\int_0^1 e^{-x}\varphi_p^2(x)\,dx = -\frac{1}{p}\int_0^1 \varphi_p(x)\,d\,[xe^{-x}\varphi_p'(x)] =$$

$$= -\frac{1}{p}\,[xe^{-x}\varphi_p(x)\varphi'_p(x)]_0^1 + \frac{1}{p}\int_0^1 xe^{-x}\varphi_p'^2(x)\,dx$$

so

$$\int_0^1 e^{-x}\left[\varphi_p^2(x) - \frac{x}{p}\varphi'^2_p(x)\right]dx = -\frac{1}{pe}\varphi_p(1)\varphi_p'(1) = a_p\varphi_p(1).$$

Now, the equations (4) and (5) give

$$\varphi_p^2(x) = \varphi_p(x)\,[\varphi_p'(x) - \varphi'_{p+1}(x)]$$

$$\frac{x}{p}\varphi'^2_p(x) = \varphi_p'(x)\,[\varphi_p(x) - \varphi_{p-1}(x)]$$

hence

$$\varphi_p^2(x) - \frac{x}{p}\varphi'^2_p(x) = \varphi_{p-1}(x)\varphi_p'(x) - \varphi_p(x)\varphi'_{p+1}(x)$$

and

$$\sum_1^n\left[\varphi_p^2(x) - \frac{x}{p}\varphi'^2_p(x)\right] = \varphi_0(x)\varphi_1'(x) - \varphi_n(x)\varphi'_{n+1}(x).$$

This shows that

$$\int_0^1 e^{-x}[\varphi_0(x)\varphi_1'(x) - \varphi_n(x)\varphi'_{n+1}(x)]\,dx = \sum_1^n a_p\varphi_p(1)$$

where

$$\int_0^1 e^{-x}\varphi_0(x)\varphi_1'(x)\,dx = -\int_0^1 e^{-x}\,dx = -1 + \frac{1}{e}.$$

To obtain the second integral, the value of n being very large, we observe that according to equation

$$\varphi_n(x) = \varphi_n'(x) - \varphi'_{n+1}(x) . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

the functions

$$\varphi_n'(x) \text{ and } \varphi'_{n+1}(x)$$

tend to the same limit.

If, therefore n is very large, the second integral, tends to

$$\int_0^1 e^{-x}\varphi_n(x)\varphi'_{n+1}(x)dx = \int_0^1 e^{-x}\varphi_n(x)\varphi_n'(x) =$$

$$= \left[\frac{e^{-x}\varphi_n^2(x)}{2}\right]_0^1 + \int_0^1 e^{-x}\varphi_n^2(x)\,dx = -\tfrac{1}{2}$$

and we obtain

$$\sum_1^{\infty} a_p\,\varphi_p(1) = -1 + \frac{1}{e} + \tfrac{1}{2}.$$

Thus, adding to this equation

$$a_0\,\varphi_0(1) = 1 - \frac{1}{e}$$

we get finally the required relation

$$\sum_0^1 a_p\,\varphi_p(1) = \tfrac{1}{2}.$$

7. In this article we wish to give a second verification of the former expansion because this leads to a very interesting integral containing BESSEL's functions. This verification is obtained by direct summation of

$$a_0 + a_1\varphi_1(x) + a_2\varphi_2(x) + \ldots$$

where

$$a_0 = 1 - \frac{1}{e} \quad \text{and} \quad a_n = \tfrac{1}{2}\left[\varphi_{n-1}(1) - \varphi_n(1)\right].$$

It appears from the equation (10) that

$$\varphi_{n-1}(1) = \frac{ne}{n!}\int_0^{\infty} e^{-\alpha}\,\alpha^{n-1}\,J_0(2\sqrt{\alpha})\,d\alpha$$

$$\varphi_n(1) = \frac{e}{n!}\int_0^{\infty} e^{-\alpha}\,\alpha^{n}\,J_0(2\sqrt{\alpha})\,d\alpha$$

therefore

$$\varphi_{n-1}(1) - \varphi_n(1) = \frac{e}{n!}\int_0^{\infty} J_0(2\sqrt{\alpha})\,d\left(e^{-\alpha}\alpha^n\right)$$

or, after partial integration

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$$\varphi_{n-1}(1) - \varphi_n(1) = \frac{e}{n!}\int_0^\infty e^{-\alpha}\, \alpha^n\, J_1(2\sqrt{\alpha})\, \frac{d\alpha}{\sqrt{\alpha}}.$$

If $n = 0$, the first member has no meaning, as $\varphi_{-1}(1)$ has not been determined. The second member however reduces to

$$e\int_0^\infty e^{-\alpha}\, J_1(2\sqrt{\alpha})\, \frac{d\alpha}{\sqrt{\alpha}} = 2e\int_0^\infty e^{-\alpha^2}\, J_1(2\alpha)\, d\alpha =$$

$$= e\sqrt{\pi}\, J_{\frac{1}{2}}\left(\frac{i}{2}\right) e^{-\frac{1}{2}-\frac{\pi i}{4}} = e - 1 = a_0 e$$

[Nielsen, Handbuch der Theorie der Cylinderfunctionen p. 185 (7)]. By applying again the equation (10), we have

$$[\varphi_{n-1}(1) - \varphi_n(1)]\varphi_n(x) = \frac{e^{x+1}}{(n!)^2}\int_0^\infty e^{-\alpha}\alpha^n J_1(2\sqrt{\alpha})\frac{d\alpha}{\sqrt{\alpha}}\int_0^\infty e^{-\beta}\beta^n J_0(2\sqrt{\beta x})\, d\beta.$$

and by summation from $n = 0$ to $n = \infty$, as

$$\sum_0^\infty \frac{\alpha^n \beta^n}{(n!)^2} = J_0(2i\sqrt{\alpha\beta})$$

$$e\sum_0^\infty a_n\varphi_n(x) = e^{x+1}\int_0^\infty e^{-\alpha} J_1(2\sqrt{\alpha})\frac{d\alpha}{\sqrt{\alpha}}\int_0^\infty e^{-\beta} J_0(2i\sqrt{\alpha\beta})\, J_0(2\sqrt{\beta x})\, d\beta.$$

Putting β^2 instead of β in the latter integral, this reduces to

$$2\int_0^\infty e^{-\beta^2}\, J_0(2i\beta\sqrt{\alpha})\, J_0(2\beta\sqrt{x})\, \beta d\beta = e^{-x+\alpha}\, J_0(2\sqrt{\alpha x})$$

(Nielsen p. 184); thus

$$\sum_0^\infty a_n\varphi_n(x) = \int_0^\infty J_0(2\sqrt{\alpha x})\, J_1(2\sqrt{\alpha})\, \frac{d\alpha}{\sqrt{\alpha}}$$

or, changing α into $\frac{\alpha^2}{4}$

$$\sum_0^\infty a_n\varphi_n(x) = \int_0^\infty J_0(\alpha\sqrt{x})\, J_1(\alpha)\, d\alpha.$$

The second member of this equation has different values according to the value of x, for

$$\int_0^\infty J_0(\alpha\sqrt{x})\, J_1(\alpha\, d\alpha) = \begin{cases} 1 & 0 < x < 1 \\ \frac{1}{2} & x = 1 \\ 0 & x > 0 \end{cases}$$

(NIELSEN p. 200), and for $x = 0$

$$\int_0^\infty J_0(\alpha\sqrt{x})\, J_1(\alpha)\, d\alpha = \int_0^\infty J_1(\alpha)\, d\alpha = 1.$$

8. Now we will apply our expansion to the problem of the momenta. In this problem the question is to determine the function $f(y)$ from the integral equation

$$a_n = \int_0^\infty f(y)\, y^n\, dy.$$

where a_n is a function which is given for all positive integral values of n.

Putting

$$f(y) = e^{-y}\,\theta(y)$$

we obtain

$$a_n = \int_0^\infty e^{-y}\, y^n\, \theta(y)\, dy.$$

Supposing $\theta(y)$ to be a function which satisfies the conditions of DIRICHLET, we have

$$\theta(y) = b_0 + b_1\,\varphi_1(y) + b_2\,\varphi_2(y) + \dots$$

so

$$a_n = \sum_0^\infty b_p \int_0^\infty e^{-y}\, y^n\, \varphi_p(y)\, dy.$$

Now, this integral has the value zero, when $p > n$, therefore

$$a_n = \sum_0^n b_p \int_0^\infty e^{-y}\, y^n\, \varphi_p(y)\, dy$$

Moreover, according to the equation (7)

$$a_n = n! \sum_0^n (-1)^p\, b_p\, C_p^n$$

so, with **(10)**

$$f(y) = e^{-y} \sum_0^\infty b_p\, \varphi_p(y) = \sum_0^\infty \frac{b_p}{p!} \int_0^\infty e^{-x}\, x^p\, I_0(2\sqrt{xy})\, dx.$$

If now we expand the function

$$g(x) = e^{-x} \sum_{0}^{\infty} b_p \frac{x^p}{p!} = e^{-x} X$$

in a power series, we have, differentiating n times, and putting $D = \frac{d}{dx}$

$$g^{(n)}(x) = D^{(n)}(e^{-x} X) = e^{-x} (D+1)^{(n)} X$$

$$= e^{-x} \sum_{0}^{n} (-1)^p C_p^n \; D^{(n-p)} X$$

where

$$D^{(s)} X = \sum_{0}^{\infty} b_{s+p} \frac{x^p}{p!}$$

which, for the value $x = 0$, gives

$$D_0^{(s)} X = b_s.$$

Introducing this value, we obtain

$$g^{(n)}(0) = \sum_{0}^{n} (-1)^p b_{n-p} C_p^n = (-1)^n \sum_{0}^{n} (-1)^p b_p C_p^n = (-1)^n \frac{a_n}{n!}$$

$$g(x) = \sum_{0}^{\infty} (-1)^n \frac{a_n}{n!} x^n$$

and finally

$$f(y) = \int_{0}^{\infty} I_0(2\sqrt{xy}) \sum_{0}^{\infty} (-1)^n \frac{a^n}{(n!)^2} x^n dx$$

This solution agrees with that of LE ROY. In his memoir the discussion of this formula for different values of a_n may be found.

Mathematics. — *"Some remarks on the coherence type η."* By Prof. L. E. J. BROUWER.

In order to introduce the notion of a "coherence type" we shall say that a set M is *normally connected*, if to some sequences f of elements of M are adjoined certain elements of M as their "limiting elements", the following conditions being satisfied:

1st. each limiting element of f is at the same time a limiting element of each end segment of f.

2nd. for each limiting element of f a partial sequence of f can be found of which it is the *only* limiting element.

3rd. each limiting element of a partial sequence of f is at the same time a limiting element of f.

4th. if m is the only limiting element of the sequence $\{m_r\}$ and

m_μ for μ constant the only limiting element of the sequence $\{m_{\mu\nu}\}$, then each of the latter sequences contains such an end segment $\{m_{\mu\nu}\}$, that an arbitrary sequence of elements $m_{\mu\nu}$ for which μ continually increases, possesses m as its only limiting element.

The sets of points of an n-dimensional space form a special case of normally connected sets.

Another special case we get in the following way: In an *n-ply ordered* set [1]) we understand by an *interval* the partial set formed by the elements u satisfying for $\varrho \leq n$ different values of i a relation of the form

$$b_i \overset{i}{<} u \overset{i}{<} c_i \quad \text{or} \quad b_i \overset{i}{<} u \quad \text{or} \quad u \overset{i}{<} c_i\ ;$$

we further define an element m to be a *limiting element* of a sequence f, if each interval containing m, contains elements of f not identical to m, and the given set to be *everywhere dense*, if none of its intervals reduces to zero. Then the *everywhere dense, countable, n-ply ordered* sets which will be considered more closely in this paper, likewise belong to the class of normally connected sets.

A representation of a normally connected set preserving the limiting element relations, will be called a *continuous representation*.

If of a normally connected set there exists a continuous one-one representation on an other normally connected set, the two sets will be said to possess *the same coherence type*.

One of the simplest coherence types is the type η already introduced by CANTOR [2]). From a proof of CANTOR follows namely:

THEOREM 1. *All countable sets of points lying everywhere dense on the open straight line, possess the same coherence type* η.

The proof is founded on the following construction of a one-one correspondence *preserving the relations of order*, between two sets of points $M = \{m_1, m_2, \ldots\}$ and $R = \{r_1, r_2, \ldots\}$ of the class considered: To r_1 CANTOR makes to correspond the point m_1; to r_2 the point m_{i_2} with the smallest index, having with respect to m_1 the same situation (determined by a relation of order), as r_2 has with respect to r_1; to r_3 the point m_{i_3} with the smallest index, having with respect to m_1 and m_{i_2} the same situation (determined by two relations of order), as r_3 has with respect to r_1 and r_2; and so on. That in this way not only all points of R, but also all points of M have their turn, i.o.w. that if among $m_1, m_{i_2}, \ldots m_{i_\lambda}$ appear $m_1, m_2, \ldots m_\nu$, *but not* $m_{\nu+1}$, there exists a number σ with the property that $m_{\nu+1} = m_{i_{\lambda+\sigma}}$,

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[1]) Comp. F. RIESZ, Mathem. Annalen 61, p. 406.

[2]) Mathem. Annalen 46, p. 504.

is evident by choosing for $r_{\nu+1}$ the point of R with the smallest index, having with respect to $r_1, r_2, \ldots r_\nu$ the same situation, as $m_{\nu+1}$ has with respect to $m_1, m_{i_2}, \ldots m_{i_\nu}$. The correspondence constructed in this way, is at the same time *continuous*; for, the limiting point relations depend exclusively on the relations of order, as a point m is then and only then a limiting point of a sequence f, if each interval containing m contains an infinite number of points of f.

The above proof shows at the same time the independence of the coherence type η of the linear continuum. For, after CANTOR it leads also to the following more general result:

THEOREM 2. *All everywhere dense, countable, simply ordered sets possess the coherence type* η.[1])

Theorem 1 may be extended as follows:

THEOREM 3. *If on the open straight line be given two countable, everywhere dense sets of points M and R, a continuous one-one transformation of the open straight line in itself can be constructed, by which M passes into R.*

In order to define such a transformation, we first by CANTOR's method construct a continuous one-one representation of M on R. Then the order of succession of the points of M is the same as the order of succession of the corresponding points of R. We further make to correspond to each point gm of the straight line *not* belonging to M, the point gr having to the points of R the same relations of order, as gm has to the corresponding points of M. In this way we get a one-one transformation of the straight line in itself, preserving the relations of order. On the grounds indicated in the proof of theorem 1 this transformation must also be a continuous one.

Analogously to theorem 3 is proved:

THEOREM 4. *If within a finite line segment be given two countable, everywhere dense sets of points M and R; a continuous one-one transformation of the line segment, the endpoints included, in itself can be constructed, by which M passes into R.*

We shall now treat the question, to what extent the theorems 1, 2, 3, and 4 may be generalized to polydimensional sets of points

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[1]) The possibility of a definition founded exclusively on relations of order, shewn by CANTOR not only for the coherence type ν, but likewise for the coherence type ϑ of the complete linear continuum, holds also for the coherence type ζ of the perfect, punctual sets of points in R_n (comp these Proceedings XII, p. 790). As is easily proved, this coherence type belongs to *all perfect, nowhere dense, simply ordered sets of which the set of intervals is countable* (an "interval" is formed here by each pair of elements between which no further elements lie).

on one hand, and to multiply ordered sets on the other hand. In the first place the following theorem holds here:

Theorem 5. *All countable sets of points lying everywhere dense in a cartesian R_n, possess the same coherence type η^n.*[1]

For, to an arbitrary countable set of points, lying everywhere dense in R_n, we can construct a cartesian system of coordinates C_m with the property that no R_{n-1} parallel to a coordinate space contains more than *one* point of the set. If now two such sets, M and R, are given, then in the special case that C_m and C_r are identical, a one-one representation of M on R preserving the n-fold relations of order as determined by $C_m = C_r$, can be constructed by Cantor's method cited above, only modified in as far as the "situation" of the points with respect to each other is determined here not by simple, but by n-fold relations of order. As on the grounds indicated in the proof of theorem 1 this representation must also be a continuous one, theorem 5 has been established in the special case that C_m and C_r are identical. From this the general case of the theorem ensues immediately.

If on the other hand we have an arbitrary *everywhere dense, countable, n-ply ordered* set Z, then its n simple *projections*[2], being everywhere dense, countable, and simply ordered, admit of one-one representations preserving the relations of order, on n countable sets of points lying everywhere dense on the n axes of a cartesian system of coordinates successively; these n representations determine together a one-one representation preserving the relations of order, thus a continuous one-one representation of Z on a countable set of points, everywhere dense in R_n. From this we conclude on account of theorem 5:

Theorem 6. *All everywhere dense, countable, n-ply ordered sets possess the coherence type η^n.*

As the n-dimensional analogon of theorem 3 the following extension of theorem 5 holds:

Theorem 7. *If in a cartesian R_n be given two countable, everywhere dense sets of points M and R, a continuous one-one transformation of R_n in itself can be constructed, by which M passes into R.*

In the special case that C_m and C_r are identical, we can namely first construct a continuous one-one correspondence between M and R in the manner indicated in the proof of theorem 5, and then make to correspond to each point gm *not* belonging to M, the point gr having to the points of R the same (n-fold) relations of order, as gm has

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[1] This theorem and its proof have been communicated to me by Prof. Borel.

[2] Comp. F. Riesz, l.c. p. 409.

to the corresponding points of M. In this way we get a one-one transformation of R_n in itself *preserving the relations of order as determined by* $C_m = C_r$. As on the grounds indicated in the proof of theorem 1 this transformation is also a continuous one, theorem 7 has been established in the special case that C_m and C_r are identical. From this the general case of the theorem ensues immediately.

The n-dimensional extension of theorem 4 runs as follows:

THEOREM 8. *If within an n-dimensional cube be given two countable, everywhere dense sets of points M and R, a continuous one-one transformation of the cube, the boundary included, in itself can be constructed, by which M passes into R.*

The proof of this theorem is somewhat more complicated than those of the preceding ones. We choose in R_n such a rectangular system of coordinates that the coordinates $x_1, x_2, \ldots x_n$ of the cube vertices are all either $+1$ or -1, and for $p = 1, 2, \ldots n$ successively we try to form a continuous transition between the $(n-1)$-dimensional spaces $x_p = -1$ and $x_p = +1$ by means of a onedimensional continuum s_{mp} of plane $(n-1)$-dimensional spaces meeting each other neither in the interior nor on the boundary of the cube, and containing each at most one point of M. In this we succeed as follows: Let $S \equiv \sum\limits_{p=1}^{n} a_p x_p = c$ be a plane $(n-1)$-dimensional space containing *no* straight line parallel to a line r_m joining two points of M, and through each point $(x_1 = x_2 = \ldots = x_{p-1} = 0, x_p = a, x_{p+1} = x_{p+2} = \ldots = x_n = 0)$ let us lay an $(n-1)$-dimensional space: $x_p + e\,(1 - a^2)\, S = a + e a_p a\,(1 - a^2)$; in this way we get a continuous series σ_e of plane $(n-1)$-dimensional spaces, and we can choose a magnitude e_1 with the property that for $e < e_1$ two arbitrary spaces of σ_e meet each other neither in the interior nor on the boundary of the cube. As further an $(n-1)$-dimensional space belongs to *at most one* σ_e, thus a line r_m is contained in an $(n-1)$-dimensional space belonging to σ_e for *at most one* value of e, and the lines r_m exist in countable number only, it is possible to choose a suitable value for $e < e_1$ with the property that no space of σ_e contains a line r_m, i.o.w. that σ_e satisfies the conditions imposed to s_{mp}.

If for each value of p we choose out of s_{mp} an arbitrary space, then these n spaces possess one single point, lying in the interior of the cube, in common. For, by projecting an arbitrary space of s_{m1} together with the sections determined in it by $s_{m2}, s_{m3}, \ldots s_{mn}$, into the space $x_1 = 0$, we reduce this property of the n-dimensional cube to the analogous property of the $(n-1)$-dimensional cube. So if we introduce as the coordinate x_{mp} of an arbitrary point H lying in the interior or on the boundary of the cube, the value of x_p in that point of the X_p-axis which lies with H in one and the same space of s_{mp}. then to each system of values $> - 1$ and < 1 for $x_{m1}, x_{m2}, \ldots x_{mn}$ corresponds one and only one point of the interior or of the boundary of the cube, which point is a biuniform, continuous function of $x_{m1}, x_{m2}, \ldots x_{mn}$. I.o.w. the transformation $\{x'_p = x_{mp}\}$, to be represented by T_m, is a continuous one-one transformation of the cube with its boundary in itself, by which M passes into a countable, everywhere dense set of points M_1 *of which no* $(n-1)$*-dimensional space parallel to a coordinate space contains more than one point.*

In the same way we can define a continuous one-one transformation T_r of the cube with its boundary in itself, by which R passes into a countable, everywhere dense set of points R_1 *of which no* $(n-1)$*-dimensional space parallel to a coordinate space contains more than one point.*

Further after the proof of theorem 7 a continuous one-one transformation T of the cube with its boundary in itself exists, by which M_1 passes into R_1, so that the transformation

$$T_r^{-1} \,.\, T \,.\, T_m$$

possesses the properties required by theorem 8.

We now come to a property which at first sight seems to clash with the conception of dimension:

THEOREM 9. *The coherence types* η^n *and* η *are identical.*

To prove this property, in an n-dimensional cube for which the rectangular coordinates of the vertices are all either 0 or 1, we consider the set M_n of coherence type η^n consisting of those points whose coordinates when developed into a series of negative powers of 3, from a certain moment produce exclusively the number 1, and together with this we consider the set M of coherence type η consisting of those real numbers between 0 and 1 which when developed into a series of negative powers of 3^n, from a certain moment produce exclusively the number $\frac{3^n-1}{2}$. The continuous PEANO representation 1) of the real numbers between 0 and 1 on the n-dimensional cube with edge 1, then determines a *continuous one-one representation of* M *on* M_n establishing the exactness of theorem 9.

That in reality theorem 9 *does not* clash with the conception of dimension, is elucidated by the remark that *not every continuous one-one correspondence between two countable sets of points* M *and* R,

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1) Comp. Math. Annalen 36, p. 59, and SCHOENFLIES, Bericht über die Mengenlehre I, p. 125.

lying everywhere dense in R_n, admits of an extension to a continuous one-one transformation of R_n in itself. If e.g. the set of the rational points of the open straight line is submitted to the continuous one-one transformation $x' = \frac{1}{\pi - x}$, this transformation *does not* admit of an extension to a continuous one-one transformation of the open straight line in itself.

A more characteristic example, presenting the property moreover that in no partial region an extension is possible, we get as follows: Let t_1 denote the set of those real numbers between 0 and 1 of which the development in the nonal system from a certain moment produces exclusively the digit 4, t_2 the set of the finite ternal fractions between 0 and 1. Let T denote a continuous one-one transformation of the set of the real numbers between 0 and 1 in itself, by which t_1 passes into $t_1 + t_2$, thus a part t_3 of t_1 into t_1, and a part t_4 of t_1 into t_2. By a PEANO representation T_1 the sets t_1, t_2, t_3, t_4 successively pass into countable sets of points s_1, s_2, s_3, s_4, lying everywhere dense within a square with side unity, and, so far as are concerned, s_1, s_3, and s_4, containing no points of the boundary of this square. The continuous one-one representation T of t_3 on t_1 now determines a *continuous one-one representation $T_2 = T_1 T T_1^{-1}$ of s_3 on s_1, not capable of an extension to a continuous one-one representation of the interior of the square in itself.* For, if such an extension would exist, it would be, for each set of points in the interior of the square, the only possible continuous extension of T_2. For s_1, however, $T_1 T T_1^{-1}$ furnishes itself such a continuous extension, which we know to be *not* a one-one representation.

The conception of dimension can now be saved, at least for the everywhere dense, countable *sets of points*, by replacing the notion of *coherence type* by the notion of *geometric type* 1). Two sets of points will namely be said to possess the same *geometric type*, if a *uniformly continuous* one-one correpondence exists between them. And it is for uniformly continuous representations that the following property holds:

THEOREM 10. *Every uniformly continuous one-one correspondence between two countable sets of points M and R, lying everywhere dense in an n-dimensional cube, admits of an extension to a continuous one-one transformation of the cube with its boundary in itself.*

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1) For closed sets the two notions are equivalent. For these they were introduced formerly under the name of *geometric type of order*, these Proceedings XII, p. 786.

For, on account of the uniform continuity of the correspondence between M and R, to a sequence of points of M possessing only one limiting point, a sequence of points of R likewise possessing only one limiting point, must correspond, and reciprocally. On this ground the given correspondence already admits of an extension to a one-one transformation of the cube with its boundary in itself of which we have still to prove the continuity in the property that a sequence $\{g_{m\nu}\}$ of limiting points of M converging to a single limiting point $g_{m\omega}$, the sequence $\{g_{r\nu}\}$ of the corresponding limiting points of R converges likewise to a single limiting point. For this purpose we adjoin to each point $g_{m\nu}$ a point m_ν of M possessing a distance $< \varepsilon_\nu$ from $g_{m\nu}$, the distance between $g_{r\nu}$ and the point r_ν corresponding to m_ν likewise being $< \varepsilon_\nu$, and for r indefinitely increasing we make ε_ν to converge to zero. Thus $\{m_\nu\}$ converging exclusively to $g_{m\omega}$, $\{r_\nu\}$ likewise possesses a single limiting point $g_{r\omega}$, and also $\{g_{r\nu}\}$ must converge exclusively to $g_{r\omega}$.

On account of the invariance of the number of dimensions [1]) we can enunciate as a corollary of theorem 10:

THEOREM 11. *For $m < n$ the geometric types η^m and η^n are different.*

As, however, for normally connected sets in general the notion of uniform continuity is senseless, the *indeterminateness of the number of dimensions of everywhere dense, countable, multiply ordered sets,* as expressed in theorem 9, must be considered as irreparable.

Mathematics. — "*An involution of associated points.*" By Prof. JAN DE VRIES.

(Communicated in the meeting of February 22, 1913).

§ **1.** We consider three pencils of quadric surfaces (a^2), (b^2), (c^2), the base curves of which may be indicated by α^4, β^4, γ^4. By the intersection of any surface a^2 with any surface b^2 and any surface c^2 an *involution of associated points,* I^8, consisting of ∞^3 groups, is generated. Any point outside α^4, β^4, γ^4 determines one group.

Through any point A of α^4 passes one surface b^2 and one surface c^2; these quadrics have a twisted quartic $(A)^4$ in common, intersected by the surfaces of pencil (a^2) in ∞^1 groups of seven points A' completed by A to groups of the I^8. The points of the three base curves are *singular.*

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[1]) Comp. Math. Annalen 70, p. 161.

The locus of the quartic $(A)^4$ corresponding to the different points A of α^4 is a surface which may be indicated by **A**. The curves $\varrho^4 = (b^2, c^2)$ passing through a given point B of β^4 lie on a c^2 meeting α^4 in eight points A; so B lies on eight curves $(A)^4$, i. e. β^4 is an eightfold curve of **A** and the same result holds for γ^4. A quadric b^2 meets α^4 in eight points A and contains therefore eight curves $(A)^4$; moreover it has with **A** the eightfold curve β^4 in common. We conclude from this that **A** is a *surface of order* 32.

§ **2.** The lines joining two points P, P' belonging to the same group of I^8 form a complex Γ; we are going to determine its order.

The curves $\varrho^4 = (b^2, c^2)$ generate a bilinear congruence [1]). Any line is chord of one ϱ^4; the points Q, Q' determined on the lines m through M by the ϱ^4 with m as chord lie on a surface $(Q)^5$ with M as threefold point; the tangential cone in M projects the ϱ^4 passing though M.

The two surfaces a^2 passing through Q and Q' cut m in two other points R, R'. The locus (R) of the points R, R' has in M a sevenfold point, any plane μ through M cutting $(Q)^5$ in a curve μ^5 with threefold point M and the surface a^2 through M in a conic μ^2; so the seven points Q common to μ^2 and μ^5 and differing from M bring seven points R in M. So (R) is a surface of order nine with sevenfold point M.

The curve ϱ^9 common to (R) and μ cuts μ^5 in $9 \times 5 - 7 \times 3 = 24$ points S differing from M, which can be arranged into two groups. In any point of the first group MS is touched by an a^2. So these points lie on the polar surface M^3 of M with respect to the pencil (a^2) [2]). Consequently the first group counts $3 \times 5 - 3 = 12$ points. In any point S of the second group a point R coincides with a point Q'; then the point Q coincides with R' in a second point S and both points S lie on the same a^2; so these points are associated and belong to the same group of I^8. So the plane μ contains six pairs P, P' collinear with M; in other words: *the pairs of points of the involution I^8 lie on the rays of a complex of order six.*

§ **3.** The complex cone of M contains the seven rays joining M to the points M' belonging with M to the same group of I^8. So

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[1]) We have treated this congruence in a paper "*A bilinear congruence of twisted quartics of the first species*", These Proceedings, vol. XIV, p. 255.

[2]) The polar surface of (y) with respect to $a^2_x + \lambda a'^2_x = 0$ is generated by means of this pencil and the pencil of planes $a_y a_x + \lambda a'_y a'_x = 0$; so it is represented by $a'_y a'_x a^2_x = a_y a_x a'^2_x$.

M is sevenfold on the locus of the pairs P, P' collinear with M, and this locus is a twisted curve $(P)^{19}$ passing seven times through M.

The curve $(P)^{19}$ is common to the surfaces $(Q)^5$ and $(R)^9$, intersecting each other moreover in the curve of order 15 common to $(Q)^5$ and the polar surface M^3; so the residual intersection consists of 11 lines. The lines are singular chords of the bilinear congruence[1]) of the curves $\varrho^4 = (b^2, c^2)$, i.e. any of these lines contains ∞^1 pairs (Q, Q'); these lines are not singular for I^8, as these quadratic involutions have only one pair in common.

Amongst these 11 lines we find two chords of β^4 and two chords of γ^4. So the complex Γ^6 contains three congruences (2, 6) and three congruences (7, 3) the rays of which are singular chords of a bilinear congruence (ϱ^4).

There are 120 lines g each of which contains ∞^1 pairs of the I^8, i.e. the common bisecants of the base curves $\alpha^4, \beta^4, \gamma^4$ taken two by two. A common bisecant of α^4 and β^4 forms, in combination with a twisted cubic, the intersection of an a^2 and a b^2; evidently any pair of the involution determined on it by the pencil (c^2) is a pair of I^8. So this involution admits 120 *singular chords.*

The curve $(P)^{19}$ cuts each of the base curves in 20 points, as the surface $(Q)^5$ corresponding to M has 20 points Q in common with α^4; the surface a^2 containing the corresponding point Q' also contains Q, i.e. Q, Q' is a pair of the I^8.

The three polar surfaces of M with respect to the pencils (a^2), (b^2), (c^2) intersect each other in M and 26 points more; in any of these points R the line MR is touched by three surfaces a^2, b^2, c^2. So R is a coincidence $P = P'$ of the I^8, the bearing line passing through M. So the twisted curve $(P)^{19}$ admits the particularity that 26 of its tangents concur in the sevenfold point M.

§ 4. If M describes a plane λ, the three polar surfaces generate three projective nets. The locus of the points of intersection consists of the plane λ and a surface Δ containing all the coincidencies of the I^8.

We deduce from

$$\begin{vmatrix} A^3_x & A'^3_x & A''^3_x \\ B^3_x & B'^3_x & B''^3_x \\ C^3_x & C'^3_x & C''^3_x \end{vmatrix} = 0$$

that this surface is of order eight.[2])

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[1]) loc cit.

[2]) This result is in accordance with a theorem of Mr. G. AGUGLIA (Sulla super-

The coincidencies of the involutions Γ^8 *lie on a surface* Δ^8 *passing through the base curves* $\alpha^4, \beta^4, \gamma^4$.

The surface Δ^8 also contains the three curves of order 14 containing the points of contact of surfaces of two of the pencils.

The three polar surfaces generate three projective pencils if M describes a line l. These surfaces generate the line l and moreover a twisted curve σ forming the locus of the coincidencies $P \equiv P'$, the bearing lines of which rest on l. If the three pencils are indicated by

$$A^3_x + \lambda A'^3_x = 0 \quad , \quad B^3_x + \lambda B'^3_x = 0 \quad , \quad C^3_x + \lambda C'^3_x = 0,$$

the twisted curve under consideration can be deduced from

$$\left\| \begin{matrix} A^3_x & B^3_x & C^3_x \\ A'^3_x & B'^3_x & C'^3_x \end{matrix} \right\| = 0.$$

So the degree of this curve is $6^2 - 3^2 - 1 = 26.$ [1])

The line l bears 8 coincidencies, so it is an eightfold secant of σ^{26}.

§ **5.** We now consider the locus of the points P' associated to the points P of the line l. The curve α^4 contains 32 points P', as l intersects $\mathbf{A}^{32}$ in 32 points. So any surface a^2 contains these 32 points and moreover the two sets of seven points P' associated to the two points common to a^2 and l. So the groups associated to the points of a line lie on a *twisted curve of order* 23, intersecting each of the three base curves in 32 points. In its points on Δ^8 the line l meets its curve λ^{23}; so l *eightfold secant* of λ^{23}.

A plane φ through l meets λ^{23} in 15 points not lying on l; as these points are associated to 15 points P of l, *the locus of the associated pairs lying in a plane is a curve of order* 15.

This curve, φ^{15}, has threefold points in the 12 traces of the curves α^4, β^4, γ^4 on φ. The curve (A^4) corresponding to any of these traces meets φ in three other points, each of which forms with A a pair of the I^8.

§ **6.** The sets of seven points P' associated to the points P of a plane φ lie on a surface Φ^{23} intersecting φ according to the curve φ^{15} containing the pairs P, P' lying in φ and to the curve σ^8 of the coincidencies lying in φ.

The curve $(A)^4$ corresponding to the point A of α^4 (§ 1) meets φ

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ficie luogo di un punto in cui le superficie di tre fasci toccano una medesima retta, Rend. del Circolo Mat. di Palermo, t. XX, p. 305).

[1]) Aguglia, l. c. p. 321.

in four points associated to A; so Φ^{23} passes four times through the base curves $\alpha^4, \beta^4, \gamma^4$. This is in accordance with the fact, that each trace of a base curve is threefold on φ^{15} and onefold on δ^8.

The curve δ^8 contains 18 coincidencies the bearing lines of which lie in the plane, for the curve δ^{26} (§ 4) corresponding to a line l of φ meets l eight times. These 18 coincidencies lie on φ^{15}; so φ^{15} and δ^8 touch one another in 18 points. Moreover they have 36 points in common in the 12 traces of the base curves; each of the remaining 48 common points belongs as coincidence to a group of the I^8 containing still one more point of φ^{15}.

§ 7. The plane φ contains a finite number of associated triplets. As these triplets have to lie on φ^{15} we determine the order of the locus of the sextuples of points P'' associated to the pairs P, P' of φ^{15}.

The surface $\mathbf{A}^{32}$ passes eight times through β^4, γ^4 and one time through α^4. As φ^{15} has threefold points in the 12 traces of the base curves it meets $\mathbf{A}^{32}$ elsewhere in $15 \times 32 - 4 \times 3 - 2 \times 4 \times 3 \times 8 = 276$ points forming 138 pairs P, P' corresponding to 138 points P'' of α^4. A surface a^2 cuts φ^{15} in the four threefold points A and in 9 pairs P, P' more, each pair of which determines six points P'' on a^2. So the locus under discussion has $138 + 6 \times 9 = 192$ points with a^2 in common and is therefore a curve φ^{96}. Of its points of intersection with φ a number of 48 lie in the points common to φ^{15} and δ^8 indicated above. Evidently the remaining 48 traces of φ^{96} are formed by 16 triplets of the I^8. So *any plane contains sixteen triplets of associated points.*

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§ 8. If the bases of the pencils $(a^2), (b^2), (c^2)$ have the line g in common, three surfaces a^2, b^2, c^2 intersect each other in *four* associated points; so we then get an involution I^4 of associated points.

Any point A of the curve α^3 completing g to the base of (a^2) belongs to ∞^1 quadruples. These quadruples lie on the twisted cubic $(A)^3$ common to the surfaces b^2, c^2 passing through A and they are determined on $(A)^3$ by the pencil (a^2).

In the same way any point B of the base curve β^3 and any point C of the base curve γ^3 belongs to ∞^1 quadruples.

We determine the order of the locus $\mathbf{A}$ of the curves $(A)^3$. By means of the points A the surfaces of (b^2) and (c^2) are arranged in a correspondence $(4, 4)$, any surface b^2 or c^2 containing four points A; so the surface $\mathbf{A}$ is of order 16.

In any plane through g the pencils (b^2), (c^2) determine two pencils in (4, 4)-correspondence with the traces B and C of β^3 and γ^3 lying outside g as vertices. So $\mathbf{A}^{16}$ is cut according to g and to a curve of order eight with fourfold points in B and C.

So, *the triplets of points associated to the points of one of the base curves lie on a surface of order sixteen, passing eight times through g and four times through each of the other two base curves.*

§ **9.** Any point G of g also belongs to ∞^1 quadruples. If G is to be a point common to three cubic curves (a^2b^2), (b^2c^2), (a^2c^2) the surfaces a^2, b^2, c^2 must admit in G the same tangential plane.

We now consider in the first place the locus Φ^4 of the curve (a^2b^2), intersection of surfaces a^2, b^2 touching one another in G. Any plane φ through g cuts these projective pencils $(a^2), (b^2)$ according to two projective pencils, the vertices of which are the traces A and B of α^3 and β^3 outside g. These pencils of lines generate a conic passing through G, the lines AG and BG determining with g two surfaces a^2, b^2 touching φ in G. So g is double line and G is threefold point of Φ^4.

In the same way the pencils (a^2) and (c^2) determine a second monoid ψ^4. The monoids Φ^4 and ψ^4 have the base curve α^3 and the line g to be counted four times in common; the residual intersection, locus of the three points associated to G, is of order nine. The cubic cones touching the monoids in G intersect in g and in five other edges; so G is *fivefold point* of the curve $(G)^9$. Any plane through g cuts Φ^4 and ψ^4 according to two conics passing through G and a point A; in each of the two other points of intersection three homologous rays of three projective pencils with vertices A, B, C concur. So g is cut, besides in G, in two more points G^*, each of which forms with G a pair of associated points. So the pairs of the I^4 lying on g are arranged in an involutory correspondence (2, 2), i. e. g bears four coincidencies. This proves moreover that g is a *sevenfold line* of the locus $\mathbf{G}$ of the curves $(G)^9$; for in the first place any point G is fivefold on the corresponding $(G)^9$ and it lies furthermore on two suchlike curves corresponding to other points of g.

The curve (a^2b^2) meeting γ^3 in a point C rests in two points G on g; so C lies on two curves $(G)^9$, i.e. γ^3 is double curve of $\mathbf{G}$. The curve (a^2b^2) contains the two triplets of points associated to the points of intersection G with g. Moreover it has in common with the surface $\mathbf{G}$ in each of these two points G seven points and two points in each of the eight points in which it rests on α^3 and β^3. So we find that $\mathbf{G}$ is of order 12. So, *the points associated to the* *points of g lie on a surface of order twelve, passing seven times through g and twice through each of the base curves.*

If the point G of g lies on α^3, the surfaces a^2 admit in G a common tangential plane, the plane through g and the tangent t in G to α^3; so these surfaces determine on the curve (b^2c^2) touching t in G an I^3 of associated points. The cone k^2 projecting α^3 out of G cuts any curve (b^2c^2) through G in a triplet of associated points; therefore these points lie on the intersection of k^2 with the monoid χ^4 containing all these curves. So, for any of the six points common to g and a base curve, $(G)^9$ breaks up into a twisted cubic and a twisted sextic.

Any common transversal d of g, α^3, β^3 and γ^3 forms with g the partial intersection of three surfaces a^2, b^2, c^2 with two more points in common; these two points form a group of the I^4 with any pair of points of g.

The transversals of g, α^3, and β^3 generate a scroll of order six with g as fivefold line; for the cubic cones projecting α^3 and β^3 out of any point G of g admit g as double edge and intersect each other in five lines of this scroll. On g this scroll has 10 points in common with γ^3, so it cuts γ^3 outside g in 8 points. So, *the base lines g, α^3, β^3, γ^3 admit eight common transversals and therefore eight pairs of points belonging to ∞^2 groups of the I^4.*

Evidently the eight lines d lie in the surface Δ^8 of the coincidencies; of this surface g is a *fivefold line.*

§ **10.** The pencils (a^2), (b^2) determine a bilinear congruence of twisted cubics ϱ^3. In general any ray m of a pencil (M, μ) is bisecant of one ϱ^3; the locus of the points Q, Q' common to m and this ϱ^3 is a curve $(Q)^4$ with a double point in M. In the manner of § 2 we introduce as auxiliary curve the locus of the points R, R' still common to m and the surfaces c^2 through Q and Q'. The surface c^2 through M cuts $(Q)^4$ in M and in six points Q; so M is a sixfold point of the curve (R) and this curve is of order eight.

The polar curve of M with respect to the pencil of intersection of (c^2) and μ intersects $(Q)^4$ in M and $4 \times 3 - 2 = 10$ other points, lying also on $(R)^8$. So $4 \times 8 - 2 \times 6 - 10 = 10$ points are arranged in associated pairs. So, *the pairs of points of the involution I^4 lie on the rays of a complex of order five.*

Any point G of g is associated to two points of g, the points common to g and to the curve $(G)^9$ corresponding to G. So g is a *singular line* of the I^4; the pairs of points lying on it generate an involutory (2,2).

Also the 27 common bisecants of α^3, β^3, γ^3 taken two by two are *singular* lines of the I^4. A common chord of α^3, β^3 bears ∞^1 pairs of points determined on it by the pencil (c^2).

§ **11.** We now consider the locus λ of the points P' associated to the points P of a line l. To the points common to l and each of the surfaces $\mathbf{A}^{16}$, $\mathbf{G}^{12}$ correspond respectively 16 points of α^3 and 12 points of g. Any surface a^2 contains these 28 points P and moreover the two triplets corresponding to the points common to a^2 and l. So the locus λ is a *curve of order* 17.

As l contains eight coincidencies $P = P'$ it is an eightfold secant of the curve λ^{17}; so any plane φ through l contains 9 points P' associated to points of l. So, *the pairs of associated points lying in a plane generate a curve of order nine.*

The curve $(G)^9$ corresponding to the trace G of g meets φ in four points; so G is a *fourfold point* of the curve φ^9. In an analogous way the nine traces A_k, B_k, C_k of the base curves are *double points* of φ^9.

The intersection δ^8 of φ and the surface of coincidencies has a fivefold point in G. So φ^9 and δ^8 intersect each other in $9 \times 8 - 4 \times 5 - 9 \times 2 = 34$ points differing from the traces of the bases. To these points belong the points of contact of the curves, corresponding to coincidencies of the I^4 the bearing lines of which are contained in φ.

In order to determine their number we consider the three pencils of conics common to φ and $(a^2), (b^2), (c^2)$. The polar curves of these pencils with respect to a point P describing a line l generate three projective pencils $(a^3), (b^3), (c^3)$. The first and the second generate a curve c^5 with G as node and passing through the three base points A_k of α^3 and the double points of the three pairs of lines. The curve b^5 generated by the pencils (a^3) and (c^3) also contains these points. So b^5 and c^5 admit $25 - 4 - 3 - 3 = 15$ points of contact of three corresponding conics forming therefore coincidencies of the I^4 with a bearing line lying in φ.

So φ^9 and δ^8 have four coincidencies in common the bearing lines of which intersect the plane φ.

Physics. — "*The diffraction of Electromagnetic waves by a crystal.*"

By Dr. L. S. Ornstein. (Communicated by Prof. H. A. Lorentz).

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In the "Sitzungsberichte der Königl. Bayerischen Akademie der Wissenschaften" [1]) M. Laue has published a theory — and together with Messrs. Friederich and Knipping experiments also — about this highly remarkable phenomenon. W. L. Bragg, in a paper entitled "The diffraction of short electromagnetic waves by a crystal" [2]) doubts of the explication of this experiments given by Laue being satisfactory. He proposes an elementary theory, in which he points out that we can describe the phenomenon of Laue by regarding all as if the Röntgen rays were reflected on the sets of planes that can be brought through the molecules of the crystal. In the following lines I will develop the theory proposed by Bragg, and at the same time I will give a provisory discussion of some experiments made in the Physical Laboratory of the University of Groningen which Prof. Haga has been so kind as to put at my disposal, for which I may cordially thank him here.

I will confine myself to a regular crystal, the extension to crystals with other Bravais or Sohnke point-systems being possible without any difficulty.

1. Let us suppose a plane beam of Röntgen rays (direction of ray: x-axis) to strike a regular crystal, of which one of the cubical axes of the point system is set parallel to the incident beam. The origin of coordinates is chosen in a molecule lying within the crystal in the middle of the part through which the rays are propagated. The y and z-axes are oriented parallel to the other cubic axis. Be the length of the side of the cubes a. The coordinates of a molecule of the crystal then are

$$x = k_1 a \qquad y = k_2 a \qquad z = k_3 a \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which k_1, k_2 and k_3 are positive or negative whole numbers.

We shall examine the influence of the rays in a point with coordinates ξ, η, ζ, at a distance r from the origin.

Now whatever may be the constitution of primary Röntgen rays, we can always imagine the disturbance of equilibrium being dissolved, according to the theorem of Fourier, into periodical movements. In

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[1]) Loc.cit. June 8 & July 6 1912. Interferenzerscheinungen bei Röntgenstrahlen.

[2]) Proc. Cambridge Phil. Soc. Vol. XVII, Part 1. The diffraction of short electromagnetic *w* by a crystal.

the same way, the movement and radiation of molecules can be described. Thus knowing the effect of the radiation from the molecules when a periodical radiation strikes them, we can from this calculate for each case the influence of a crystal on RÖNTGEN rays. I will therefore consider the problem of a radiation of the wavelength λ striking the crystal. Under the influence of this radiation the molecules will emit spherical waves. I will indicate the vector of radiation for the radiation emitted by a molecule situated at the origin, by

$$\frac{A}{r} \cos 2\pi \left(\frac{t}{T} - \frac{r}{\lambda}\right) \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2),$$

this formula representing the vector of radiation in the point $\xi \eta \zeta$, while A depends on the direction. The radiation of a point (1) in the point $\xi \eta \zeta$ is now represented by

$$\frac{A}{\varrho} \cos 2\pi \left(\frac{t}{T} - \frac{\varrho}{\lambda} - \frac{k_1 a}{\lambda}\right),$$

where ϱ denotes the distance of $\xi \eta \zeta$ from (1). This distance is given by

$$\varrho = r - \frac{a}{r}(\xi k_1 + \eta k_2 + \zeta k_3) + \frac{a^2}{2r}(k_1^2 + k_2^2 + k_3^2) + \frac{a^2}{2r}\left(\frac{\xi}{r} k_1 + \frac{\eta}{r} k_2 + \frac{\zeta}{r} k_3\right)^2 \ldots$$

Substituting in the amplitudo ϱ by r (which is allowed since $k_1 a$ is small compared with r etc.) then we get for the vector of light considered

$$\frac{A}{r} \cos 2\pi \left(\frac{t}{T} - \frac{r}{\lambda} - \frac{a}{\lambda}\left\{\left(1 - \frac{\xi}{r}\right) k_1 - \frac{\eta}{r} k_2 - \frac{\zeta}{r} k_3\right\} - \right.$$
$$\left. - \frac{a^2}{2r\lambda}\left\{(k_1^2 + k_2^2 + k_3^2) + \left(\frac{\xi}{r} k_1 + \frac{\eta}{r} k_2 + \frac{\zeta}{r} k_3\right)^2\right\} \quad . \; . \; . \quad (3)$$

And in order to find the total vector of radiation we have to sum up the expression (3) over all molecules struck (or rather put into vibration) by the primary radiation. In doing so we obtain the formula given by LAUE and with that, his cones of maximal intensity.

However, we can show that there are other maxima still, besides the cones of LAUE. I will suppose r to be so great that we can neglect the fourth term.

The maxima that do not appear in LAUE's theory can be made to appear by first taking into account the interference of the points for which

$$k_1 \left(1 - \frac{\zeta}{r}\right) - \frac{\eta}{r} k_2 - \frac{\zeta}{r} k_3 = 0$$

Further I wil substitute $^{\xi}/_{r}$ by α, $^{\eta}/_{r}$ by β, $^{\zeta}/_{r}$ by γ, then $\alpha^2 + \beta^2 + \gamma^2 = 1$, thus in this notation we have to fix our attention upon the interference of the radiation from those points for which the numbers k satisfy the equation

$$k_1\,(1-\alpha) - \beta\,k_2 - \gamma\,k_3 = 0.$$

Now if this equation determines a great number of points, the pulses originating from the molecules will interfere without difference of phase.

This will be the case when the plane

$$x\,(1-\alpha) - y\,\beta - z\,\gamma = 0$$

passes through the molecules of the crystal. Now, a plane through molecules may in general be represented by

$$\mathfrak{a}\,x + \mathfrak{b}\,y + \mathfrak{c}\,z = 0 \quad \ldots\ldots\ldots \quad (4)$$

where $\mathfrak{a}\,\mathfrak{b}\,\mathfrak{c}$ are whole numbers, that we constantly suppose to be reduced to their smallest values possible. The values of $\alpha\beta\gamma$, where maximal intensity is thus to be found on account of the cooperation of the points of a plane, we can find by putting

$$\frac{1-\alpha}{\mathfrak{a}} = -\frac{\beta}{\mathfrak{b}} = -\frac{\gamma}{\mathfrak{c}}$$

while $\alpha^2 + \beta^2 + \gamma^2$ must be 1. From this we find $\beta = 0$, $\gamma = 0$, $\alpha = 1$ (i. e. the light transmitted directly, a point of interference that is not observable) and

$$\left.\begin{aligned} \alpha &= \frac{\mathfrak{b}^2 + \mathfrak{c}^2 - \mathfrak{a}^2}{\mathfrak{a}^2 + \mathfrak{b}^2 + \mathfrak{c}^2} \\ \beta &= \frac{-2\,\mathfrak{a}\,\mathfrak{b}}{\mathfrak{a}^2 + \mathfrak{b}^2 + \mathfrak{c}^2} \\ \gamma &= \frac{-2\,\mathfrak{a}\,\mathfrak{c}}{\mathfrak{a}^2 + \mathfrak{b}^2 + \mathfrak{c}^2} \end{aligned}\right\} \quad \ldots\ldots\ldots \quad (5)$$

Now we can easily show the direction thus found to agree with the direction in which the RÖNTGEN-beam would be reflected if the chosen plane rich in molecules should be a mirror. For the angle of the normal of (4) forms with the x-axis an angle of which the cosine is $\dfrac{\mathfrak{a}}{\sqrt{\mathfrak{a}^2 + \mathfrak{b}^2 + \mathfrak{c}^2}}$, the plane of incidence has for equation: $\mathfrak{c}y - \mathfrak{b}z = 0$, the direction cosines of the reflected ray are $\alpha'\beta'\gamma'$. Thus we have

$$\left.\begin{aligned} (\alpha' + 1)\,\mathfrak{a} + \beta'\,\mathfrak{b} + \gamma'\,\mathfrak{c} &= 0 \\ \beta'\,\mathfrak{c} - \gamma'\,\mathfrak{b} &= 0 \\ \alpha'^2 + \beta'^2 + \gamma'^2 &= 1 \end{aligned}\right\} \quad \ldots\ldots \quad (6)$$

The set of values (5) satisfies (6).

In this way we have shown the maximum to lie really in the direction of reflection. We can see this without calculation, and I principally gave the above calculation to show the connection between LAUE's considerations and mine.

For if P the origin of rays, and L the point of observation, both are situated at a distance from the molecules of a plane which is infinite with respect to the dimensions of the plane of which A and B are arbitrary molecules, then the way $PAL = PBL$, and there is interference of the light emitted by the molecules, if the angles of PA and AL with the normal of the plane are equal. Thus there is interference in L, if the point lies in the direction of the ray reflected in the plane. For the rest the disturbance of equilibrium, if N is the number of particles of the plane, will be N times as great as the disturbance caused by one particle, and therefore the intensity will be N^2 times as great.

The intensity of the maximum is of the order of the number of molecules in a plane, i. e therefore, of the order of the "two-cone" maxima of LAUE. As we may now presume, all pulses will interfere in the same direction which originate from planes in the crystal parallel to the one considered. The equation of similar planes is

$$\mathfrak{a}x + \mathfrak{b}y + \mathfrak{c}z = \pm sa$$

where I must be a whole number, xyz being whole multiples of the side a, the coefficients $\mathfrak{a}$, $\mathfrak{b}$, and $\mathfrak{c}$ also being whole numbers.

Expressed in $\alpha\beta\gamma$ the equation takes the form

$$x(1-\alpha) - y\beta - 2\gamma = d.$$

We therefore have

$$\frac{\mathfrak{a}}{1-\alpha} = -\frac{\mathfrak{b}}{\beta} = -\frac{\mathfrak{c}}{\gamma} = \frac{sa}{d} = \lambda$$

which gives for $\alpha\beta\gamma$ the same values as in the preceding formula, whereas we have

$$d = \frac{2\mathfrak{a}}{\mathfrak{a}^2 + \mathfrak{b}^2 + \mathfrak{c}^2}\, sa$$

or

$$a\{k_1(1-\alpha) - k_2\beta - k_3\gamma\} = \frac{2s\,\mathfrak{a}\,a.}{\mathfrak{a}^2 + \mathfrak{b}^2 + \mathfrak{c}^2}.$$

It is easy to introduce into this formula the smallest distance of the planes under consideration. It amounts to $\frac{a}{\sqrt{\mathfrak{a}^2 + \mathfrak{b}^2 + \mathfrak{c}^2}}$. For if

$ax + by + cz = d$ is a plane, we pass to another plane of the same kind by putting:

$$ax + by + cz = d + (\alpha_1\mathfrak{a} + \beta_1\mathfrak{b} + \gamma_1\mathfrak{c})a$$

where $\alpha_1\,\beta_1\,\gamma_1$ are whole numbers. Now the distance of the two planes considered is

$$\frac{a}{\sqrt{\mathfrak{a}^2 + \mathfrak{b}^2 + \mathfrak{c}^2}}\,(\alpha_1\mathfrak{a} + \beta_1\mathfrak{b} + \gamma_1\mathfrak{c})$$

which, $\mathfrak{a}\,\mathfrak{b}\,\mathfrak{c}$ being given, must be a minimum. This minimum is reached if $\alpha_1, \beta_1, \gamma_1$, are such that

$$\alpha_1\mathfrak{a} + \beta_1\mathfrak{b} + \gamma_1\mathfrak{c} = 1.$$

$\mathfrak{a}$, $\mathfrak{b}$ and $\mathfrak{c}$ being given, this equation can always be satisfied in ∞^2 ways. The minimum distance of the planes I will represent by l_m. We may still observe that in applying the above results we have the means of easily comparing the number of molecules lying in the different planes. The number of molecules that each plane contains will be greater, the greater the distance of the planes of a given kind is. If the number of molecules pro unit of volume is $\mathfrak{r}$, then a plane with parameters $a\,b\,c$, contains $\frac{\mathfrak{r}}{\sqrt{a^2 + b^2 + c^2}}$ molecules pro unit of surface.

The plane of the kind considered, denoted by the parameter s, contains N_s molecules. The contribution to the vector of radiation, originating from this plane, thus amounts to

$$\frac{NsA}{r}\cos 2\pi\left(\frac{t}{T} - \frac{r}{\lambda} - \frac{2s\,\mathfrak{a}\,l_m}{\lambda\sqrt{\mathfrak{a}^2 + \mathfrak{b}^2 + \mathfrak{c}^2}}\right)$$

Taking the sum with respect to s over all possible values, then we obtain the total vector of radiation originating from the emission of molecules. Generally, however, the contributions to the vector of radiation here considered and originating from parallel planes, are incoherent, unless, which may exceptionally occur, λ and $\frac{\mathfrak{a}\,l_m}{\sqrt{\mathfrak{a}^2 + \mathfrak{b}^2 + \mathfrak{c}^2}}$ are mutually measurable. If we have to do with several wave-lengths, this will certainly cause incoherence.

Now, the intensity of the maxima observed can easily be found if for a moment we imagine an equal number of points getting into vibration in all planes considered. Then, if n is the number of planes considered, the intensity is

$$nN^2,$$

where nN^2 is therefore substituted for

$$\Sigma\, N_s^{\,2}$$

Taking into consideration that nN represents the total number of the molecules struck by radiation $\mathfrak{R}$, then we see that the intensity of the maxima is proportional to

$$\mathfrak{R}N$$

so that the spots are the more intense according as they are caused by planes in which the number of molecules pro unit of plane is greater.[1] We can even to some degree extend what was observed above, so as to come to a conclusion which perhaps can be controlled by experiments. Take an x-axis in the direction of the normal of the planes, then x will pass through the values $\pm l_m \pm 2l_m \pm kl_m$ etc., in which the same positive and negative value ought to be taken for γ, when the origin is chosen in the centre of the plate. For each value of $\varkappa$ the part cut off from the plane by the incident beam can be calculated. Be this part $S_\varkappa$, the number of molecules pro unit of plane is νl_m, the contribution to the intensity of the plane $S_\varkappa$, therefore

$$\nu^2 l_m^2 S_\varkappa^2$$

and the total intensity is therefore $\nu^2 l_m^2 \Sigma S_\varkappa^2$, for which we may approximately write

$$\nu^2 l_m \int S^2 \, dx.$$

By applying this formula in different cases, we may come to a further trial of the theory; however, we do not yet possess the necessary photometrical experimental measurements. The intensity of the maxima now under consideration is greater than that of the "two-cone" maxima of LAUE (of the order 10^7 times as great), it is, however, of the order 10^7 times as small as that of the 3 cone maxima of LAUE. However, the experiment forces us to such a degree to accept the explication by reflection, that probably in no other way than in the one described above the photograms may be explained, as I will show below.

We may still observe, that in the consideration as given above, the molecules are assumed to contain only one electron. We can, however, easily get rid of this supposition by multiplying N and ν by s, where s is the number of electrons pro molecule. Perhaps, by taking this into account, we may derive an estimation of the proportion of the numbers of electrons pro molecule in different crystallised matter.

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[1] We may here observe, that by this we have the means of comparing the numbers N, in matter with given density, for planes that are struck by equal radiation under similar circumstances.

We may also observe, that in the direction of the propagation of the primary radiation too an interference can be noticed between the secondary pulses emitted and the primary radiation. At this interference a difference of phase shows itself, which to such a degree diminishes the primary radiation as is necessary to deliver the energy of secondary pulses emitted in the directions of reflection.

We can still somewhat nearer consider the influence of a single plane. Be the reflecting plane chosen as yz-plane, be the xy-plane the plane of incidence, and α the angle of incidence. Let us now consider the vector of radiation in a point

$$x = r\cos\alpha, \qquad y = r\sin\alpha + \eta, \qquad z = \zeta.$$

The vector of radiation is given by

$$\frac{A}{r}\sum_{k_1}\sum_{k_2}\cos 2\pi\left(\frac{t}{T}-\frac{r}{\lambda}+\frac{k_1 a}{\lambda r}\eta+\frac{k_2 a}{\lambda r}\zeta\right).$$

which, when summed up with respect to k_1 and k_2, will give

$$\frac{\alpha_1 A}{r}\cos\alpha\pi\left(\frac{t}{T}-\frac{r}{\lambda}\right)\cos N\frac{a\eta}{2\lambda}\pi\cos N\frac{a\zeta}{2\lambda}\pi\sin(N+1)\frac{a\eta}{2\lambda}\pi\sin(N+1)\frac{a\zeta\pi}{2\lambda}:$$

$$\sin\frac{a\eta\pi}{2\lambda}\sin\frac{a\zeta\pi}{2\lambda}$$

For $\eta=0$ $\zeta=0$ we obtain the maximum found above (diffraction maximum of the order zero) with the intensity there given.

A second maximum (first maximum of diffraction) could appear if $\frac{\eta a}{2\lambda}=1$, or $\frac{a\zeta}{2\lambda}=1$, or thus if $\eta=\frac{2\lambda}{a}$ or $\zeta=\frac{2\lambda}{a}$. Now r is about 4 in the experiments, and a is of the order 10^{-8}; should λ be much smaller than a, then this second maximum would be observable. In the photograms we do not find diffraction-rings of this kind. Thus if the wavelength is very small with respect to 10^{-8} then such images do not occur, but if λ is of the order of a or not much smaller, then we can neither observe such images, the latest estimation giving for λ a quantity of the order 10^{-9}. This might well thought to be consistent with the result that circular fringes do not appear on the plates.

Bragg has explained the form of the spots, — ellipses whose long axis has the direction of the line perpendicular to the plane of incidence which belongs to the plane observed — by observing that the different layers are struck by waves not wholly parallel. However, he does not take into account that in each point the radiation of molecules of all the planes interferes. The form might rather be explained by observing that the intensity in the said direction approaches less rapidly to zero than that in the direction perpendicular to it, whereas we have also to take into account that the distance between the source of radiation and the point of observation is not infinitely great with respect to the dimensions of the plane struck by radiation. Trying to explain the form of the spots by assuming a rectilinear propagation we do not come to the right result. E. g., if we have to do with a reflecting plane lying oblique to the beam, then the photographic plate would cut the reflected cylindre just in an ellipse, whose longest axis is perpendicular to the direction in the plane already considered, whereas on the photograms we observe just the contrary.

In the pencil the beams are not wholly parallel. What is the influence of this on the diffraction image? If the beams forming a small angle will have to give the same reflected beam then the reflecting planes must form a small angle too, and otherwise. Now if $ax + by + cz = 0$ is the plane rich in molecules, then a plane very little differing from it as to its direction will be

$$\left(a - \frac{1}{p}\right)x + \left(b + \frac{1}{q}\right)y + \left(c + \frac{1}{r}\right)z = 0\,,$$

where p, q, r are large whole numbers; or,

$$qr\,(pa + 1) + (bq + 1)\,pz + (cq + 1)\,pq = 0\,.$$

This plane however will be very poor since l_m here becomes $\frac{1}{\sqrt{q^2r^2(pa+1)^2+\dots}}$, which is very small. The forming of the patterns is thus exclusively ruled by the planes very rich in molecules. Of course, each of the pencils in the incident beam gives a reflected pencil to a plane rich in molecules, but since the incident beams differ but a little, the reflected ones will not do so either. Always, when among the planes considered one is rich in molecules the spot will be formed by the influence of one of the pencils.

When we want to consider directly very thin pulses, we come to a problem which agrees in some way with the one treated by Prof. LORENTZ[1]. However, we can now directly consider the pulses reflected by the molecules, which were dealt with in this treatise, to be combined to pulses formed by the planes rich in molecules, since in this case each of such planes gives only one pulse. This fact hinders the coinciding of the pulses considered in the publication mentioned. Take e. g. pulses originating from a definite set of planes, be the dimension in the direction of the normal l, then we have $\frac{l}{l_m}$ pulses,

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[1] Verslagen Kon. Akad. v. Wet. XXI 1912 13 p. 911. „Over den aard der Röntgenstralen”.

of pulse thickness Δ, together having a thickness $l' = \frac{l}{l_m} \Delta$ or $\frac{l'}{l} = \frac{\Delta}{l_m}$, which is a small quantity so long as Δ is small with respect to l_m, as is generally the case. When the pulses do coincide, which again will be the case when we take into account the primary disturbances of equilibrium emitted successively by the anticathode, then the considerations developed by Prof. LORENTZ must be applied. Thus also when operating with the hypothesis that the RÖNTGEN rays exist in pulses, the incoherence of the pulses originating from the different parallel planes is a matter of fact, and therefore also on this assumption the intensity of the spots in the photogram will be proportional to the number of molecules pro unity of surface of the corresponding plane. We may suppose that in this direction also the solution is to be found of the question why the effect of the motion of heat which causes the molecules to vibrate around the corners of the net, is so small.

Now we may still with a single word discuss the photograms which were at our disposal.

The way in which they were taken agrees in many points with that of LAUE, only it has been somewhat less complicated. In order to shorten the time of exposition, a fluorescent screen was used. The spots occurring on the plates may be arranged very conveniently into ellipses, hyperbolas, straight lines and sometimes parabolas; as BRAGG has already explained, points of such a conical section originate from the reflection on planes rich in molecules, which have a line rich in molecules in common. The conic section then will be the inter-section of the photographic plate and a cone, produced by letting the incident beam turn about the said line rich in molecules.

The photograms at my disposal were:

1. Rock-salt. The direction of incidence was lying along a cubical axis. The diagram produced agrees with the one for zinc-blende. The distance of the crystal from the photographic plate was 4 cm., while 3.56 in LAUE's experiment. By magnifying LAUE's pattern in the corresponding proportion I got one *perfectly* congruent with that of Prof. HAGA. Only a few ellipses were missing or were represented less intense, which may be attributed to the fact that with NaCl the net is centric cubical, whereas ZnS shows cubes with centric cube faces. This agrees with the crystallographically deducted cleavability, which lies in the direction of the plane richest in molecules. The fact that the patterns for matters of totally different kinds are identical, is a strong proof for the above developed theory.

2. CaF^2 transmitting the radiation along a triangular axis, gave a pattern identical with ZnS.

3. Topaz, transmitting radiation in the direction of the bisectrix of the acute angle of the optical axes, gave a pattern which can be explained by assuming the net of the molecules to be built up from parallellograms with equal sides in the plane perpendicular to the bisectrix, and by points perpendicularly placed above the net points obtained in this way.

From the photogram I calculated the angle of the *pg*. It amounts to 66°10′. A trying of this angle with the angles of the planes of the prism, known from crystallographic data, gives a suitable agreement. I hope to have an opportunity to calculate the proportion of sides etc. for more types of Bravais nets. We may suppose that in this way we shall obtain the possibility of deciding between the different structure theories, and of coming to a rational description of crystals.

4. The experiment of reflecting Röntgen rays on the cleavage plane published by Bragg in "Nature" of 23 of Dec., was repeated with mica. Because of the plate being longer exposed this time, there appeared on the plate, besides the reflected spot upon the planes parallel to the cleavage plane already found by Bragg, also a number of other points of which by far the greater part were lying upon an ellipse rather changed into a circle. For plane of incidence the principal cross-section had been chosen, the photographic plate was placed perpendicular to the plane of incidence. The circle was lying asymmetrically, although the plane of incidence had been chosen in a principal cross-section.

Supposing the monoclinic net for mica to exist in a rectangle (in the cleavage-plane) and a side inclining with respect to this rectangle, lying in a plane perpendicular to the cleavage plane, then in order to explain the patterns we must take for the proportion of the sides of the rectangle and the inclining side 8 : 13 : 100, and besides we must suppose the angle of the cleavage plane and the inclining side to amount to 85°. The pattern obtained can still better be explained by using the second net of the monoclinic system. The basis then is a *pg* with very long and almost equal sides, and an angle of about 85° between the short diagonal and one of the sides. The third side is perpendicular to the *pg* considered, the rectangle through the short diagonal of the basis is centric. The cleavage plane then is // to this rectangle. This structure shows for mica an approach to the hexagonal type.

The same results were shown by the pattern obtained when mica was crossed by a radiation in a direction perpendicular to the cleavage plane. The photogram so obtained was much weaker, although the time of exposition was taken equally long, and although the intensity of the primary radiation was the same. This may be explained by observing that in the reflection the cleavage plane rich in molecules gives a spot, which does not appear with the transmitted radiation. But the other images are to be taken with respect to corresponding planes. The explication therefore must run otherwise. In both cases a cylindrical pencil with cross-section of about 1 mm. strikes the plate. Consequently the part struck by radiation of the plane richest in molecules, the reflection taking place under an angle α near 90°, is a good deal greater, namely in the proportion $\frac{1}{\cos \alpha}$, the number of working layers being the same. In the most unfavourable case of the vector of radiation lying in the plane of incidence, the working vector of radiation, if $\alpha = 90 - \beta$ where β is a small angle, is $- S \sin 2\beta$. The intensity of the image reflected thus will be proportional to $\frac{I^2 \sin^2 2\beta (o\omega)^2}{\sin^2 \beta}$ (where o is the diameter of the pencil, ω the number of particles pro unit of surface). For the case of the vector of radiation lying in the plane of incidence, $\sin 2\beta$ in the numerator is to be substituted by the unity; then the intensity will be great. As the incident pencil is not polarised, we have to expect a stronger effect with the reflection than with the light being directly transmitted.

5. The reflection on rock-salt (perpendicular to a cubical axis) again gave a set of spots very clearly observable, situated on conical sections through the central spot. The spots were lying close together on the plate; as may be supposed they are partly to be assigned to different not wholly parallel layers in the crystal.

Anatomy. — *"Nerve-regeneration after the joining of a motor nerve to a receptive nerve."* By Prof. J. Boeke.

(Communicated in the meeting of February 22, 1913).

After the primary discoveries of Fontana, Monro, Cruikshank, at the end of the 18th century, no phenomenon of life has been more closely studied than the process of nerve-regeneration. Attention was drawn to the primary degeneration of the peripheral portion of a cut nerve deprived of its trophic centre, the ganglion cells (Waller), and the' manner after which a new nervous union was established by the growing out of the fibers of the central end into the old path of the peripheral nerve-portion became better and better known. It was seen how the new nerve-fibers growing out from the cut-end may extend to the organs normally supplied by the nerve in question, form new end-organs and how thus even a functional regeneration may take place. It was seen how regenerating nerve-fibers may even grow into a nerve-path belonging to another (cut) nerve, and how motor fibers from the cut-end of the nervus accessorius for example may grow into the peripheral degenerated portion of a cut facialis nerve and thus in the end provide with motor nerve-endings the atrophying muscle-fibers of the mimic muscles.

This phenomenon leads naturally up to the question, whether it would be possible, after a nerve containing motor and receptive fibers has been severed in its course, that motor nerve-fibers from the cut-end grow into degenerated receptive fibers of the peripheral portion of the nerve, and vice-versa.

This question, which was studied for the first time by Bidder in 1849 and more closely by Philipeaux and Vulpian in 1863 and 1873, and by different authors in the course of the years, has been answered almost universally in a negative sense. Even Langley and Anderson, who studied the question as late as 1904, denied the functional and trophic regenerative union of motor and receptive fibers, and Bethe, who studied the question for (as far as I could gather) the last time in 1907 [1], gives as the results of his investigations the following statement: "dass auch unter den für die Vereiniging günstigeren Bedingungen (nach Durchschneidung der motorischen Warzeln) eine functionelle oder auch nur trophische Verwachsung zwischen rezeptorischen und motorischen Fasern nicht eintritt." (l. c. page 481).

And yet, notwithstanding these statements, the question must be answered in a positive sense.

To study the question, the same course was taken as that followed by Philipeaux and Vulpian making their classic experiments in 1863 and 1873 (Vulpian). The nervus lingualis and the nervus hypoglossus of the same side were both cut through. Only I did not join the central end of the lingualis to the peripheral portion of the nervus hypoglossus [2], as was done by the investigators mentioned above, but followed the example given by Bethe in 1903, and joined the

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[1] Pfluger's Archiv, 116 Bd. 1907.

[2] In a second note I hope to describe the results of this line of experiments.

central end of the n. hypoglossus to the peripheral portion of the nervus lingualis. The two other nerve-ends were both exstirpated as far as they could be reached.

The entire cycle of experiments was the following:

a. In a number of fullgrown hedge-hogs (14 in all) the right nervus hypoglossus was cut through, and the ends joined together. After a lapse of several days, weeks or months the animals were killed, the bloodvessels were rinsed by means of the fluid of RINGER-LOCKE, and the tissues were preserved by means of an injection of a very slightly alcaline solution of formalin into the aorta; afterwards the nerves and the nerve-endings inside the tongue were stained by the BIELSCHOWSKY-method, and cross-sections or sagittal sections of the tongue examined under the microscope.

The phenomena of regeneration of the motor fibers after the reunion of the severed ends of the n. hypoglossus I will not discuss here. In this connection it only interests us to know, that in preparations made of the tongue of animals killed 5 to 10 days after they were operated upon, all the fibers of the n. hypoglossus of the right half of the tongue were entirely degenerated, the fibers of the nervus lingualis having of course remained entirely intact. In this way I obtained a very accurate insight into the topographical relations, the course and distribution of both nerves throughout the tongue. These relations are very systematic, so that when we only take care to compare analogous cross-sections of different tongues with each other we are able to tell immediately in a given cross-section the places where the nerve-fibers of the n. lingualis and those of the n. hypoglossus (at least the larger rami) are to be found. For a safe and accurate judgment of the results of the following group of experiments (*b*) these preliminary experiments are absolutely necessary.

b. In another series of full-grown hedge-hogs at the right side of the neck the nervus lingualis and the nervus hypoglossus were cut through, great care being taken to make as small a wound as was possible and to injure no other elements. After this the central cut-end of the n. hypoglossus was joined with the peripheral portion of the n. lingualis, the two other ends were exstirpated as far as possible, and the wound closed. After a lapse of some weeks or months the animals were killed, and stained sections through the tongue examined after the manner described above. To prevent ulcerative processes to occur in the lamed and anaesthetic half of the tongue, before the operation all the teeth of the right side of the mouth were stripped of their crowns. After that ulcerative processes in the tongue did not occur any more.

Examination of the place of section of the nerves showed in the first place that in the greater half of the cases, viz. in 11 of the 20 aminals of group *b* which were operated upon, a complete union of the heterogeneous nerves had taken place. The central cut-end of the hypoglossus adhered firmly to the peripheral portion of the lingualis, and after one or two months the peripheral portion of the joined nerve had turned white again, viz. had become myelinised. After a due lapse of time even the place of union of the nerves, the cicatrice itself, was white. I however got the impression, that the process of union of the cut-ends has a somewhat longer duration than after the dissection and joining of homogeneous nerve-portions. The experiments of group *a* showed, that already after the lapse of one month regenerating nerve-fibers were visible in the tongue, and after one and a half month regenerating motor endplates were visible on the muscle-fibers even at the tip of the tongue. In the experiments of group *b* it was only after 2 or 3 months. that I was able to detect the regenerating fibers inside the tongue.

These results were confirmed in all points by the microscopic examination. The regenerating nerve-fibers of the hypoglossus had grown through the cicatrice, had reached the peripheral portion of the lingualis and had grown into it just as in the regenerative union of homogeneous nerve-ends. Sections through the place of union tend to show the same intertwisting of the neurofibrillar bundles, the regenerating axons, in the cicatrice, the slow forward movement, and at the end the same picture of the regenerating axons penetrating into the channel of the degenerated peripheral portion, in casu the n. lingualis. Nearly all the regenerating fibers of the hypoglossus penetrate into the peripheral nerve-end, in casu the n. lingualis. A few fibers only pass alongside and are seen growing out into the surrounding tissue, the perineural connective tissue.

The examination of the microscopic sections gave me however the same impression as the macroscopic inspection, viz. that the process of regeneration, especially of the penetrating of the regenerating axons into the peripheral nerve-end (lingualis) has a somewhat longer duration and slower movement than in the union of homogeneous nerve-ends. The intertwisting of the axons is more dense, and a greater number of the so-called spirals of Perroncito are formed. As however the nervus hypoglossus possesses a far greater number of nerve-fibers than the nervus lingualis, finally the peripheral nerve-end (lingualis) becomes entirely filled-up with the regenerating axons of the hypoglossus nerve.

The examination of the cross-sections through the tongue gives corresponding results. When we examine such a cross-section in a successful experiment (and only those are considered), we find all the sections of the branches of the n. lingualis filled with regenerating nerve-fibers, whilst those of the n. hypoglossus are entirely (or nearly so) devoid of them, showing only the so-called bands of BÜNGNER of the degenerated nerve-tubes.

This is — and that gives us the answer to the question mentioned above, why no *physiological* regeneration is to be found — not only the case with the larger branches, but also the smaller and smallest branches present the same aspect. When the larger branches of the hypoglossus are devoid of regenerating axons, no trace of these is to be found even in the smallest branches of the hypoglossus, whilst even the smallest branches of the lingualis are full of regenerating axons, and a dense plexus of regenerated nerve-fibers is present in the mucous membrane of the tongue, in the connective tissue of the submucosa, but not a single motor nerve-plate is to be found on any of the muscle-fibers, in sharp contrast to what we find after the regeneration of the nerve-fibers of the hypoglossus into the peripheral end of the hypoglossus itself (group *a*), where we find everywhere the regenerating end-plates on the muscle-fibers.

When regenerating nerve-fibers have penetrated into the old channel of a peripheral degenerated nerve, it clearly is impossible for them to get out of it and they are compelled to travel it to the end. Nowhere is this rule demonstrated so clearly as it is done here. The branches of the lingualis nerve wind their way towards the final station, the mucous membrane, between the bundles of muscle-fibers, and often seem to come into close contact with them, as is clearly shown by the examination of the sections in the experiments of group *a*. And yet not a single nerve-fiber of the regenerating hypoglossus nerve leaves the channel of the lingualis in group *b* to form an endorgan on the muscle fibers as it is to be seen everywhere in the experiments of group *a* [1]).

Now the question might be asked, whether these regenerating nerve fibres growing into the peripheral end of the nervus lingualis are in reality hypoglossus fibres, and whether it is not more probable that the ingrowing fibres are after all lingualis fibres, which grew out from the central end of the lingualis and have found their way into the old nerve channel. To exclude this source of errors, in a number of animals, in which 3 and 4 months ago the central end of the n. hypoglossus had been joined to the peripheral end of the

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[1]) J. BOEKE, Ueber De- und Regeneration motorischer Endplatten, etc in Verhandl. der Anat. Gesellsch. Versamml. in München. April 1912. S. 152

n. lingualis (group *b*), the cicatrice was opened again, and after it had been ascertained, that the nerve-ends had grown together and that the peripheral portion was myelinised already, the central cut-end of the nervus lingualis was prepared again, and cut out with a part of the surrounding connective tissue as far as it was possible to reach it, the connective tissue being exstirpated because it might be possible that some nerve fibres from the central end of the lingualis had grown into the connective tissue and from there had reached the point of joining of the two nerve-ends. Ten days were allowed to the eventually cut nerve fibres to degenerate, and after that time the animals were killed and prepared after the manner described above. Ten days may be supposed to be entirely sufficient for the degeneration of all the nerve fibres eventually supplied by the central portion of the lingualis nerve.

One of these experiments, which looked entirely successful, was studied as accurately as possible, and gave the following results: from the central portion of the lingualis nerve not a single nerve fibre entered the peripheral lingualis, nor had any other nerve (a small muscle nerve for example) regenerated into the peripheral lingualis, except the nervus hypoglossus. From the central cut-end of the hypoglossus, which was in full process of regeneration, a large number of regenerating nerve fibres had grown out and had all penetrated into the peripheral end of the nervus lingualis. Only a very few fibres had grown into the perineural connective tissue around the lingualis nerve. Inside the tongue all the lingualis branches were full of regenerating fibres, the hypoglossus branches were entirely devoid of them.

The regenerating fibres, which here could have no other source than the hypoglossus, had followed the course of the lingualis nerve down to the smallest branches of the nerve plexus in the mucous membrane of the tongue. Of so-called autogenic regeneration (A. BETHE) no trace was found (only full-grown animals were used for experiments).

The fibres of the hypoglossus nerve, having arrived at the end of the terminal branches of the lingualis, begin to form nerve-endings of different patterns. It is here not the right place to describe elaborately the differences in form and in extension of the nerve-endings. I hope to do that in extenso elsewhere. Here I will only mention two or three points.

It is certainly an interesting fact that the hypoglossus fibres after having penetrated into and arrived at the end of the lingualis tract, begin to form terminal branchings and different end-bulbs. But not only that they form nerve-endings in the connective tissue, but they even penetrate into the epithelium. In most cases the terminal fibrillae do not penetrate far into the epithelium, but remain in the basal layers, where they form small endnets around different epithelial cells, but sometimes they penetrate into the upper layers of the epithelium (fig. 1 *e*).

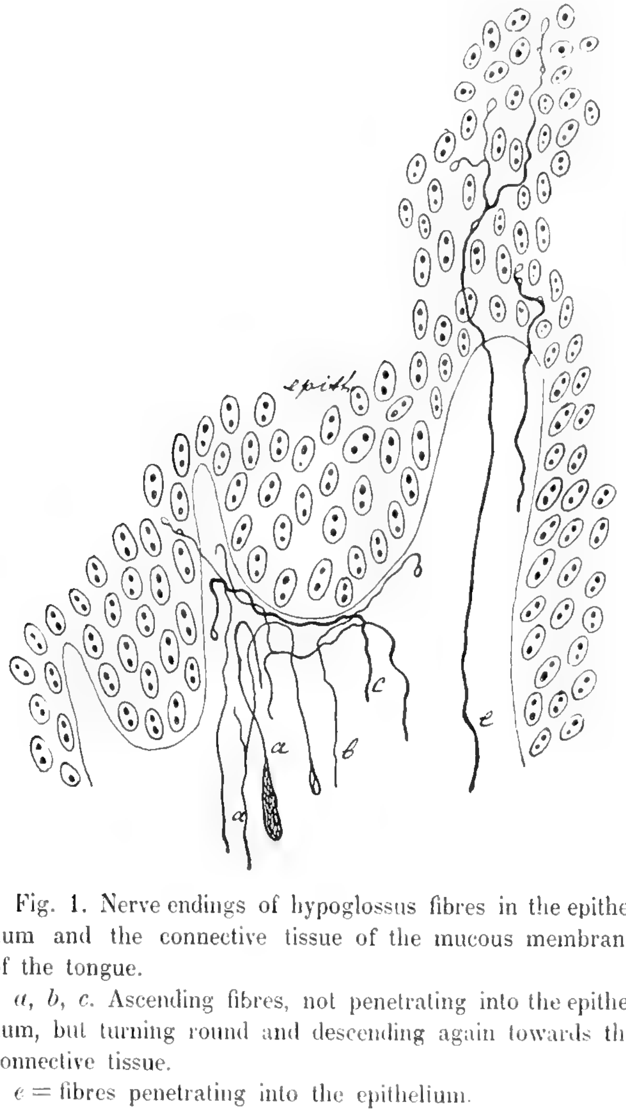

Fig. 1. Nerve endings of hypoglossus fibres in the epithelium and the connective tissue of the mucous membrane of the tongue.

a, *b*, *c*. Ascending fibres, not penetrating into the epithelium, but turning round and descending again towards the connective tissue.

e = fibres penetrating into the epithelium.

It seems however that the epithelium offers a certain resistance against the ingrowing fibrillae, that makes it difficult for them to penetrate into the epithelial membrane. In the normal half of the tongue at all points of the epithelium the neurofibrillae may be seen to penetrate far into the epithelium, sometimes as far as the superficial layers of cells. In the other half of the tongue, where the fibres of the hypoglossus nerve are regenerating along the nerve paths of the lingualis, one sees often strikingly how the nervous fibrillae grow right up against the basal side of the epithelium, but then do not penetrate it, but turn round and descend again, ending inside the connective tissue with an endknob or endnet, or run for a shorter or longer distance along the basal side of the epithelium as if seeking entrance, and then turn round and end between the elements of the connective tissue as described above (fig. 1 *a*, *b*, *c*).

In the second place it is an interesting fact, that the terminal branches of the hypoglossus nerve fibres often show a striking resemblance to the endplates formed on the muscle fibres during regeneration after simple cutting of the hypoglossus nerve (*a*-group of experiments). An example is given in the figs. 2 and 3. In fig. 2 is drawn a set of terminal branches formed by a hypoglossus nerve fibre against the basal membrane of the epithelium, in fig. 3 is drawn a regenerated motor end-plate on a muscle fibre of the tongue after

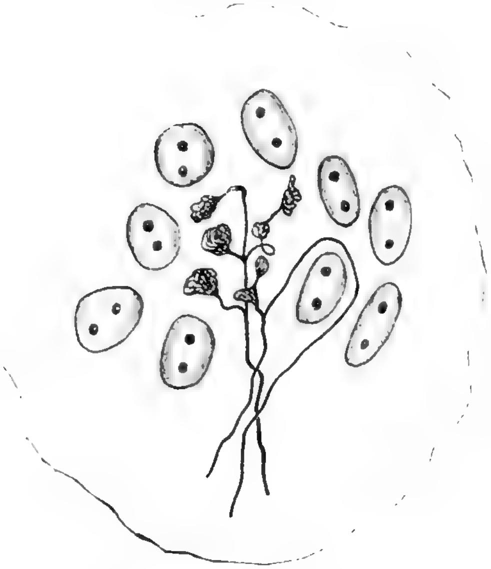

Fig. 2 Terminal branches of a hypoglossus nervefibre in the connective tissue of the mucous membrane of the tongue (group *b*).

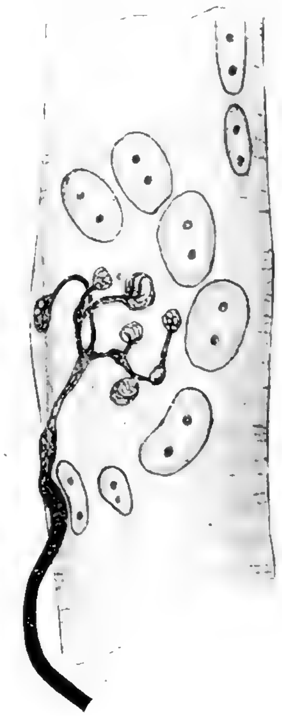

Fig. 3. Regenerated motor endplate on a muscle fibre of the tongue (hedgehog group *a*).

the cutting of the hypoglossus nerve. It is certainly interesting, that even in such atypic surroundings the hypoglossus nerve fibres try to build up their proper typical endformations.

In the third place the following point may be mentioned. In the course of the branches of the lingualis nerve are distributed groups of ganglion cells of sympathetic nature, probably belonging to the chorda-tympani part of the lingualis nerve. The fibres of the lingualis (chorda tympani?) form a beautifully impregnated network with meshes and interwoven fibrillae on the surface of these cells. After the cutting of the lingualis nerve this network of fibrillae disappears entirely, the cells themselves undergoing apparently no alteration. The fibers of the hypoglossus nerve appear to be unable to regenerate this network of neurofibrillae, at least in all my preparations, even there where the nerve plexus in the mucosa and the submucosa was very well regenerated, and all the branches of the lingualis nerve were full of regenerating fibres, no trace of the above mentioned network could be found.

To conclude, it appears from these facts that fusion of heterogenic nerve-ends is not only possible, but may lead to distinct regenerative processes which do not differ much from these following on the fusion of homogenic nerve-ends. A functional (physiological) regeneration however does not take place, because the regenerating fibres are not able to reach their proper destination, and no contact with the muscle fibres is acquired.

And yet a certain amount of *functional* regeneration may be obtained after all. Firstly some fibres of the hypoglossus nerve will grow out, not into the neural tubes of the lingualis, but in the connective tissue of the perineural sheath. These fibres after a time will reach their destination, the tongue, and these fibres will have no difficulty in coming into contact with the adjoining muscle fibres and will form new motor end-plates on them. Secondly here and there in the preparations a fibre was found, which in forming terminal branches in the connective tissue of the mucous membrane of the tongue, had come in contact with the end of a muscle fibre, and was seen to run alongside it for a distance (towards the centre of the tongue) and then to form a small end plate on the surface of the muscle fibre. This last mode of functional regeneration I met with however only in a few cases.

Leiden, 18 February 1813.

Physiology. — "*The effect of fatty acids and soaps on phagocytosis*".[1]

By Prof. Hamburger and J. de Haan.

(Communicated in the meeting of February 22, 1913.)

In our former paper[2]) we drew the attention to the particularly noxious effect of fatty acids on phagocytosis.

Already at a concentration of 1 : 1000,000 the pernicious influence of propionic acid became manifest. The law of division-coefficients, obeyed by all the other fat-dissolving substances, examined by us, did not lead us to expect such a poisonous effect of propionic acid.

How could this abnormal action of propionic acid, and likewise of butyric acid, which was also examined by us, be explained?

Is it caused by a noxious effect of ions of H, or perhaps also by a specifically injurious effect of the anion of fatty acid?

At that time we failed to supply an answer to this question.

In order to determine to what extent the ions of H are responsible for the noxious effect of the fatty acids we exposed the

TABLE I.

Comparison of sulphuric acid- and propionic acid solutions with equal percentages of ions of H. The solutions act upon the leucocytes during $^5/_4$ hours; the leucocytes are brought into contact with carbon during 25 minutes.

	NaCl-solution in which has been dissolved:	Number of leucocytes examined	Number of leucocytes having taken up carbon	Percentage of phagocytosis
	nothing	349	101	**29** %
1	H_2SO_4 $^1/_{100000}$	208	0	0 »
	Proprionic acid $^{1.5}/_{100000}$	301	0	0 »
2	H_2SO_4 $^1/_{500000}$	194	13	6.7 »
	Proprionic acid $^{1.5}/_{500000}$	180	0	0 »
3	H_2SO_4 $^1/_{2500000}$	148	33	22.2 »
	Propionic ac. $^{1.5}/_{2500000}$	215	52	24.2 »

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[1]) A more detailed account will be published in the Archiv. f. (Anat. u.) Physiologie.

[2]) The effect of substances which dissolve in fat on the mobility of Phagocytes and other cells. These Proceedings Vol. XIV p. 314.

leucocytes to the action of fatty acid and of sulphuric acid-solutions *containing the same percentage of ions of H*, and determined subsequently its phagocytarian power.

The table on p. 1290 will need no further explanation.

It follows from this series of experiments that the noxious effect of aqueous sulphuric acid- and propionic acid-solutions manifests itself at the same concentration of ions of *H*.

This renders it in a high degree probable that the noxious effect of a strongly diluted solution of propionic-acid must be attributed to the action of ions of H.

If this view was the correct one, if it was not *the anion of propionic acid*, but the ion of *H* which had to be reckoned with, it might be expected that the propionate of sodium, in the corresponding dilution, would have *no* bad effect.

This was indeed not the case, as appears from the following table.

TABLE II.

Effect of Na-propionate on phagocytosis. The propionate acts upon the leucocytes during half an hour. The leucocytes are brought into contact with carbon during half an hour at 37°.

NaCl-sol. 0.9 $^0/_0$ in which has been dissolved:	Number of leucocytes examined	Number of leucocytes having taken up carbon	Perc. of phagocytosis
nothing	768	373	48.5 $^0/_0$
	323	163	50.4 »
Na-propionate 1 : 100 (i.e. 1 gr. propionate dissolved in 100 ccm. NaCl)	923	535	57.9 »
Na-propionate 1 : 250	549	332	60.4 »
» 1 : 1000	781	460	58.6 »
» 1 : 5000	412	247	59.9 »
	344	83	24.1 » ?
» 1 : 25000	891	437	49 »
» 1 : 100.000	633	321	50.7 »

A hurtful effect of anions of *H*, even in much greater concentrations than those in which the anion was used in the propionic acid experiments, is evidently out of the question. The propionate 1 : 25000 and 1 : 100000 leave the phagocytarian power intact; propionic *acid* in this concentration destroys all the leucocytes.

But what is much more remarkable than this result is the favourable effect of still higher concentrations of propionate (1 : 100; 1 : 250; 1 : 1000) *on phagocytosis.*

By dissolving for instance 1 gramme of propionate in 250 ccm. of NaCl 0.9 % the phagocytosis is found to increase by 100 %.

This increase, which was also caused by *the Na-salts of butyric acid and formic acid*, was all the more remarkable, as the fluid was made strongly hyperisotonic by the addition of these soaps, and as was shown hyperisotony has nearly always a highly injurious effect upon phagocytosis.

This is clearly confirmed by the following experiment in which isosmotic NaCl-solutions, with and without propionate, are compared with each other.

The comparison relates to the following isosmotic solutions:

NaCl 0,9% and NaCl 0,9%
NaCl 1, % ,, NaCl 0,9% + Na-Propionate 0,165%
NaCl 1,1% ,, NaCl 0,9% + ,, ,, 0,33 %
NaCl 1,2% ,, NaCl 0,9% + ,, ,, 0,5 %
NaCl 1,3% ,, NaCl 0,9% + ,, ,, 0,66 %

These fluids acted for half an hour upon fresh leucocytes; then

TABLE III.

Effect of isosmotic NaCl and NaCl-Propionate-solutions.

Solution	Percentage of leucocytes having taken up carbon	NaCl-solution 0.9% +	Percentage of leucocytes having taken up carbon
NaCl 0.9%	$\frac{132}{465} \times 100 = 28.2\%$	nothing	$\frac{68}{266} \times 100 = 25.5\%$
» 1 »	$\frac{113}{457} \times 100 = 24.7$ »	Na-Propionate 0.165%	$\frac{42}{325} \times 100 = 12.9$ »
» 1.1 »	$\frac{62}{400} \times 100 = 15.5$ »	» 0.33 »	$\frac{113}{316} \times 100 = 35.9$ »
» 1.2 »	$\frac{69}{524} \times 100 = 13.1$ »	» 0.5 »	$\frac{193}{643} \times 100 = 30$ »
» 1.3 »	$\frac{6}{272} \times 100 = 2.2$ »	» 0.66 »	$\frac{116}{428} \times 100 = 27.1$ »

the suspensions were brought into contact with coal for ½ hour at 37°, and the preparations were made.

This result is indeed interesting, for we find that when by the application of a strongly hyperisotonic NaCl-sol. (1.1 % the phagocytosis has been reduced by 50 % (from 28 % to 15,5 % a NaCl-solution, isosmotic with the former, in which, however, part of the NaCl has been replaced by propionate, promotes phagocytosis to a considerable extent (to 35.7 %).

A similar result was obtained with leucocytes which had been left in serum containing citrate of Na during one night, and which had consequently lost part of their phagocytarian power.

After the results obtained with the propionate it might be expected that also the butyrate and the formate would give the same results.

This was indeed the case.

We subjoin a table, showing the results obtained with butyrate.

This table shows that Na-butyrate in a dilution of 1 : 1000 has

TABLE IV.

Effect of butyrate of Na on phagocytosis. The NaCl-solutions containing butyrate have acted upon the leucocytes for half an hour at room-temperature; then they were brought into contact with carbon for half an hour.

NaCl-solution 0.9 % +	Percentage of leucocytes having taken up carbon
nothing	$\frac{132}{449} \times 100 = 29.3\ \%$
	$\frac{132}{488} \times 100 = 27$ „
Na butyrate 1 : 100	$\frac{130}{448} \times 100 = 29$ „
„ 1 : 250	$\frac{138}{479} \times 100 = 28.8$ „
„ 1 : 1000	$\frac{321}{841} \times 100 = 38.1$ „
„ 1 : 5000	$\frac{306}{808} \times 100 = 37.8$ „
„ 1 : 25000	$\frac{260}{554} \times 100 = 39.7$ „

increased phagocytosis (from 28% to 38%), and that this increase is still more obvious in a dilution of 1 : 25000.

As regards the *formiate,* here too a dilution of 1 : 1000 caused an important increase, which continued at 1 : 2000, and which was still clearly visible at 1 : 10000.

An attempt at an explanation of the facts observed.

How must the favourable effect of propionate and of other soaps on phagocytosis be explained?

Is the cause the same as that which we adduced to explain the effect of lipoid-dissolving substances such as iodoform, chloroform, chloral, etc.?

Also in the case of these soaps we might think that propionate — for convenience sake we shall only mention propionate when we should also name the other two soaps which were experimented upon — dissolves in the lipoid surface of the phagocytes, softens them and facilitates in this way the amoeboid motion.

Numerous experiments, however, showed that propionate is absolutely insoluble in olive-oil.

We have then tried to find another explanation, and it occurred to us that *soaps have in a high degree the property of lessening the surface tension of oil.*

The reader knows GAD's experiment: if oil is brought into contact with a soap solution, an extremely fine emulsion is formed.

As far as we know these experiments have only been carried out with soaps of higher fatty acids (sapo medicatus or olive-oil containing some fatty acid).

Therefore we have repeated them with soaps containing a smaller number of *C* atoms in their molecules.

It appeared indeed that the propionate, butyrate and formiate of Na have an emulgent effect on olive-oil. The formiate of Na was more active than the two others.

We may conceive that the soaps lay themselves against the surface of the phagocytes, reduce the surface-tension, and in this way facilitate the amoeboid motion.

The following observations point in the same direction.

By way of an illustration we beg the reader to glance at Table III.

In this series of experiments the leucocyte suspensions, after having been in contact with carbon for $^3/_4$ hours at 37°, were suddenly cooled down by water at 13°. Then the phagocytes were fixed by means of a drop of an osmium-solution.

Microscopical examination showed that in the NaCl-solution of 1,1°/₀, 1,2°/₀, and 1,3°/₀ all the leucocytes had regained their round shape, while in the isosmotic NaCl-propionate solution nearly all the cells still had pseudopodia.

Even in the NaCl-solution 0,9°/₀ relatively few leucocytes with pseudopodia were found, and yet the phagocytosis had reached about the same stage as in the latter fluid, which contained much propionate (12,7°/₀ and 15°/₀ respectively).

It follows from this that propionate has the property of influencing the amoeboid motion of the leucocytes in a favourable sense; one might be inclined to say that they are made more resistant.

For what was observed to take place?

In the NaCl-solution 0,9°/₀ the leucocytes drew back their protrusions owing to the lower temperature, but in the propionate-sol. with the same degree of phagocytosis they remained, notwithstanding this low temperature.

Similar results were arrived at in the experiments of Table II: in NaCl 0,9°/₀ no pseudopodia, in NaCl combined with propionate 1 : 100, 1 : 250 and 1 : 1000 many pseudopodia, in propionate 1 : 5000 fewer, and in 1 : 25000 and 1000.000 none.

Now it would be incorrect to look upon the promotion of phagocytosis and the capacity of resistance of the pseudopodia as being identical.

First there are a number of leucocytes which protrude pseudopodia, but which show no phagocytosis, and secondly it appeared from another series of experiments with propionate and $CaCl_2$ where both substances equally promoted phagocytosis, that after being cooled down and fixed, the microscopic pictures were entirely different. In the $CaCl_2$-solution namely the lower temperature had caused the pseudopodia to disappear almost entirely, in the propionate-solution on the other hand, this was not the case.

But since the formation of pseudopodia is *one of the conditions* for phagocytosis, it may be concluded from the observation with propionate that propionate by influencing the formation of pseudopodia in a favourable sense has contributed to the promotion of phagocytosis.

That the effect of propionate is due to a surface-action and not to a direct action on the contents of the cells appears from *volumetrical determinations*,

The volumes of two equal amounts of blood corpuscles, exposed to the action of isosmotic solutions, are equal, as we know, *but only on condition that the substances do not penetrate into the blood corpus-*

cles and that therefore the phenomenon remains restricted to an interchange of water between the cells and the surrounding fluid.[1])

Conversely it may be concluded that if two isosmotic solutions give the same volume to the blood-corpuscles, the latter are impermeable to these substances [2]).

Therefore we have investigated to what extent a certain amount of blood-corpuscles in a solution of NaCl 1,2 °/₀ had the same volume as a solution, isosmotic with the former and which contained 0,9 °/₀ NaCl and 0.5 propionate of Na.

If the volumes were equal then it might be concluded that propionate did not penetrate or hardly into the cells.

The experiments showed that only traces of propionate could have penetrated into the blood-corpuscles.

Consequently Na-propionate acted upon the red blood corpuscles like for instance NaBr and other anorganic Na-salts.

Now it might be objected that the permeability of the red and the white blood-corpuscles need not be alike. As regards this we may observe that none of the many researches carried out in this direction, have established any difference.

The agreement goes even so far that the same hyperisotonic salt solution causes the same relative decrease in volume in the red and in the white blood corpuscles [3]). And this also applies to the hypisotonic one.

The analogy also appears from the way in which anisotonic salt-solutions act upon phagocytosis [4]).

We arrive, therefore at the conclusion that until now we have discovered three causes which may increase phagocytosis.

1. *Traces of a calcium-salt*; there can be hardly any doubt but here we have to do with an action of Ca on the cell-protoplasm. It has not been verified as yet whether the Ca also acts upon the surface.

2. *Fat-dissolving substances* such as iodoform, chloroform, chloral, turpentine, etc. When applied in homoiopathic quantities (e.g. Chlo-

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[1]) *Perfectly* equal when the isosmotic solutions are isotonic. *Hedin*, Pflüger's Archiv **60**, 198, p. 300

[2]) Only urea, as appears from investigations by Grijns and myself, makes an exception.

[3]) Hamburger. Archiv. f. (Anat u.) Physiol. 1898 S. 317; Osmot. Druck u. Ionenlehre I. S. 337.

[4]) Hamburger and Hekma. Biochem. Zeitschr. **7**, 1907, 102. Further Hamburger, Physik. Chem. Unters. über Phagocyten u. s. w. Wiesbaden, J. F. Bergmann. 1912.

roform 1:500000, Propionic acid 1:10000000, they restrict their action to the lipoid surface, which they weaken thus facilitating the amoeboid motion.

When applied in somewhat greater quantities a second factor becomes of importance viz. the noxious effect of these substances on the protoplasm. All these substances indeed penetrate easily into the cells, thus causing paralysis.

3. *Soaps*, such as propionate, butyrate and formiate. These substances, unlike the fat dissolving substances, do *not* enter into the phagocytes. Their action upon the phagocytes is therefore entirely different from that of the fat-dissolving substances, for even when applied in high concentrations (1:250), in concentrations in which the fat dissolving substances would inevitably kill the cells, *they have a very favourable effect upon phagocytosis.*

When applied in still greater quantities their action is a pernicious one, but this may be due to the solution being too hyperisotonic.

Further it is a remarkable fact — and in this respect the soaps are distinguished from calcium as well as from the fat dissolving substances — that within rather wide limits, the degree to which phagocytosis is promoted is independent of the amount of soap, found in the solution. (Cf. Tables II and IV.)

The researches, described above, have given rise to different questions, which, owing to the present circumstances we cannot enter into now.

Physiological Laboratory. *Groningen*, January, 1913

Astronomy. — "*A proof of the constancy of the velocity of light*". By Prof. W. DE SITTER.

(Communicated in the meeting of February 22, 1913).

In the theory of RITZ light emitted by a source moving with velocity u is propagated through space in the direction of the motion of the source with the velocity $c+u$, c being the velocity of light emitted by a motionless source. In other theories (LORENTZ, EINSTEIN) the velocity of light in always c, independent of the motion of the source. Now it is easily seen that the hypothesis of RITZ leads to results which are absolutely inadmissible.

Consider one of the components of a double star, and an observer situated at a great distance Δ. Let at the time t, the projection of the star's velocity in the direction towards the observer be u. Then from the law of motion of the star we can derive an equation:

$$u = f(t - t_0) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The light emitted by the star at the time t reaches the observer at the time $\tau = t + \Delta/c - \alpha u$. In RITZ's theory we have, neglecting the second and higher powers of u/c, $\alpha = \Delta/c^2$. In other theories we have $\alpha = 0$. If now we put $\tau_0 = t_0 + \Delta/c$, we have

$$u = f(\tau - \tau_0 + \alpha u) \qquad \text{or} \qquad u = \varphi(\tau - \tau_0) \quad . \quad . \quad . \quad . \quad (2)$$

The function φ will differ from f, unless αu be immeasurably small. Therefore if one of the two equations (1) and (2) is in agreement with the laws of mechanics, the other is not. Now α is far from small. In the case of spectroscopic doubles u also is not small, and consequently αu can reach considerable amounts. Taking e.g. $u = 100 \frac{KM}{sec}$, and assuming a parallax of 0".1, from which $\Delta/c = 33$ years, we find approximately $\alpha u = 4$ days, i. e. entirely of the order of magnitude of the periodic time of the best known spectroscopic doubles.

Now the observed velocities of spectroscopic doubles, i. e. the equation (2), are as a matter of fact satisfactorily represented by a Keplerian motion. Moreover in many cases the orbit derived from the radial velocities is confirmed by visual observations (as for δ Equulei, ζ Herculis, etc.) or by eclipse-observations (as in Algol-variables). We can thus not avoid the conclusion $\alpha = 0$, i. e. the velocity of light is independent of the motion of the source. RITZ's theory would force us to assume that the motion of the double stars is governed not by NEWTON's law, but by a much more complicated law, depending on the star's distance from the earth, which is evidently absurd.

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In a manner similar to that in which, in the previous communications, we considered the saturation line under its own vapour pressure we can also consider the conjugated vapour line. Instead of the two-phase complex $F + L$ we now, however, take, the complex $F + G$ and if in the three-phase equilibrium $F + L + G$ no phase reaction occurs, we must in the conversion of $F + G$ again distinguish three cases.

Let us now take the case generally occurring in which, on a change in pressure in the one direction $F + G$ is converted into $F + L' + G'$, and into $F + G''$ on a change in pressure in the other direction. Hence, on a change of pressure in the one direction liquid is formed, but not when in the other direction.

In the previous communication we have deduced: if $F + L$ is converted into $F + L' + G'$ with increase in volume, the conjugation line solid-liquid will, on lowering the pressure turn towards the vapour point. If $F + L$ is converted into $F + L' + G'$ with contraction of volume, the conjugation line solid-liquid turns in the opposite direction.

In a similar manner we may now deduce: if $F + G$ is converted into $F + L' + G'$ with increase in volume, the conjugation line solid-vapour, on lowering the pressure, turns away from the liquidum point, and on increasing the pressure it turns towards the same. If $F + G$ is converted into $F + L' + G'$ with contraction of volume the conjugation line solid-vapour will turn in the opposite direction.

The conversion of $F + L$ into $F + L' + G'$, or as we may also call it the formation of vapour from $F + L$ generally takes place with increase in volume and only on certain conditions with a decrease in the same. The conversion of $F + G$ into $F + L' + G'$, or in other words the formation of vapour from $F + G$ takes place as a rule with decrease in volume and only in definite conditions with an increase of the same.

In the previous communication (V) we have demonstrated that the rule for the rotation of the conjugation line solid-liquid is in conformity with the saturation lines under their own vapour pressure as deduced in communication (I): in the same manner we may now also show that this is the case with the movement of the conjugation line solid-vapour.

Let us imagine in fig. 7 (I) a tangent to be drawn through F on the vapour saturation curve of F under its own vapour pressure, therefore, on curve $M_1 a_1 m_1 b_1$. As on a change in pressure in either direction the new conjugation line solid-vapour falls outside the first three-phase triangle, the system $F + G$, in this particular case, is converted on a change in pressure in the one direction into $F + G'$ and by a change in the other direction into $F + G''$. Hence, no liquid is formed either on an increase or a decrease in pressure. At an infinitesimal change in pressure nothing happens but evaporation of a little solid substance F in, or else a slight deposit of solid F from the vapour G.

On evaporation of F, the volume will as a rule increase; as the gas then draws nearer to the point F, the pressure along the vapour saturation curve, starting from the point of contact, will decrease towards F and increase in the other direction. This is in agreement with fig. 7 (I) and 12 (I) but not so with fig. 13 (I); from the deduction of this last figure; however, it is more to be expected that the curve $M_1\,m_1$ is either circumphased or exphased, but is then situated at the other side of F like curve Mm.

Let us now consider the case when the vapour saturation curve of F under its own vapour pressure possesses a form like curve $a\,m\,b$ in fig. 4 (V); the saturation line should then be supposed to lie more towards the right. We may then draw through F tangents to the vapour saturation line with the points of contact R, R', X and X'.

In the point R' (X') now also takes place the above considered conversion of $F+G$ into $F+G'$ and $F+G''$. In the point R, however, the system $F+G$ is converted, on change in pressure, in the one direction, into $F+L'+G'$, and by a change in the other direction into $F+L''+G''$. Hence, liquid is formed on increase as well as on decrease in pressure. At an infinitesimal change in pressure, only a little solid substance F evaporates into, or else a little of this is deposited from the vapour; hence, when starting from the point of contact, the pressure along the vapour-saturation curve will decrease towards F, but increase in the other direction.

We have noticed above that the rotation-direction of the conjugation line solid-liquid depends on the change in volume when vapour is formed from $F+L$, whereas that of the conjugation line solid-vapour depends on the change in volume when liquid is formed from $F+G$. In the three-phase equilibrium $F+L+G$ we may now suppose four cases to occur.

1. The formation of vapour from $F+L$ takes place with increase, the formation of liquid from $F+G$ with decrease in volume.

2. The formation of vapour from $F+L$ takes place with decrease, the formation of liquid from $F+G$ with increase in volume.

3. The formation of vapour from $F+L$ and that of liquid from $F+G$ both take place with increase in volume.

4. The formation of vapour from $F+L$ and that of liquid from $F+G$ both take place with decrease in volume.

Let us first take the case mentioned sub 1 which is also the one usually occurring; from what has already been communicated it follows that, on increase in pressure, the conjugation line solid-liquid turns towards the vapour point and that the conjugation line solid-vapour turns away from that point.

Hence, on increase of the pressure, the three-phase triangle turns in such a manner that the conjugation line solid-vapour gets in front; on diminution of the pressure the three-phase triangle turns in the opposite direction, but in such a manner that the conjugation line solid-liquid precedes.

On increase in pressure the two three-phase triangles of fig. 3 (I) with their conjugation line solid-vapour in front, will therefore move towards each other; on diminution in pressure they move away from each other, with the conjugation line solid-liquid in front, to be converted, for instance, into fig. 8 (I). If in fig. 11 (I) we suppose each liquid to be united with its correlated vapour and the solid substance F we notice that the three-phase triangle moves in conformity with the above mentioned rule.

It is evident that we must not look upon this rotation of the three-phase triangle as if this turns in its entirety without a change in form; during this rotation not only the length of the conjugation lines solid-liquid and solid-vapour is changed, but also the angle formed by the two lines.

In the case mentioned sub 2 the changes in the volumes have the opposite sign to that mentioned in the case sub 1; the three-phase triangle then of course will turn in the opposite direction namely in such a manner that on increase in pressure the conjugation line solid-vapour gets in front.

A similar case we meet in fig. 12 (I), if in this we take two three-phase triangles, one at each side, and adjacent to the straight line $F m m_1$; the two triangles turn the conjugation line solid-vapour towards each other. On lowering the pressure the two triangles must move towards each other and on increasing the pressure they must part from each other, which is in conformity with fig. 12 (I).

In the case mentioned sub 3, the two conjugation lines, solid-liquid and solid-vapour, of the three-phase triangle will, on increase in pressure, move towards each other, and on decrease in pressure part from each other; in the case mentioned sub 4 they move in opposite directions.

Let us suppose that the exphased vapour saturation line of F, in fig. 13 (I) is situated at the other side of F. We now take a liquid close to the point m so that its conjugated vapour is adjacent to the point m_1. The three-phase triangle then forms in F an angle of nearly 180°. As here occurs the case mentioned sub. 3, the two conjugation lines solid-liquid and solid-vapour must draw nearer each other on increase in pressure. And this is in agreement with fig. 13 (I).

If we take a liquid close to the point M and hence a vapour

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adjacent to the point M_1, the case mentioned sub 4 occurs and the movement of the conjugation lines is in conformity with the rule deduced above. The cases mentioned sub 3 and sub 4 also occur in other figures, for instance also in fig. 12 (I).

In the above considered conversion of $F+L$ we can distinguish three special cases.

1. The case, mentioned above sub A 2 and A 3, which has already been discussed in detail, when no vapour is formed at an infinitesimal change in pressure or in volume.

2. At an infinitesimal change in volume the quantity of the liquid does not alter (its composition, of course, changes).

3. At an infinitesimal change in volume the quantity of solid matter does not change.

In each of these cases one of the sides of the three-phase triangle will occupy a special position. We have already noticed previously that in the case mentioned sub 1 the conjugation line solid-liquid meets the saturation line under its own vapour pressure.

In the case mentioned sub 2, dm in the formula given in the previous communication V (p. 1213) must be taken $=0$; from that it follows that the tangent drawn in the liquidum point to the saturation line under its own vapour pressure is parallel to the conjugation line solid-vapour.

In the case mentioned sub 3 dn in the said formula must be taken $=0$; this signifies that the conjugation line liquid-vapour touches in the liquidum point the saturation line under its own vapour pressure.

In the saturation curves deduced previously diverse examples of these cases are to be found.

It is evident that in the system $F+G$, three corresponding cases may be distinguished; these then relate to the direction of the tangent in the vapour point of a vapour saturation line under its own vapour pressure.

We will now consider the case already mentioned in the previous communication sub B, when a phase reaction between the three phases takes place. The three phases are then represented by three points of a straight line and the pressure for the system $F+L+G$ is then a maximum or a minimum.

Let us first take the case mentioned sub B 1 when the reaction $F \rightleftarrows L+G$ occurs; the point F then falls between the points L and G as, for instance, in fig. 4 (I), if in these figures we suppose a_1 to have coincided with b_1 and a with b. We then obtain fig. 5 (I) in which the points m_1, F, and m correspond with the homonymous points in fig. 7 (I).

If now we suppose first that the reaction $F \rightleftarrows L + G$ proceeds from the left to the right with increase in volume, the system $L+G$ will then appear at lower pressures and the systems $F + L$ and $F + G$ at higher ones. Hence, on lowering the pressure, fig. 5 (I) will be converted into fig. 6 (I) and on increasing the same into fig. 4 (I), which is in agreement with our previous considerations. As, on increase of pressure, fig. 5 (I) is converted into fig. 4 (I) the pressure for the system $F + L + G$ in fig. 5 (I) is consequently a minimum.

If we had assumed that the conversion $F \rightleftarrows L + G$ took place from the left to the right with decrease in volume, the pressure would be a maximum. Such a change in volume can only occur when the liquid differs but little in composition from F, and when F melts with contraction of volume. If we imagine in fig. 13 (I) the curve $M_1 m_1$ to have shifted so far to the other side of F that M_1 gets situated at the other side of F, this case will occur in the system F + liquid M + vapour M_1.

Let us now take the case mentioned sub B 2, namely when the reaction $F + L \rightleftarrows G$ takes place, so that the point G lies between the points F and L. This is, for instance the case in fig. 9 (I). Let us now assume first that the reaction takes place from the left to the right with increase in volume. The system $F + L$ will then appear at a higher, the systems $F + G$ and $L + G$ at a lower pressure. In agreement with our previous considerations fig. 9 (I) will be converted, on increase in pressure, into fig. 8 (I) and on lowering of the pressure into fig. 10 (I). As on increase of pressure fig. 9 (I) is converted into fig. 8 (I) the pressure for the system $F + L + G$ in fig. 9 (I) is a minimum. This is also in harmony with the situation of the points m_1 m, and F in figs. 11 (I) and 13 (I).

Let us now just take a system $F + L_1 + G_1$ in which L_1 differs but little from L, and G_1 but little from G; this system will then be represented by a triangle situated in the vicinity of the line $F m m_1$. As the reaction $F + L \rightleftarrows G$ takes place with increase in volume, the conversion of $F + L_1$ into $F + L'_1 + G'$ in the infinitesimally differing system $F + L_1 + G_1$ will take place with increase in volume and the conversion of $F + G_1$ into $F + L'_1 + G'_1$ with decrease in the same. We have noticed previously that, in this case the three-phase triangle must turn in such a manner that, on increase in pressure, the conjugation line solid-vapour gets in front and that on reduction of pressure the conjugation line solid-liquid precedes. This also is in agreement with figs. 8 (I) and 9 (I). On lowering the pressure, the first figure is converted into the second and we notice that in this conversion both three-phase triangles turn in such a manner that the conjugation line solid-liquid gets in front.

In the case now considered when the reaction $F + L \rightleftarrows G$ takes place from the left to the right with increase in volume, the pressure can also be a maximum; I will elucidate this with a single example.

We take a saturation line of the solid substance F at the pressure P; this is represented in fig. 1 by the curve fgh; within this saturation line is situated a vapour region encompassed by a heterogeneous region, of which the liquidum line is drawn and the vapour line dotted.

On lowering the pressure the vapour region expands and at a certain pressure P_M the saturation line of F and the liquidum line of the heterogeneous region meet each other in M. There is now formed the three-phase equilibrium solid $F +$ liquid $M +$ vapour M_1 represented by three points of a straight line, whereas the vapour phase M_1 lies between the points F and M. Hence, the reaction is $F + L \leftrightarrows G$ namely from the left to the right with increase of volume, whilst the pressure P_M is a maximum.

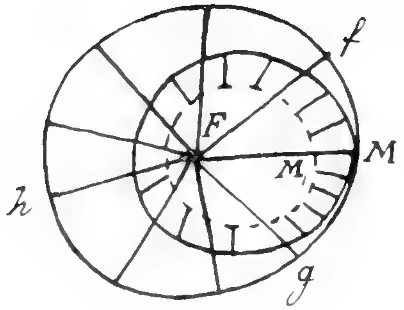

Fig. 1.

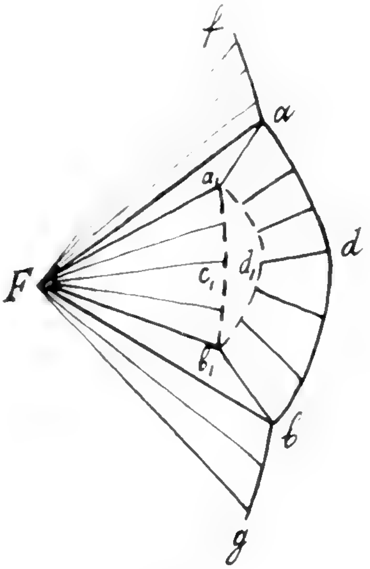

Fig. 2.

At a pressure somewhat lower than P_M is now formed a diagram as in fig. 2 in which, however, we must imagine the only partially drawn saturation line af and bg of F to be closed. The vapour saturation line $a_1 c_1 b_1$, the liquidum line $a d b$ and the vapour line $a_1 d_1 b_1$ have been drawn only to the extent where they represent stable conditions.

We have noticed previously that from the system $F + L + G$, which exists at the pressure P_M, are formed, on increase in pressure, the systems $F + G$ and $L + G$; we find this confirmed here also in figs. 1 and 2. We also notice, in agreement with the rule given above that the two three-phase triangles Faa_1 and Fbb_1 turn, on reduction in pressure, in such a manner that the conjugation line solid-liquid gets in front; on increase of pressure the conjugation line solid-gas precedes.

I must leave the consideration of the other cases to the reader.

In our previous considerations we have compared the course of the saturation- and vapour-saturation lines under their own vapour pressure with the change in volume that takes place in the conversion of $F + L$ and of $F + G$ into $F + L' + G'$. In the same manner we might compare the course of the boiling point-line and the vapour-boiling point line with changes in entropy occurring in these reactions. Instead of increasing, or decreasing the volume of the systems $F + L$ and $F + G$ we must either supply, or withdraw, a little heat to, or from the same.

If we distill a ternary liquid at a constant temperature, then, as is well known, the pressure continuously decreases during the distillation. The liquid and the at each moment distilling vapour proceed along a curve which we distinguish as the distillation curve of the liquid and of the vapour. We obtain, as is well known, clusters of these distillation curves which emanate from one or more definite points (the distillation points) and meet in one or more definite points.

If now at the temperature of distillation a solid substance F also occurs, this can modify the course of the distillation lines; of course, not the theoretical but the experimental course.

According to whether the initial and terminal points of the distillation curves are situated within or without the saturation line of F under its own vapour pressure, we may now distinguish several cases, of which we will only take a single one.

Let us choose a temperature below the minimum melting point of the solid substance F, so that its saturation line under its own vapour pressure is circumphased. In fig. 3 has been drawn a part of this saturation line with the point of maximum pressure M and of minimum pressure m; the dotted curve $M_1 s_1 a_1 b_1$ is a part of the correlated vapour line.

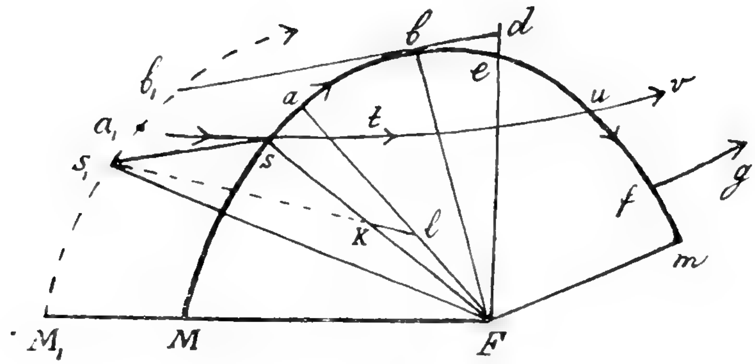

Fig. 3

From the situation of the points M and m it is now evident that the arrows do not, as in the previous figures, indicate here the direction of the increasing pressure, but that of the decreasing one.

Let us now imagine in fig. 3 to be drawn the distillation curve of a liquid and its conjugated vapour curve. It is now evident that if the first does not intersect the saturation line under its own vapour pressure, the second will also not intersect the vapour saturation line and reversedly. We further perceive at once that in this case the distillation curve will suffer no change owing to the appearance of the solid substance.

When, however, the distillation curve, such as the curve $r\,s\,t\,u\,v$ in fig. 3, intersects the saturation line under its own vapour pressure, matters are different; the arrows on this curve $r\,s\,t\,u\,v$ indicate the direction of decreasing pressure, hence also the direction in which the liquid moves during the distillation. It is now evident that with a point of intersection s of the distillation curve of the liquid and the saturation line of F under its own vapour pressure must correspond a point of intersection s_1 of the distillation curve of the vapour and the vapour saturation curve of F under its own vapour pressure. As s_1 represents the vapour which can be in equilibrium with the liquid s, the distillation curve of the liquid must meet the line ss_1 in s.

If no solid F occurred, the liquid r would, on distillation, proceed along the curve $r\,s\,t\,u\,v$; now however, when it has arrived in s something else takes place. For if we withdraw from the liquid s a small quantity of vapour s_1 the new liquid will be represented by a point of the line aF; we must then suppose the point a to be situated adjacent to s. The new liquid will now resolve into solid F and the solution a of the saturation line under its own vapour pressure. The liquid, therefore, does not proceed along the distillation curve $s\,t\,u$, but moves, with separation of F, along the saturation line under its own vapour pressure from *s* towards *a*. If now we again generate a little vapour which can be in equilibrium with the liquid *a*, therefore the vapour a_1, the liquid *a* moves, with separation of *F*, along the saturation line under its own vapour pressure in the direction of *b*.

If, as assumed for the point *b* in fig. 3, the conjugation line liquid-vapour (the line b_1 *b*) meets the saturation line under its own vapour pressure in the liquidum point *b*, then, as we have seen previously, the system $F + L$ is converted, at an infinitesimal change in pressure, into $F + L' + G'$ without any solid substance either dissolving or crystallising. If, however, we withdraw a little more vapour, so that the liquid *b* is converted into *d*, *F* is dissolved and *d* is converted into liquid *e*. Hence, on distillation the liquid *s* will traverse a part of the saturation curve of *F* under its own vapour pressure, first with separation of solid *F* and afterwards with solution of the same. The point *f* in which all solid substance has again disappeared will, as a rule, not coincide with the point *u* of the distillation curve *r s t u v*. Starting from the point *f*, the liquid, on continued distillation, proceeds along a distillation curve *fg*.

If no solid substance *F* did occur the liquid *r* would, on distillation, traverse the distillation curve *r s t u v*; as now, however, solid matter *F* appears, it first proceeds along curve *rs*, then along curve *s b f* and finally along curve *fg*. From the foregoing considerations it follows: if a distillation curve meets the saturation line under its own vapour pressure it proceeds starting from this point of intersection, along a part of the saturation line under its own vapour pressure and abandons it in another point along a distillation line which, with regard to the first one, has shifted.

We may also express this as follows: If during the distillation of a liquid a solid substance *F* separates, the liquid leaves the distillation curve in order to proceed along a part of the saturation line of *F* under its own vapour pressure. As soon as, on continued distillation, the solid substance *F* again disappears, the liquid again proceeds along a distillation curve which, however, does not coincide with the prolongation of the first. The occurrence of the solid substance has, therefore transferred the liquid to another distillation curve.

Although, as stated above, the appearance of a solid substance generally causes the shifting of a distillation line, yet in some cases no shifting can take place so that the liquid after the disappearance of the solid matter traverses the prolongation of the original distillation curve. This will be the case when the vapour contains only one of the three components; the distillation curves of the liquid then become straight lines, those of vapour and distillate are reduced to a single point.

When a distillation curve of a liquid meets the saturation line of F under its own vapour pressure in the point b, it will not penetrate within the heterogeneous region, but meet this saturation curve in b; its vapour distillation curve will then also meet the vapour saturation curve.

Among all distillation curves intersecting the saturation line of F under its own vapour pressure there is one that behaves in a particular manner: it is the one that intersects the saturation line in the point M and, therefore, meets the line MM_1 in M. If we withdraw from the liquid M a little of the vapour M_1, M will not change its composition, but the reaction: liquid $M \rightarrow$ solid $F +$ vapour M_1 will appear. If now the vapour is continuously distilled off, the liquid M will disappear without change in pressure and only the solid substance F will remain. The distillation curve arriving in M, therefore, terminates in this point without proceeding any further along the saturation curve of F.

What follows next is dependent on the temperature; this, as we have presupposed has been chosen lower than the minimum melting point of F. We now can distinguish two cases.

1. The distillation temperature is higher than the maximum sublimation point of F. The saturation curve and the vapour saturation curve of F under their own vapour pressure then possess a form like in fig. 7 (I), the isothermic-isobaric diagrams are as shown in figs. 1 (I)—6 (I).

After, on distillation, the liquid M has disappeared and only the solid substance F remains, the pressure conforming with fig. 2 (I) will fall to the pressure to which fig. 5 (I) applies. At this pressure, the reaction solid $F \rightleftarrows$ liquid $m +$ vapour m_1 now occurs. If now the vapour is continually driven off, the solid substance F will disappear and the liquid m will remain, without any change in pressure. On further distillation, the liquid transverses the distillation curve, starting from point m in fig. 3.

The liquid, therefore, proceeds first along a distillation curve terminating, at the pressure P_M in the point M, and then along another one starting from m at the pressure P_m; at the transfer of the liquid from the one to the other distillation curve, hence, between the pressures P_M and P_m, it is converted into the solid substance F.

2. The distillation temperature is lower than the maximum sublimation

point of F. The saturation- and the vapour-saturation curve of F under their own vapour pressure then have a form as in fig. 11(I), the isothermic-isobaric diagrams as in figs. 1(I), 2(I), 3(I), 4(I), 8(I), 9(I) and 10(I).

As soon, as on distillation, the liquid M has disappeared and, consequently, only the solid substance F remains, the pressure conforming with fig. 2 (I) will fall. If now, however, the pressure P_m, which now conforms with fig. 3 (I) has been attained, the solid matter F will not be capable of splitting, as in the previous case. On further lowering of the pressure, fig. 10 is formed; hence, the substance F will only appear in the solid condition. On further decrease in pressure the vapour saturation curve of fig. 10 (I) undergoes contraction and finally, at a definite pressure, coincides with the point F. The solid substance F can now be in equilibrium with vapour of the composition F, or in other words: the substance F sublimes.

Hence, the liquid first traverses, at a pressure P_M, a distillation curve terminating in the point M, where it is converted into the solid substance F, which at a further lowering of the pressure sublimes at a definite pressure. The distillation of the liquid is, therefore, finally changed into a sublimation of the solid substance F.

We will now investigate what happens when we distill a liquid saturated with a solid substance F. We take a liquid s (fig. 3) and the solid substance F in such proportion that the complex is represented by point K of the line sF. We now withdraw from this complex K a little vapour s_1, which can be in equilibrium with this complex; the complex now arrives in l and hence, is resolved into liquid $a +$ solid F. The little straight line Kl is now an element of the curve which the complex K will traverse on distillation; we will call this curve the complex distillation curve. From the deduction of this curve it now follows at once that the tangent drawn in the point K at the complex distillation curve which passes through this point, passes through the point s_1. Further, it is evident that this applies to all complexes situated on the line Fs. From this follows: in order to find the direction of the tangent to a complex distillation curve in a point (k) we should take the three-phase triangle, whose conjugation line solid-liquid (sF) passes through this point K. The line which connects this point (K) with the vapour point (s_1) of the three-phase triangle is the looked for tangent. We may express this also as follows: in the point of intersection of a complex distillation curve with a conjugation line solid-liquid the tangent to this curve passes through the vapour point correlated to that conjugation line.

From this follows: if we intersect a cluster of complex distillation curves by a conjugation line solid-liquid, the tangents in these points of intersection form a cluster of straight lines which all pass through the vapour point appertaining to that conjugation line. Further, it is evident that the vapour distillation curve representing the vapour distilling over at each moment is the vapour saturation line of F under its own vapour pressure.

We can now demonstrate that a complex distillation curve turns in each point its convex side towards the correlated vapour point and that a definite point will be a point of inflexion if the tangent which passes through this point meets the vapour saturation line of F under its own vapour pressure and if this latter point of contact is not itself a point of inflexion.

If we intersect a cluster of complex distillation curves by a conjugation line solid-liquid, then as we have seen previously, the tangents in these points of intersection all pass through the vapour point correlated to this conjugation line. If now, in the proximity of this vapour point the vapour saturation curve under its own vapour pressure is situated outside the three-phase triangle none of the above mentioned points of intersection will be a point of inflexion.

We can imagine a curve transmitted through the points of inflexion of the complex distillation curve, which we will call the point of inflexion curve; this curve may be found in the following manner. We draw to the point X of the vapour saturation line under its own vapour pressure a tangent; the point of intersection of this tangent with the conjugation line solid-liquid appertaining to the point X we will call S. If now the point X traverses the saturation curve under its own vapour pressure the point S will traverse the looked for point of inflexion curve.

This point of inflexion curve always passes through the points M_1 and m_1 of the vapour saturation curve [Fig. 7 (I), 11 (I), 12 (I)] and if we can draw through F a tangent to this vapour saturation curve also through the point F. For our purpose, only the part of the point of inflexion curve which is situated within the heterogeneous region has any significance, that is in so far as it intersects the conjugation line solid-liquid between the points indicating the solid substance and the liquid.

In the points of intersection of the saturation curve under its own pressure with the point of inflexion curve, the conjugation line liquid-vapour meets the vapour saturation curve.

In the proximity of a maximum or a minimum point of the three-phase equilibrium $F + L + G$ the three-phase triangle is very narrow and as noticed previously, we can distinguish many cases. From a consideration of these cases appears the following.

We represent, as before, the liquid with the maximum pressure by M the correlated vapour by M_1 the liquid with the minimum pressure by m and the correlated vapour by m_1. The complex distillation curves have, in the vicinity of the line FM (Fm) a direction about parallel to this line from F towards M(m) or reversedly so. If, however, the vapour point M_1 (m_1) is situated between F and M (m) they proceed from F and M (m) towards the point M' (m_1) or reversedly so, and in the vicinity of this point they inflect in definite direction away from the line FM(Fm) or towards that line.

Let us take the case of a distillation temperature lower than the maximum sublimation point of the solid substance F; the saturation line of F under its own vapour pressure and the correlated vapour line then possess a form as in fig. 11 (I). In fig. 4 a part $Mdbm$ of this saturation line has been drawn but the correlated vapour line has been omitted. From a consideration of the three-phase triangles we can readily deduce the course of the complex saturation curves; the arrows indicate the direction in which the complex moves on distillation. If these complex distillation curves are intersected by a straight line passing through the point F the tangents and curvatures in these points of intersection must then satisfy the conditions deduced therefor.

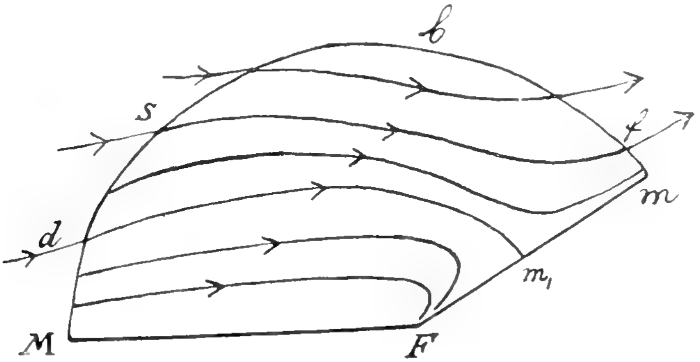

Fig. 4.

If in the vicinity of the line Fm_1m we imagine a three-phase triangle so that the vapour point is adjacent to m_1 and the liquidum point adjacent to m, we notice that a part of the complex distillation curves must proceed towards the point F and another part towards the point m, whilst there is one that, without bending towards F or m, draws near to the point m_1. This is represented by dm_1. The point b of fig. 4 corresponds with the homonymous one of fig. 3; it is, therefore, that point of the saturation line under its own vapour pressure in which the side liquid-gas of the three-phase triangle meets this saturation line. The points d and b divide the branch $Mdbm$ of the saturation line under its own vapour pressure into three parts.

On distilling the liquid d a complex $F + L$ is formed which traverses the complex distillation curve dm_1; the pressure therefore falls from P_d to the minimum pressure P_m and the liquid itself traverses the curve dbm. As the pressure gets nearer P_m, the liquid and the solid substance F will be left behind more and more in that proportion in which the vapour m_1 can be formed from them; at the last moments of the distillation we notice the solid matter and the liquid to disappear simultaneously.

Let us now take a liquid c of the branch Md. On distillation of this liquid, a complex $F + L$ is formed which traverses the complex distillation curve proceeding from c towards F. The pressure, therefore, falls from P_c to the minimum pressure P_m and the liquid itself traverses the branch cbm. The nearer the pressure gets to P_m the less liquid will be retained in the complex which finally will practically consist of the solid substance F only.

Let us now take a liquid s of the branch db; this on distillation forms a complex $F + L$ which traverses the complex distillation curve sf. Hence, the pressure falls from P_s to P_f and the liquid itself proceeds along the curve sbf; the liquid s is, therefore, converted into the liquid f at first with separation of solid matter which is then again redissolved.

We notice from this that the point d is a point of demarcation and in such a manner that all the liquidum distillation curves which meet the saturation line under its own vapour pressure between d and M do not leave the heterogeneous region, whereas those meeting this curve between d and b abandon that region.

If we take a distillation temperature higher than the maximum sublimation point but lower than the minimum melting point of the substance F the saturation- and vapour-saturation curve under their own vapour pressure will have a form as in fig. 7 (I). All liquidum distillation curves which meet this saturation curve abandon the heterogeneous region. I must leave the consideration of the other cases to the reader.

(*To be continued*).

Chemistry. — *"Equilibria in Ternary Systems"* VII. By Prof. F. A. H. SCHREINEMAKERS.

Up to now we have only considered the occurrence of a single solid substance F; we will now take the case when a second solid substance F' also appears.

Let us first investigate what happens if a mixture of both substances F and F' is brought together.

If, at a low temperature, we introduce a mixture of the substances F and F' in an evacuated space, a vapour G is formed causing the equilibrium $F + F' + G$ to appear. The vapour G is of course represented by a point of the line FF'.

According to the composition of the vapour G or in other words according to the position of the three points in regard to each other, the following reactions can occur at a supply or withdrawal of heat or at a change in volume, P and T being constant.

1. If the point G is situated between F and F' the reaction $F + F' \rightleftarrows G$ occurs. Hence, if F and F' are placed in an evacuated space a part of each of the solid substances evaporates. We will call this a congruent sublimation.

2. If the point F' is situated between F and G the reaction $F' \rightleftarrows F + G$ takes place. Hence, if both substances are placed in an evacuated space only a part of F' will evaporate while solid F is being deposited. The formation of vapour is, therefore, accompanied by a transformation of F' into F. We will call this an incongruent or transformation sublimation.

3. If the point F is situated between F' and G the reaction $F \rightleftarrows F' + G$ occurs. This case is quite analogous to that mentioned sub 2. so we call this also an incongruent or transformation sublimation.

4. As a transition case between 1 and 2 or 3 the point G can also coincide incidentally with F' or with F.

At an elevation of temperature, the vapour pressure of the system $F + F' + G$ increases when G, of course, alters its composition; hence, in a P,T-diagram we obtain a curve such as $a''D$ of fig. 1 which we will call the sublimation curve of $F + F'$. If, between the three phases occurs the reaction mentioned sub 1 we call $a''D$ a congruent, if the reaction mentioned sub 2 or 3 takes place we call $a''D$ an incongruent or transformation sublimation curve. It is evident that the one part of a curve may be a congruent and the other part a transformation sublimation curve.

On further heating the system $F + F' + G$ a temperature T_D

and its correlated pressure P_D is attained at which an infinitesimal quantity of liquid L is formed. The sublimation curve, therefore, terminates in a point D of fig. 1 representing the temperature T_D and the pressure P_D which we will call the maximum sublimation point of $F+F'$. The liquid L which forms in the point D will as a rule not be represented in an x,y-representation, by a point of the line FF'. As, however, the quantity of this liquid L is as yet but infinitely small, the vapour corresponding with the point D will still be represented by a point of the line FF'.

If the temperature is increased still further, still more liquid is formed and the four-phase equilibrium $F+F'+L+G$ appears. As, however, a finite quantity of liquid is now present, L and G must be in opposition in regard to the line FF'; only incidentally, L and G may fall both on this line.

At a constant P and T one of the following reactions takes place between the four phases on increase or withdrawal of heat or on a change in volume.

1. $F+F' \leftrightarrows L+G$ 2. $F' \rightleftarrows F+L+G$ 3. $F \rightleftarrows F'+L+G$.

We will call the reaction 1 a congruent reaction, the reactions 2 and 3 incongruent ones. Which of these reactions takes place depends on the situation of the four points in regard to each other. As the system $F+F'+L+G$ has formed from $F+F'$ it is evident that in this four-phase equilibrium L and G are always present in such proportions that both disappear simultaneously in the above reactions.

Hence by warming the system $F+F'+G$ we have arrived on the four-phase line $F+F'+L+G$. As on this line the three components are present in four phases, this system is a monovariant one, so that to each temperature appertains a definite vapour pressure.

Hence, the four-phase line in a P,T-diagram will be represented by a curve; a part of this curve is represented in fig. 1 by DS; we shall see later that it continues in the points D and S. This curve, as we shall see meets the sublimation curve of $F+F'$ in its terminal point D.

We now take a T and P at which is formed from $F+F'$ a liquid without vapour, hence the system $F+F'+L$. The liquid will then, of course, be represented by a point of the line FF'. According to the situation of L in regard to the points F and F', the following reactions may occur at a constant P and T on a supply, or withdrawal of heat, or on a change in volume.

1. If the point L lies between F and F' the reaction $F+F' \rightleftarrows L$

takes place. The liquid is, therefore, formed by the fusion of a part of each of the solid substances. We will call this a congruent or mutual fusion of $F+F'$.

2. If the point F' is situated between F and L the reaction $F' \rightleftarrows F + L$ occurs. Hence, the liquid is formed because a part of F' melts with separation of F. The formation of liquid is thus accompanied with a conversion of F' into F. We will call that an incongruent or transformation fusion.

3. If the point F lies between F' and L the reaction $F \rightleftarrows F' + L$ occurs. This case is quite analogous to the previous one.

If we change the temperature we must, of course, also change the pressure in order to keep together the three phases F, F', and L. The liquid L then also changes its composition. In a P, T-diagram we thus obtain a curve like $d''S$ in fig. 1, which we will call the melting point line of $F+F'$.

If between the three phases occurs the reaction mentioned sub 1 we call $d''S$ a congruent or mutual melting point line of $F+F'$; if the reaction sub 2 or sub 3 occurs we call $d''S$ an incongruent melting point line or the transformation melting point line of $F+F'$.

We now allow the system $F+F'+L$ to traverse the melting point line $d''S$ in such a direction that the pressure diminishes; at a definite pressure P_D and its correlated temperature T_D an infinitely small quantity of vapour will form so that the four-phase equilibrium $F+F'+L+G$ again appears. The complex therefore passes from the melting point line on to the four-phase line DS. The melting point line therefore terminates in the point S and, as we shall see presently, comes into contact with the four-phase line in this point. We will call S the minimum melting point, or the melting point of the complex $F+F'$ under its own vapour pressure. The vapour G forming in the point S will as a rule, not be represented by a point of the line FF', but the liquid L will, of course, still be represented by such a point.

The sublimation line $a''D$ and the melting point line Sd'' of the complex $F+F'$ are therefore connected with each other by the part DS of the four-phase curve. The fact that the points D and S will not, as a rule coincide may be perceived in the following manner. In the maximum sublimation point the points F, F', and G, in the minimum melting point F, F', and L are situated on a straight line. Hence, both points will coincide only then when incidentally the four phases of the system $F+F'+L+G$ lie on a straight line.

The course of the sublimation curve, of the four-phase curve and of the melting point line is, as we will see presently, determined by the relation:

$$T\frac{dP}{dT}=\frac{\Delta W}{\Delta V} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

ΔW is the quantity of heat which must be supplied, ΔV the change in volume occurring when, between the phases in equilibrium at a constant T and P, a reaction takes place in the one or in the other direction.

Let us first consider the sublimation curve $a''D$. For each of the reactions mentioned sub 1—3 taken in such a direction that vapour is formed, ΔW and ΔV are positive.

From (1) it thus follows, as drawn in fig. 1, that, at an elevation of temperature, the sublimation curve must proceed towards higher pressures. The point D lies as well on the sublimation- as on the four-phase curve. As, however, in this point D, the quantity of liquid of the four-phase equilibrium is still but infinitesimal, ΔW and ΔV are the same for both systems so that the two curves must meet in D.

Let us now consider the melting point line Sd''. We take each of the reactions mentioned sub 1—3 in such a direction that liquid is formed so that ΔW is positive. At the congruent and incongruent fusion of $F+F'$ ΔV may, however, be positive as well as negative. The melting point line can therefore, proceed from S towards the right as well as to the left; in fig. 1 the first case has been drawn. The fact that the melting point line and the four-phase line meet each other in S follows in the same manner as that given above for the meeting of the two curves in D.

In order to deduce formula (1) for the sublimation or the melting point curve, we consider the equilibrium $F+F'+G$ or $F+F'+L$. We represent the composition of F by α, β, that of F' by α', β', that of L or G by x, y. We call the volumina of these phases v, v' and V, the entropies η, η' and H, the thermodynamic potentials ζ, ζ' and Z.

As F and F' are in equilibrium with L (G) we have:

$$Z-(x-\alpha)\frac{\partial Z}{\partial x}-(y-\beta)\frac{\partial Z}{\partial y}=\zeta \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$Z-(x-\alpha')\frac{\partial Z}{\partial x}-(y-\beta')\frac{\partial Z}{\partial y}=\zeta' \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

From the condition that the three points F, F' and L (G) are situated on a straight line, follows:

$$(x-\alpha)(y-\beta')=(x-\alpha')(y-\beta) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

From these relations between the four variables x, y, P and T follows:

$$\{(x-\alpha)\, r + (y-\beta)\, s\}\, dx + \{(x-\alpha)\, s + (y-\beta)\, t\}\, dy = AdP - BdT \quad (5)$$

$$\{(x-\alpha')\, s + (y-\beta'\, t\}\, dx + \{(x-\alpha')\, s + (y-\beta')\, t\}\, dy = A'dP - B'dT \quad (6)$$

$$(\beta-\beta')\, dx = (\alpha-\alpha')\, dy \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

If from this we wish to deduce the relation between dP and dT we may divide (5) by (6). In consequence of (4) we get:

$$\frac{x-\alpha}{x-\alpha'} = \frac{AdP - BdT}{A'dP - B'dT} \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

or after reduction:

$$\frac{dP}{dT} = \frac{(\alpha'-\alpha)\, H + (x-\alpha')\, \eta + (x-\alpha)\, \eta'}{(\alpha'-\alpha)\, V + (x-\alpha')\, v + (x-\alpha)\, v'} \quad . \quad . \quad . \quad . \quad (9)$$

which corresponds with formula (1).

Hence, as we have seen above, if we choose the exact conditions, we can compel the complex $F+F'$ to traverse the sublimation curve $a''\,D$, the four-phase curve $D\,S$ and the melting point curve Sd''. We will now investigate which conditions of the complex $F+F'$ are represented by points situated outside these curves. We distinguish therein different cases.

1. The complex $F+F'$ has a congruent sublimation line, four-phase line and melting point line.

Let us first introduce the complex $F+F'$ in a point of the sublimation curve so that $F+F'+G$ is formed. From a consideration of what happens on supplying or withdrawing heat or on a change in volume we deduce: at the right of and below the line $a''D$ are situated the regions $F+G$ and $F'+G$, at the left of and above curve $a''D$ is situated the region $F+F'$.

Acting in a similar manner with points of the other curves we find:

at the left of and above $a''DSd''$ is situated the region $F+F'$.
at the left of and below $a''D$ are situated the regions $F+G$ and $F'+G$
,, ,, ,, ,, ,, ,, DS ,, ,, ,, ,, $F+L+G$ and $F'+L+G$
,, ,, ,, ,, ,, ,, Sd'' ,, ,, ,, ,, $F+L$ and $F'+L$.

Let us enter the region $F+L+G$ from a point of the fourphase curve in a horizontal direction. We then, at a constant pressure, raise the temperature of the system $F+L+G$. The liquid and the vapour of this system then traverse a part of the boiling point and vapour boiling point curve of the substance F.

If we enter the region $F+L+G$ from a point of the four-phase curve in a vertical direction we then, at a constant temperature, lower the pressure of the system $F + L + G$; the liquid and the vapour of this system then traverse a part of the saturation- and vapour saturation curve of the substance F under its own vapour pressure.

The same applies if we enter the region $F' + L + G$ from a point of the four-phase curve. In order to find the limitation of the different regions we draw in fig. 1 the sublimation curve aK, the three-phase curve KF and the melting point curve Fd of the compound F and the same curves $a'K'$, $K'F'$ and $F'd'$ of the compound F'. We will assume that F and F' also melt with increase in volume. The curves Fe and Kf have the same significance as the homonymous curves in fig. 3 (III); the same applies to the curves $F'e'$ and $K'f'$. The question now arises: where are these curves situated in regard to the corresponding curves of the complex $F + F'$.

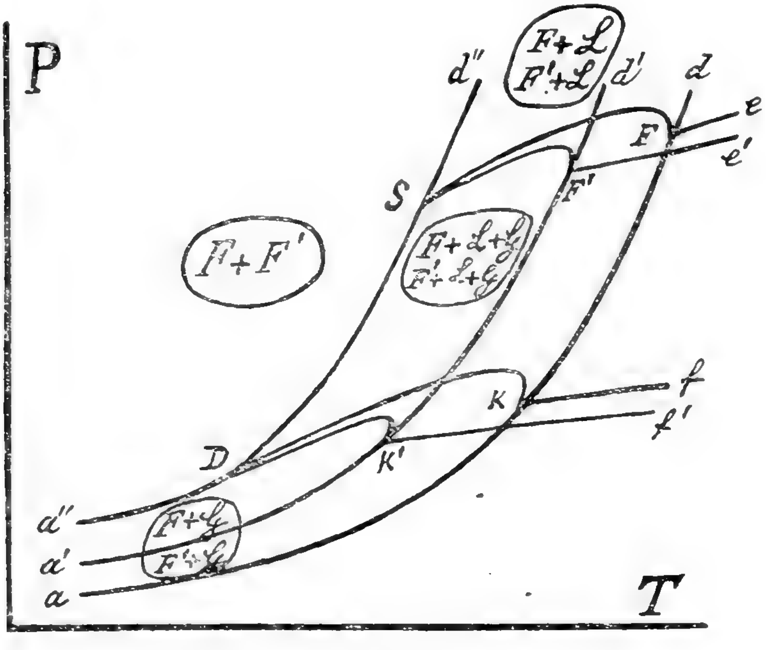

Fig. 1.

Let us first take a pressure so high that F and F' as well as their complex $F + F'$ have a melting point. Now, as is well known, the mutual melting point of $F + F'$ is situated lower than than of each of the components individually. A horizontal line intersecting the three melting point lines must therefore intersect the melting point line of $F + F'$ at lower temperature than the two other melting point lines.

In the same manner we find that a horizontal line which intersects the three sublimation curves must cut those of $F+F'$ at a lower temperature than in the case of the two other ones.

Curve $a''DSa''$ must, therefore, be situated in regard to the curves $aKFd$ and $a'K'F'd'$ as in Fig. 1.

The regions $F+L$ and $F+L+G$ are separated from each other by means of a curve, where $F+L$ appears in the proximity of an infinitesimal amount of vapour. We call this system $F+L+G^\circ$; G° signifies here that the other phases can be in equilibrium with a vapour of the composition G but that only an infinitesimal amount of that vapour is present.

If, owing to solution of large quantities of F in a small quantity of L, the system $F+L+G^\circ$ approaches to solid $F+$ liquid $F+G^\circ$ the system $F+L+G^\circ$ then approaches the minimum melting point of the substance F.

If from $F+L+G^\circ$ the solid substance F' is separated, so that the system $F+F'+L+G^\circ$ is formed, we find ourselves in the minimum melting point of complex $F+F'$.

Hence, the P, T-curve of the system $F+L+G^\circ$ proceeds in fig. 1 from S towards F.

In the previous communication IV we have already extensively considered this system $F+L+G^\circ$. The liquid L of this system traverses at an elevation of temperature a straight line passing, in the x, y-representation, through the point F, for instance the line ZF or Z_1F in fig. 1 (IV). The P,T curve corresponding with this line is represented in fig. 4 (IV) by curve ZF or Z_1F. The curve SF must, therefore as a rule come into contact with the melting point line Fd in the point F. In fig. 1 it has been assumed that curve SF corresponds with branch ZF of fig. 4 (IV).

The regions $F'+L$ and $F'+L+G$ are separated from each other by a curve $F'+L+G^\circ$; in a similar manner as above we find that this is represented by a curve SF'. In fig. 1 we have drawn the two curves SF and SF' in agreement with branch ZF of fig. 4 (IV) ; we might have drawn both or one of them also in agreement with branch Z_1F of this figure. The boundary curve of the regions $F+L+G$ and $F+G$ is formed by the system $F+L^\circ+G$; that of the regions $F'+L+G$ and $F'+G$ by the system $F'+L^\circ+G$. L° signifies here that the other phases may be in equilibrium with a liquid L, but that only infinitely little of that liquid is present. In an analogous manner as above we find that the P, T-curves of these systems are represented in fig. 1 by the curves SK and SK'. These curves meet in K and K' the curves

$a\,d$ and $a'\,d'$. On both curves a point with a maximum pressure and one with a minimum temperature is supposed to occur.

Besides the regions whose limitations we know now we find at the right of curve $a'\,d'$ also the regions $L + G$, L and G which, however, are not drawn in the figure.

In order to survey the connection of these regions we might draw a representation in space; for this we imagine the composition of the complex $F + F'$ to be placed perpendicularly to fig. 1. Instead of the spacial representation itself we will here consider its sections with planes.

If we place a plane perpendicularly to the concentration-axis we get a P,T-diagram which applies to a definite complex, if we place a plane perpendicularly to the T-axis we get a pressure-concentration diagram which applies to a definite temperature, and if we place a plane perpendicularly to the P-axis we get a temperature-concentration diagram which applies to a definite pressure.

Let us place first a plane, which intersects the three sublimation curves, perpendicularly to the T-axis; we then obtain a section as in fig. 2 in which F and F' represent the two compounds F and F'. Perpendicularly to this line FF' is placed the P-axis.

In order to be able to indicate readily the different regions occurring in this and the following diagrams we will represent:

The liquidum region by L, the vapour region by G, the solid region by $F + F'$, the region $F + G$ by 1, $F' + G$ by 2, $F + L$ by 3, $F' + L$ by 4, $L + G$ by 5, $F + L + G$ by 6 and $F' + L + G$ by 7.

If in fig. 1 we suppose a straight line, which intersects the three sublimation curves, to be drawn parallel to the P-axis, we notice that in fig. 2 the regions $F + F'$, $1 = F + G$, $2 = F' + G$ and the region G must appear. The points s, s' and s'' represent the sublimation pressures of the solid substances F and F' and of their complex $F + F'$; the complex, therefore, has a higher sublimation pressure than each of its components by itself.

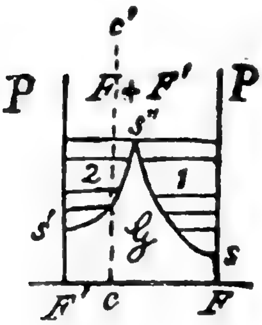

Fig. 2.

The curve ss'' represents the vapours which can be in equilibrium with solid F, curve $s's''$ those which can be in equilibrium with solid F'; these curves have in s and s' a horizontal tangent.

We now take a complex $F + F'$ of the composition c, so that the complex itself is represented by a point of the line cc'. As this line intersects the regions $F + F'$, 2 and G, then according to the pressure chosen, there is formed either $F+F'$ or $F'+G$ or G. If the complex has such a composition that the line cc' intersects the regions $F+F'$, 1 and G either $F+F'$ or $F+G$ or G is formed.

Let us now take a pressure concentration diagram for a temperature higher than the maximum sublimation point, but lower than the minimum melting point of the complex $F+F'$. If in fig. 1 we draw a vertical line which intersects curve DS we notice that this diagram may be represented by fig. 3.

Besides the regions G, $F+F'$, 1 and 2 which appear already in fig. 2 we also find here the regions:

$$5 = L + G, \qquad 6 = F + L + G \quad \text{and} \quad 7 = F' + L + G.$$

If from $F+F'$ is formed one of the systems G, $F+G$ or $F'+G$, the vapour G always has a composition that can be represented by a point of fig. 3; the same applies to the liquid L if from $F+F'$ is formed one of the systems L, $F+L$ or $F'+L$.

If, however, $L+G$ is formed as in the systems $L+G$, $F+L+G$ and $F'+L+G$, such, as we have seen previously, is no longer the case and neither L nor G can be represented by a point of the diagram.

Let us take for example a complex K (not drawn in the figure); this complex is resolved into a liquid L and a gas G, both situated outside the plane of fig. 3. If L is situated above this plane, G lies below the same and reversedly so and in such a manner that their conjugation line intersects the region 5 in the point K.

If we take a complex K' within the region 6 (7), we then suppose this to be resolved first into F (F') and a complex K of $L+G$; the complex K is, of course, represented by a point of fig. 3. To this complex now applies the same as to the complex K within the region 5.

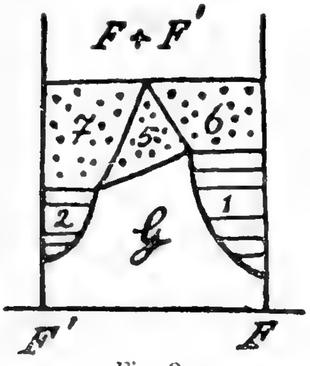

Fig. 3.

Hence, if from $F+F'$ is formed a system in which $L+G$ appears, the complex $L+G$ is certainly represented by a point of fig. 3 but L and G separately are not; one of these phases lies in front of, the other behind the plane of fig. 3. By way of distinction from the other regions, the regions 5, 6, and 7 are dotted; we may imagine that these points represent the points of intersection of fig. 3 with the conjugation lines liquid-gas. We have noticed previously that in some systems occurs only an infinitesimal quantity of L or G; of a similar complex L^0+G or $L+G^0$ the gas is represented by a point of the diagram in the first case; the liquid in the second case.

The line of demarcation of the regions 1 and G represents the vapours which can be in equilibrium with solid F, that of the regions 2 and G those which can be in equilibrium with solid F'. The line of demarcation of the regions 5 and G represents the equilibrium $L^\circ + G$, that of the regions 5 and 6 the complex $L + G$ of the system $F + L + G$ and that of the regions 5 and 7 this same complex of the system $F' + L + G$.

If in agreement with fig. 1 we take a temperature higher than the minimum melting point S of the complex $F + F'$ and lower than the maximum sublimation point K' of the substance F' we obtain a diagram as in fig. 4. If in agreement with fig. 1 we take a temperature higher than the maximum sublimation point K of the substance F and lower than the minimum meltingpoint F' of the compound F' we obtain a diagram as in fig. 5. If finally we take a temperature higher than the minimum melting point F of the compound F we obtain a diagram as in fig. 6.

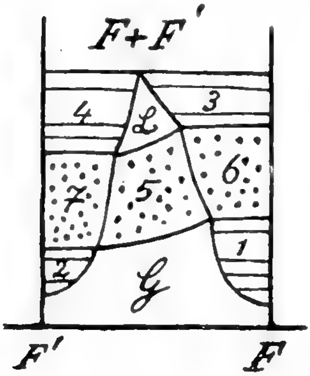

Fig. 4.

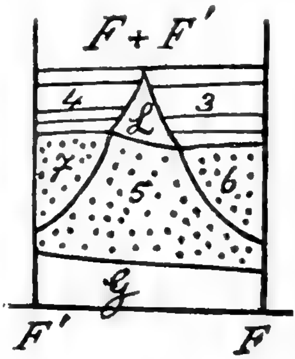

Fig. 5.

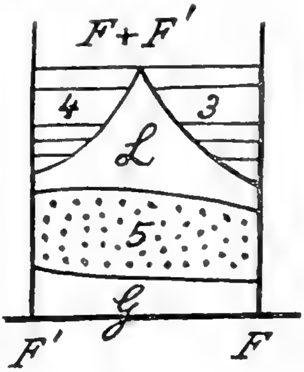

Fig. 6.

Between the diagrams figs. 2—6 exist different transition forms; we must also consider the possibility that, in fig. 1, we can draw lines parallel to the P-axis which cut the curves DK, DK', SF and SF' in two points. We will not, however, discuss here these transition forms.

When deducing the diagrams it has also been assumed that the points D, K', K, S, F' and F are situated in regard to each other as drawn in fig. 1. But this may be different.

As a rule, the points S, F', and F and also the points D, K' and K will lie in regard to each other as assumed in fig. 1. The minimum melting point of the complex $F + F'$ is therefore, as a rule situated at a lower temperature and pressure than the minimum melting point of each of the substances F and F' separately.

For in fig. 1 we have assumed that curve SF corresponds with branch ZF of fig. 4 (IV) and that S is situated on the rising part of this branch and is removed far from the point with the maximum pressure. If, however, S lies on this branch somewhere between the point with the maximum pressure and that with the maximum temperature the curve SF in fig. 1 no longer exhibits a pressure maximum but only a temperature maximum; the pressure in the minimum melting point of $F+F'$ is then higher than that in the minimum melting point of F.

If S is situated on branch ZF somewhere between the point with maximum temperature and the point F, curve SF in fig. 1 proceeds from S towards lower temperatures and pressures. In that case not only the pressure but also the temperature of the minimum melting point $F+F'$ is situated higher than that of F.

From our previous considerations as to curve ZFZ_1 of fig. 4 (IV) it follows that the latter case can occur only then when the liquid formed at the minimum melting point of $F+F'$ differs but little in composition from the substance F.

From these considerations follows: at a constant pressure the melting point of the complex $F+F'$ is always lower than that of each of the substances F and F' separately. As a rule the minimum melting point of $F+F'$ is also lower than that of each of the compounds individually. By way of exception, the minimum melting point of $F+F'$ may, however, be somewhat higher than that of one or even of both of the substances F and F'.

We shall see later that in this case at the temperature of the minimum melting point of $F+F'$, the saturation curve of F or F' under its own vapour pressure is exphased.

A similar consideration applies to the maximum sublimation points of the complex $F+F'$ and the compounds F and F'.

Let us now bring a complex $F+F'$ of a definite composition c_0 to a temperature T_0 and a pressure P_0. In order to investigate in which of the 10 possible conditions this complex will now occur we take a pressure concentration diagram of the temperature T_0 and place in this the concentration c_0 and the pressure P_0 of the complex. If now the figurating point lies for instance in region 7, $F'+L+G$ is formed, if in region 3, $F+L$ is formed, if it lies in region G it is converted wholly into gas, in region L wholly into liquid, etc.

Besides the pressure concentration diagrams considered above we may also deduce from fig. 1, or its corresponding spacial representation, temperature concentration diagrams for a complex of a definite composition; I will, however, not go into this any further.

2. The complex $F + F'$ has an incongruent sublimation line, four-phase line, and melting point line.

We will assume that both liquid and vapour have such a composition that on the sublimation curve $a''D$ (fig. 1) occurs the reaction $F' \rightleftarrows F + G$, on the four-phase curve DS the reaction $F' \rightleftarrows F + L + G$ and on the melting point curve Sd'' the reaction $F' \leftrightarrows F + L$. Hence if F' is placed in an evacuated space and if gas is generated, then according to the capacity of this space $F + F' + G$ or $F + G$ is formed or merely a vapour G of the composition F'; if liquid and vapour are generated $F + F' + L + G$ is formed, or $F + L + G$, or $L + G$; if liquid is generated $F + F' + L$ is formed or $F + L$ or merely a liquid of the composition F'.

From F' according to the conditions chosen, one of the complexes $F + F' + G$, $F + G$, G, $F + G$, $F + F' + L + G$, $F + L + G$, $L + G$, $F + F' + L$, $F + L$ or L will form or else the compound F' may remain unchanged. If only L or G is formed these will, of course have the same composition as the compound F'. Hence, we can never obtain from the compound F one of the complexes $F' + G$, $F' + L + G$ or $F' + L$ unless these appear in a metastable condition.

In fig. 1 all curves relating only to the compound F' ($a'K'$, $K'F'$, Fd' $F'e'$ and $K'f'$) and the regions encompassed by them, therefore represent only metastable conditions of the compound F'; hence, they cannot be realised in the stable condition. If, therefore, the compound F' is introduced into an evacuated space it will not occur in the conditions which correspond with the P, T-diagram of F', but with those corresponding with the P, T-diagram of the complex $F + F'$.

The terminal point D of the sublimation curve $a''D$ is here not only the highest sublimation point of the complex $F + F'$, but it also represents the highest pressure at which the conversion of F' into F takes place by the side of gas; the initial point S of the melting point curve Sd'' is here not only the lowest melting point of the complex $F + F'$, but represents also the lowest pressure at which the conversion of F' into F takes place in presence of liquid.

From a consideration of what happens with the complex $F + F'$ on supply or withdrawal of heat or on a change in volume we deduce:

At the loft of and above $a''DSd''$ is situated the region $F + F'$
,, ,, right ,, ,, below $a''D$,, ,, ,, ,, $F + G$
,, ,, ,, ,, ,, ,, DS ,, ,, ,, ,, $F + L + G$
,, ,, ,, ,, ,, ,, Sd'' ,, ,, ,, ,, $F + L$.

These regions are, therefore, situated, with regard to the curve $a''DSd''$, in the same manner as in fig. 1. It is also evident therefrom that in the P,T-diagram the regions $F' + G$, $F' + L + G$ and $F' + L$ are wanting.

In order to survey the connection of these regions we might draw a representation in space by now also placing perpendicularly to fig. 1 the composition of the complex $F + F'$. From this spacial representation we might then deduce the pressure concentration the temperature concentration and the P,T-diagrams for definite concentrations. We will, however, not go into this matter any further just now.

3. Some other cases.

Up to now, we have supposed that F and F' melt with increase in volume and that this is also the case with the congruent and incongruent melting of the complex $F + F'$; in agreement therewith, the temperature on each of the three melting point curves in fig. 1 increases with elevation of pressure.

We now see at once that there are many cases to be distinguished; the reader himself can easily introduce the necessary alterations.

Further, we have supposed sub 1 that in each point of the curve $a''DSd'$ occurs a congruent reaction and sub 2 that in each point of this curve an incongruent reaction appears. It is evident that in this respect also many cases may be distinguished of which I will briefly mention a few.

We imagine on the sublimationcurve a point l; on the part $a''l$ occurs, between the phases of the complex $F + F' + G$, the congruent reaction $F' + F \rightleftarrows G$; on the part lD the incongruent reaction $F' \rightleftarrows F + G$. In the point l itself the compound F will then take no part in the reaction but the reaction $F' \rightleftarrows G$ takes place in which G has the same composition as F'.

Hence, in the point l occurs the complex $F + F' +$ vapour F'; in l therefore, also exists the complex $F' +$ vapour F'. From this follows that l is not only a point of the sublimation curve $a''D$ but also of the sublimation curve $a'K'$.

Now, the direction of these curves in each point, therefore also in l is determined by $T\frac{dP}{dT} = \frac{\Delta W}{\Delta V}$. As, however in the point l the reaction in the two systems $F + F' +$ vapour F' and $F' +$ vapour

F' is the same (namely, $F' \rightleftarrows$ vapour F') ΔW and ΔV are also the same for both systems. The curves $a''D$ and $a'K'$ must, therefore meet in the P, T-diagram in the point l.

A corresponding property holds when a corresponding point l is situated on the four-phase curve, or on the melting point curve of the complex $F + F'$.

Hence, if the sublimation line, the four-phase line or the melting point line of the complex $F + F'$ is in a part a congruent and in a part a transition curve, the curve of the complex in the P,T-diagram will meet in its transition point the corresponding curve of that compound which is being converted.

If there are two transition points, many cases may present themselves, according to their situation, the compound converted etc., which we will not discuss here any further.

(*To be continued*).

Chemistry. — "*The system sodium sulphate, manganous sulphate and water at* 35°[1]). By Prof. F. A. H. SCHREINEMAKERS and D. J. VAN PROOIJE.

In this system occur as solid phases, which can be in equilibrium at 35° with saturated solutions: anhydrous Na_2SO_4, the hydrate $MnSO_4 . H_2O$ and the two anhydrous double salts:

$$D_{9.10} = (Mn\,SO_4)_9 . (Na_2\,SO_4)_{10} \text{ and } D_{1.3} = Mn\,SO_4 . (Na_2\,SO_4)_3.$$

The double salts previously described:

$$Mn\,SO_4 . Na_2\,SO_4 , 2H_2O \text{ and } Mn\,SO_4 . Na_2\,SO_4 . 4\,H_2O$$

have not been found by us, whereas on the other hand those now noticed have not been described up to the present. Moreover, the accurate preparation and solubility of the salts previously described are but insufficiently known, so that it is difficult to decide whether these are perhaps metastable or whether the presence of two metastable salts was, perhaps, due to accident.

The equilibria occurring at 35° are indicated schematically in the figure; the two double salts are represented by the points $D_{9.10}$ and $D_{1.3}$, the salt $MnSO_4 . H_2O$ is represented by the point Mn_1. The isotherm consists of four branches, namely

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[1]) MARIGNAC and GEIGER, A. Min. [5] **9**. 15. Mag. Pharm. **11** 27.

ab the saturation line of Na_2SO_4
bc ,, ,, ,, ,, $D_{1.3}$
cd ,, ,, ,, ,, $D_{9.10}$
de ,, ,, ,, ,, $MnSO_4 . H_2O$

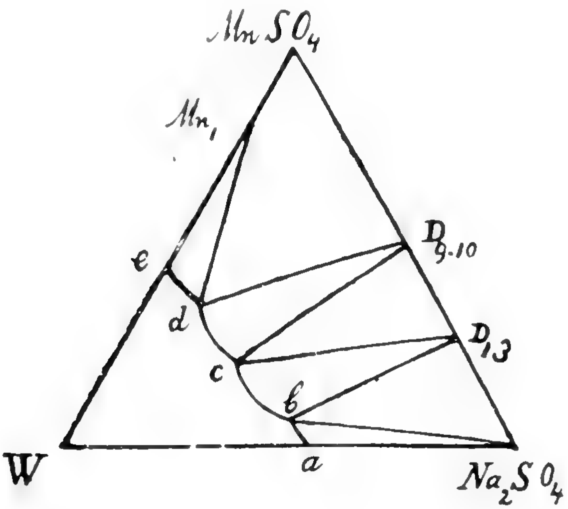
The exact position of these branches can be drawn with the aid of the determinations recorded in table I.

TABLE I.

Composition in % by weight of the solutions saturated at 35° and of the residues.

Solution		Residue		Solid phase
% $MnSO_4$	% Na_2SO_4	% $MnSO_4$	% Na_2SO_3	
39.45	0	—	—	$MnSO_4 . H_2O$
33.92	5.23	43.84	4.50	,,
33.06	7.97	50.85	23.22	$MnSO_4 . H_2O + D_{9.10}$
32.76	7.71	49.35	14.71	,,
32.92	7.42	43.49	7.76	,,
31.05	9.20	39.21	28.73	$D_{9.10}$
27.67	10.76	33.44	21.81	,,
22.14	14.28	37.44	35.46	,,
14.58	20.01	31.06	35.50	,,
13.96	21.91	24.51	40.65	$D_{9.10} + D_{1.3}$
12.19	22.49	18.63	47.18	$D_{1.3}$
10.45	23.41	18.40	49.53	,,
7.43	26.58	18.53	55.45	,,
5.69	29.31	17.02	55.00	,,
5.11	30.52	9.11	61.58	$D_{1.3} + Na_2SO_4$
2.96	31.33	1.46	67.40	Na_2SO_4
0	33	—	—	,,

From the table it is shown that the composition of the solution saturated with $MnSO_4 . H_2O + D_{9.10}$ has been determined three times. In order to be able to deduce the composition of the solid substances with which the solutions are saturated, the composition of such a solution has been determined and in addition that of the correlated residue.



As shown in the table, four solutions of branch *cd* and their correlated residues have been determined besides the two terminal points; if these are introduced into the figure and the conjugation lines are drawn, these intersect the side $MnSO_4$— Na_2SO_4 in a point indicating 48.89 °/₀ of $MnSO_4$ and consequently 51.11 °/₀ of Na_2SO_4. The double salt $MnSO_4 . Na_2SO_4$ contains, however, 51.53 °/₀ of $MnSO_4$, therefore, 48.47 °/₀ of Na_2SO_4, so that the solid substance with which the solutions of branch *cd* are saturated cannot be the double salt $MnSO_4 . Na_2SO_4$ or one of its hydrates. If from the composition (°/₀ by weight) of the point of intersection we calculate the molecular composition we find: $(MnSO_4)_9 (Na_2SO_4)_{10} = D_{9.10}$.

As shown in the table, four solutions of branch *bc* and their correlated residues have been determined besides the two terminal points *b* and *c*; these four conjugation lines intersect the side $MnSO_4$—Na_2SO_4 in a point indicating the composition of the double salt: $MnSO_4 (Na_2SO_4)_3 = D_{1.3}$. This double salt contains 26.16 °/₀ of $MnSO_4$ and consequently 73.84 °/₀ of Na_2SO_4.

The behaviour of both double salts in regard to water is shown at once in the figure if we connect therein the apex W with the points $D_{1.3}$ and $D_{9.10}$. As the line $W.D_{1.3}$ intersects the curve *bc* and the line $W.D_{9.10}$ the curve *cd*, it is evident that at 35° both double salts are soluble in water without decomposition.

Botany. — *"On intravital precipitates"*. By Prof. C. van Wisselingh. (Communicated by Prof. Moll).

(Communicated in the meeting of February 22, 1913).

The precipitates caused by basic substances in living plant cells have long attracted the attention of investigators and the literature on this subject is already voluminous. Charles Darwin was the first to investigate these precipitates. He [1]) first mentions the phenomenon in his work on insectivorous plants, and calls it aggregation. As de Vries [2]) has pointed out, Darwin includes two different phenomena under this name: in the first place, the movements which he discovered in the protoplasm of the cells of the glands of Drosera rotundifolia and other insectivorous plants, movements which occur whenever stimulation causes an increased secretion, and in the second place the precipitates which occur in the protoplasm when ammonium carbonate is used as a stimulus.

As Ch. Darwin [3]) has shown, precipitates with ammonium carbonate and with ammonia are also formed in many other cases in living plant cells. He stated that the precipitates no longer occur when the preparations are heated in water for 2 to 3 minutes to the boiling point and on this account he was inclined to consider the reaction as a vital one. With regard to the chemical nature and physiological significance of the substance of which the precipitates are composed Darwin expressed himself very cautiously. He supposed that they consist of protein and considered that we have to deal with an excretion product. He concluded his last-mentioned paper as follows: "But I hope that some one better fitted than I am, from possessing much more chemical and histological knowledge, may be induced to investigate the whole subject". From this it follows that Darwin may have thought that another explanation of the phenomenon he had discovered was also possible.

Fr. Darwin [4]) defends his father's views, as far as the chemical nature of the precipitate is concerned, which ammonium carbonate produces in the tentacles of Drosera rotundifolia. De Vries [5]) is

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[1]) Charles Darwin, Insectivorous plants. 1875, p. 38. Chapter III.

[2]) Hugo de Vries, Ueber die Aggregation im Protoplasma von Drosera rotundifolia. Bot. Zeit. 44. Jahrg. 1886, p. 1.

[3]) Charles Darwin, The Action of Carbonate of Ammonia on the Roots of certain Plants. The Journal of the Linnean Society. Botany. Vol. XIX. 1882, p. 239.

[4]) Francis Darwin, The process of aggregation in the tentacles of Drosera rotundifolia. Quarterly journal of microsc. science. Vol. XVI. 1876, p. 309.

[5]) l. c. p. 42 ff. and 57 ff.

also of the opinion that the precipitate belongs to the group of the proteins, as far as its behaviour towards reagents is concerned.

The precipitates caused by ammonium carbonate in the cell-sap of Spirogyra and of other plants, have also been investigated by PFEFFER[1]. In his opinion they are composed of protein tannate and give reactions both with protein- and with tannin-reagents.

LOEW and BOKORNY[2]) have written numerous papers on the subject of precipitation in living plant cells by various basic substances. In these publications, the same points generally have been stated, so that they can here be dealt with together.

In the opinion of these two investigators the precipitates which have been caused in the cells by ammonium carbonate, antipyrine and caffeine consist of active protein. The bodies of which the precipitates are composed, called by these writers proteosomes, can be formed both in the protoplasm and in the cell-sap. According to LOEW and BOKORNY the formation of proteosomes is a real vital reaction. When the cells have been killed, the reagents mentioned cannot any longer bring about the phenomenon, because the active protein has been changed into passive protein.

The two authors describe peculiarities of the precipitates and mention positive results which they obtained with various protein reagents. The precipitates are stated to be composed either exclusively of active protein or they contain also other substances, such as tannin, but it is emphatically declared in this connection, that the admixture of other substances is "unwesentlich".

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1) W. PFEFFER, Ueber Aufnahme von Anilinfarben in lebenden Zellen. Untersuchungen aus dem botan. Institut zu Tübingen. 2. Bd. 1886—1888. p. 239 ff.

2) O. LOEW und TH. BOKORNY, Ueber das Vorkommen von activem Albumin im Zellsaft und dessen Ausscheidung in Körnchen durch Basen. Bot. Zeit. 45. Jahrg. 1887. p. 849. — Ueber das Verhalten von Pflanzenzellen zu stark verdünnter alkalischer Silberlösung. Bot. Centralblatt. 10. Jahrg. 1889. XXXVIII. Bd. p. 581 and 614. XXXIX. Bd. p. 369. XL. Bd. p. 161 and 194. — Versuche über aktives Eiweiss für Vorlesung und Praktikum. Biologisches Centralblatt. 1891. XI. p. 5. — Zur Chemie der Proteosomen. Flora. 1892. Ergänzungsb. p. 117. — Aktives Eiweiss und Tannin in Pflanzenzellen. Flora. CI. 1911. p. 113—116. Autoreferat. Botan. Centralblatt. 32. Jahrg. 1911. I. Halbjahr. Bd. 116. 1911. p. 361.

TH. BOKORNY, Neue Untersuchungen über den Vorgang der Silberabscheidung durch actives Albumin. Jahrb. f. wiss. Bot. XVIII. Bd. 1887. p. 194. — Ueber die Einwirkung basischer Stoffe auf das lebende Protoplasma. l. c. Bd. XIX. 1888. p. 206—220. — Ueber Aggregation, l. c. Bd. XX. 1889. p. 427. — Zur Kenntniss des Cytoplasmas. Ber. d. d. bot. Gesellsch. Bd. VIII. 1890. p. 101. — Zur Proteosomenbildung in den Blättern der Crassulaceen. l. c. Bd. X. 1892. p. 619. — Ueber das Vorkommen des Gerbstoffes im Pflanzenreiche und seine Beziehung zum activen Albumin. Chemiker-Zeit. 1896. No. 103. p. 1022.

The views of LOEW and BOKORNY that precipitates caused in living plant-cells by ammonium carbonate, ammonia, antipyrine, caffeine and other basic substances are protein precipitates have been contested by AF KLERCKER [1]), KLEMM [2]) and CZAPEK [3]). All these consider that the precipitates are in reality tannin precipitates. On treating these and the cell-sap with protein reagents they always obtained negative results, while on the other hand tannin reagents gave positive ones.

It is worthy of notice that KLEMM in connection with his experiments with methylene-blue regards tannin as of secondary importance in the case of Spirogyra. Here another as yet unknown substance might cause the precipitate.

CZAPEK states that the precipitates may sometimes take up other substances, such as colouring-matter from the cell-sap and lipoids. Also, in spite of the negative results of experimental investigation, he thinks that the precipitates sometimes may contain protein substances, because the latter occurs in the cells.

There is a divergence of opinion between the last-mentioned investigators as to the place where the precipitates occur. AF KLERCKER holds that they occur in the cell-sap. KLEMM thinks that detailed study will probably show more and more, that they are formed exclusively in the cell-sap and not in the protoplasm or in both, as BOKORNY wrongly asserts for the Crassulaceae. On the other hand CZAPEK believes, that they can occur in the cell-sap and in the cytoplasm as, inter alia, may be the case in the leaf of Echeveria.

In 1897 an interesting investigation by OVERTON [4]) was published. He experimented on Spirogyra with ammonia, amines, caffeine, pyridine, quinoline, piperidine, and alkaloids. He has no doubt at all that the precipitates which are found in the cell-sap are compounds of tannin with the above substances. He describes in detail the phenomena which are brought about by solutions of caffeine of different strength, namely, when successively stronger or weaker solutions are added. In explanation it is said that the compound of tannin and caffeine are in a condition of hydrolytic dissociation.

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[1]) J. E. F. AF KLERCKER, Studien über die Gerbstoffvakuolen. Inaug. Diss Tübingen 1888.

[2]) P. KLEMM, Beitrag zur Erforschung der Aggregationsvorgänge in lebenden Pflanzenzellen. Flora 1892, p. 395. — Ueber die Aggregationsvorgänge in Crassulaceenzellen Berichte d d. bot. Gesellsch. Bd. X. 1892, p. 237.

[3]) F. CZAPEK, Ueber Fällungsreaktionen in lebenden Pflanzenzellen und einige Anwendungen derselben. Ber. d.d. bot. Gesellsch. Bd. XXVIII. 1910. Heft V. p. 147.

[4]) E. OVERTON, Ueber die osmotischen Eigenschaften der Zellen in ihrer Bedeutung für die Toxikologie und Pharmakologie. Zeitschr. f. Physikal Chemie XXII. Bd. 1897, p. 189.

Shortly before the appearance of CZAPEK's publication quoted above I [1]) made a preliminary communication on the demonstration of tannin in the living plant and on its physiological significance. While searching for a method of studying the physiological significance of tannin in Spirogyra my attention was also drawn to antipyrine and caffeine, substances which had not then been used for that purpose. Like OVERTON I described the precipitates as tannin precipitates and have never for a moment thought of regarding them as protein precipitates. All the results were in agreement with the view that they were tannin precipitates. In the paper referred to above I drew attention to the fact that they were earlier described erroneously by LOEW and BOKORNY [2]) as protein precipitates. To this these authors [2]) soon replied.

In connection with the various views on the chemical nature of intravital precipitates, I have further considered whether protein might occur in them and subsequently performed some experiments on Spirogyra maxima (Hass.) Wittr. which in my opinion render much more certain the view that the precipitates contain no protein, than was already the case. It follows moreover from these experiments that the precipitates occur in the cell-sap and not in the cytoplasm. I will first explain this point.

BOKORNY [3]) assumes that in *Spirogyra* proteosomes are formed in the cytoplasm as well as in the cell-sap. He thinks he has furnished proof of this by combining the formation of proteosomes with abnormal plasmolysis.

He placed *Spirogyra* in a mixture of equal parts of a 10°/₀ solution of potassium nitrate and a 0.1°/₀ solution of caffeine. After the action proteosomes were observed in the cytoplasm as well as in the contracted vacuole. KLEMM [4]) agrees with BOKORNY with respect to the localisation of the precipitate in Spirogyra. KLEMM first allowed the precipitate to occur and then to be plasmolysed.

When BOKORNY [5]) first brought about abnormal plasmolysis with a

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[1]) C. VAN WISSELINGH, Over het aantoonen van looistof in de levende plant en over hare physiologische beteekenis. Verslagen der Koninkl. Akad. van Wetenschappen te Amsterdam, Maart 1910. On the tests for tannin in the living plant and on the physiological significance of tannin. These Proc XII, p. 685.

[2]) O. LOEW and TH. BOKORNY, Aktives Eiweiss und Tannin in Pflanzenzellen. l.c.

[3]) TH. BOKORNY, Neue Untersuchungen über den Vorgang der Silberabscheidung durch actives Albumin. l. c. p. 206.

[4]) P. KLEMM, Beitrag zur Erforschung der Aggregationsvorgänge in lebenden Pflanzenzellen. l. c. p. 407.

[5]) TH. BOKORNY, Ueber die Einwirkung basischer Stoffe auf das lebende Protoplasma. l. c. p. 209.

10% solution of potassium nitrate and subsequently allowed basic substances to act, he found only proteosomes in the contracted vacuole and explains this by assuming that on the death of the protoplasm the active protein is changed into passive and that then no more proteosomes can be formed, so that a vital reaction is given no longer.

Without considering this explanation for the present, I content myself with pointing out that, when the above experiments are repeated, careful observation already shows that so far as the localisation of the precipitate is concerned, BOKORNY's view, accepted by KLEMM, is incorrect.

When first abnormal phasmolysis is produced with a 10% solution of potassium nitrate and this is followed by application of a 10% solution of potassium nitrate which contains in addition 1% antipyrine or 0.1% caffeine or if a rod with ammonia is then held above the preparation, precipitation takes place exclusively in the contracted vacuole. If the reagents are allowed to act simultaneously or in reverse order, i.e. if the precipitation is first produced by the antipyrine or caffeine solution and is followed by abnormal plasmolysis, then it is seen that the contraction of the vacuole is accompanied by continued expulsion of the precipitate which is surrounded by cytoplasm. If the whole process is not followed under the microscope, but if the final result alone is observed, then it is easy to imagine that precipitation has also taken place in the cytoplasm and thus to draw an erroneous conclusion, as did BOKORNY.

As already mentioned, some investigators have obtained all possible protein reactions with the intravital precipitates, whilst others have only got negative results. I may remark that protein reactions at our disposal are in general not sensitive as microchemical reactions. When these reactions, namely, the test with sugar and sulphuric acid, the biuret test, MILLON's test and the nitric acid test, are tried on minute pieces of coagulated egg-white, the various colorations can indeed be easily seen, but yet it is noticed that most of the reactions can have no great value for microscopic investigation. With MILLON's reaction, and the nitric acid and biuret tests the colour with very thin pieces of egg-white is very faint.

With a minute object such as the protoplast of Spirogyra which in addition to protein contains also other substances, little is to be expected from the three last-mentioned reactions. In accordance with this I did not obtain favourable results, but the reaction with sugar and sulphuric acid yielded better ones. The objects were left in a sugar solution for some time and then sulfuric acid was allowed to flow in. I used a mixture of 9 parts by weight of concentrated sulphuric acid and one part by weight of water, therefore sulphuric acid of $85^1/_2\,\%$. This mixture has a much smaller carbonising action on the sugar than concentrated sulphuric acid and is therefore to be preferred. With small pieces of egg-white the reaction is very striking. At first the colour is red (compare Klincksieck et Valette, Code des Coleurs, 1908, N°. 16 and 21), sometimes with a very weak violet tint, then pure red (Kl. et V. N°. 41) and afterwards orange-red (Kl. et V. N°. 51). With very thin pieces the colour is still observable. The reaction is also very suitable for microchemical use. In Spirogyra the protoplasts are coloured a distinct light red, the nucleus with the nucleolus and the pyrenoids are darker.

At this point I mention a reaction which is indeed not a real protein reaction, but which may sometimes serve for the indirect microchemical demonstration of protein, namely, the test with tannin and iodine in potassium iodide solution. In botanical papers I have found it stated that iodine in potassium iodide solution gives a precipitate with a tannin solution and can be used to demonstrate tannin microscopically. I have not been able to confirm this and it is moreover in conflict with what is generally stated in chemical handbooks, namely, that a tannin solution is coloured violet by means of an iodine solution such as iodine in potassium iodide. Of course care must be taken that the violet colour is not masked by the addition of much iodine. In chemical books I have found no mention of a precipitate.

When hide-powder or pieces of egg-white are brought into contact with a tannin solution, washed with water after some time and then treated with iodine in potassium iodide solution, they usually show a dirty brown colour; after repeated washing with water a fine violet colour (Kl. et V. 591, 596) appears, however.

This reaction can also be applied to Spirogyra, but in this case the tannin solution is unnecessary, because Spirogyra itself contains tannin in solution in its cell-sap. The filaments of Spirogyra are warmed to 60° in water. They are then killed, the tannin leaves the vacuole and partly combines with the protein of the protoplast. If the filaments are now treated with iodine in potassium iodide solution and afterwards washed with distilled water until the iodine reaction of the starch disappears, it is then found that those parts of the protoplast which are rich in protein, are coloured violet. The nuclei with the nucleoli are finely coloured, the pyrenoids more faintly.

I have been no more able to find protein in the intravital precipitates with caffeine, antipyrine and ammonium carbonate than were Af Klercker, Klemm and Czapek; neither when the precipitates with caffeine and antipyrine had been treated according to BOKORNY's[1] method with $^1/_{10}$ °/₀ ammonia and had thus become insoluble.

Nor have I been able to obtain a protein reaction when the precipitates were some weeks old and had become insoluble. Spirogyra can, it should be noted, remain alive for several weeks in a 1 °/₀ antipyrine-solution and in a 0.1 °/₀ caffeine-solution. At first the precipitates aggregate and form globules; gradually their solubility diminishes. When the filaments are then transferred into water, the globules leave vesicles behind, which have disappeared after some days. After a few weeks the globules seem altogether insoluble. In dead cells brown globules are found, which are also insoluble in water. Neither the globules nor their insoluble residues gave even a protein reaction with sugar and sulphuric acid, whilst the protoplast became distinctly coloured red. On the other hand the globules gave tannin reactions.

It is remarkable that LOEW and BOKORNY[2]), who have repeatedly insisted on the protein nature of the precipitates, assert in one of their latest publications that the colour-reactions for protein substances, such as that of MILLON and the biuret reaction, are not the most important protein tests, although they formerly relied on these. Now they prefer coagulation by rise of temperature, by alcohol and by acids.

I treated Spirogyra-filaments, with precipitates produced by 1°/₀ solution of caffeine, by BOKORNY's method with a saturated caffeine solution containing 20 °/₀ alcohol or I exposed the filaments for a short time to the action of 10 °/₀ nitric acid or warmed them to 60° in a 1 °/₀ solution of caffeine. In the first two cases I observed solution, in the last case coalescence. The results by no means proved the protein nature, as is especially evident from the following experiments.

When I mixed 1 °/₀ solutions of gallnut- or of Spirogyra-tannin with an equal quantity of a 1 °/₀ caffeine-solution and heated the mixture to 60° or added 10 °/₀ nitric acid, the precipitate which was formed underwent a modification. It agglutinated more or less and a portion had clearly become much less soluble in water, so that after some days in an excess of water there was still a considerable resinous residue undissolved. It is possible that LOEW and BOKORNY succeeded by heating and by the action of nitric acid to transform part of the precipitate in the cells into an insoluble modification, but this is by no means a proof of its protein nature.

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[1]) TH. BOKORNY, Zur Kenntnis des Cytoplasmas. l.c. p. 106.

[2]) O. LOEW und TH. BOKORNY. Aktives Eiweiss und Tannin in Pflanzenzellen. l.c

LOEW and BOKORNY[1]) declare the formation of protosomes with ammonium carbonate, antipyrine and caffeine to be a true vital reaction. They say that when the cells are dead, formation of protosomes can no longer take place, because the active protein has become passive. I shall proceed to show how, starting from dead material, precipitates can be produced with antipyrine, caffeine and other basic substances, which completely agree with those observed in living material.

That in dead cells of Spirogyra no precipitates occur with the above basic substances, is simply due to the fact that the dead protoplast and the cell-wall allow the tannin to escape. A portion of the tannin gets outside the cell and another portion enters into combination with the protein-substances present in the cell. It is specially fixed in the nuclei and the pyrenoids. Now antipyrine, caffeine and other basic substances can obviously no longer cause any precipitate in the vacuole.

It can be proved as follows that in dead Spirogyra part of the tannin passes out. Pieces of Spirogyra-filaments are placed between slide and cover-slip in a 1 % solution of egg-white or in a $^1/_2$ % gelatin or glue solution. These colloids do not penetrate into the cells and cannot therefore form any precipitate with the tannin of the cell-sap. When carefully heated above a micro-flame, the cells are successively killed. The tannin passes through the protoplasmic layer and cell-wall and forms a precipitate in the egg-white-, gelatin- or glue-solution. On careful heating the precipitate lies immediately against the Spirogyra-filament. The cells which are still alive are not surrounded by a precipitate. It can be established by using solutions of ferric salts, and other tannin reagents, that the precipitate formed outside the filament is a tannin precipitate.

When Spirogyra has been slowly heated in water to 60° in a test-tube placed in a water-bath, it dies. In this case much tannin usually combines with the protein present in the protoplast and only a little leaves the cell. When a large quantity of Spirogyra was heated to 60° in very little water, the liquid sometimes gave after filtration only a very weak tannin reaction with ferric salts, whilst the nuclei and pyrenoids always gave a distinct reaction. The nuclei and pyrenoids also gave a distinct tannin reaction with iodine in potassium iodide solution. When sufficiently washed out with water they show a fine red violet coloration.

When starting with dead material, it is desired to produce with

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[1]) O. LOEW and TH. BOKORNY, Ueber das Verhalten von Pflanzenzellen zu stark verdünnter alkalischer Silberlösung. Bot. Centralbl. Bd. XXXVIII. p. 614.

antipyrine, caffeine and other basic substances precipitates which agree with those occurring in living cells, the following method may be adopted. A number of Spirogyra-filaments are taken, washed out with distilled water, which is allowed to drip off as much as possible and then they are heated to 60°, dried as well as possible by means of gentle pressure between filter-paper, and extracted 2 or 3 times with a mixture of 4 parts of ether and 1 part of alcohol, such as is used in the extraction of tannin from gallnuts; the fluid obtained is filtered and evaporated in a vacuum. The residue, which resembles gallnut-tannin, is dissolved in a little distilled water and filtered. We thus obtain a solution, which gives all the possible tannin reactions, with ferric salts, potassium bichromate, egg-white and gelatin solutions, caffeine, antipyrine etc.

The precipitates with antipyrine and caffeine solutions, with pyridine and quinoline-vapour, and other basic substances completely resemble those occurring in living cells: little spheres or globules which show Brownian movement and gradually aggregate to larger masses, which on the addition of water dissolve and behave towards reagents as tannin precipitates, all of which completely resembles what we observe in living cells.

From the above experiments it is evident that what LOEW and BOKORNY take to be reactions of active protein are in reality none other than reactions of tannin and the proteosomes none other than precipitates of different basic substances with tannin. It is further evident that after death these precipitates can be as distinctly produced as in living cells and can therefore hardly be called vital reactions.

The question what substances the precipitates can contain in addition to tannin-compounds is more difficult to answer than it was to demonstrate the tannin character of the precipitates in living cells. That other substances may be present in the precipitates, is already clear from observations on cells containing red colouring matter as well as tannin in solution in the cell sap. The precipitates take up the red colouring-matter and large red-coloured spheres finally arise through the aggregation of many globules.

The question whether the intravital precipitates can contain protein will now be dealt with. As already stated PFEFFER[1]) assumes that the precipitate which is produced in Spirogyra by ammonium carbonate, consists of protein and tannin, which, according to him, both occur in solution in the cell-sap. The acids present in the

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[1]) l. c. p. 239.

cell-sap are supposed to prevent the precipitation of the protein by the tannin. When these acids are neutralised a protein-tannin precipitate is produced according to PFEFFER.

PFEFFER thinks that the formation of the precipitate in Spirogyra must be explained otherwise than the precipitation of tannin by ammonium carbonate, because in Spirogyra filaments a precipitate occurs with ammonium-carbonate at greater dilution than in solutions of tannin. Af KLERCKER [1]) has erroneously considered this observation incorrect. I have indeed found it to be correct and I have also come to the conclusion that organic acids can entirely or partly prevent the precipitation of protein and gelatin by tannin.

On the other hand, in order to explain his observations PFEFFER assumes various factors, without proving their existence, whilst he takes no account of other existing factors. In the first place PFEFFER ought to have considered whether the tannin in Spirogyra is really identical with gallnut-tannin. It is quite possible that the tannin in Spirogyra is a different chemical body from gallnut-tannin and behaves rather differently towards ammonium-carbonate. Then PFEFFER has failed to demonstrate the presence of organic acids in the cell-sap. Also he has not proved the presence of protein in the precipitate and moreover he has not investigated whether the formation of the precipitaie may be influenced by other substances.

As to the first point, I have found that gallnut-tannin and Spirogyra-tannin in general behave similarly towards reagents and solvents. Also a solution of ammonium-carbonate must be more concentrated in order to produce in a solution of Spirogyra-tannin a precipitate than is necessary to produce it in the living cells of Spirogyra. The first point may therefore be left.

It is otherwise with the presence of acids in the cell-sap. When Spirogyra is washed out and then disintegrated, the mass has a faint acid reaction to litmus paper but a solution of gallnut-tannin and of Spirogyra-tannin are likewise acid. A suitable microchemical method for demonstrating free acids in the cell-sap, does not appear te exist. No value can be attached to LOEW and BOKORNY's [2]) method. They lay filaments of Spirogyra in a potassium iodide solution and seeing that no iodine is set free, they infer the absence of free acid in the cell-sap. The liberation of iodine by free acid cannot be explained chemically, for although dilute acids might set free hydriodic acid from potassium iodide, they cannot liberate iodine.

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[1]) l. c. p. 37 ff.

[2]) O. LOEW and TH. BOKORNY, Ueber das Vorkommen von activem Albumin im Zellsaft und dessen Ausscheidung in Körnchen durch Basen. l. c.

I attempted to demonstrate free acid in the living cells of Spirogyra as follows. I placed Spirogyra in a solution of potassium iodide ($0.1\,^{0}/_{0}$) and of potassium iodate ($0.025\,^{0}/_{0}$), but no separation of iodine by free acid was indicated ($5KI + KIO_3 + 6HCl \rightarrow 6KCl + 6I + 3H_2O$).

On heating Spirogyra for some time in a $0.1\,^{0}/_{0}$ solution of citric acid, before placing it in the solution of potassium iodide and iodate a very faint blue colour in the starch and faint violet coloration of the nuclei was to be seen; the latter had taken up tannin from the cell-sap, for in the meantime the cells had perished. This result points to light absorption of citric acid and separation of iodine by this acid. The method seems to yield useful results and probably in the first experiment iodine would also have been liberated, in case Spirogyra contained free acid.

It should be noted that Spirogyra is very sensitive to dilute solutions of organic acids. In a $0.1\,^{0}/_{0}$ solution of citric acid, tartaric acid, malic acid, quinic acid, it quickly dies.

On these grounds it is very improbable that Spirogyra contains so much acid that protein and tannin should be able to appear together in soluble form in the cell-sap. The experiments which I am about to describe, also show that PFEFFER has incorrectly interpreted his observations.

Whilst with many reagents it is quite easy to demonstrate tannin in the cell-sap of Spirogyra because the cell-wall and protoplasm are permeable to these reagents, the most important tannin-reagents, namely, those which belong to the protein group cannot permeate. For this reason I heated Spirogyra in egg-white-, gelatin- or glue-solutions.

On the death of the protoplasts the tannin passes through the protoplasmic layer and the cell-wall and a precipitate is formed outside the cell. If, instead of allowing the tannin to pass out, a little protein solution could be introduced into the cell-sap which contains the tannin and if we could investigate the result, this would go a long way in my opinion towards solving the problem of whether in the cell-sap protein exists in solution as well as tannin. Should the cell-sap remain clear, one might be able to assume that the cell-sap, was of such composition as to contain dissolved tannin and protein side by side. If, on the other hand, a small amount of protein-solution produced a precipitate, then this might be taken to exclude the simultaneous presence of the two substances.

I will proceed to explain how I succeeded in introducing a protein-solution into the cell-sap, causing a precipitate which on closer investigation was found to be a compound of tannin and protein.

As I[1]) have previously described, the cytoplasm in Spirogyra possesses an alveolar structure. The hyaloplasm forms the walls of the alveoli, which are filled with a watery solution. By the action of reagents the structure is destroyed without the immediate onset of death. Often the hyaloplasm is seen to form a wall, which separates different portions of the contents. If abnormal plasmolysis is produced with, for example, 10°/₀ potassium-nitrate solution then the hyaloplasm forms a wall round the contracted vacuole.

As I[2]) have previously stated, it may not be assumed that this wall is a special organ and accurately represents that part of the protoplast which in the cell constitutes the lining of the vacuole.

If dilute chloral-hydrate or phenol solutions act on the living cells, other phenomena are again observed[3]). Cytoplasm collects round the nucleus and, taking up water, forms a vesicle whose wall again consists of hyaloplasm and whose content except for the nucleus is chiefly an aqueous solution. Smaller vesicles are formed on the suspensory threads.

If instead of the last mentioned solutions a 5 °/₀ solution of ether (5 parts by weight of ether and 95 parts by weight of distilled water or ditch water) is used, then the death of the protoplasts is accompanied by the following phenomena. Cytoplasm flows towards the nucleus and collects there; the suspensory-threads are detached and are taken up by the protoplasmic mass, which has a granular appearance; round the nucleus a vesicle forms, which lies quite free in the cell sap. The wall of the vesicle is again composed of a hyaloplasmic layer; the nucleus is seen lying inside the vesicle and between the protoplasmic wall of the vesicle and the nucleus there is an aqueous solution, in which some granules can be distinguished. The protoplasmic wall is at first fluid and stretched. When the protoplast dies, this changes; the protoplasmic-wall becomes rigid and often acquires folds and creases. The nuclear-wall also, which is stretched as long as the protoplast lives, contracts irregularly. By the walls different fluids are at first separated; this also is changed by death. When the nuclear wall contracts, we may assume that its content comes into contact with that of the vesicle, but this is not accompanied by any noticeable phenomenon. It is otherwise when the content of the vesicle and the cell-sap

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[1]) C. VAN WISSELINGH, Zur Physiologie der Spirogyrazelle. Beih. zum Botan. Centralblatt. Bd. XXIV (1908). Abt. I. S. 190 ff.

[2]) l. c. p. 185 ff and 192 ff.

[3]) C. VAN WISSELINGH, Untersuchungen über Spirogyra. Botan. Zeitung. 1902. Heft VI. S. 121 ff.

come into contact. This takes place at one or more points on the circumference of the vesicle. At these points precipitates are produced, but it cannot be seen whether at first small openings or tears occur in the vesicle. It is often possible to distinguish two parts in the precipitates: the one is compact and seems to lie within the vesicle; the other is looser and occurs outside the wall of the latter.

When the precipitates are investigated with reagents, they are found to consist of protein and tannin. With sugar-solution and $85\frac{1}{2}\,\%$ sulphuric acid they become very distinctly red, especially the more compact portion; after treatment with iodine in potassium iodide solution and washing out with water they show a reddish violet colour. With ferric acetate they become blue-black, with potassium bichromate brownish-red.

From these results I think the following conclusions may be deduced. The vesicle contains a solution of protein, which is derived from the cytoplasm and probably occurs there in soluble condition in the alveolar fluid. When the protein-solution and the cell-sap containing tannin come into contact with each other, the above mentioned precipitates are formed, from which it follows, in my opinion, that in addition to tannin protein in solution cannot be present in the cell-sap. They would at once form an insoluble compound with each other. It is thus impossible that, as LOEW and BOKORNY assume, the precipitates, which are formed in the cell-sap by basic substances, are protein-precipitates or, as PFEFFER assumes, precipitates of protein and tannin.

In reality they are tannin precipitates. Although the possibility is not excluded that other substances are sometimes present in small quantity, experimental investigation yields the proof, that there can be absolutely no thought of protein-substances in the first place.

Tannin and protein are separated in the living cells in a remarkable manner. Tannin in solution occurs in the cell-sap; proteins can be demonstrated in the nucleus, the chromatophores and the cytoplasm. They are either solid, as for example, the pyrenoids of the chromatophores or dissolved, as in the cytoplasm. The nucleoli which contain a viscous substance, in which the two nucleolus-threads lie [1]) give specially clear protein-reactions.

There still remains the question why a solution of ammonium-carbonate which causes a precipitate in the cell-sap of Spirogyra, may be much more dilute than that which produces a precipitate in a solution of gallnut-tannin or of Spirogyra-tannin.

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[1]) C. VAN WISSELINGH, Ueber den Nucleolus von Spirogyra. Bot. Zeit. 1898, p. 202 — Ueber abnormale Kernteilung, l. c. 1903, p. 217.

It is obvious that in the water in which Spirogyra grows and also in the cell-sap salts are present and I have on this account traced the influence of various salts on the precipitation of gallnut- and Spirogyra-tannin by ammonium carbonate. I found that precipitation is favoured by salts; expecially is this the case with calcium salts. The formation of a precipitate in the cell-sap at greater dilution of ammonium carbonate is therefore readily explicable.

Intravital precipitates can in many case also be brought about by aniline dyes. PFEFFER [1]) has described this in detail. In particular he recommended methylene-blue which gradually produces a precipitate in the living cells of Spirogyra with a very dilute solution.

In PFEFFER'S [2]) opinion the tannin is completely precipitated as a methylene-blue compound. The precipitate is also supposed to contain protein. When the solution of methylene-blue is sufficiently dilute, the precipitation is regarded as innocuous to the vital processes. The explanation which PFEFFER gives of the phenomenon he has observed is incorrect, whilst he greatly overestimates the value of the results obtainable by his method.

PFEFFER [3]) writes: "In allen Fällen werden also Methylenblau und andere Farbstoffe wertvolle Reagentien sein, mit deren Hülfe, ohne Schädigung, Aufschlüsse über Vorkommen und Verteilung gewisser Körper in der Zelle zu erhalten sind. Mit solcher vielseitig ausnutzbaren Methode lässt sich unter richtiger Erwägung nach vielen Richtungen hin eine Kontrole des jeweiligen Zustandes des Zellsaftes und der Veränderungen dieses im Laufe der Entwicklung erreichen."

PFEFFER frequently writes of the harmlessness of his method to life. As a proof of this he cites for instance the growth of Spirogyra-filaments. In two cases this amounted in four days to 12 and 26°/₀. I must here remark that PFEFFER has made no comparative experiments. If the rate of growth of Spirogyra cells in ditch water is studied, it is seen to be much greater. After two days the increase in length in 14 cases was found to be 25 to 75°/₀ and after four days in 18 other cases 40 to 75°/₀. From PFEFFER'S results it is therefore clear that dilute solutions of methylene-blue also are harmful.

My own experiments on Spirogyra maxima with methylene-blue (methylene-blue pro usu interno, the hydrochloride), indicated that it was very harmful. In a solution of 1 part in 10000 parts of

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[1]) l. c.

[2]) l. c. p. 183 and 218.

[3]) l. c. p. 191.

ditch-water all the cells perished in one day. In solution of 1 part in 500.000 parts of ditchwater or Knopp's fluid many dead cells were seen after one day and in a solution prepared with distilled water of the same strength the number of dead cells was still greater. No growth was observed. The poisonous action of methylene-blue is the reason why there can be no question of "Kontrole des jeweiligen Zustandes des Zellsaftes und der Veränderungen dieses im Laufe der Entwicklung", as Pfeffer imagines.

It has been already demonstrated above that the cell-sap of Spirogyra contains no dissolved protein. The precipitate with methylene-blue cannot therefore as Pfeffer believes, contain protein. In his opinion the precipitate is actually a compound of tannin with methylene-blue, which cannot be brought into agreement with the fact that solutions of methylene-blue, even stronger than those used by Pfeffer remain clear with solutions of gallnut- and Spirogyra-tannin. This is not explained by Pfeffer.

It is noteworthy that when Spirogyra is placed in a dilute methylene-blue solution (1 in 500.000) there is no gradual formation of a precipitate which is coloured blue from the beginning, but there is first a colourless or almost colourless precipitate and that this is then gradually coloured a deeper and deeper blue. Of this Pfeffer makes no mention.

On examination of the precipitate with reagents tannin reactions could be obtained, for example, the black coloration with ferric acetate. It may therefore be assumed that tannin is precipitated. The quantity of the precipitate even in Spirogyras with much tannin was however, small compared with other tannin precipitates.

Hence I doubted whether the tannin is completely precipitated. After one day I could not, indeed, demonstrate any tannin in the cell-sap in addition to the precipitate, but it seems that the cells may lose tannin by exosmosis. For when, for example, pieces of Spirogyra-filaments were placed in a dilute solution of methylene-blue, containing $^1/_2\,^0/_0$ gelatin, a precipitate was formed outside the cells and between the layers of the cell-wall which separated from each other. The precipitate was a compound of gelatin with tannin and became coloured black with ferric acetate. I cannot therefore venture to assume with Pfeffer, that a complete precipitation of tannin takes place in the cell-sap.

It seems to me that various factors play their part in the production of the precipitate. In the first place the harmful action of the methylene-blue, of causing great modifications in the organism. Further the presence of salts appear to assist the formation of precipitate. In a solution of one part of methylene-blue in 500.000 parts of distilled water the phenomenon was not so clear as in a solution of the same strength made with ditch-water or KNOPP's fluid. A number of experiments in test tubes with methylene-blue, salts, gall-nut- and Spirogyra-tannin led to the conclusion that the appearance of a precipitate is not only affected by the presence of salts but that also atmospheric oxygen comes into play and finally, that methylene-blue itself has no precipitating action, but that in one way or another a tannin precipitate is formed which gradually takes up more and more of the dye. How the precipitate is produced I cannot definitely say, but its formation does certainly not depend on a simple precipitation of tannin by methylene-blue, as PFEFFER assumes.

Chemistry. — *"The influence of surface-active substances on the stability of suspensoids"*. By Dr. H. R. KRUYT. (Communicated by Prof. P. VAN ROMBURGH.)

In the chemical literature of the colloids it is generally stated that electrolytes exert a great, and non-electrolytes no action on the stability of suspensoids, at least when those non-electrolytes are not colloids themselves. BODLÄNDER[1]) found that the formation of sediment in a suspension of colloids was much accelerated by electrolytes, "dagegen sind die Nichtleiter wirkungslos". And FREUNDLICH[2]) states of a series of organic substances that they "in grossen Ueberschuss selbst bei tagelanger Einwirkung, keinen Einfluss auf die Beständigkeit des Arsensulphidsols ausübten." This, however, merely shows that these substances themselves do not cause a coagulation in a direct manner.

If, however, we take the standpoint of the ingenious theory developed by FREUNDLICH[3]), the complete absence of any influence on the stability is absurd. For when the stability is determined by the electric charge of the particle (HARDY[4]), BURTON[5])) and when this charge is formed by the selective ion-adsorption (FREUNDLICH l.c.) a cause which exerts an influence on the adsorption cannot be inert towards the stability.

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[1]) Nachr. Göttingen 1893, 267.

[2]) Diss. Leipzig, 1903, p. 13, Zeitschr. f. physik. Chem. **44**, 129 (1903).

[3]) Consult his Kapillarchemie, Leipzig 1909.

[4]) Zeitschr. f. physik. Chem. **33**, 385 (1900).

[5]) Phil. Mag. [6] **12**, 472 (1906).

Now an adsorbed substance is displaced by another adsorbed substance; this is dependent on the degree to which that second substance is itself adsorbed[1]; if to a suspensoid system is added a substance which itself becomes strongly adsorbed it would be astonishing indeed if it left the stability of the system unmodified.

As a rule, we possess a measure for the stability of a system in the limitation value.[2] Meanwhile it is as well to consider in how far we must attach value to this relation. A complete coagulation in a short time occurs when of an added electrolyte so much gets dissolved that the colloid has become isoelectric. But this adsorption will also be modified by an added substance.

If, for instance, we have a As_2S_3 sol this consists of particles of arsenious sulphide dispersed in water; these particles at their preparation have adsorbed hydrogen sulphide in such a manner that an electric double layer has formed in such a way that the layer of S''-ions lies at the side of the solid particle and the H-ion layer at that of the liquid. If now we add a substance A which is adsorbed positively, the condition of that double layer will be modified because A displaces H_2S, S'' as well as $H^{\cdot}$. When effectuating coagulation by means of an electrolyte such as $BaCl_2$, adsorption also takes place of $BaCl_2$, $Ba^{\cdot\cdot}$ and Cl' and the limitation value will be attained when the quantities of $Ba^{\cdot\cdot}$ and $S^{\cdot}$ are equivalent.[3] But this adsorption process also experiences a similar influence from the substance A. The change in the limitation value under the influence of A is therefore the resultant of those two actions. Perhaps these might just neutralise each other? This seems to have always been an assumption not mentioned. Although we know as yet but little about the displacement in the capillary layer, such a symmetry did not seem to me probable and therefore the subjoined investigation was carried out, provisionally for the purpose of orientation.

The substance to be admixed should give rise to a strongly positive adsorption and hence, according to GIBBS's principle it must strongly reduce the surface tension. In this relation account must, of course, be taken of the surface tension solid-liquid; the measurement thereof is, as yet, almost impracticable, but experience has taught us up to the present (and theoretically this may be expected) that the surface tension must as a rule proceed similarly to that for liquid gas. Hence, as strongly adsorbable components were chosen those which strongly lessen the surface tension of water.

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[1] Cf. FREUNDLICH and MASIUS, Gedenkboek VAN BEMMELEN (Helder 1910), 88.

[2] A version of the German word "Schwellenwert".

[3] Cf. WHITNEY and OBER, Zeitschr. f. physik. Chem. **39**, 630 (1902).

The subjoined investigations were, therefore, carried out to demonstrate in the first instance the existence of the influence of surface-active substances on the limitation value. Hence, they were carried out by means of an arbitrary colloid As_2S_3 sol with an arbitrary electrolyte $BaCl_2$ with addition of substances, which in diverse degrees lower the surface tension of water, namely first of all, isoamyl alcohol, isobutyl alcohol, propyl and ethyl alcohol the σ-c lines of which (σ surface tension, c molecular concentration) had been determined by TRAUBE[1]).

TABLE I. *Isoamyl alcohol.*

Conc. of the alcohol	Limitation value		Limitation value relat.
	water	alc. mixture	
0	1.08	—	1.00
66	1.08	1.16	1.07
78	1.07	1.32	1.23
92	1.07	1.38	1.29

TABLE II. *Isobutyl alcohol.*

0	0.87	—	1.00
101	0.87	0.96	1.10
201	0.87	1.02	1.17
302	0.87	1.13	1.30

TABLE III. *Propyl alcohol.*

0	0.92		1.00
197	0.92	1.06	1.15
393	0.92	1.14	1.24
787	0.92	1.30	1.41

TABLE IV. *Ethyl alcohol.*

0	0.87	—	1.00
1560	0.87	0.97	1.12

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[1]) Lieb. Ann. d. Chem. **265**, 27 (1891).

To 10 cc. of the sol were added with constant shaking 5 cc. of a solution of the organic substance (or water for the blank experiments which were repeated each time) and about 15 minutes later 1 cc. of a $BaCl_2$ solution. The whole was then again shaken and then once more two hours afterwards; the $BaCl_2$ concentration, which was just incapable to cause a *complete* coagulation, represented the limitation value. Those values may be taken as being accurate within two units in the second decimal.

In the tables are given the concentrations relating to the final total volume in millimols. per Litre. In the last column the limitation values have been recalculated so as to make the value for pure water = 1.00.

From these tables it is indeed evident that the alcohol concentration has an influence on the limitation value; this influence appeared to vary for the different alcohols and therefore it was thought desirable to make a comparison of their influence on the capillarity of water, with their adsorbing properties, and consequently with their power of displacement.

This comparison may be readily effected with the aid of the subjoined figure constructed from data obtained by TRAUBE l.c. (The line for phenol will be discussed presently). σ_{H_2O} is taken therein as 76.0.

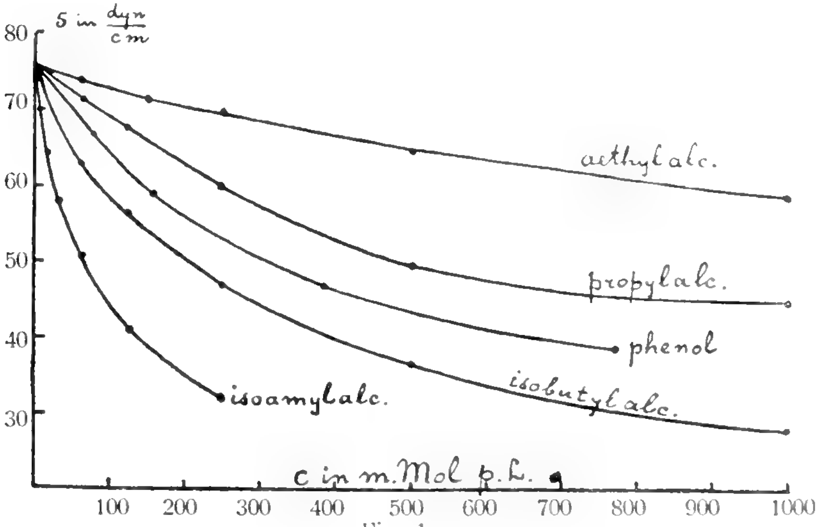

Fig. 1.

From the tables I—IV we now notice that the order of the admixed substances in which they effectuate an increase of the limitation value is: isoamyl, isobutyl, propyl, and amyl alcohol, while, according to the figure the order for the power of lowering the surface tension is the same.

This result is, therefore, undoubtedly in harmony with the adsorption theory. The only question still to be answered is why the added substances *increase* the limitation value. This however, was to be expected on account of the manner in which displacement takes place as shown from the research of FREUNDLICH and MASIUS (l.c.). What they found is as follows: Let substance A be adsorbed according to the equation:

$$\frac{x}{m} = a\, c^{\frac{1}{n}}$$

or expressed in logarithms

$$log \frac{x}{m} = log\, a + \frac{1}{n} log\, c$$

(x the quantity adsorbed, m the amount of adsorbent, c the concentration of the liquid in equilibrium, a and n constants).

If now a substance B is added in definite concentration, the adsorption of A takes place according to the equation:

$$log \frac{x'}{m} = log\, a' + \frac{1}{n'} log\, c$$

The investigation always showed that $\frac{1}{n'}$ is smaller than $\frac{1}{n}$. As the dependency of log $\frac{x}{m}$ on *log* c is represented by a straight line, we readily perceive that the reduced coefficient causes a stronger displacement of A by B in the higher concentrations of A than in the lower ones.

If now in the experiments described above the alcohol is added to the sol the concentration of the liquid in stability-promoting ions will be exceedingly small in comparison with the concentration of $BaCl_2$ when the limitation value is attained. If now we assume that the adsorption of each of these substances by itself is about the same, it will be readily perceived that the displacing influence will hinder the *charge* of the particle in a much lesser degree than the *discharge*. Hence an *increase* in the limitation value.

Meanwhile it will be as well to dispense with further theories until the matter cited above has been extended by the investigation of more colloids and other organic substances as well as of other (particularly uni- and trivalent) coagulating ions. With this investigation I have already made a start.

The following fact has already been disclosed: aromatic substances are always adsorbed much more strongly than might be surmised from their influence on the surface tension [1]). I determined stalagmometrically the σ-c figure for phenol (also given in the figure); although it appeared to lie between that of isobutyl and propyl alcohol, the influence exerted by addition of phenol is greater than that caused by isobutyl alcohol, exactly as was to be expected. This investigation is being continued, also in connection with a direct investigation as to the adsorption of the substances added.

A more extended investigation in various directions appears to me desirable all the more because the results may elucidate several other problems in the chemistry of the colloids. I will again refer to this matter in due course.

Meanwhile the results obtained are interesting when taken in connection with the researches of H. LACHS and L. MICHAËLIS [2]), who found that surface-active non-electrolytes exert no influence on the adsorption of electrolytes: the above described investigation, however, makes us surmise that although these two kinds of substances should not be put on a par with each other without further evidence, a displacement takes place nevertheless. The effect of the displacement, however, seems to elude the direct measurement, but it may be demonstrated by measurements of the limitation values. Hence, the said investigators could find a displacement effect for isoamylalcohol only, just the very alcohol which according to our research exerts the strongest power of displacement.

Utrecht, March 1913. VAN 'T HOFF-*Laboratory*.

Microbiology. — "*Potassium sulfur, and magnesium in the metabolism of Aspergillus niger.*" By Dr. H. J. WATERMAN. (Communicated by Prof. M. W. BEIJERINCK).

In earlier investigations I have shown that the elements carbon, nitrogen, and fosfor occur in large quantities in young mould material, but that, when it grows older, a considerable portion is again excreted as carbonic acid, ammonia, and fosforic acid [3]). During the development the plastic aequivalent of the carbon lowers to the half; as to the nitrogen, there is a threefold accumulation, whereas the quantity of fosfor in a young mould layer is ten times as large as that

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[1]) Compare for instance I. TRAUBE, Verh. d. deutschen physik Ges **10**, 880 (1908). In the Table on p. 901, Aniline the only aromatic compound, occupies a quite special position.

[2]) Zeitschr. f. Elektrochemie **17**, 1 (1911)

[3]) Folia microbiologica Bd. 1 p. 422, 1912. These Proceedings 1912.

TABLE I. *POTASSIUM.*

a. Nutrient liquid: Distilled water, 2 % glucose, 0,2 % ammoniumnitrate, 0,1 % magnesiumsulfate [illegible] ammonium fosfate, 0,02 % calciumnitrate (free from water), 0,04 % manganesechloride ($MnCl_2 . 4$ Aq.). $t = 34°$ C.

Nr.	Addition of KCl		Growth and spore formation after					
	milligr.	gram-mol. p. L.	1	2	3	4 5	10	30 days
1	0	0	+	+	+, few spores	+, few spores	few spores	+, hardly any spores
2	0,1	$\frac{1}{37500}$	+	+++ few spores	++, beginning sp. formation	+++, rather many sp.	rather many sp.	++++, few spores
3	0,6	$\frac{6}{37500}$	+	+++	++++, beg. sp. formation	++++, many spores	many spores	+++++, rather many sp,
4	1,0	$\frac{1}{3750}$	+	++++	+++++,beg. sp. formation	++++++, many spores	„ „	++++++, many spores
5	2,0	$\frac{2}{3750}$	+	++++	+++++, few spores	++++++. rather many sp.	„ „	++++++, many spores

b. Nutrient liquid: Distilled water, 2 % glucose, 0,15 % ammoniumnitrate, 0,1 % magnesiumsulfate (7 Aq.), 0,05 % fosforic acid (crystallised), 0,01 % $MnCl_2 . 4Aq.$ $t = 34°$ C.

Nr.	Addition of KCl		Growth and spore formation after				
	milligr.	gram-mol. p. L.	1	2	3	4	8 days
1	0	0	+	+++, no spores	++, no spores	++, few spores	++, hardly any spores
2	0,001	$\frac{1}{3750000}$		„ „	„ „	„ „	„ „ „
3	0,01	$\frac{1}{375000}$		„ „	„ „	„ „	+++, no spores
4	0,1	$\frac{1}{37500}$		++, beginning spore formation	+++, beg. sp. formation	+++, rather many spores	+++++, beginning spore formation
5	1	$\frac{1}{3750}$		+++, very few spores	+++++++, few spores	++++++, beg. spore formation	++++++, rather many spores
6	2	$\frac{2}{3750}$		++++, very few spores	„ „	+++++++, few spores	+++++++, many spores
7	5	$\frac{5}{3750}$		„ „	„ „	„ „	„ „
8	12	$\frac{12}{3750}$		„ „	„ „	„ „	„ „
9	15,5	$\frac{15,5}{3750}$		„ „	„ „	„ „	„ „
10	35,5	$\frac{35,5}{3750}$		„ „	„ „	„ „	„ „
11	85,5	$\frac{85,5}{3750}$		„ „	„ „	„ „	„ „

contained in a similar old one. Various influences on the metabolism, such as temperature, concentration, hydrogenions, boric acid, manganese, rubidium, etc., were studied, in which only changes of velocity were observed.

I have now continued these experiments, more qualitatively, with potassium sulfur, and magnesium and obtained the following results.

a. Potassium. I used a nutrient liquid of the composition given in Table I. The constituents of the solution in the series of experiments *b* were the same as those of *a*, only no calcium had been added, because, as I have shown before, the non-adding of this element under the mentioned circumstances, has no influence on the velocity or the nature of the metabolism. This was also the case with chlorine.

The cultivation was always effected in ERLENMEYER flasks of Jena glass and of 200 cm^3. capacity, the volume of the medium being 50 cm^3. The distilled water was once more purified in an apparatus of Jena glass. These experiments prove that the quantity of produced mould, even in the Nrs. *a* 1 and *b* 1, where no potassium was added, is not inconsiderable. This may be ascribed to the difficulties accompanying the exclusion of traces of this element. Further we see that by excess of potassium the spore formation is temporarily inhibited. Compare Nr. 5 with Nr. 4, after 4 and 5 days (Table *a*), and Nr. 6 and following Nrs. with 5, after 4 days (Table *b*). This inhibition of spore formation by an excess of a necessary element finds its cause in the cells being able to accumulate reserve food. [1]).

Finally Table I shows that deficiency of potassium does provoke production of mycelium but no spore formation (Nrs. 1—3, Table I *b*). Only at $\frac{1}{37500}$ gr. mol. KCl. p. L. spore forming begins after 8 days.

Formerly [2]) I have shown that potassium can but partly be replaced by rubidium. Whereas the production of mycelium is possible as well with potassium as with rubidium, spore formation takes only place with a certain percentage of potassium and not at all with rubidium. It was likewise proved that manganese is necessary for the latter process. The results given in Table I prove that at very low concentrations the action of potassium is quite analogous to that of rubidium: mycelium is formed, but hardly any spores, and this in spite of the presence of large quantities of manganese.

In the physiological action of potassium thus, two functions are to be distinguished, one corresponding with that of rubidium, the other with that of manganese.

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[1]) These Proceedings, 1912.

[2]) These Proceedings, 1912.

b. Sulfur. The results of the experiments on the action of different sulfate concentrations are found in Table II.

Here we see that in the culture tubes (N° 1), where no sulfur was added, development takes place, just as had before been observed for the nitrogen, the fosfor, and the potassium. A considerable spore formation took place after 2 days already in Nrs. 1—7, which had a deficiency of sulfur, whilst in the experiments with more sulfur the production of spores was at first slackened. Nrs. 8—20 had only few spores. After 3 days Nrs. 14—20 had hardly any, whilst in all other culture tubes an important spore formation had already occurred. After 4 days these differences were less marked; after 40 days all the mould layers were covered with a considerable number of spores. The explanation of this temporary inhibition of the spore production is the same as for the elements treated before. In other respects, too, the sulfur quite corresponds with the other elements. *Like the carbon, nitrogen, and fosfor, the sulfur accumulates in the cells and is afterwards partly excreted.*

Indirectly this could already be shown by the following considerations.

We see that in Nr. 8, after 3 days only 34,5 %, after 3 days in Nr. 9, 36 %, after 40 days already 48 % of the glucose has been assimilated, notwithstanding after 3 days no sulfate was left in the solution. Evidently during the development of the organism by the dissimilation of an intermediary product, sulfate is set free in the liquid so that the assimilation of the glucose can go on. This is still more obvious in Nrs. 11—13. After 3 days the assimilation of the glucose was 49 %, after 4 days it mounted to 61 %, and after 40 days already 82 % of the glucose had been used, whereas, here too, after 3 days already, all the sulfate had disappeared from the solution. By direct analysis was shown that an old, mature mould layer indeed contains less sulfur than a young one obtained in quite the same way and under the same conditions.

To this end the mould was, after frequent washing with distilled water, destroyed by fuming nitric acid, in a closed tube at 300° C. The sulfate was precipitated in the usual way.

It was here proved that of 4 mature mould layers (70 and 40 days old), treated in this way, after 3 to 4 hours' heating on a low flame, no precipitate was formed, whereas 4 young moulds (3 and 4 days old)[1], likewise treated, did give a precipitate after heating. In what condition the sulfur, temporarily withdrawn from the liquid, exists in the organism, must for the moment be left undiscussed.

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[1] These were the mould layers of Nrs. 14, 18, 15, 16 (Table II).

TABLE IV. *Activation of magnesium by zinc.*

Nutrient liquid: 50 cm³ of distilled water in a Jena glass apparatus, in which dissolved 2 % glucose, 0,15 % ammoniumnitrate, 0,1 % potassiumsulfate, 0,05 % potassiumchloride, 0,05 % fosforic acid (crystallised), 0,01 % manganese sulfate.

N⁰.	Added	Development after 1	3	4	12 days
1	—	—	—	—	?
2	—		—	—	—
3	—		—	—	—
4	0 001 mgr. $ZnSO_4 . 7$ Aq		Germination	+	++++
5	0,01 " " "		?	+	+
6	0,001 " $MgSO_4$ 7 Aq		—	—	—
7	0,001 " $MgSO_4 . 7$ Aq + 0,001 mgr. $ZnSO_4$ 7 Aq		—	—	Germination
8	0,001 " $MgSO_4 . 7$ Aq + 0,001 mgr. Cadmiumsulfate		—	—	—
9	0,001 " $MgSO_4 . 7$ Aq + 0,01 mgr. strontiumnitrate		—	—	?
10	0,001 " $MgSO_4 . 7$ Aq + 0,001 mgr. $HgCl_2$			—	—
11	0,005 " $MgSO_4 . 7$ Aq		—	—	—
12	0,005 " $MgSO_4 . 7$ Aq + 0,001 mgr. $ZnSO_4 . 7$ Aq		—	+ (slight)	+
13	0,005 " $MgSO_4 . 7$ Aq + 0,01 mgr. $ZnSO_4 . 7$ Aq		—	?	Germination
14	0,01 " $MgSO_4 . 7$ Aq		?	+ (slight)	+
15	0,05 " " "		Germination	+	++, no spores
16	0,1 " " "		+	++, no spores	++, no spores
17	0,3 " " "	+	++, beginning sp. formation	+++, beg. sp. formation	++++, beg. sp. formation
18	0,5 " " "	+	+++, beg. sp. formation	++++, beg. sp. formation	+++++, rather many sp.
19	1 " " "	+	++++, no spores	++++++, beg. sp. form.	++++++, many spores
20	5 " " "	+	++++++, few spores	++++++, rather many sp.	++++ +, many spores

It may finally be called to mind that with deficiency of a necessary element the metabolism of *Aspergillus niger* remains unchanged. This follows from the amounts found for the plastic aequivalent of the carbon. The table shows, namely, that only trifling differences are found for all the simultaneous determinations. We see, moreover, that those mould layers, which are more developed, possess a correspondingly lower plastic aequivalent.

c. Magnesium. Whilst in the study of the other required elements it was found that even the slightest quantities cause a perceptible growth, magnesium behaves quite otherwise. Relatively great quantities $\left(\frac{1}{2470000}\text{ gr. mol. } MgSO_4\ 7\text{ Aq. per L.}\right)$ did not, even after a prolonged cultivation, produce any macroscopically perceptible mycelium, whereas stronger concentrations $\left(\frac{2}{247000}\text{ gr.mol. } MgSO_4\ 7\text{ Aq. p. L.}\right)$, only after some days caused a considerable growth.

This result warns us to be cautious in the computation of a production in a way as suggested by MITSCHERLICH [2]) even in a relatively simple case such as the present. The results of the referring experiments are found in Table III.

The explanation of the above fact has not yet been found. It might be supposed that the metabolism of the magnesium is extremely slow; whereas for each individual cell much magnesium should be wanted. More acceptable, however, is the supposition that by absence or deficiency of magnesium some unknown factor in the medium is allowed to exert its noxious influence which may be counteracted by addition of more magnesium. Beryllium, lithium, manganese, and calcium cannot replace magnesium. (See Table III). Zinc can replace it, as is shown by the experiments, whose results are exposed in Table IV.

For cadmium, strontium, and mercury I have not as yet been able to find an action analogous to that of zinc. Nrs. 12 and 13 are in particular convincing as they show *that even the slightest quantities of zinc are sufficient to activate magnesium* (0,02 mgr. $ZnSO_4$. 7 Aq. p. L.).

The abundant growth in Nrs. 4 and 5 is also remarkable as not any magnesium was added there. This does not, however, prove that the magnesium is here replaced by zinc, as it is always possible that slight quantities of magnesium are present in the solution, so that in this case, too, the influence of the zinc may be only an

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[2]) MITSCHERLICH, Bodenkunde für Land- und Forstwirte, 2te Aufl. Berlin 1913.

activating one. This effect is the more important as hitherto I have not succeeded in the usual way to demonstrate a favourable influence of zinc.

Laboratories for Microbiology and Organical Chemistry of the Technical University

Delft, March 1913.

Physics. — *"On the law of partition of energy"*. II. By J. D. VAN DER WAALS Jr. (Communicated by Prof. J. D. VAN DER WAALS).

§ 6. It is obvious that the chance that the value of one of the variables p or q lies between specified limits cannot be represented by a normal frequency curve. If however we investigate a region of the spectrum, which is very narrow, but yet contains many elementary vibrations, then we find another probability curve than for one single elementary vibration. If the region is sufficiently small, then the radiation will appear to us to be homogeneous. Only an observation during a long time (i.e. very long compared with one period) will reveal the want of homogeneity by the increase and decrease of the amplitude in consequence of beats. In order to describe the momentaneous condition we can represent one elementary vibration by:

$$a \sin \frac{2\pi t}{T} + b \cos \frac{2\pi t}{T}$$

and the total vibration of the spectral region by:

$$(\Sigma a) \sin \frac{2\pi t}{T} + (\Sigma b) \cos \frac{2\pi t}{T}.$$

In this expression the separate a's and b's may have all kinds of values. The chance that they lie between specified limits is not represented by a normal frequency curve. But this does not detract from the fact that the chance for a specified value of $(\Sigma a) = A$, is represented by a normal curve, at least if the sum contains a sufficiently great number of terms.

Let us imagine that the decrease of the amplitude of the vibrators in consequence of the radiation has such a value, that they are perceptibly set vibrating by a great number of elementary vibrations whose period does not differ too much from the fundamental period of the vibrators, then MAXWELL's law will hold for the chance that the velocity of a vibrating particle lies between specified limits. The mean energy of a linear vibrator is probably rightly represented by the formula of PLANCK:

$$U = \frac{h\nu}{e^{\frac{h\nu}{\theta}} - 1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

so the chance that the velocity of a vibrating particle has the value s will be represented by:

$$Ce^{-\frac{\frac{1}{2}ms^2}{\frac{1}{3}U}}ds \quad \text{where} \quad {}^1/_2\,\overline{ms^2} = \frac{1}{2}\,U = \frac{1}{2}\,\frac{h\nu}{e^{\frac{h\nu}{\theta}} - 1}.$$

It is true that the formula (11) has been calculated with the aid of an equation of the form. (1) p. 1177 and that such an equation cannot hold good. But here a difference between the theory of PLANCK and the conception indicated in this communication comes to light. For if the quanta-hypothesis is right, the equation (1) cannot even approximately be fulfilled, and it is to be considered as the merest chance if it leads to the exact value for U. According to the here developed conception however, the equation (1) cannot be rigorously satisfied, but it can hold with a rather high degree of approximation, and the sharpness of the lines of the spectra seems to indicate that this is really the case. For this reason it seems to me that we have reason to expect, that we can find the average kinetic evergy of rotating particles, or of particles describing paths disturbed by collisions, with the aid of the ordinary fundamental equations of classical mechanics and electromagnetics. For this purpose we have to investigate the motions which those particles would perform according to those equations in an electromagnetic field whose partition of energy is that of the normal spectrum. According to the quanta-hypothesis it would seem doubtful whether such a calculation would yield the right value for the velocity of the particles.

These conclusions would not be justified, if it should appear that the equations of motion of the electrons cannot be approximately represented by equation (1). In this case we should have no reason to expect that the velocities of the vibrating particles are distributed according to MAXWELL's law for the partition of the velocities. It seems probable to me that the normal probability-curve will rather apply to the momenta than to the velocities. If the mass is constant we have no reason to make this difference, but in the case that the mass of the particles is variable, the fact that the normal probability curve did hold good for the momenta would involve that it could not apply to the velocities. For LORENTZ-electrons the deviations from MAXWELL's law for the distribution of the velocities, occasioned by the variability of the mass, would remain small for temperatures which are practically reached. The average kinetic energy of electrons of that nature in the normal radiation field can probably be calculated as if the mass were constant.

When we differentiate the value of the kinetic energy which we find in this manner, according to the temperature we find c_v as is well known, if only we add to it another term which accounts for the potential energy.

§ 7. *The potential energy. The distribution in space.*

For the distribution in space of particles of mass we have according to classical mechanics the following law: if n represents the number of particles per unit volume and ε the potential energy of one particle, the expression

$$n\, e^{\frac{\varepsilon}{\theta}} = \text{a constant throughout the space.} \quad . \quad (12)$$

For a mixture an expression of the same kind holds good for each of the components. If we wish to take into account the volume of the particles we may write that

$$\frac{1}{V-2b}\, e^{\frac{\varepsilon}{\theta}} = \text{constant} \quad . \quad . \quad . \quad . \quad . \quad . \quad (12a)$$

where V represents the volume of the molecular weight in grams of the substance, and $V-2b$ the "available space" present in this volume. The logarithm of this expression is, as is well known, equal to the thermodynamical potential [1]) of the component, to which the expression has relation. All thermodynamical equilibria, as well those for simple substances as those for mixtures, and also those in which electrically charged particles play a part, can be derived from the equation (12a), which was for the first time used by BOLTZMANN.

We will now consider the question how the space-distribution must be according to modified mechanics. Will this law of BOLTZMANN hold also according to them? This question must be answered negatively.

Let us imagine two coexisting phases e.g. liquid and vapour. Even if we assume that in each of the two phases MAXWELL's law for the distribution of the velocities is satisfied, the mean kinetic energy of the molecules in the two phases will be different. Of

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[1]) Or at least it differs from it only in a function of the temperature which is immaterial for the existence of thermodynamical equilibrium.

course this difference will be exceedingly small at ordinary temperatures and will only get a noticeable value at extremely low temperatures, at which the molecules in the liquid phase which can be regarded as vibrators of a shorter period than those of the vapour, have less kinetic energy than they should have according to the equipartition-law. This will of course have influence on the density of the vapour phase, which will be found to be smaller than we should expect according to classical statistical mechanics.

Corresponding considerations apply to the contact difference of potential at very low temperatures. .

Besides the distribution of particles in space there are other problems which may be treated with the aid of considerations of the same kind, e.g. the orientation of the axes of polar particles under the influence of directing forces. The probability that the axis of such a particle, with moment m, in a field of forces, whose intensity is $\mathfrak{H}$, forms an angle α with the direction of this force, is according to classical statistical mechanics equal to

$$e^{\frac{m\mathfrak{H}\cos\alpha}{\theta}}\frac{\sin\alpha}{2}d\alpha \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

According to our considerations the probability that it has a considerable amount will at low temperatures be smaller than is indicated by this formula. Accordingly we find e.g. the CURIE-point at a higher temperature than would be deduced from this formula, at least for those substances, for which this point lies so low, that at the CURIE-temperature the mean kinetic energy of the rotations of the molecules is smaller than it should be according to the equipartition law.

§ 8. It is obvious that the above considerations have an exceedingly provisional character. Many problems are referred to, but not for a single one have we found a sufficiently conclusive solution. I hope to be able to treat some problems more in detail on a later occasion.

In the meantime I think that I have shown that the drawing up of a new system of mechanics as aimed at in my former communication upon this subject is of the highest importance for all thermodynamic questions. I have done this with a view to draw the attention of the mathematicians to the problem and more in particular to the integral equation (5a) or a corresponding equation [1],

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[1] I say a corresponding equation because, as I have already remarked on p. 1180 I was not perfectly sure that I was right in leaving the "proper coordinates" of the electron in this equation out of consideration. It is possible that the

the solution of which would bring us an important step nearer to the drawing up of the new system of mechanics.

Some phenomena are at present often considered in connection with the quanta-hypothesis of which it is not clear from the above how they are connected with the new system of mechanics, from which we expect the solution of the question concerning the partition of energy. Specially this is the case with the question of the emission of electrons under the influence of light- or RÖNTGEN rays.

In the thermodynamical applications it appears to me that we may expect from the quanta-hypothesis, that it will yield results which are sometimes quantitatively and always qualitatively accurate. For it has the tendency to lower the kinetic energy of vibrators of short period in agreement with the observations to an amount smaller than would agree with the equipartition law. And it is only this mean energy which is observed in thermodynamics, or the distribution in space which is closely connected with it.

Whether on the other hand the application of the quanta-hypothesis on the emission of electrons is justified seems doubtful to me. From a theoretical point of view it appears to me that no reason for the accuracy of the considerations can be found. And whether the agreement with experiment is sufficient to warrant the validity of the considerations seems to me to be still doubtful.

If in particular we take the theory of SOMMERFELD for these phenomena with the aid of the quanta of "action", then it appears to me that this theory (though perhaps accurate in itself) can be in no way connected with any possible theory for the normal spectrum. Let us imagine e.g. two equal guns with equal projectiles but with unequal charges of gunpowder. The projectile with the greatest gunpowder charge will obtain the greater kinetic energy and that in the smaller time. And so we can assume that the molecular action is of such a nature that always the greater change of energy requires the shorter time in the way as is assumed by SOMMERFELD. This is a question of the law of action of molecular forces; it has nothing to do with the laws of mechanics, and in particular it is not contradictory to the laws of classical mechanics. I at last cannot discover any contradiction. But if indeed the theory of SOMMERFELD can be reconciled with classical mechanics then it can also be reconciled with the spectral formula of RAYLEIGH and leads by no means to the spectral formula of PLANCK.

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function ε must depend besides on the p's and the q's also on the "proper coordinates" and that we, in connection with this, must add the differentials of the proper coordinates to the product of the differentials $dp_1 \ldots dq_n$.

Physiology. — "*The electrocardiogram of the foetal heart.*" By Prof. J. K. A. Wertheim Salomonson.

In 1906 Cremer published an electrocardiogram of a human embryo in utero, taken in a healthy woman during the last period of pregnancy. The curve showed oscillations caused by the heart of the mother, between which less conspicuous deviations could be seen, caused by the foetal heart-action. These latter had the form of monophasic deviations, but probably they should not be considered as a true representation of the actual electrical potential differences.

Cremer's investigations were repeated by Foa, who was not able to extend our knowledge in this respect and could only confirm Cremer's statement.

I have tried to get some further insight in the peculiarities of the foetal electrocardiogram by investigating it in the embryo of the chicken. This very obvious way was clearly indicated, as Zwaardemaker had shown that an electrocardiogram could be taken from partly-hatched eggs. He published a foetal electrocardiogram in his Treatise of Physiology.

Though my researches on this subject were commenced about a year ago and are not yet completed owing to a lengthy interval during the autumn and winterseasons, I may be permitted to show some of the results of my experiments.

Long before the conclusion of the first 60 hours of the incubating period, we can see in the chicken's embryo a strongly pulsating tubular heart, slightly curved to an s-form. In this early condition I have not been able to register any electrical potential difference [1]. The reason is that probably at that time the potential differences caused by the heart beats are exceedingly small. The electrical resistance of the substance in which the foetal heart is embedded and which contains albuminous and fatty matter is rather high. This combination of a low potential difference acting on a high resistance makes it very difficult even with an instrument so delicate as the string-galvanometer to detect the potential difference. The string-electrometer gave me no better results.

In the end of the first week we can generally without any particular difficulty lead off electrical oscillations from the foetal heart. These are very regular, isochronic with the heart beats, and show a simple monophasic deviation. Generally the ascending part has a slighter slope than the descending part. The descending part is followed immediately, without an isoelectric interval, by the next

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[1] I have since succeeded in doing so.

deviation, so as to give a regularly rising and falling line. No

Fig. 1.

difference between the different beats could be observed. The maximal P.D amounts to about 20—30 microvolts.

On the 8th day we get a curve which is perfectly differentiated. Instead of a series of continuous simple, nearly sinusoidal deviations we get deviations which may be grouped in series of 3 each, each group belonging to one heart beat. In each group the first and second deviation have the same polarity and are followed by a third peak of opposite polarity. The first peak seems to be somewhat higher than the others. I suppose that we may consider these three deviations as identical with the summits P, R, and T in the normal human electrocardiogram. The largest potential difference, that of the P-deviation, amounts to some 50 or 60 microvolt. The duration of P is of the order of 0.07 second. The R-peak has a shorter duration. In a few records I believe I have also found slight indications of a Q and an S-peak. The electrical activity represented by the T-peak extends over 0.15—0.18 second.

Fig. 2.

I am not yet prepared to speak about the extremely important question as to how the differentiated electrocardiogram of the 8th day develops from the undifferentiated curves derived before the 6th day.

After the 8th day, as the foetal heart grows stronger, the electrocardiogram also grows stronger. It shows more markedly all the points generally visible in the electrocardiogram of the full-grown embryo and in that of the new-born chicken. This latter shows some similarity to the mammalian or human electrocardiogram.

On the 12th and 14th day electrocardiograms with higher potential oscillations, up to 0,5 millivolt, can easily be recorded. After that time the maximal PD rises very slowly till the chicken is fully

Fig. 3.

hatched. In the last week no further changes in the form of the curve are to be found.

Fig. 4.

During my experiments, the results of which have been here broadly summarized, I found a few other noteworthy details. So a record taken on the 14th day gave a definite biphasic oscillation instead of the ordinary monophasic P-peak. Another complication in the form of the curve was caused by an unusual form of the T-peak, which also showed a tendency to alter into a diphasic

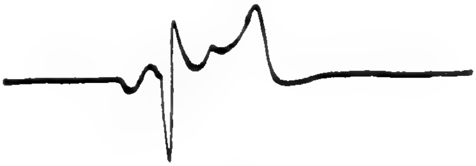

Fig. 5.

deviation (figs. 4 and 5) and to start before the R-deviation had completely subsided (fig. 5).

Contrasting with these rather complicated forms, I sometimes found more simplified ones in which it was not possible to differentiate with certainty more than two elementary summits.

Lastly I found no small number of complexes which had to be considered as pathological forms. The principal of these were caused by block; even isolated P-deviations could be found. The form represented in fig. 6 seems to me to be also a pathological form.

Fig. 6.

The pathological processes in these cases are probably caused by changes in the temperature, by lesions occurring during the preparation, or by the gradual death of the heart itself.

Mathematics. — *"On a class of surfaces with algebraic asymptotic curves."* By Prof. W. A. VERSLUYS. (Communicated by Prof. J. CARDINAAL).

§ 1. Let a twisted curve $C\begin{pmatrix} p, q, s \\ a, b, c \end{pmatrix}$ be given by the equations:

$$x = at^p \quad , \quad y = bt^q \quad , \quad z = ct^s \, , \quad . \quad . \quad . \quad . \quad . \quad (1)$$

t being the arbitrary parameter, a, b, c constants and p, q, s positive integers not admitting a common divisor. In general we suppose

$$p < q < s.$$

By assigning to a, b, c all possible values we get a system of ∞^3 curves, which will be denoted as *the system* $C(p, q, s)$. All the curves of this system contain the origin O and the point at infinity on the axis OZ; through any other point of space only one curve of the system $C(p, q, s)$ passes. The curve determined by the point A shall be indicated by $C_A(p, q, s)$ or by C_A.

Let $P_1(x_1, y_1, z_1)$ be the point of the curve $C\begin{pmatrix} p, q, s \\ a, b, c \end{pmatrix}$ corresponding to the value t_1 of the parameter t; then

$$x_1 = at_1{}^p \quad , \quad y_1 = bt_1{}^q \quad , \quad z_1 = ct_1{}^s .$$

The equation of the osculating plane in P_1 to C_{P_1} is:

$$\begin{vmatrix} x - x_1 & y - y_1 & z - z_1 \\ p\,a\,t_1{}^{p-1} & q\,b\,t_1{}^{q-1} & s\,c\,t_1{}^{s-1} \\ p\,(p-1)\,at_1{}^{p-2} & q\,(q-1)\,bt_1{}^{q-2} & s\,(s-1)\,ct_1{}^{s-2} \end{vmatrix} = 0,$$

or reduced

$$\begin{vmatrix} x - x_1 & y - y_1 & z - z_1 \\ px_1 & py_1 & sz_1 \\ p^2x_1 & q^2y_1 & s^2z_1 \end{vmatrix} = 0,$$

or worked out

$$\frac{s-q}{p}\left(\frac{x}{x_1} - 1\right) + \frac{p-s}{q}\left(\frac{y}{y_1} - 1\right) + \frac{q-p}{s}\left(\frac{z}{z_1} - 1\right) = 0 \quad . \quad . \quad (2)$$

By putting

$$\frac{s-q}{p} = P \quad , \quad \frac{p-s}{q} = Q \quad , \quad \frac{q-p}{s} = S, \quad . \quad . \quad . \quad . \quad (3)$$

and replacing $P + Q + S$ by the value $-PQS$, equal to it, the equation of the osculating plane becomes

$$P\frac{x}{x_1} + Q\frac{y}{y_1} + S\frac{z}{z_1} + PQS = 0. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

§ 2. We now propose the question how to determine the three functions $\varphi_1, \varphi_2, \varphi_3$ in such a way that the twisted curve

$$x = \varphi_1(u) \quad , \quad y = \varphi_2(u) \quad , \quad z = \varphi_3(u)$$

admits in the point $P_1(x_1, y_1, z_1)$ corresponding to the value u_1 of u the plane (2) as osculating plane.

The twisted curve φ under discussion has to cut the plane (2) thrice in the point $u = u_1$, i. e. the equation

$$P\left(\frac{\varphi_1(u)}{x_1} - 1\right) + Q\left(\frac{\varphi_2(u)}{y_1} - 1\right) + S\left(\frac{\varphi_3(u)}{z_1} - 1\right) = 0$$

must admit three roots $u = u_1$.

This gives the conditions:

$$P\frac{\varphi'_1(u_1)}{\varphi_1(u_1)} + Q\frac{\varphi'_2(u_1)}{\varphi_2(u_1)} + S\frac{\varphi'_3(u_1)}{\varphi_3(u_1)} = 0. \quad . \quad . \quad . \quad . \qquad (5)$$

$$P\frac{\varphi''_1(u_1)}{\varphi_1(u_1)} + Q\frac{\varphi''_2(u_1)}{\varphi_2(u_1)} + S\frac{\varphi''_3(u_1)}{\varphi_3(u_1)} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (6)$$

As the equation (5) must hold for any value of u_1 the first differential coefficient of the first member must disappear. This gives by taking (6) into account:

$$P\left\{\frac{\varphi'_1(u_1)}{\varphi_1(u_1)}\right\}^2 + Q\left\{\frac{\varphi'_2(u_1)}{\varphi_2(u_1)}\right\}^2 + S\left\{\frac{\varphi'_3(u_1)}{\varphi_3(u_1)}\right\}^2 = 0 \quad . \quad . \quad . \qquad (7)$$

As the equations (5) and (7) must hold for any value of u_1 they lead to the two sets of solutions:

$$\frac{\varphi'_1(u) : \varphi_1(u)}{p} = \frac{\varphi'_2(u) : \varphi_2(u)}{q} = \frac{\varphi'_3(u) : \varphi_3(u)}{s} \quad , \quad . \quad . \quad . \quad . \qquad (8)$$

and

$$\frac{\varphi'_1 : \varphi_1}{p(-p+q+s)} = \frac{\varphi'_2 : \varphi_2}{q(p-q+s)} = \frac{\varphi'_3 : \varphi_3}{s(p+q-s)} \quad . \quad . \quad . \qquad (9)$$

By representing the three equal ratios (8) by $\psi(u)$ we find

$$\varphi_1 = ae^{p\int \psi(u)\,du}$$

which passes, by replacing $\int \psi(u)\,du$ by t, into

$$x = \varphi(u) = at^p \quad , \quad y = bt^q \quad , \quad z = ct^s,$$

i. e. into a curve of the system $C(p, q, s)$.

Likewise the ratios (9) furnish

$$x = \alpha\tau^{p_1} \quad , \quad y = \beta\tau^{q_1} \quad , \quad z = \gamma\tau^{s_1},$$

i. e. a second curve belonging to a system $C(p_1, q_1, s_1)$ determined by the relations

$$\left.\begin{aligned} p_1 &= p\,(-p+q+s) \\ q_1 &= q\,(p-q+s) \\ s_1 &= s\,(p+q-s) \end{aligned}\right\} \quad . \; . \; . \; . \; . \; . \quad (10)$$

So we have the theorem:

The equation (2) *represents the osculating plane in the arbitrarily chosen point* $P_1(x_1, y_1, z_1)$ *to both the curves* $C_{P_1}(p, q, s)$ *and* $C_{P_1}(p_1, q_1, s_1)$.

We also find easily for the equation of the osculating plane in P_1 to the curve $C_{P_1}(p_1, q_1, s_1)$

$$\frac{s_1-q_1}{p_1}\left(\frac{x}{x_1}-1\right)+\frac{p_1-s_1}{q_1}\left(\frac{y}{y_1}-1\right)+\frac{q_1-p_1}{s_1}\left(\frac{z}{z_1}-1\right)=0$$

so that

$$P_1=\frac{s_1-q_1}{p_1}=\frac{q-s}{p}=-P$$

and likewise

$$Q_1=-Q \quad , \quad S_1=-S \quad . \; . \; . \; . \; . \; . \quad (11)$$

§ 3. *Definition.* We call $C(p_1, q_1, s_1)$ *the complementary system* of $C(p, q, s)$.

By determining the complementary system of $C(p_1, q_1, s_1)$ we find again the original $C(p, q, s)$, as we have

$$\begin{aligned} p_1(-p_1+q_1+s_1) &= p(-p+q+s)(p-q+s)(p+q-s), \\ q_1(p_1-q_1+s_1) &= q(-p+q+s)(p-q+s)(p+q-s), \\ s_1(p_1+q_1-s_1) &= s(-p+q+s)(p-q+s)(p+q-s). \end{aligned}$$

Therefore an exception presents itself if and only if we have

$$(-p+q+s)(p-q+s)(p-q+s)=0.$$

For $p<q<s$ this reduces to the possibility $p+q-s=0$; on this supposition we find $s_1=0$ and $p_1=q_1$, i. e. the system $C(p_1, q_1, s_1)$ is the system of the right lines intersecting the axis OZ and the line at infinity of the plane $z=0$.

We find $s_1>0$ for $s<p+q$ and $s_1<0$ for $s>p+q$; p_1 and q_1 are always positive.

For $p=0$ we also find $p_1=0$; then the two complementary systems $C(p, q, s)$ and $C(p_1, q_1, s_1)$ are both systems of plane curves situated in planes $x=$ constant.

If two of the three numbers p, q, s. e. g. p and q are equal, we find $p_1=q_1=ps$ and both systems $C(p, q, s)$ and $C(p_1, q_1, s_1)$ consist in plane curves complanar with the axis OZ.

The identities

$$\left.\begin{aligned} pP+qQ+sS &= 0, \\ p^2P+q^2Q+s^2S &= 0. \end{aligned}\right\} \quad . \; . \; . \; . \; . \; . \quad (12)$$

can immediately be verified. Likewise one finds

$$p_1 P_1 + q_1 Q_1 + s_1 S_1 = 0$$

and as according to (11) $P_1 = - P$, etc. we find

$$\left.\begin{aligned} p_1 P + q_1 Q + s_1 S &= 0, \\ \text{and also} \qquad p_1^2 P + q_1^2 Q + s_1^2 S &= 0. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

§ 4. Let O_{cc_1} be a surface determined by the equations

$$\left.\begin{aligned} x &= a u^p v^{p_1}, \\ y &= b u^q v^{q_1}, \\ z &= c u^s v^{s_1}, \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

where the coordinate lines $v =$ constant are curves of the system $C(p, q, s)$ and the coordinate lines $u =$ constant curves of the complementary system $C(p_1, q_1, s_1)$. The two coordinate lines passing through any point $P_1 (x_1, y_1, z_1)$ of O_{cc_1} admit in this point the same osculating plane. This common osculating plane contains the tangents in P_1 to both the coordinate lines and as the director cosines of these tangents are proportional to

$$\left.\begin{aligned} & p x_1, \; q y_1, \; s z_1, \\ \text{and} \qquad & p_1 x_1, q_1 y_1, s_1 z_1, \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

these tangents do not coincide and the common osculating plane is at the same time the tangent plane of O_{cc_1} in P_1.

This proves the theorem:

The two systems of coordinate lines are the systems of asymptotic curves of the surface O_{cc_1} given by (14).

In any point P_1 of O_{cc_1} the tangents to $C_{P_1}(p,q,s)$ and $C_{P_1}(p_1,q_1,s_1)$ are the principal tangents as these curves are the asymptotic curves. So in any real point of O_{cc_1} the principal tangents (see (15)) are real and different from one another; so we have the theorem:

All the points of O_{cc_1} are hyperbolic.

The equation of the surface O_{cc_1} is:

$$\left(\frac{x}{a}\right)^{Pk} \left(\frac{y}{b}\right)^{Qk} \left(\frac{z}{c}\right)^{Sk} = 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

k being the lowest common multiple of the numerators P, Q, S of (3) after reduction of these fractions to their simplest values. Indeed the values (14) of the coordinates of any point of O_{cc_1} satisfy the equation (16) for arbitrary values of u and v, as according to (12) and (13) we have the identities

$$pP + qQ + sS = 0,$$

$$p_1 P + q_1 Q + s_1 S = 0.$$

On account of $p < q < s$ we have $Q < 0$; so we prefer to trasnform (16) into

$$x^{Pk}\, z^{Sk} = B y^{-Qk} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

Corollary I. The degree of the surface O_{cc_1} is $(P+S)k$.

For we have:

$$P + Q + S = - PQS > 0,$$
$$P + S > - Q.$$

Corollary II. The surfaces O_{cc_1} on which the lines of the systems $C(p, q, s)$ and $C(p_1, q_1, s_1)$ are the asymptotic curves form a pencil.

Corollary III. The base curve of the pencil of surfaces O_{cc_1} is formed by the sides of the skew quadrilateral $OX_\infty Y_\infty Z_\infty O$, each of these sides counted a certain number of times.

Corollary IV. The complex of the principal tangents of the pencil of surfaces O_{cc_1} is formed by the tangents to the curves of both the systems $C(p, q, s)$ and $C(p_1, q_1, s_1)$.

§ 5. Reversely we start from the equation

$$x^L\, y^M\, z^N = B \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

where L, M, N are integers admitting no factor common to all three, in order to investigate under which restrictions with respect to these numbers the surface represented by (18) admits as asymptotic curves the lines of a system $C(p, q, s)$ and therefore also those of the complementary system $C(p_1, q_1, s_1)$. This will be the case if the surface (18) contains curves of both systems; to that end we must have

$$\left.\begin{array}{r} pL + qM + sN = 0 \\ \text{and} \quad p_1L + q_1M + s_1N = 0, \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

or

$$(p+q+s)\,(pL+qM+sN) - 2\,(p^2L + q^2M + s^2N) = 0,$$

what can be replaced, on account of (19), by

$$p^2L + q^2M + s^2N = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

where p, q and s are integers.

From (19) and (20) we deduce:

$$\frac{p}{q} = \frac{- LM \pm \sqrt{\{- LMN\,(L+M+N)\}}}{L\,(L+N)}.$$

As p and q have to be integers the expression $- LMN\,(L+M+N)$ under the root sign must be positive and a square; so L, M, N cannot have the same sign. Let a^2 be the highest integer square by which LMN and b^2 the highest integer square by which $L+M+N$ can be divided, so that $LMN : a^2$ and $(L+M+N) : b^2$ contain prime factors only occurring only once in each expression; then we must have

$$LMN : a^2 = -(L+M+N) : b^2 \quad . \quad . \quad . \quad . \quad . \quad (21)$$

By substituting the value of $-(L+M+N)$ following from it into the expression for $p:q$ given above we easily find:

$$\frac{p}{M(a \pm bN)} = \frac{q}{-a(L+N)} = \frac{s}{M(a \mp bL)} \quad . \quad . \quad . \quad (22)$$

So, as soon as L, M, N satisfy the condition (21) we find sets of numbers (p, q, s), (p', q', s') and therefore also two sets of curves $C(p, q, s)$, $C(p', q', s')$ lying on the surface (18). After some reductions we find $p' : q' : s' = p_1 : q_1 : s_1$ as the deduction of (p, q, s) and (p', q', s') requires. So we have proved the theorem:

A surface

$$x^L y^M z^N = B$$

admits as asymptotic curves the curves of the systems

$$C\,(M\,(a+bN),\, -a\,(L+N),\, M\,(a-bL)),$$

and

$$C\,(M\,(a-bN),\, -a\,(L+N),\, M\,(a+bL)),$$

as soon as L, M, N *satisfy the condition*

$$L + M + N = -\frac{b^2}{a^2} LMN,$$

a *and* b *being integers.*

The simplest example of a surface $x^L y^M z^N = B$, where the condition $L+M+N = -\frac{b^2}{a^2} LMN$, holds, is the hyperbolic paraboloid

$$xz = By.$$

In this case the equations (22) become

$$p = 0, \quad q = s \quad \text{and} \quad s_1 = 0, \quad p_1 = q_1 .$$

The systems $C(0, 1, 1)$ and $C(1, 1, 0)$ are systems of right lines forming on the paraboloid the asymptotic lines.

§ 6. Any surface O_{cc_1} contains besides the two systems of asymptotic lines $C(p, q, s)$ and $C(p_1, q_1, s_1)$ other systems of curves belonging to the systems

$$C\,(p + \lambda p_1, q + \lambda q_1, s + \lambda s_1)$$

and this holds for any rational value of λ either positive or negative.

Let, in order to show this, $P_1\,(x_1, y_1, z_1)$ be any point of O_{cc_1}, so that we have

$$x_1^{Pk} z_1^{Sk} = B y_1^{-Qk},$$

then O_{cc_1} contains any point of the curve

$$x = x_1 t^{p+\lambda p_1}, \quad y = y_1 t^{q+\lambda q_1}, \quad z = z_1 t^{s+\lambda s_1}$$

as from the identities (12) and (13) we can deduce

$$P(p+\lambda p_1) + Q(q+\lambda q_1) + S(s+\lambda s_1) = 0.$$

If λ_1 and λ_2 represent any two definite values of λ, the cross ratio of the four tangents in a point P_1 of O_{cc_1} to the curves through P_1 of the systems

$$C(p, q, s), C(p_1, q_1, s_1), \quad C(p+\lambda_1 p_1, q+\lambda_1 q_1, s+\lambda_1 s_1),$$
$$C(p+\lambda_2 p_1, q+\lambda_2 q_1, s+\lambda_2 s_1),$$

is always equal to $\lambda_1 : \lambda_2$ and therefore independent of x_1, y_1, z_1. So this cross ratio is constant all over the surface.

If we put e.g.

$$\lambda_1 = 1 : (p+q+s)$$
$$\lambda_2 = (p_1+q_1+s_1) : (-p+q+s)(p-q+s)(p+q-s),$$

the two systems of curves corresponding to these two values of λ are the systems $C(p^3, q^2, s^2)$ and $C(p_1^2, q_1^2, s_1^2)$.

So the cross ratio of the tangents in any point of O_{cc_1} to the four curves through this point belonging to the systems

$$C(p, q, s), \quad C(p_1, q_1, s_1), \quad C(p^2, q^2, s^2), \quad C(p_1^2, q_1^2, s_1^2),$$

is therefore

$$\lambda_1 : \lambda_2 = \frac{(-p+q+s)(p-q+s)(p+q-s)}{(p+q+s)(p_1+q_1+s_1)} = p_1 q_1 s_1 : \{pqs(p+q+s)(p+q_1+s_1)\}.$$

This cross ratio becomes zero or infinite if two of the four tangents coincide with each other; then the curves touching these coinciding lines also coincide. For p, q, and s positive and $p<q<s$ the cross ratio becomes zero under the condition $p+q=s$ only and infinite for $p_1+q_1+s_1$ only. In the first case the systems $C(p_1, q_1, s_1)$ and $C(p_1^2, q_1^2, s_1^2)$ coincide, in the second case the systems $C(p, q, s)$ and $C(p_1^2, q_1^2, s_1^2)$.

Reversely, if a curve of a system $C(p', q', s')$ lies on the surface O_{cc_1} it will always be possible to find a value of λ for which the system $C(p+\lambda p_1, q+\lambda q_1, s+\lambda s_1)$ coincides with the system $C(p', q', s')$.

So we have to prove that it is possible to find values λ and μ satisfying the three equations:

$$p + \lambda p_1 + \mu p' = 0,$$
$$p + \lambda q_1 + \mu q' = 0,$$
$$s + \lambda s_1 + \mu s' = 0.$$

These three equations are not mutually independent; multiplying the first members by P, Q and S and adding the results we get $0 = 0$. for the condition under which the curve $C(p', q', s')$ lies on O_{cc_1} is

$$Pp' + Qq' + Ss' = 0.$$

For this proof we have not made use of the fact that the two systems $C(p, q, s)$ and $C(p_1, q_1, s_1)$ are complementary; so this theorem also holds for any surface generated by curves of the system $C(p, q, s)$ meeting a curve of a system $C(p_2, q_2, s_2)$.

§ 7. Let $P_1(x_1, y_1, z_1)$ be once more an arbitrary point of O_{cc_1}. Then the two ruled surfaces osculating O_{cc_1} along the curve through P_1 of the system $C(p+\lambda p_1, q+\lambda q_1, s+\lambda s_1)$ are the surfaces the generatrices of which are the principal tangents of O_{cc_1} in the points of this curve. So these two osculating ruled surfaces are represented by the following two sets of equations:

$$\left.\begin{aligned} x &= x_1 t^{p+\lambda p_1}(1+pv), \\ y &= y_1 t^{q+\lambda q_1}(1+qv), \\ z &= z_1 t^{s+\lambda s_1}(1+sv). \end{aligned}\right\} (I) \qquad \left.\begin{aligned} x &= x_1 t^{p+\lambda p_1}(1+p_1 v), \\ y &= y_1 t^{q+\lambda q_1}(1+q_1 v), \\ z &= z_1 t^{s+\lambda s_1}(1+s_1 v). \end{aligned}\right\} (II)$$

As soon as two surfaces are generated by curves of a same system $C(p, q, s)$ the intersection of these surfaces consists exclusively of curves of this system, whether single or degenerated ones; for the curve $C(p, q, s)$ passing through any common point of the two surfaces must lie on both. So, as the two surfaces I and II osculating O_{cc_1} partake of the property of O_{cc_1}, of being generated by curves of the system $C(p+\lambda p_1, q+\lambda q_1, s+\lambda s_1)$, or $C(\lambda)$ for short, the intersection of each of these two surfaces with O_{cc_1} and their mutual intersection must break up into curves of the system $C(\lambda)$.

In the case $\lambda = 0$, i.e. if the system $C(\lambda)$ coincides with the system $C(p, q, s)$, the ruled surface I is developable. If $C(\lambda)$ coincides with the system $C(p_1, q_1, s_1)$ the ruled surface II is developable.

For $\lambda_2 = -\lambda_1$ the cross ratio $\lambda_1 : \lambda_2 = -1$ (see § 6) and the four tangents form a harmonic quadruple. Then the tangents to the curves of the systems $C(\lambda_1)$ and $C(-\lambda_1)$ are two conjugate diameters of the indicatrix, the tangents to the curves of the systems $C(p, q, s)$ and $C(p_1, q_1, s_1)$ being the asymptotes of the indicatrix. So the two systems of curves corresponding to λ_1 and $-\lambda_1$ are *conjugate* on O_{cc_1}.

So the developable enveloping O_{cc_1} according to a curve of the system $C(\lambda_1)$ is represented by the equations

$$\left.\begin{aligned} x &= x_1 (1 + v(p - \lambda_1 p_1))\, t^{p+\lambda_1 p_1}, \\ y &= y_1 (1 + v(q - \lambda_1 q_1))\, t^{q+\lambda_1 q_1}, \\ z &= z_1 (1 + v(s - \lambda_1 s_1))\, t^{s+\lambda_1 s_1}. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (III)$$

Indeed this ruled surface proves to be developable, as it is possibe to determine v in such a way that the director cosines of the tangent to the curve of the system $C(\lambda_1)$ situated on this surface III and corresponding to this value of v become proportional to the director cosines of the generatrices.

Indeed it is possible to find values v and w satisfying the equations

$$p + \lambda_1 p_1 + v(p^2 - \lambda_1^2 p_1^2) + w(p - \lambda_1 p_1) = 0,$$
$$q + \lambda_1 q_1 + v(q^2 - \lambda_1^2 q_1^2) + w(q - \lambda_1 q_1) = 0,$$
$$s + \lambda_1 s_1 + v(s^2 - \lambda_1^2 s_1^2) + w(s - \lambda_1 s_1) = 0,$$

as the sum of the three first members, multiplied respectively by P, Q, and S disappears.

This developable also cuts O_{cc_1} according to curves of the system $C(\lambda_1)$ to which also belongs the curve of contact.

§ 8. By assuming for λ_1 the value $-\dfrac{s}{s_1}$ we find $s - \lambda_1 s_1 = 0$ and the system $C(\lambda)$ becomes the system $C(p(s-p), q(s-q), 0)$. The conjugated system, i.e. the system corresponding to the value $\lambda_2 = -\lambda_1 = s:s_1$, is then the system $C(pq, pq, s_1)$. Then the first system consists of curves lying in the planes $z =$ constant and the second of curves lying in planes through the axis OZ.

The developable D circumscribed to O_{cc_1} along a curve of the system $C(p(s-p), q(s-q), 0)$ is generated by the tangents to the curves $C(pq, pq, s_1)$ and admits therefore the equations:

$$x = x_1 (1 + pqv)\, t^{p(s-p)},$$
$$y = y_1 (1 + pqv)\, t^{q(s-q)},$$
$$z = z_1 (1 + s_1 v),$$

x_1, y_1, z_1 satisfying the relation

$$x_1^{Pk} z_1^{Sk} = B y^{-Qk}.$$

As the system of curves conjugated to the curves of contact consists of curves situated in planes through the axis OZ, the developable must be a cone (according to the theorem of KOENIGS[1]), the vertex of which lies on OZ. It is easily verified that all the generatrices of D pass through the point $\left\{0, 0, z_1\left(1 - \dfrac{s_1}{pq}\right)\right\}$.

The developable D' circumscribed to O_{cc_1} along a curve of the system $C(pq, pq, s_1)$ is represented by the equations:

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[1] G. DARBOUX, Théorie gén. des surfaces T. I § 91.

$$x = x_1 \{1 + p(s-p)r\} t^{pq},$$

$$y = y_1 \{1 + q(s-q)r\} t^{pq},$$

$$z = z_1 t^{s_1}.$$

The direction of the generatrices of this developable being constant, D' is an enveloping cylinder.

For $\lambda_1 = -p : p_1$ and $\lambda_1 = -q : q_1$ we obtain analogous results. So the theorems hold:

I. *The plane sections of O_{cc_1} by planes through any edge of the tetrahedron of coordinates are conjugated to those by planes containing the opposite edge.*

II. *The developable circumscribed to O_{cc_1} along a plane curve, the plane of which contains an edge of the tetrahedron of coordinates is a cone the vertex of which lies on the opposite edge.*

III. *Any of these enveloping cones cuts O_{cc_1} according to curves of the system $C(\lambda)$ to which belongs the curve of contact.*

§ 9. Let $A(a, b, c)$ be an arbitrary point. Then the curve of contact of the enveloping cone of O_{cc_1} with A as vertex lies on O_{cc_1} itself, the equation of which surface is

$$x^{Pk} y^{Qk} z^{Sk} = B,$$

and on the first polar surface of A with respect to O_{cc_1} with the equation

$$Pax^{Pk-1} y^{Qk} z^{Sk} + Qbx^{Pk} y^{Qk-1} z^{Sk} + Scx^{Pk} y^{Qk} z^{Sk-1}$$
$$- (P+Q+S) B = 0.$$

By eliminating B between these two equations we find:

$$Payz + Qbxz + Scxy - (P+Q+S)\,xyz = 0 \quad . \quad . \quad . \quad (23)$$

So the curve of contact always lies on a cubic surface O^3_A represented by (23). The equation (23) of O^3_A being independent of B, this surface O^3_A is the same for all the surfaces O_{cc_1}; so we have theorem:

The locus of the curves of contact of all the surfaces O_{cc_1} with the enveloping cones with common vertex A is a cubic surface O^3_A.

The tangential planes of O_{cc_1} being at the same time the osculating planes of the systems $C(p, q, s)$ and $C(p_1, q_1, s_1)$, the surface O^3_A is also the locus of the points P for which the osculating planes to $C_P(p, q, s)$ and to $C_P(p_1, q_1, s_1)$ pass through A; this can easily be proved directly by making use of the equations (4).

The surface O^3_A containing the six edges of the tetrahedron of coordinates, four of which also lie on O_{cc_1}, the intersection of O_{cc_1}

and O^3_A breaks up into the curve of contact and these four edges. The tangential plane of O^3_A in any point of one of these edges is the same for all the points of this edge and different from the faces of the tetrahedron of coordinates. As we always have $S < - Q$ and we suppose provisionally that $P > - Q$, the tangential planes of O_{cc_1} along the four edges coincide with faces of the tetrahedron of coordinates. So each of the four edges belongs to the intersection a number of times indicated by its multiplicity on O_{cc_1}.

Now the edge OX_∞ is always Sk-fold on O_{cc_1} and $Y_\infty Z_\infty$ is always $(S+Q+P)k$-fold, while for $P > - Q$ the edge $X_\infty Y_\infty$ is Sk-fold and the edge OZ_∞ is $-Qk$-fold. So the four edges represent together $(3S+P)k$ common right lines. The total intersection of O^3_A and O_{cc_1} being of the order $3(P+S)k$, there remains a curve of contact of order $2Pk$.

In the case $P < - Q$ the edge $X_\infty Y_\infty$ counts $(P+Q+S)k$ times on O_{cc_1} and the edge OZ_∞ counts Pk times. Then the four edges represent $(3S+3P+2Q)k$ common right lines belonging to the intersection and therefore the curve of contact is of order $-2Qk$.

For $P = - Q$ which implies $S = S + P + Q$ the tangential plane of O_{cc_1} along OZ_∞ is no more constant and therefore this plane does not coincide with the tangential plane of O^3_A along this edge which is constant; likewise for the edge $Y_\infty Z_\infty$. So the multiplicity of these edges as parts of the intersection still remains equal to their multiplicity on O_{cc_1}.

Now the edge $X_\infty Y_\infty$ is Sk-fold on O_{cc_1} and the edge OZ_∞ is Pk-fold. The order of the curve of contact is $2Pk = - 2Qk$.

From $P = - Q$ we deduce

$$(s-p-q)(q-p) = 0,$$

i. e. either $s = q + p$, or $p = q$. In the first case O_{cc_1} is a ruled surface (see § 3, § 14), in the second a plane (see § 3).

As in general the point A does not lie on the surface O_{cc_1} it neither lies on the curve of contact and the order of the enveloping cone to O_{cc_1} with vertex A is equal to the order of the curve of contact. So we find the theorem:

The order of the enveloping cone to O_{cc_1} with an arbitrary vertex A is the larger of the two numbers $2Pk$ and $-2Qk$.

If A lies in one of the faces of the tetrahedron of coordinates, O^3_A breaks up into the plane of that face and into a quadratic cone the vertex of which coincides with the opposite vertex of the tetrahedron.

If A lies on one of the edges of the tetrahedron of coordinates,

O^3_A breaks up into the two faces through A and into a third plane. Then the curve of contact is plane (see § 8).

§ 10. The class of the enveloping cone is equal to the class of O_{cc_1}; the class of O_{cc_1} being $(P+S)\,k$, as we shall see immediately, the class of the enveloping cone also is $(P+S)\,k$.

The class of O_{cc_1} is equal to its order, the reciprocal polar figure of O_{cc_1} being also a surface O_{cc_1}. The homogeneous plane coordinates $(\alpha, \beta, \gamma, \delta)$ of a tangential plane to O_{cc_1}, i. e. of an osculating plane to a curve $C(p, q, s)$ satisfy the conditions (see § 1, equation 4):

$$\frac{\alpha}{P : x_1 u_1^{p} v_1^{p_1}} = \frac{\beta}{Q : b u_1^{q} v_1^{q_1}} = \frac{\gamma}{S : c u_1^{s} v_1^{s_1}} = \frac{\delta}{PQS};$$

where (x_1, y_1, z_1) are the coordinates of any point of O_{cc_1} and u_1, v_1 the parameter values corresponding to the point of contact. By replacing $1 : u_1$ and $1 : v_1$ by u' and v' we find:

$$\alpha : \delta = \frac{u'^{p} v'^{p_1}}{QSx_1},$$

$$\beta : \delta = \frac{u'^{q} v'^{q_1}}{PSy_1},$$

$$\gamma : \delta = \frac{u'^{s} v'^{s_1}}{PQz_1}.$$

So, but for constant factors, the coordinates of the pole of the tangential plane to O_{cc_1} with respect to the quadric

$$x^2 + y^2 + z^2 + 1 = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

are equal to the coordinates of a point of O_{cc_1} (see § 4, equation 14).

So, if the equation of O_{cc_1} is

$$x^{Pk} y^{Qk} z^{Sk} = B,$$

the equation of the reciprocal polar figure with respect to (24) is

$$x^{Pk} y^{Qk} z^{Sk} = \frac{1}{B \left\{ P^{S+Q}\, Q^{P+S}\, S^{P+Q} \right\}^{k}}.$$

So the product of the parameters corresponding to two reciprocal polar surfaces of the pencil O_{cc_1} is constant, viz.

$$\left\{ P^{Q+S}\, Q^{S+P}\, S^{P+Q} \right\}^{-k}.$$

§ 11. In the case $s_1 = 0$ the asymptotic lines of the system $C(p_1, q_1, s_1)$ are right; so according to a known theorem four arbitrary asymptotic curves of the system $C(p, q, s)$ must intersect all the generatrices in four points with a constant cross ratio. This theorem not only holds for the ruled surfaces on which the curves

$C(p, q, s)$ are asymptotic curves, but also for any ruled surface generated by these curves.

Proof: Let the ruled surface be represented by the equations

$$\left.\begin{aligned} x &= (a + \alpha v)\, t^p \\ y &= (b + \beta v)\, t^q \\ z &= (c + \gamma v)\, t^s \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (25)$$

Let P_1, P_2, P_3, P_4 be the four points of intersection of the four curves $C(p, q, s)$ corresponding to the four parameter values v_1, v_2, v_3, v_4, with the generatrix corresponding to the parameter t_1. The cross ratio of these four points is equal to that of the four projections of these points on the axis OX and in its turn this cross ratio is equal to that of the four points of OX for which the x coordinate has the values

$$a + \alpha v_1 \quad , \quad a + \alpha v_2 \quad , \quad a + \alpha v_3 \quad , \quad a + \alpha v_4 .$$

These four coordinates being independent of t, the cross ratio of the last group of four points does not vary with t_1. So the cross ratio of the four points P_1, P_2, P_3, P_4 is independent of t_1, i. e. this cross ratio is the same for any group of four points determined by the four curves $C(p, q, s)$ corresponding to the parameter values v_1, v_2, v_3, v_4 on any generatrix.

Example. The curves of the system $C(1, 2, 3)$ intersecting a given right line lie on a ruled surface of order four, for which one of the twisted cubics $C(1, 2, 3)$ is double curve (nodal curve, isolated curve or cuspidal curve). According to the theorem just proved any definite group of four curves of the system $C(1, 2, 3)$ cuts all the generatrices in four points with a constant cross ratio.

§ 12. In the case of a rectangular system of coordinates we easily find for the first differential coefficient of the length of arc σ in the point $P(x, y, z)$ of the curve $C_P(p, q, s)$ corresponding to the parameter value t the expression

$$\frac{d\sigma}{dt} = \frac{1}{t} \left\{ p^2 x^2 + q^2 y^2 + s^2 z^2 \right\}^{\frac{1}{2}} .$$

Let $\Delta\theta$ be the angle between the binormals of the curve $C(p, q, s)$ in the points corresponding to the values t and $t + \Delta t$; then we easily find:

$$\frac{d\theta}{dt} = \frac{PQS \left\{ p^2 x^2 + q^2 y^2 + s^2 z^2 \right\}^{\frac{1}{2}}}{t\, x\, y\, z \left\{ \dfrac{P^2}{x^2} + \dfrac{Q^2}{y^2} + \dfrac{S^2}{z^2} \right\}} .$$

So the radius of torsion ϱ becomes:

$$\varrho = \frac{d\sigma}{d\theta} = \frac{xyz}{PQS}\left(\frac{P^2}{x^2} + \frac{Q^2}{y^2} + \frac{S^2}{z^2}\right).$$

For the radius of torsion ϱ_1 of the curve $C_p(p_1, q_1, s_1)$ in the same point we get

$$\varrho_1 = \frac{x\,y\,z}{P_1 Q_1 S_1}\left(\frac{P_1^{\,2}}{x^2} + \frac{Q_1^{\,2}}{y^2} + \frac{S_1^{\,2}}{z^2}\right),$$

and, as $P_1 = -P$, $Q_1 = -Q$, $S_1 = -S$ (see § 2, equation 11),

$$|\,\varrho\,| = |\,\varrho_1\,|$$ [1].

Of the screws osculating the asymptotic lines of the surface O_{cc_1} in any point the one is righthanded, the other lefthanded, as the determinant

$$\begin{vmatrix} x' & x'' & x''' \\ y' & y'' & y''' \\ z' & z'' & z''' \end{vmatrix} = \frac{xyz}{t^6}\, p^2 q^2 s^2 \,(P + Q + S)$$

assumes opposite signs for the two asymptotic lines.

Let X, Y, Z represent the director cosines of the binormal and d the distance of the origin to the osculating plane in the point (x, y, z); then we easily find:

$$1 : \varrho = XYZ \left\{\frac{P^2}{x^2} + \frac{Q^2}{y^2} + \frac{S^2}{z^2}\right\}^{\frac{1}{2}} = XY\,\frac{S}{z} = YZ\,\frac{P}{x} = ZX\,\frac{Q}{y}\,;$$

$$\varrho = \frac{d}{XYZ\,PQS} = \frac{xyz\,PQS}{d^2}\,.$$

Let $\Delta\varphi$ be the angle between the tangents to a curve of the system $C(p, q, s)$ in the points corresponding to the values t and $t + \Delta t$; then we have:

$$\frac{d\varphi}{dt} = \frac{pqs\,xyz \left\{\frac{P^2}{x^2} + \frac{Q^2}{y^2} + \frac{S^2}{z^2}\right\}^{\frac{1}{2}}}{t\,(p^2x^2 + q^2y^2 + s^2z^2)}$$

by means of which we find for the radius of curvature R:

$$R = \frac{d\sigma}{d\varphi} = \frac{(p^2x^2 + q^2y^2 + s^2z^2)^{\frac{3}{2}}}{pqs\,xyz\left(\frac{P^2}{x^2} + \frac{Q^2}{y^2} + \frac{S^2}{z^2}\right)^{\frac{1}{2}}}\,,$$

or, if α, β, and γ are the angles between the tangent and the axes of coordinates

$$\frac{1}{R} = \cos\alpha\,\cos\beta\,\cos\gamma\,\left\{\frac{P^2}{x^2} + \frac{Q^2}{y^2} + \frac{S^2}{z^2}\right\}^{\frac{1}{2}}$$

So we get :

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[1] Pascal, Rep. di Mat. Sup. Cap. 16; § 9.

$$R = \frac{d}{PQS \cos\alpha \cos\beta \cos\gamma},$$

and

$$\frac{R}{\varrho} = \frac{XYZ}{\cos\alpha \cos\beta \cos\gamma}.$$

Likewise, if $\alpha_1, \beta_1, \gamma_1$ are the angles between the tangent in the point P (x, y, z) to C^P (p_1, q_1, s_1) and the axes of coordinates, and R_1 is the radius of curvature of this curve in this point, we find:

$$R_1 = \frac{d}{P_1 Q_1 S_1 \cos\alpha_1 \cos\beta_1 \cos\gamma_1},$$

and therefore

$$\frac{R}{R_1} = \frac{\cos\alpha_1 \cos\beta_1 \cos\gamma_1}{\cos\alpha \cos\beta \cos\gamma}.$$

§ 13. The tangent in the point P_1 to the curve $C_P\,(p_1, q_1, s)$ admitting the director cosines

$$p'x_1 \;,\; q'y_1 \;,\; s'z_1 \;,$$

this line is normal, in the case of rectangular axes, in P_1 to the quadric of the pencil

$$p'x^2 + q'y^2 + s'z^2 = \mu \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

passing through P_1. So the surfaces of this pencil (26) cut all the curves of the system $C(p, q, s)$ and consequently also all the surfaces generated by curves of the system $C(p, q, s)$ under right angles. Moreover the pencil (26) cuts any surface generated by curves $C(p, q, s)$ according to the orthogonal trajectories of these curves.

The surface O_{cc_1} being generated by curves of any system $C(\gamma)$, see § 7, we find the theorems:

I. *Any quadric of the net*

$$px^2 + qy^2 + sz^2 + \lambda\,(p_1x^2 + q_1y^2 + s_1z^2) = \mu \quad . \quad . \quad . \quad . \quad (27)$$

cuts any surface O_{cc_1} under right angles.

II. *The orthogonal trajectories of the curves $C(\lambda_1)$ situated on O_{cc_1} are the intersections with surfaces of the pencil.*

$$px^2 + qy^2 + sz^2 + \lambda_1\,(p_1x^2 + q_1y^2 + s_1z^2) = \mu.$$

III. *Any curve of order four forming the base of a pencil of quadrics belonging to the net (27) cuts any surface O_{cc_1} under right angles.*

IV. *In particular the orthogonal trajectories of the asymptotic curves of O_{cc_1} are determined by the intersection with the two pencils of quadrics*

$$p\,x^2 + q\,y^2 + s\,z^2 = \mu\,,$$
$$p_1x^2 + q_1y^2 + s_1z^2 = \mu_1.$$

§ 14. We now suppose $s = p + q$; then the numbers p, q, s are mutually prime two by two. We then find $p_1 = q_1 = 2\,pq$, $s_1 = 0$; so the complementary system $C'(p_1, q_1, s_1)$ is a system of right lines resting on the axis OZ and on $X_\infty Y_\infty$. The surface O_{cc_1} is a ruled surface with two right director lines.

Furthermore we find:

$$P = 1\,,\; Q = -1\,,\; S = \frac{q-p}{q+p}\,;$$

so the lowest common multiple of the denominators of P, Q, S is either $q+p$ or $(q+p):2$ according to the numbers q and p being either one even and the other odd, or both odd.

We suppose in the first place that one of the numbers p, q is even (see § 15, examples I and III).

Then the equation of the ruled surface O_{cc_1} is:

$$x^{q+p} z^{q-p} = B y^{q+p}\,;$$

so the ruled surface is of order $2q$. The enveloping cone is of order $2Pk = 2\,(q+p)$, see § 9, and of class $2q$..

If p and q are both odd and therefore $p - q$ and $p+q$ both even (see § 15, examples II, IV and V), the equation of O_{cc_1} is

$$x^{(p+q):2}\, z^{(p-q):2} = B y^{(p+q):2}\,,$$

so O_{cc_1} is a ruled surface of order q. The enveloping cone with arbitrary vertex A is of order $q+p$, see § 9, and of class q.

The ruled surface osculating O_{cc_1} along a generatrix l is generated by the principal tangents of O_{cc_1} in the points of l which do not coincide with l, i.e. by the tangents of the curves of the system $C(p, q, p+q)$. So this osculating ruled surface is represented by the equations:

$$x = x_1\,(1+pv)\,t$$
$$y = y_1\,(1+qv)\,t.$$
$$z = z_1\,\{1 + (p+q)\,v\}.$$

or by the equation

$$\frac{xy_1 - yx_1}{px_1y - qy_1x} = \frac{z-z_1}{(p+q)\,z_1}\,.$$

§ 15. *Example I.* Suppose $p = 1$, $q = 2$, $s = 3$; then we have $s = p + q$, $p_1 = q_1 = 4$, $s_1 = 0$, $P = -Q = 1$, $S = \frac{1}{3}$. So the equation of the ruled surface with the twisted cubics of the system $C(1, 2, 3)$ as asymptotic lines is

$$x^3 z = By^3.$$

Example II. For $p = 1$, $q = 3$, $s = 4$; we find $s = p + q$, $q_1 = p_1 = 6$, $s_1 = 0$. $P = - Q = 1$, $S = \frac{1}{2}$.

So the surface admitting as asymptotic lines the twisted quartics of the system $C(1, 3, 4)$ with two stationary tangents, is the cubic surface

$$x^2 z = By^2.$$

The section of O_{cc_1} by a plane $x =$ constant breaks up into the line at infinity of this plane and a curve of the system $C(0, 1, 2)$. The ruled surface osculating O_{cc_1} along this section is represented by the equations:

$$x = x_1 (1 + v),$$
$$y = y_1 (1 + 3v) t,$$
$$z = z_1 (1 + 4v) t^2.$$

The equation of this osculating ruled surface is

$$y^2 z_1 (4x - 3x_1) = z y_1^2 (3x - 2x_1)^2.$$

The intersection of this cubic surface and O_{cc_1} consists of the conic of contact counted thrice and of the two right directors of O_{cc_1}.

Example III. Suppose $p = 2$, $q = 3$, $s = p + q = 5$. Then O_{cc_1} is a ruled surface of order $2q = 6$, the equation of which is

$$x^5 z = By^5.$$

So this ruled surface admits a system of asymptotic lines of order five.

Example IV. Suppose $p = 1$, $q = 5$, $s = p + q = 6$. Then O_{cc_1} is a ruled surface of order $q = 5$ with the equation

$$x^3 z^2 = By^3.$$

So this ruled surface of order five admits a system of asymptotic lines of order six.

Example V. Suppose $p = 3$, $q = 5$, $s = p + q = 8$. Here O_{cc_1} is a ruled surface with the equation

$$x^4 z = By^4.$$

Example VI. If the first system of asymptotic lines is formed by curves of the system $C(1, 3, 6)$, then the asymptotic lines of the second system belong to the system $C(2, 3, -3)$. So both systems are curves of order six.

The equation of O_{cc_1} is

$$x^9 z = By^5.$$

Example VII. If the first system of asymptotic lines belongs to the system $C(1, 2, 4)$ the second system belongs to the system $C(5, 6, -4)$.

Then the equation of O_{cc_1} is

$$x^8 z = By^6.$$

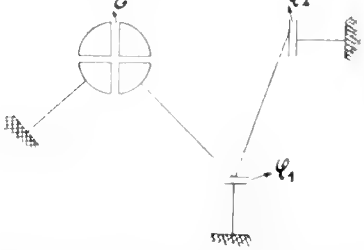
Physics. — *"On piezo-electric and pyro-electric properties of quartz at low temperatures down to that of liquid hydrogen."* By H. Kamerlingh Onnes and Mrs. Anna Beckman. Communication N°. 132*f* from the Physical Laboratory at Leiden.

(Communicated in the meeting of February 22, 1913).

§ 1. *Introduction.* As many qualities of solid bodies are much simplified at very low temperatures by the considerable decrease of the caloric motion, it seemed desirable to examine also the piezo- and pyro-electric effects under these probably favourable circumstances. In order to make a preliminary inquiry into this branch of the subject we have measured the piezo-electric modulus of quartz, perpendicular to the axis, down to the temperatures of liquid hydrogen.

Then we have also, at the temperatures of liquid air and liquid hydrogen, observed the pyro-electric phenomenon of quartz, which Friedel, Curie and others have examined at higher temperatures.

§ 2. *Measurements of the piezo-electricity of quartz at low temperatures.* The measurements were effected by the generation of electricity on a quartz plate, which was kept at low temperatures and compared with a similar plate at ordinary temperature. The generated charge was measured with a quadrant electrometer. Both the plates were of the same sort as is used in the ordinary Curie's instrument, that is to say, they were cut out of the crystal parallel to the optical axis and with the broadest side perpendicular to one of the electrical axis.



They were 7—8 cm. long, 2 cm. broad and 0.06 cm. thick. The two broad, sides were coated with tin [1]). One of the tin coatings of each plate was earthed, the two others were metallically connected with one another and, with one pair of quadrants of the electrometer, as is shown in the figure. The other pair of quadrants was earthed.

All the connections were enclosed in brass tubes, which were in

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[1]) The tinfoils were apt to get loose from the plate in the liquid oxygen, which gave rise to blisters; it would of course be better to employ a platinized quartz plate, silvered: Then, too, the use of cementing material between the metal coating and the quartz would be obviated.

connection with the earth. The electrometer needle was kept at a constant potential of 120 volts.

The quartz plate Q_1 was suspended in an earthed metal case and carried a scale pan, on which weights could be placed, in order to stretch the plate: Q_2 was put in a DEWAR glass; its lower end was fastened in a brass support, which was carried by the cap of the vacuum vessel; the uppermost end was suspended by a brass rod to one arm of a balance, whose other arm carried a scale, which could be loaded with weights. In order to be able to close the vessel hermetically (which was quite necessary), and at the same time make the free movement of the rod through the cover possible, it was simplest, for these preliminary measurements, to use an elastic india rubber tube which closed round the rod and the tube in the cap. As we shall see this had only a slight effect on the relative measurements.

Within the glass the quartz plate and the support were surrounded by a brass net in connection with the earth.

The measurements were made in the following way: first the plate Q_1 was stretched by a weight (500 gr.) and the deviation of the electrometer needle was observed. Then this plate was earthed, and when the connection with the earth was broken, the weight was removed and the deviation of the electrometer to the other side was observed. The sum of these deviations is proportional to the quantity of electricity generated. Then the electricity which was generated on Q_2 was measured in the same way. Immediately before and after the measurements the electrometer was calibrated with a WESTON element. The sensibility changed very little.

The insulation was generally very good, so that there was seldom any need of making corrections for leakage.

Always five or seven turnings of the electrometer needle were observed. From these the eventual corrections for incomplete insulation could be calculated.

§ 3. *Results.* I. Both the quartz plates at room temperature ($T = 290^\circ$ K.).

The deflections were

						mean values
Q_1	126.7	127.2	127.0	127.6	127.4	127.2
Q_2	163.7	164.0	163.6	163.2	163.3	163.6

The WESTON element (1.018 Volt) gave 34.4.

The capacity of the electrometer, of the connections to Q_1 and of Q_1 itself was about 150 cm.; that of the connection to Q_2 and of Q_2 was about 100 cm. By the cooling of Q_2 its capacity changes.

II. Q_2 in oxygen boiling under a pressure of 21 cm. $T = 78°.5$ K.

			mean values
Q_1	130.6	130.1	130.3
Q_2	165.2	165.7	165.4

One WESTON element 34.4.

III. Q_2 in boiling hydrogen, $T = 20°.3$ K.

				mean values
Q_1	129.6	130.5	130.0	130.0
Q_2	165.4	165.5	165.4	165.4

One WESTON 34.4.

IV. Q_2 at ordinary temperature, $T = 290°$ K.

						mean values
Q_1	127.1	127.4	127.1	126.8	127.0	127.0
Q_2	162.5	163.0	162.8	163.1	162.7	162.8

One WESTON 34.3.

In order to examine the influence of the elastic connection between Q_2 and the cap of the vacuum vessel, two measurements were made without the elastic tube, one at ordinary temperature and the other in liquid air. These gave

V. Q_2 at ordinary temperature, $T = 290°$ K.

						mean values
Q_1	126.2	126.8	127.7	127.5	127.1	127.0
Q_2	167.4	168.1	168.1	167.8	168.3	167.9

One WESTON 34.3.

VI. Q_2 at the temperature of liquid air, $T = 80°$ K.

						mean values
Q_1	129.3	129.6	129.8	129.7	129.9	129.7
Q_2	168.8	169.3	170.1	169.2	169.4	169.4

One WESTON 34.3.

By immersing Q_2 into the bath of low temperature the deviations are thereby changed for both the plates. The change was at the measurement

II	($T = 78°.5$ K.)	Q_1 + 2.4%	Q_2 + 1.1%
III	20.3	2.2	1.0
VI	80.0	2.1	0.9

The electricity generated on Q_2 was thus at all events less than at ordinary temperature. The decrease was 1.3 $^0/_0$, 1.2 $^0/_0$, 1.2 $^0/_0$.

The influence of the elastic connection falls within the limits of errors of observation. In the absolute measurements the connection causes a decrease of about 3 $^0/_0$.

Thus we may conclude that the cooling from 290° K. to 80° K. causes a decrease of 1.2 $^0/_0$ in the piezo-electric modulus. A further cooling from 80° to 20° causes a much smaller change, it appears even less than 2 $^0/_{00}$. The importance of this result is perhaps that the change in the piezo-electricity by cooling to low temperatures seems to take place chiefly above the temperature of liquid air.

§ 4. *Pyro-electricity of quartz.* As has already been said, we also made some observations on the pyro-electricity of quartz at the temperatures of liquid air and hydrogen. The pressure under which the liquid round Q_2 boiled was changed. By the change of temperature, which is the consequence thereof, a pyro-electric charge is generated on Q_2. The deflections of the electrometer were

for 90° K	to 86.5° K	+ 27.5 mm.	or per degree	+ 8.5 mm.	mean value per degree 7.8 mm.
86.5	,, 82.5	+ 27.0	,, ,, ,, ,,	+ 6.5 ,,	
82.5	,, 78.5	+ 27.5	,, ,, ,, ,,	+ 8.5 ,,	
78.5	,, 90	— 89.0	,, ,, ,, ,,	— 7.5 ,,	
20.3° K	,, 15.2° K	+ 6.5	,, ,, ,, ,,	+ 1.4 mm.	1.6
15.2 ,,	,, 20.3 ,,	— 7.8	,, ,, ,, ,,	— 1.6 ,,	
between 20.3,,	and 15.8,,	± 14.3	(double deflect.)	± 1.7 ,,	

The deviation 7.8 per degree at the temperatures of liquid oxygen
1.6 per degree at the temperatures of liquid hydrogen

has by an increase of temperature the same direction as by a stretching of the plate.

We note that the generated pyro-electric charge is about proportional to the absolute temperature.

We wish to record our heartiest thanks to Mr. G. HOLST, assistant at the physical laboratory, for his assistance at our experiments.

Physics. — "*Measurements on resistance of a pyrite at low temperatures, down to the melting point of hydrogen.*" By Bengt Beckman. Communication N°. 132*g* from the Physical Laboratory at Leiden. (Communicated by Prof. H. Kamerlingh Onnes).

(Communicated in the Meeting of February 22, 1913).

In an earlier publication [1]) I examined resistance as a function of temperature in the case of a pyrite crystal from Gellivare, Malmberget, Sweden. Those measurements embraced the temperature interval + 100° C. to — 193° C. The resistance was well represented by the formula

$$W = W_0 e^{at}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where W_0 is the resistance at 0° C. and t the temperature on the centrigrade scale. The spec. resistance at 0° C. in ohms per cube of 1 cm. was $w_0 = 0{,}00294$; a was 3.53×10^{-3}.

The measurements were made with a Wheatstone bridge. The ends of the crystal were galvanized with copper; as electrodes amalgamated copper plates were used. The resistance at 0° C. was 0.101 ohms. To determine the magnitude and the variation of the contact resistances and of the connections with the temperature, a little copper prism of the same dimensions as the crystal was placed between the electrodes and short-circuited, and the resistance of the short-circuited crystal support and the connections were measured at the various temperatures.

I have now had an opportunity of continuing these measurements on a pyrite through a larger temperature interval (down to — 258° C.). This last investigation was made in the cryogenic laboratory of the University of Leiden, and for the opportunity I owe the director of the laboratory, Prof. H. Kamerlingh Onnes, great thanks.

To obtain these measurements I have used another method, which eliminates the possible errors of the contact resistances. The crystal was pressed between two copper electrodes, through which the current was conveyed to it. Two other electrodes were firmly pressed against the longest side of the crystal. The voltage between these was measured with the compensation apparatus [2]).

In Table I the results of the measurements in Upsala 1910 are

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[1]) Bengt Beckman: Uppsala Univ. Årsskrift 1911. Mat. o. naturvetenskap 1, p. 28.

[2]) See H. Diesselhorst, Zeitschrift f. Instrumentenkunde 26, p. 182, (1906), where Fig. 2 gives a survey of the mounting.

TABLE I.

Change of the resistance of pyrite with the temperature. Measurements in Upsala 1911.

	$\left[\frac{W}{W_0}\right]_{obs.}$	$\left[\frac{W}{W_0}\right]_{calc.}$
+ 100°.9 C.	1.422	1.436
+ 54 .2	1.223	1.215
+ 44 .5	1.180	1.173
0	1	1
— 78 .6	0.726	0.754
— 193	0.508	0·495

TABLE II.

Change of the resistance of pyrite with the temperature. Measurements in Leiden, 1912.

t	$\left[\frac{W}{W_0}\right]_{obs.}$	$\left[\frac{W}{W_0}\right]_{calc.}$
+ 15°.8 C.	1.063	1.058
— 183	0.519	0.520
— 252.8	0.405	0.404
— 258	0.390	0.396

given and in Table II these last results of 1912. The values $\left[\frac{W}{W_0}\right]_{cal}$ are calculated from the formula (1), where now

$$a = 3.59 \times 10^{-3}.$$

The results are well represented by this formula. The values of $\frac{W}{W_0}$ at low temperatures that were found in the last observations are in better agreement with the formula than the earlier ones.

The results for $t = -78°.6$ C. and $-193°$ C. in these deviate a little from the calculated values, but in different directions. The deviations do not exceed 4%, which corresponds to a difference of 0.004 ohms at the most.

The last measurements may also serve to control whether the results of the earlier ones were not fully accurate owing to the contact resistances. The deviations that I have just mentioned might arise from this source of error, but, as they go in different directions at $t = -78°.6$ C. and $t = -193°$ C. one is inclined to think that these deviations may originate in other errors too, for instance in variations of the temperature bath at $t = -78°.6$ C. (solid carbonic acid and ether).

O. REICHENHEIM [1]) and J. KOENIGSBERGER [2]) have examined pyrite from Val Ginf, Graubünden and have found a minimum of resistance at about $t = -10°$ C. This pyrite has a specific resistance of 0.0240 at 0° C., thus eight times larger than mine. An explanation of this difference of the conductivity is given by J. KOENIGSBERGER [3]).

My pyrite shows no minimum of resistance above —258° C. The resistance throughout the whole temperature interval follows the formula (1), which is the same, mathematically, as

$$\frac{1}{W}\frac{dW}{dt} = const.$$

It seems very probable that there does not exist any minimum below — 258° C., but that the resistance at still lower temperatures approaches asymptotically to a limit value, as is the case in, for instance, not perfectly pure gold and platinum.

A. WESELY [4]) has recently examined a pyrite crystal from the same place af origin, Malmberget, Gellivare. He found a still smaller spec. resistance, $w_0 = 0.00247$ and a temperature coefficient at 0° C. of 0.00228.

Physics. — *"Investigation of the viscosity of gases at low temperatures. I. Hydrogen."* By H. KAMERLINGH ONNES, C. DORSMAN and SOPHUS WEBER. Communication N°. 134*a* from the Physical Laboratory at Leiden by H. KAMERLINGH ONNES.

§ 1. *Introduction.* [5]) The investigation of the dependence of the viscosity of gases upon the temperature at densities near the normal,

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[1]) O. REICHENHEIM, Inaug. Dissert. Freiburg 1906.

[2]) J. KOENIGSBERGER, Jahrbuch der Rad. u. Elektr. **4**, p. 169, 1907.

[3]) J. KOENIGSBERGER, Phys. Zeitschr. 13, p. 282, 1912.

[4]) A. WESELY, Phys. Zeitschr. 14, p. 78, 1913.

[5]) This Comm. includes the paper on the same subject by KAMERLINGH ONNES and DORSMAN, which is referred to in Comm. Suppl. No. 25. (Sept. 1912) § 6, note 1.

is chiefly of importance for the knowledge of the mechanism of the impact of two molecules, or, more simply in monatomic gases, of two atoms. In the nature of the case it is desirable to extend this investigation with one substance over the largest possible range of reduced temperature. This gives a particular significance to very low temperatures and substances such as hydrogen, neon, and helium.

The pupils of DORN [1]) at Halle have made systematic researches into the viscosity of different gases. By these both absolute values and temperature coefficients have been determined, and they have gone as low as the temperature of liquid air.

In our researches we particularly wished to investigate hydrogen temperatures, while the viscosity apparatus was so arranged that it could be used without alteration for helium at helium temperatures. But it was natural for us to extend our investigation to the viscosity of our gases at less low temperatures. It then appeared that besides being of value for the confirmation of the above mentioned researches as far as the temperature of solid carbonic acid, it was also of value for the knowledge of viscosity in the field of the temperature of liquid air.

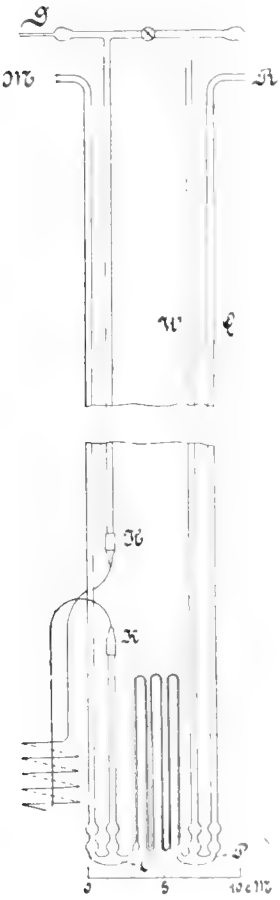

Fig. 1.

In the field of hydrogen temperatures we found the viscosity of hydrogen while flowing through a capillary tube dependent upon the mean pressure. From MAXWELL's [1]) researches we know that the viscosity of gases at normal density is independent of the pressure, and WARBURG and VON BABO have shown in the investigation of carbon dioxide, that in dense vapours, it increases with the density. There is, therefore, every reason to further investigate the dependence of the viscosity upon the pressure in hydrogen vapour.

§ 2. *Method.* The measurements were made according to the transpiration method. This presents experimentally perhaps the greatest difficulties, but it seems to allow

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[1]) There is a survey of these researches by K. SCHMITT. Ann. d. Phys. (30). p. 393, 1909.

[2]) For the older litterature see H. KAMERLINGH ONNES and W. H. KEESOM. Leiden Comm. Suppl. N⁰. 23, page 86.

better than any other the fulfilment of the conditions which are assumed in the theoretical deduction.

The form which we choose (diagrammatically represented in fig. 1, compare further fig. 2) is distinguished by the following special features:

1. the pressure at both ends of the capillary tube through which the gas flows, can be kept constant as long as desired at any height.

2. the mean pressure and the difference of pressure are immediately measured at both ends of the capillary.

3. before it enters the capillary the gas flows through a copper tube (in our case 70 cm. long) where it acquires the desired temperature.

The calculation of the measurements got by the transpiration method was made by the formulas of O. E. Meyer and M. Knudsen[1]; for the amount of gas that passes through a capillary they give:

$$Q = \frac{\pi}{8} \cdot \frac{1}{\eta} (p_1 - p_2)\, p\, \tau \frac{R^4}{L} \left(1 + \frac{4\,\zeta}{R}\right)$$

in which

$$\frac{\zeta}{\lambda} = 1.05 - \frac{1}{5 + \frac{\lambda}{R}} \quad \text{and} \quad p\,\lambda = \sqrt{\frac{\pi}{8}} \cdot \frac{1}{0{,}30967} \cdot \frac{\eta}{\sqrt{\varrho_1}}$$

η = coefficient of viscosity.
R = radius of the capillary.
L = length of the capillary.
τ = time of flow.
$\bar{p} = \frac{p_1 + p_2}{2}$ = mean pressure.
p_1 = pressure at beginning of capillary.
p_2 = pressure at end of capillary.
Q = the quantity that has flowed through, measured by the product of volume and pressure, and corrected for the temperature of the capillary.
ζ = the gliding coefficient which is determined by the two last equations, in which ϱ_1 is the density of the gas.

The units are those of the *C. G. S.* system.

§ 3. *Arrangement of the apparatus.* The manner in which the various quantities in these formulas were determined in the measurement, will easily be understood with the help of fig. 2.

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[1] M. Knudsen: Ann. d. Phys. 28, 1909. p. 75.

The pure gas [1]) from a store cylinder is first let into a pipette *P*, in which it can be brought to a suitable pressure by means of mercury. By a high pressure regulating tap it is then conducted by a brass capillary to *A*, where the capillary forks. One branch leads to a mercury-water differential manometer, in which the level of the water is kept constant by the regulation of the tap *C*. At first we worked with oil manometers, which allow an easy adjustment at any pressure required. With these no constant values were found for the viscosity coefficient, which was perhaps in consequence of oil vapour solidifying on the capillary. On this account the oil manometers were replaced by mercury-water differential manometers.

The other branch of the capillary at *A* leads the gas through a steel capillary *EFG* to the viscosity apparatus in the cryostat.

Between *D* and *E* is a *U* tube of charcoal immersed in liquid air, by means of which the last possible traces of air would be kept back.

A vertical glass tube carried the gas further. To this was soldered the spiral copper capillary of about 70 cm. length, in which the above mentioned cooling of the gas took place, which had been shown to be indispensible. This terminated at *K*, from where the gas was carried to *L*. In *L*, which was a small reservoir, the tube divides into two branches viz. the capillary and the tube *LMN* to the mercury manometer *O*. *L* and *P* could be directly connected by a tube in parallel with the capillary and provided with a stopcock. This was necessary during the exhaustion. The transition from the capillary tube into *L*, in which the gas may be considered as at rest, is very gradual. This is of importance for the correction of HAGENBACH, which can be omitted in these circumstances. From *S* a branch *TO* leads further to a second mercury manometer *V*, which registered the pressure p at the beginning of the capillary tube. Through the capillary tube, (about 65 cm. long, with a diameter of 0.122 mm.) the gas flowed into *P*. As at *L* a tube *PQR* leads from here to the other end of the mercury manometer *O*. By means of this manometer we could thus read the difference $p_1 - p_2$. Another tube *WMYZ* leads the gas from *P* to *Z*. *Z* is connected on one side to the mercury-water differential manometer *b*, and on the other side by *a* to *c*. At *a* there is a regulating tap, which enables us to keep the level of the manometer *b* at a constant height during the experiment. By doing this during the experiment we can keep $p_1 - p_2$

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[1]) The gas was purified by passing over a spiral cooled by liquid hydrogen (Comm. N⁰. 83). A trace of air was afterwards found in the gas, this may have been absorbed during the compression in spite of the precautions taken.

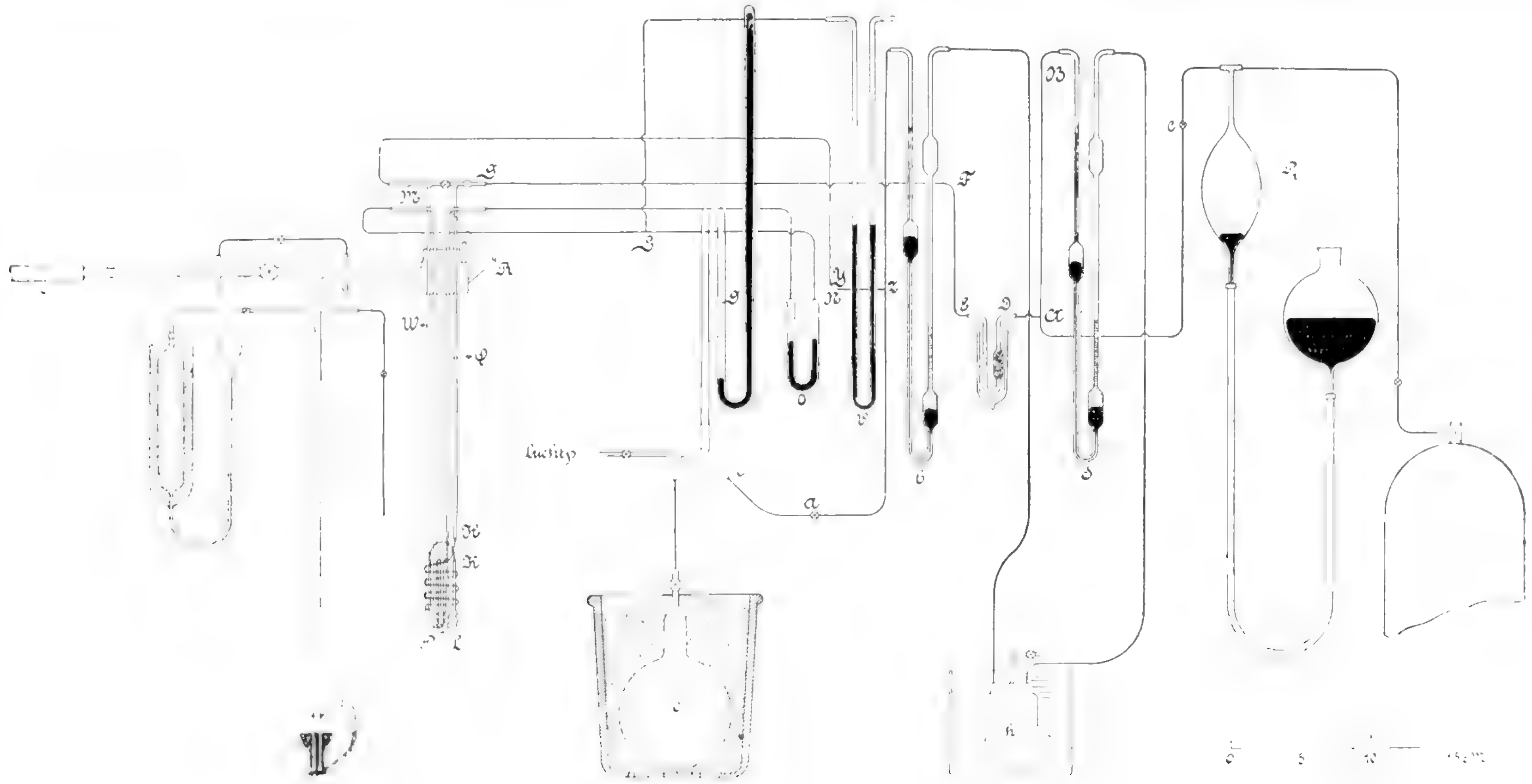

Fig. 2.

and p_1 steady, except for the small irregularities due to the regulation of the taps. The tube e is connected to a vessel e of about 4 L. placed in ice, intended for the determination of the volume. The gas pressure in this reservoir was determined before and after every experiment, by reading the manometer g. As can be seen, a small portion of this volume is not reduced to 0° C., it remains at about the temperature of the room. This portion is only about 1.5 % of the whole volume.

The three manometers were read by a kathetometer, and were so placed that they could all be viewed by turning the kathetometer.

The temperature of the viscosity capillary was determined by a platinum resistance thermometer placed beside it, which was reduced to the hydrogen thermometer of the Laboratory by comparison with a standard resistance thermometer.

For the arrangement of the cryostat with stirrer see Com. N°. 123. The measuring apparatus were immersed in a cryostat glass exactly like that of the helium cryostat. As we said in § 1, it is our intention to determine the viscosity of helium at helium temperature with the same apparatus. The cryostat glass was covered by a cap, which is like that of the helium cryostat, but simplified in an obvious way. In fig. 2 the cryostat glass with stirrer and thermometer are omitted.

§ 4. *Course of the experiments.* When the tightness of the apparatus had been properly tested and all found to be in order, the experiment was made in the following way. The volumenometer and the whole apparatus were pumped out and the tap a was closed. Then tap c was opened, and regulated so that the manometers b and d were at the desired height. When this was attained the experiment was begun, and simultaneously with the beginning of the regulation of tap a the knob of a chronometer was pressed. During the experiment, as already said, the taps a and c were so regulated that the differential manometers which acted as indicators, kept constant, at the same time the manometers O and V were read, and the small irregularities which at the most were 1 % were noted as well as was possible. By the determination of a mean-value we find from these readings the pressure difference, which existed between the extremities of the capillary tube during the experiment. If we reduce the readings of the manometer v by $\frac{p_1-p_2}{2}$, we find the mean pressure $\overline{p}$.

The chronometer was compared with the standard clock of the laboratory immediately after pressing the knob. The latter served as the actual time measurer. The end of the experiment was registered in the same way At the same time tap a was closed. Then the pressure in the volumenometer was read, and herewith the necessary data were obtained.

The distribution of temperature in the cryostat during the evaporation of the bath, may be a source of error, as it affects the distribution of the density in the tubes leading to the capillary tube. These tubes and the time of flow were therefore so chosen that the errors which might arise from this were negligible.

The experiments were usually made at a mean pressure of about $^1/_2$ atmosphere.

RUCKES[1]) has proved that REYNOLDS' criterion applies also to gases. When we determine the critical velocity for our experiments at hydrogen temperatures, we find 3253 cm./sec. while the greatest which occurred in the experiments was 419 cm./sec.

§ 5. *Results.* In the first measurements made with hydrogen in the manner described above, the viscosity became higher and the higher, which can be explained by the hydrogen still containing some traces of air which froze in the capillary tube. On this account we introduced the tube with charcoal described above. The later determinations gave constant results.

The whole observational material is collected in Table I. The first column contains the temp. in Kelvin degrees, the second and third the difference of pressure and the mean pressure. These results, as already said, are calculated from a great number of observations, the deviations from the mean were about $2^0/_{00}$. The fourth column contains the time of flow in seconds, the fifth the increase of pressure in the volumenometer.

This increase of pressure combined with the volume, gives the amount of gas which flows through, and this must be reduced to mean pressure and temperature of the tube through which it flows. For this purpose the equation of state was used, which had been deduced from the measurements of KAMERLINGH ONNES and DE HAAS (Comm. N°. 127) and KAMERLINGH ONNES and BRAAK (Comm. N°. 97*a*).

The two first observations were used to calibrate the apparatus, in which we assumed with MARKOWSKI[2]) $\eta_0 = 841.10^{-7}$, while for C in SUTHERLAND's formula 83 was taken.

By this means the values were determined which are given under

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[1]) W. RUCKES Ann. d. Phys. 25, 1908 pag. 983.

[2]) H. MARKOWSKI loc. cit. and K. SCHMITT loc. cit.

TABLE I.

$T°$ K.	$\Delta p_{\text{cm.Hg}}$	$p_{\text{cm.Hg}}$	τ_{sec}	ΔP_{cmHg}	$\eta'.10^7$	$\eta.10^7$
293.90	11.455	41.83	12739	1.479	"	887.2
293.88	10.750	42.61	16814	1.866	"	
170.2	10.315	43.42	4755.5	1.282	616.8	609.2
170.2	10.310	43.43	6600.5	1.777	617.0	609.4
89.60	6.020	39.47	4760.0	1.999	399.4	392.1
89.65	5.545	40.39	3472.5	1.374	399.4	392.1
89.65	8.485	38.86	3045.0	1.773	399.8	392.5
70.9	6.010	39.48	2610.0	1.711	323.1	316.7
70.9	8.385	38.91	2301.5	2.056	326.2	319.8
70.9	8.300	38.92	1834.0	1.614	327.7	321.3
20.06	4.648	39.08	1264.2	6.565	114.1	111.5
20.04	4.651	39.16	1264.0	6.628	113.5	110.9
20.03	4.630	39.70	1265.5	6.694	113.5	110.9
20.04	3.945	20.40	1684.1	4.021	108.5	106.0
20.04	4.190	19.12	1576.3	3.799	107.0	103.5
20.04	4.580	20.71	1625.0	4.575	108.4	105.9
20.04	4.603	20.37	1357.6	3.787	108.2	105.7

$\eta'.10^7$. They were corrected for the change of R^4/L with the temperature and for the gliding. The corrected values are in column 7 under $\eta.10^7$.

From Table I we can immediately see the degree of accuracy that may be ascribed to the measurements with regard to accidental errors. As we have said before the determinations were usually made at a mean pressure of half an atmosphere. At and above oxygen temperatures a determination at one pressure is sufficient, at hydrogen temperatures this appeared to be no longer the case. Table I shows that there the viscosity changes with the density, and in the same direction as was found by WARBURG and BABO for carbon dioxide. Our differential manometers were not yet arranged, as we intend to do, for working with different mean pressures, and the apparatus was thus not very suitable for determining the influence of the pressure. In order to perform a few experiments with a different pressure, the two differential manometers were connected to an artificial atmosphere h, as can be seen in the plate.

For the further experiments which we intend to make (see § 1) concerning the dependence of the viscosity upon the density, it may appear that where it is a case of relative determinations only, the oscillation method is perhaps the most suitable.

TABLE II.

T° K	$\eta_{obs.} . 10^7$	$\eta_s . 10^7$	$\eta_{calc.} . 10^7$
457.3*	1212	1203	1207
373.6*	1046	1050	1052
293.95	—	887.2	886
287.6*	877	874	875
273.0*	844	843	843
261.2*	821	814	816
255.3*	802	800	803
233.2*	760	747	757
212.9*	710	697	709
194.4*	670	648	666
170.2	609.3	582	608
89.63	392.2	326	389
[78.2*	374.2	284	354]
70.87	319.3	257	329
20.04	105—111	58	137

In Table II our results are put together with those of MARKOWSKI and of KOPSCH[1]) (the last are marked with an asterisk). Fig. 3 shows that our measurements correspond well with the previous ones. KOPSCH's determination in liquid air forms an exception. The cause of this is probably an insufficient fore-cooling in KOPSCH's apparatus, as it is improbable that the density should have an important influence[2]) here.

In column 3 under $\eta_s . 10^7$ are given the values calculated by SUTHERLAND's formula with $\eta_0 = 841.10^2$ and $C = 83$. The differences become very great at the lower temperatures, in liquid hydrogen more than 100 %.

KOPSCH has already pointed out that SUTHERLAND's formula no longer holds for hydrogen at the temperature of liquid air, and although the deviation which he found seems to be partly ascribable

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[1]) H. MARKOWSKI. Ann. d. Phys. 14. 1904 pag. 742.

[2]) Observations for *He* which will be treated in a following paper, show that there is no such dependence on the density.

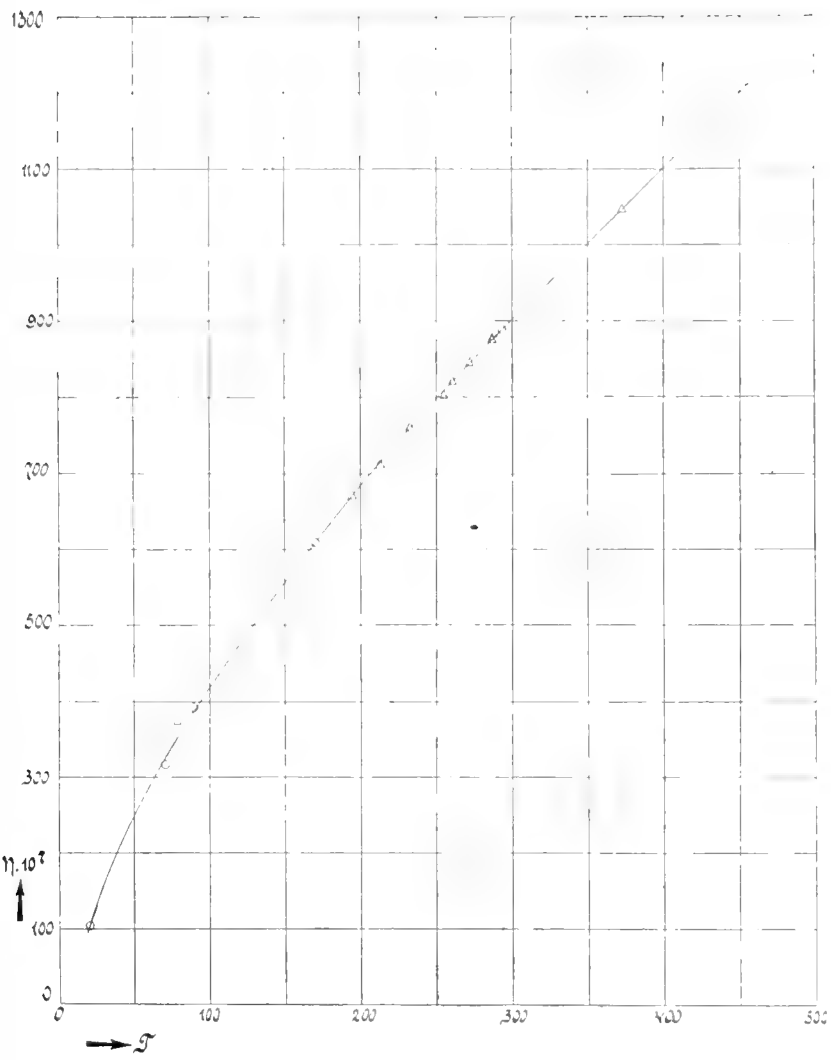


Fig. 3

to insufficient fore-cooling his conclusion remains correct, as the amount of the deviation of the observations from the formula even at the temperature of liquid air is larger than that of the deviation which is due to insufficient cooling.

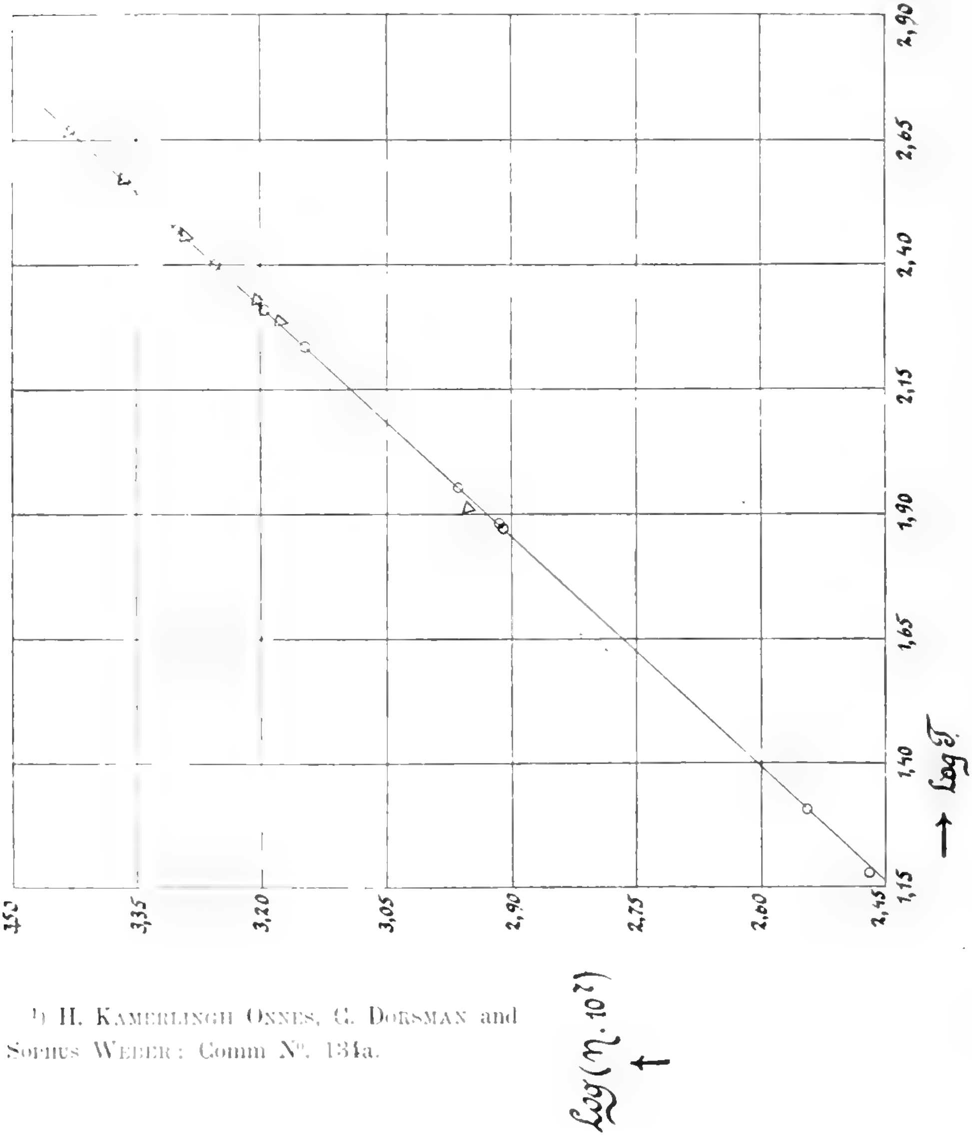
We endeavoured to find a simple relation between *log* η and *log* T, which would correspond to the observations better than SUTHERLAND's formula. Column 4 under $\eta_{calc.} 10^7$ contains the values of η calculated by the formula

$$\eta = \eta_0 \left(\frac{T}{273}\right)^{0.695}$$

The correspondence is satisfactory as far as the temperature of reduced oxygen. We shall return to this question in the following paper about the viscosity of helium, in which we shall further deal with the change of the nucleus volume b_w with the temperature, as it follows from our experiments.

Physics. "*Investigation of the viscosity of gases at low temperatures.* II. *Helium*". By Prof. KAMERLINGH ONNES and SOPHUS WEBER. Communication N°. 134*b* from the physical Laboratory at Leiden by Prof. H. KAMERLINGH ONNES.

§ 1. *Results.* With the same apparatus as was used for the investigation of the viscosity of hydrogen[1], a series of measure-



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[1] H. KAMERLINGH ONNES, C. DORSMAN and SOPHUS WEBER: Comm N°. 134a.

ments were made for helium. According to REYNOLDS the critical velocity would be 2960 $^{cm}/_{sec}$; in our experiments the greatest velocity was 105 $^{cm}/_{sec}$. All our observations are brought together in Table I. The notations are the same as in the previous paper about hydrogen.

Again the first two experiments were used for the calibration of the apparatus, for which purpose we assumed as K. SCHMITT[1] does, $\eta_0 . 10^7 = 1887$ and C in SUTHERLAND's formula $= 78.2$. In this way we got the values given under $\eta_0 . 10^7$. These were corrected for the change in $\frac{R^4}{L}$ with the temperature and for the gliding. The corrected values stand in column 7 under $\eta_t . 10^7$.

As can be seen, most of the measurements were made under a mean pressure of 40 cm. mercury. At 20°.1 K. we also took some measurements at 12 cm. mercury pressure. A glance at the table shows that the viscosity does not depend upon the density.

TABLE I.

Viscosity of helium at about normal density, observations and results.

$T°$ K.	p_{cmHg}	p_{cmHg}	$\tau_{\text{sec.}}$	ΔP_{cmHg}	$\eta' . 10^7$	$\eta . 10^7$
294°.50	10.83	36.81	13475	1.565	—	1994
294.55	7.892	44.43	13372	1.370	—	
250.3	9.870	42.98	9540.5	1.539	1806	1788
203.1	8.471	45.65	7828.5	1.622	1591	1564
170.5	8.522	42.60	7191.2	1.851	1420	1392
89.7	10.173	41.07	3201.0	2.709	943.7	917.9
89.8	8.480	44.60	2933.4	2.241	945.6	919.2
75.5	9.744	42.57	1828.1	1.999	841.8	817.6
74.7	7.037	45.30	3220.0	2.810	838.2	813.2
20.17	5.121	41.61	921.1	4.600	362.5	349.9
20.15	5.566	39.49	881.0	4.516	364.6	352.0
20.20	4.540	40.10	846.8	4.540	360.0	347.6
20.16	4.528	11.15	1788.8	2.113	362.9	351.5
20.16	4.530	12.28	1967.2	2.573	362.0	350.7
15.00	3.374	42.73	922.8	5.010	304.1	293.1
15.00	3.962	40.31	821.4	4.921	305.2	294.2
15.00	1.270	41.55	1514.1	2.981	307.5	296.4

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[1] K. SCHMITT: Ann. d. Phys. 30, 1909, p. 393.

In Table II our measurements are placed together with those made at Halle by **Schierloh** and **Schmitt**, which are marked with an asterisk. From this table and from fig. 1 it can be seen that our results correspond very well with the previous ones. Only **Schmitt**'s result in liquid air seems to be too high, which perhaps may be explained, as in **Kopsch**'s experiments with hydrogen, by the gas not being sufficiently cooled before it came into the capillary tube.

TABLE II.

Viscosity of helium at about normal density and representation of the dependence on the temperature by empirical formulae.

$T°K$	$\eta_{obs.} \cdot 10^7$	$\eta_S \cdot 10^7$	$\eta_{calc.} \cdot 10^7$
456.8*	2681	2682	2632
372.9*	2337	2345	2309
294.5	—	1994	1982
291.8*	1980	1979	1970
290.7*	1967	1974	1965
250.3	1788	1771	1783
212.2*	1587	1563	1603
203.1	1564	1513	1558
194.6*	1506	1460	1516
170.5	1392	1317	1389
89.75	918.6	745	918.5
[[79.9*	894.7	659	852.1]
75.5	817.6	628	821.3
74.7	813.2	621	815.5
20.17	349.8	135	348.9
15.00	294.6	92	288.7

§ 2. *Representation of the observations by a formula.* In the same table under $\eta_S \cdot 10^7$ the values are given which **Sutherland**'s formula gives with the assumed values of η_0 and C. **Schmitt** has already found that at the temperature of liquid air a distinct deviation appears. For this observation the same is true as we said about that of

Kopsch with regard to the deviation from Sutherland's formula of the observations on hydrogen at liquid air temperatures.

At hydrogen temperatures Sutherland's formula is shown to be entirely unsuitable for expressing our results. It gives a value two or three times too small. We have tried to represent the series of measurements by another formula, and in column 4 under $\eta_{calc.} \cdot 10^7$ we have given the values which we have calculated by the following formula.

$$\frac{\eta}{\eta_0} = \left(\frac{T}{273.1}\right)^{0.647}$$

As can be seen, this empirical formula agrees remarkably well with the values found over the whole extensive field of temperatures. In a following paper we shall discuss the values for

$$\frac{\eta_0 \sqrt{T}}{\eta_t \sqrt{T_0}}$$

which follow from our experiments, and further the viscosities at various temperatures for different substances in connection with the law of the corresponding states.

Physics. — *"Investigation of the viscosity of gases at low temperatures. III. Comparison of the results obtained with the law of corresponding states".* By H. Kamerlingh Onnes and Sophus Weber. Communication N°. 134*c* from the Physical Laboratory at Leiden by Prof. H. Kamerlingh Onnes.

§ 1. *Dependence of the viscosity upon temperature.* We have already discussed this in our previous papers. It was shown that Sutherland's formula in no way corresponded to the observations at low temperature, either for hydrogen or for helium [1]. Reinganum's formula although founded upon acceptable hypotheses about the constitution and mutual action of the molecules, is even worse so long as we regard C in it as constant. This can be easily understood when we consider that Sutherland's formula can be taken as a first approximation to Reinganum's, and that the terms left out must lead to a further divergence from the observations. Neither is it possible to come to an even approximate agreement at low tem-

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[1] Shortly after our paper an important article by Eucken appeared in the Phys. Zeitschrift (April 15th 1913) in which observations concerning the viscosity of helium and hydrogen taken from an as yet unpublished paper by Vogel were communicated. Within the limits of accuracy, which in Vogel's observations are given at $5^0/_0$ at hydrogen temperature, these confirm our measurements, of which the accuracy at hydrogen temperatures is to be put at about $1^0/_0$.

perature with the empirical correction of REINGANUM's C which RAPPENECKER has suggested.

We might for instance with helium take $C = C'' T \log T$, to come to agreement with the observations. But then REINGANUM's formula would simply be converted into our interpolation formula.

KEESOM, in Suppl. N°. 25 and 26 of these communications has shown, that the second virial coefficient in the equation of state for hydrogen, at temperatures at which this gas may be regarded as di-atomical, can be very statisfactorily explained by the supposition that hydrogen molecules are hard spheres with electric doublets in the centra. His formula for the virial of the collisional forces under these circumstances gives a change of the radius of the molecule with the temperature, which for higher temperatures agrees fairly well with that deduced from the viscosity by $\frac{\eta_t \sqrt{T_0}}{\eta_{t_0} \sqrt{T}}$. At lower temperatures at which hydrogen behaves like a monatomic gas, the formula for hard spheres with a central force according to the law r^{-q} becomes applicable, and KEESOM finds this again confirmed by the change of the viscosity with the temperature.

But when we go down to −193° C. deviations appear, in accordance with what we said above about SUTHERLAND's formula, and at lower temperatures the value of the viscosity becomes much too small.

None of the formulas deduced from theoretical suppositions can represent the observations for helium; for the present we can only use our empirical representation for this substance, which for hydrogen also holds good for lower temperatures than the theoretical formulas, viz. as far as the temperature of reduced oxygen. As regards the formula for helium, it is not impossible, that the straight line in the logarithmic diagram must be replaced by one that at low temperatures, and perhaps at higher ones also, curves somewhat towards greater values of the viscosity.

§ 2. *Application of the principle of mechanical similarity upon the comparison of the viscosities in corresponding conditions.*

If two substances may be taken as mechanically similar systems of molecules, it follows [1]) that the viscosities for both in corresponding conditions must be in a constant ratio which may be calculated from the ratios of the units of length, time, and mass in both systems. On the other hand from the values of

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[1]) H. KAMERLINGH ONNES. Verh. Kon. Akad. Amsterdam 21, p. 22. 1881 Beibl. 5. p. 718. 1881.

$$-\frac{1}{2}\log\frac{\eta}{\sqrt{T}\sqrt{M}} = \log\sigma - \log c$$

where M is the molecular weight, σ the mean radius of a molecule, as it is effective in viscosity, and c a constant, the same for all substances, we may, when the curves which express the connection between η and $\frac{T}{T_k}$ are the same, infer the ratio between the units of length which have to be ascribed to the two mechanically similar [1]) systems. With the help of the viscosity we can, therefore, make a comparison of the just defined mean molecular radii and we may inquire how far the ratio found corresponds to that of the mean molecular radii, determined in the way that is necessary in the deduction of the equation of state. If this correspondence were complete, then, when the expression of σ given above, is expressed in reduced quantities, the curves which express the logarithm of the reduced σ as a function of the logarithm of the reduced temperature for the various substances, would coincide. The accompanying diagram shows in how far this is the case. In the construction $M^{-1/2}\,T_k^{-1/6}\,p_k^{2/3}$ has been used as the ratio by which the viscosities [2]) are deduced to the same imaginary system. In this we have taken p_k and T_k which hold for the critical state [3]), as determining quantities, and postponed the consideration of deviation functions still later[4]).

The first thing that strikes one is the great deviation of helium. In § 1 we remarked that the character of the viscosity of helium can be expressed by replacing the constant c, which may be understood as a measure for the attraction between the molecules, in REINGANUM's formula (differing by a constant factor from c in KEESOM's formula) by $c'\,T\log T$. Perhaps this points to an increase with the temperature of the quantity which determines the attraction of helium.

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[1]) More correctly: mechanically and statistically similar.

[2]) H. KAMERLINGH ONNES Leiden Comm. No. 12, p. 9.

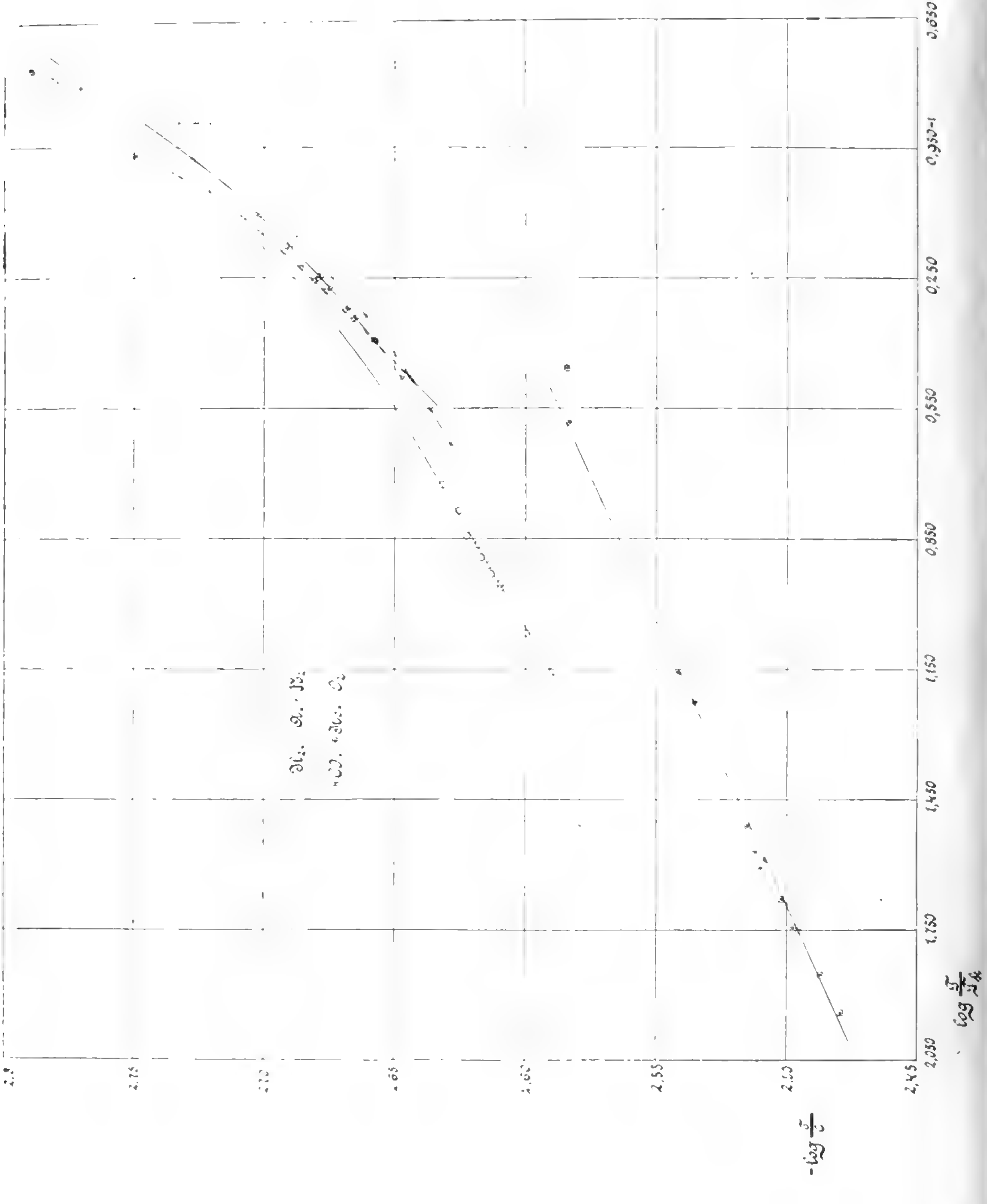
[3]) The cristical dates we have used are the following.

	p_k (Atm.)	T_k
H_2	15.0	32°.0 K.
He	2.26	5 .25
O_2	50.0	155 .0
N_2	33.0	127 .1
Ar	48.0	150 .7
CO	35.9	132 0

[Note added in the translation].

[4]) KAMERLINGH ONNES and KEESOM. Suppl No. 23, § 38. The ratios found by KEESOM in Suppl. No. 25, p. 12, note 3, give 6 % deviation for hydrogen and argon, those used here 9 %.

Kamerlingh Onnes was also led to assume a similar increase of the attraction with the temperature, to explain peculiarities in liquid helium, and Keesom in discussing the second virial coefficient of helium at higher temperatures, found that peculiarities of this coeffi-



cient might be ascribed to the same cause; in this case the receding of the attraction sphere (or the greater receding than in other substances) might be the cause of a slighter decrease of the viscosity at the reduction to lower temperatures. There might, however, also be an expansion of the molecule (in this case the atom) with temperature, and finally both phenomena might be dependent upon one cause, and go together. The possible small curvature for helium of the line in the logarithmic diagram [that we mentioned in § 1] in the opposite sense to that of the other lines which expresses the difference between helium and other substances, could be ascribed to this change in the attraction.

That which might explain the deviation for helium of the slope of the line from that which holds for a large range of temperatures for other substances, may also possibly help to explain the deviation from REINGANUM's formula at low temperatures, by the quantity which determines the attraction becoming smaller.

With hydrogen at the temperature of liquid air there is a distinct change in the slope of the curve. It is remarkable that the same is found with nitrogen, and perhaps also with oxygen and carbon monoxide, and that the point at which it occurs seems to lie at the same reduced temperature for hydrogen and nitrogen and perhaps also for oxygen and carbon monoxide. If this is the case, then the change which in the hydrogen molecules may according to KEESOM be taken as a change from hard spheres with electric doublets into hard spheres with a central force $r-q$ as far as the vis cosity, is concerned would be a similar process for all these different substances, determined by the same units of length, time, and mass as hold for the critical quantities, while this point only coincides with the point of transition in the specific heat of diatomic substances in the special case of hydrogen.

We must further notice the systematic differences between the different substances which appear from the non coincidence of the curves. It is remarkable that most of them (except a part of argon) can be removed by shifting the curves. The mean value of the molecular radius which comes into consideration for the viscosity seems thus to differ from the mean value which comes into consideration for the equation of state at the critical temperature, but both are in a fixed relation for the various materials over the whole field of temperature. This might be ascribed for instance, to a more elongated shape of the molecules in substances which give the smallest viscosity.

Physics. — "*Magnetic Researches. VIII. On the susceptibility of gaseous oxygen at low temperatures*". By H. Kamerlingh Onnes and E. Oosterhuis. (Communication N°. 134*d* from the Physical Laboratory at Leiden.) Communisated by Prof. H. Kamerlingh Onnes.

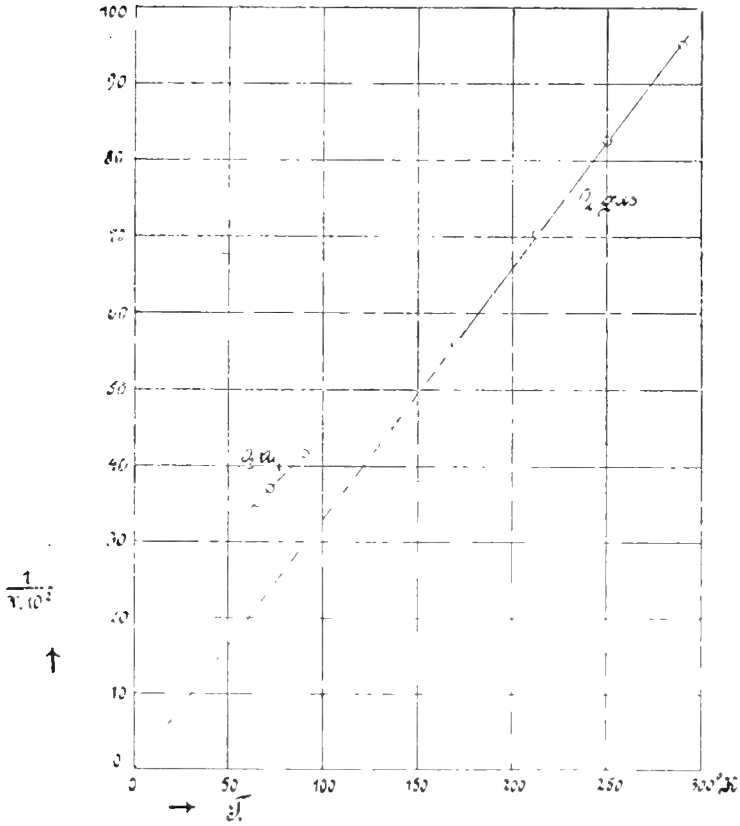
§ 1. *The susceptibility of compressed oxygen between* 17° C. *and temperatures near the critical temperature of oxygen.* In our last paper in connection with our investigations of various cases in which a molecular field of Weiss with opposite sign can be assumed with paramagnetic substances, we mentioned the continuation of the experiments by Kamerlingh Onnes and Perrier which have already been projected and the continuation of which may soon be expected, and which have for their object to investigate the influence, with oxygen, of bringing the molecules to various densities upon the deviations from Curie's law. Working in the same direction, we have endeavoured to ascertain whether in gaseous oxygen below the ordinary temperature and above the critical temperature a Δ appears. For this purpose we have measured the susceptibility of oxygen between 17° C. and — 126°.7 C. We used the attraction method in the same form as described for the paramagnetic salts in our previous paper. A copper tube, closed underneath, 10 cm. long, 8 mm. external and 6 mm. internal diameter, provided with a capillary tube above, by which it could be filled with oxygen under pressure, and closed, one time with a fine tap in which the capillary tube ended, another time by pinching this capillary, and then soldering up after it had served for filling, was filled with oxygen at ordinary temperature to 100 atmospheres. The experiment was then repeated with the evacuated tube in the same baths. For results: (see table I p. 1405).

The experiments should be regarded as comparative for the question under consideration, but the absolute value of the susceptibility was also determined at 289°.9 K. It corresponds pretty well to that of Weiss and Piccard. As manometer we used a metal manometer which was compared with a hydrogen manometer going to 120 atmospheres. The density of oxygen was taken from Amagat. χT appears to be constant, within the limits of accuracy (which is about 1 %) as far as the boiling-point of ethylene (169°.6 K.). The two points in ethylene, evaporating under reduced pressure, deviate a little, but this need not be considered as of much importance, as these temperatures were not accurately known. Moreover the proximity of the critical temperature made the distribution of density in the tube uncertain.

We may draw the conclusion that within the limits of accuracy

TABLE I. Gaseous oxygen ($\rho_N = 100$)
$H = 10$ to 18 kilogauss.

T	$\chi . 10^6$	$\chi . T . 10^4$	Bath.
289°.9 K.	105	304	In air.
249.7	121	302	Liquid methyl chloride.
212.1	142	301	
169.6	179	304	Liquid ethylene.
[157.7	188	296]	
[146.6	201	295]	



in the measurements a Δ does not yet appear in oxygen above the critical temperature at densities which are 100 times the normal. From this it seems all the more probable that Δ only appears for oxygen at great densities, and in liquid oxygen can rise to the considerable value of 71° as the density rises to 1000 times the normal.

In the accompanying figure our observations concerning gaseous oxygen and those of Kamerlingh Onnes and Perrier which we confirmed in our last paper, are combined in a graphic representation; the uncertain points near the critical temperature are not given. The point of intersection of the line for gaseous oxygen with the production of the line for the liquid state, appears to have no physical meaning; as we supposed in our last paper, it is due to the value of the constants, that the temperature which indicates the intersection of these lines happens to be about the ordinary one, at which amongst others, the observations of Weiss and Piccard fall, and below which as yet no observation had been made for gaseous oxygen.

(*To be continued.*)

Physics. — "*Further experiments with liquid helium.* H. *On the electrical resistance of pure metals etc.* VII. *The potential difference necessary for the electric current through mercury below* 4°.19 K." By Prof. H. Kamerlingh Onnes. Communication N°. 133*a* and 133*b* from the Physical Laboratory at Leiden.

(Communicated in the meetings of February 22 and March 22, 1913).

§ 1. *Difficulties involved in the investigation of the galvanic phenomena below* 4.°19 K. In a previous Communication (No. **124*c*** of Nov. 1911) we related that special phenomena appeared when an electric current of great density was passed through a mercury thread at a temperature below 4°.19 K., as was done to establish a higher limit at every temperature for the possible residual value of the resistance. Not until the experiments had been repeated many times with different mercury threads, which were provided with different leads chosen so as to exclude any possible disturbances, could we obtain a survey of these phenomena. They consist principally herein, that at every temperature below 4°.18 K. for a mercury thread inclosed in a glass capillary tube a "*threshold value*", of the current density can be given, such that at the crossing of the "threshold value" the phenomena change. At current density below the "threshold value" the electricity goes through without any perceptible potential difference at the extremities of the thread being necessary. It appears therefore that the thread has no resistance, and for the residual resistance which it might possess, a higher limit can be given determined by the smallest potential difference which could be established in the experiments (here $0.03 \,.\, 10^{-6}\, V$) and the "threshold value" of the current. At a lower temperature the threshold value becomes higher and thus the highest limit for the possible residual resistance can be pushed further back. As soon as the current density rises above the *"threshold value"*, a potential difference appears which *increases more rapidly than the current*; this seemed at first to be about proportional to the square of the excess value of the current above the initial value, but as a matter of fact at smaller excess values it increases less and at greater excess values much more rapidly.

It appears that the phenomena at least for the greater part are due to a heating of the conductor. It has still to be settled whether this heating is connected with peculiarities in the movement of electricity through mercury, which for a moment I thought most probable in connection with various theoretical suppositions (comp. § 4), when this metal has assumed its exceedingly large conductivity at low helium temperatures; or whether it can be explained by the ordinary notions of resistance and rise of temperature of a conductor carrying a current, perhaps with the introduction of extra numerical values for the quantities that influence the problem. A further investigation of this with mercury in the most obvious directions, such as cooling the resistance itself with helium, presents such difficulties that I have not pursued it, as it would not be possible to prepare the necessary mercury resistances by the comparatively simple process of freezing mercury in capillary tubes. When I found (Dec. 1912) that, as I shall explain in a following Comm., (see VIII of this series Comm. N°. 132*d*) tin and lead show properties similar to those of mercury, the investigations were continued with these two metals. Thus the experiments with mercury which are described below may be regarded as a first complete series.

Various circumstances combined to make even the investigation of the mercury inclosed in capillary tubes difficult. A day of experiments with liquid helium requires a great deal of preparation, and when the experiments treated of here were made, before the latest improvements in the helium circulation were introduced, there were only a few hours available for the actual experiments. To be able to make accurate measurements with the liquid helium then, it is necessary to draw up a programme beforehand and to follow it quickly and methodically on the day of experiment. Modifications of the experiments in connection with what one observes, must usually be postponed to another day on which experiments with liquid helium could be made. Very likely in consequence of some delay caused by the careful and difficult preparation of the resistances, the helium apparatus would have been taken into use for something else. And when we could go on with the experiment again, the resistance sometimes became useless (e. g. § 3) because in the freezing the fine mercury thread separated, and all our preparations were labour thrown away. Under these circumstances the detection and elimination of the causes of unexpected and misleading disturbances took up a great deal of time.

§ 2. *Confirmation of the sudden disappearance of the resistance at* 4°.19 K. *and first observations concerning the potential phenomena at low temperature.* The first experiments which showed the phenomena to be discussed were made in October 1911, with the resistance described in the previous Comm. (N°. 124*c*).

a. Before discussing them let us consider for a moment the measurements which were made with this resistance at 4°.23 K. and add something to what we said about them in the previous Comm.[1]). In the measurements which we are considering we could take advantage[2]) of the presence of Hg_5 to measure the portions between Hg_1 and Hg_5 and between Hg_5 and Hg_4 separately and afterwards the two in series. The result was $Hg_1 Hg_5 = 0.0518\,\Omega$, $Hg_5 Hg_4 = 0.0617\,\Omega$, together $0.1135\,\Omega$. This gave a necessary check on the determination of the two in series $Hg_1 Hg_4 = 0.1142\,\Omega$[3]). These values, considering

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[1]) For a survey of the observations concerning mercury at the lowest temp. in three figs. with rising scale the reader is referred to Rapport du Comité Solvay, Nov. 1911, fig. 11, 12 and 13 (in which read 13 for 12, and 12 for 13, Leiden Comm. Suppl. N⁰. 29).

[2]) The measurements with a view to which the tube Hg_5 was added (see Plate I in Comm. N⁰. 124*c*) were not made then, but postponed till later. (See § 5). They were to enable us to judge of the dependence on the section.

[3]) The resistance at the boiling point of hydrogen was 3.27 Ω. A further Comm. will refer to the difference of the ratio of the values at 273° K. and 20° K. to those in previous measurements, which is here of no consequence and is due to different ways in which the mercury freezes. In the experiments described here, similar differences were constantly found.

It should be mentioned that the glass was tested at all temperatures for its insulation and also that when the potential difference at the terminals was found to be zero, it was always ascertained that the resistance of the galvanometer circuit which served to measure the P. D. had not changed materially.

that they belong to about 65 Ω (calculated for solid mercury at 0° C.) correspond pretty well to the results obtained in the experiments in May 1911 Comm. N°. 122*b*, July 1911, viz. that a resistance of about 40 Ω (calculated for solid mercury at 0° C.) becomes 0.084 Ω at the boiling point 4°.25 K.

β. In these experiments the validity of OHM's law was confirmed above the point where the almost sudden disappearance of the resistance begins which was treated in the previous Comm. by one measurement at a current strength of 3 and another of 6 milliampères which within the limits of accuracy gave the same result (0.0837 at 3, and 0.0842 at 6 m.A.). In connection with the experiments in Comm. N°. 122*b* July 1911 we may mention that they were made with a resistance of a different kind from that[1] which was used for the experiments in Oct. 1911, viz. the one which appears in the Plate of Comm. N°. 123 as Ω_{Hg} (of about 40 Ω calculated for solid mercury at 0° C.). Narrow tubes alternately going up and down were connected by expansion heads (as in the Plate in Comm. N°. 124*b*) and connected to platinum leading wires by fork-shaped turned down wide pieces[2], which can be seen distinctly on magnification on the Plate in Comm. N°. 123 (where the resistance is shown in the cryostat).

γ. After this digression about the change in the resistance between ordinary temperature and the boiling point of helium, let us return to the experiments in and below the region of the sudden fall of resistance, which as has been said at the beginning of this § were made with a mercury resistance with mercury leads, and which were treated of in § 3 and fig. 1 of the previous Comm. (Dec. 1911) about the resistance at helium temperatures (experiments of Oct. 1911).

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[1] This was a ramification of solid mercury threads consisting of a U divided at both ends, allowing measurements as well by the method of CALENDAR as by the potentiometer method. (Note added in the translation).

[2] In the resistances which were used for the first experiments with mercury, the platinum leading in wires were simply sealed into the wider portions of the resistance tube at the ends (the expansion heads). When the mercury cannot be poured into the tube in vacuo but has to be boiled in the tubes in order that they may afterwards be exhausted without any chance of the mercury separating there is some fear of platinum amalgam being formed which might penetrate into the current circuit. In order to prevent this the wide ends of the tubes are according to a suggestion of Mr G. HOLST, made fork-shaped, the prongs which contain the sealing place being turned down. In this manner mercury leads may in general be replaced by platinum leads without any trouble being experienced with regard to the resistance of the current circuit. By a comparison with experiments with mercury leads it had been found that the mercury-platinum contacts could be allowed in the potential circuit

At 4°.20 K. we find ourselves in the higher part of the almost sudden change. In the case that we are now about to treat it had almost become complete. With a current of 7.1 m.A. it was a considerable time before the condition became stable. When this had taken place, the resistance of $Hg_1 Hg_4$ was found to be 0.000746 Ω [1]).

At a further cooling of the mercury to $4°.19^5$ K. with the same strength of current the result was only $Hg_1 Hg_4 < 1.4 . 10^{-5}$ Ω.

d. At 4°.19 K. we come into the lower part of the region with which this Comm. deals in particular. The strength of the current had to be increased to 14 m.A. to give a perceptible potential difference at the ends of the resistance but even then it remained doubtful. It became distinct at a current strength of 0.02 amp. and was then $2.5 . 10^{-6}$ V. At 0.023 amp. it became $5 . 10^{-6}$ V, and at 0.0288 amp. $16 . 10^{-6}$ V.

When the mercury thread was cooled by helium which evaporated at a mercury pressure of 40 cm. that is at about 3°.65 K., with a strength of current of 0.49 amp. there was no potential difference to be observed at the extremities, the current had to be increased to the threshold value of 0.72 amp. to make the potential difference observable.

ε. The highest limit of the value which the residual resistance can have in the case of the lowest temperature, is therefore in these last experiments again considerably reduced by the application of stronger currents, viz. in this case (3°.65 K.) to 10^{-9} of the resistance at 0° C. (calculated for solid mercury) while in Comm. N°. 122*b* June 1911 at 3° K. it could only be put at $< 10^{-7}$.

§ 3. *Appearance of the same potential phenomena in a revised arrangement of the experiment.* The appearance of the peculiar phenomena immediately above the "threshold value" of the current, gave rise to the question whether the just established limit would not have to be put lower when it should be possible to avoid the disturbances, which might still exist, and perhaps showed themselves in the above mentioned phenomena. The most obvious thing in the first place was to prevent the possibility with great current density of heat, developed in places in the main circuit where the temperature is higher, penetrating to the resistance that is being measured. By this, from both ends, the thread would be brought over part of

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[1]) Here and in the following we speak repeatedly of resistance, without wishing to give it beforehand any other meaning than: calculated by OHM's law from the strength of current and the potential difference observed.

its length above the vanishing temperature, which would immediately cause considerable potential differences. In this connection we thought particularly of JOULE heat. PELTIER heat, which we had noticed before (Comm. N°. 124*c*) but which for the present we attributed to impurities in the mercury in the legs, and assumed to be present only in the neighbourhood of the transition from solid to liquid, I took to be as far as possible excluded by the fact that the whole current system was of pure solid mercury at the very low temperatures. Now this belief may be untrue, because owing either to tension caused by a difference of expansion to that of glass which it seems can be fairly great as the mercury sticks to the glass, or through the contact between crystals of different kinds or sizes, even in the purest mercury considerable thermopowers may possibly appear. But then they have their seat, as shown by the previous experiments, chiefly in places above the temperature of liquid air and PELTIER heat in these places need not be feared. To avoid disturbances of the sort to which we referred the experiment was repeated with resistances of such a kind that the conduction of any kind of heat from a part of the apparatus where there was higher temperature was made very difficult. The accompanying figure, which should be compared with figs. 1 and 2 on the Plate in the previous Comm. N°. 124*c* (VI of this series) shows the form chosen. The mercury threads which lead the current to and from the apparatus, run first through the liquid helium downwards, before they come out into the widened parts of the resistance. The potential wires do the same[1]. Close to the surface of the liquid the leading

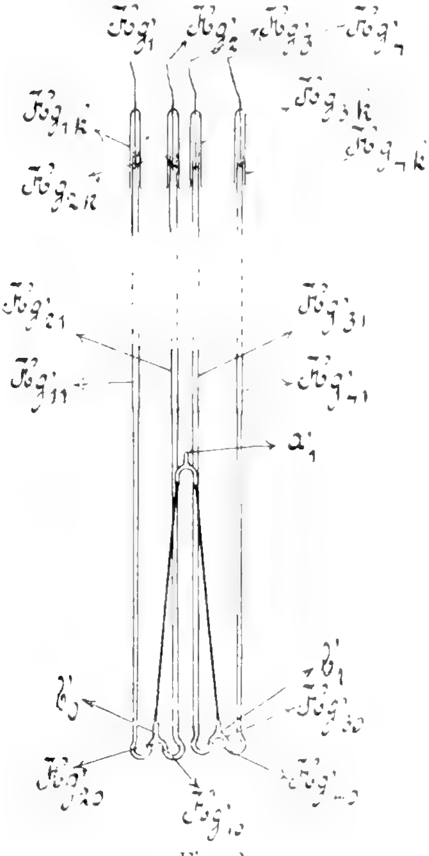

Fig. 2.

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[1] Corresponding parts are indicated by the same letters, modified parts by the addition of an accent. A small additional improvement was further introduced into the contacts at the upper end, the four leading tubes were simply left open

wires can be thin on account of the low temperature. There were two resistances of the same kind in the cryostat, one of 50 Ω and the other of 130 Ω, the section of the tubes was about 0.004 mm² and 0.0015 mm². They were intended to investigate the influence of the section of the tubes upon the phenomena examined, a thing that had been aimed at already before (see § 2) but did not succeed and the preparation of the narrowest one in particular had given great difficulties. It gave way during the experiment, so that the question of the influence of the section had again to be solved later on (see § 5). The experiments which were of chief importance for the matter under consideration were made in Dec. 1911 with the smallest of the two resistances, the section of the narrow resistance tube was here a little smaller than the mean in the resistance which was used for the experiments in Comm. N°. 124*c*.

On the whole the results were the same as by previous measurements. Although great care[1]) was again given to the distillation of the mercury with the help of liquid air[2]), the mercury legs, as has

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(which made it easy to add mercury which the contraction during the freezing made necessary), and bell shaped tubes *Hgk* were placed over the extremities in which the platinum wires *Hg'* etc. are sealed, which connect the resistance to the current sources and the measuring apparatus. Platinum amalgam (see note 2, p. 4) need not be feared in this case, so that the complication of the inverted forks was superfluous.

We do not need here to enter into particulars of precautions such as the protection of contacts against changes of temperature, and others which have reference to the special circumstances under which the resistance measurements were made

Fig. 2.

[1]) In § 9 it is demonstrated that in repeating the experiments not so many precautions would have been sufficient.

[2]) In the distillation the mercury was not heated above 65° and 70° C. while the cooling was effected with liquid air. In order not to have to wait too long to procure a sufficient quantity it was done in an apparatus shown in fig. 2 at $^1/_3$ of the actual size. The mercury is brought into the double walled tube *a b* (with the reception beaker *c*), which was sealed off below at *e*. It is exhausted through tube *d*, while the mercury is warmed and then sealed off at *f*.

The lowest part is immersed in warm water; in the hollow *a* liquid air is poured. In 3 hours about 2 cm³ goes over; the condensed mercury in *c* is afterwards poured out at *f*.

been observed, gave considerable thermo-power; the legs with the smallest thermo-power were chosen as potential wires[1]).

There was some indication that the resistance of the mercury in narrower tubes falls a trifle less than in wider ones, when the tubes are cooled to 4°.25 K. (boiling point of helium). The new experiments also raised the question whether the almost sudden changes were found at a slightly different temperature of the bath in the narrower than in the wider tubes. But all this concerns particulars which can probably be explained by differences of crystallization and of heating by the current.

That the almost sudden change begins at 4°.21 K.[2]) and ends

TABLE I.

Potential difference of the extremities of mercury threads carrying a current.

Temperature	Current density in ampères per mm²		Potential difference in microvolts	
	October 1911	December 1911	October 1911 $l = 7 \times 20$ cm	December 1911 $l = 20$ cm
3°.65K.	0.49 × 190		0	
		0.510 × 260		0
	0.56		0	
		0.665		0.5
	0.72		7 × 1.14	
		0.890		4.7
		1.10		12.7
4°.19K.	0.010		0	0
	0.014		7 × 0.017	
		0.016		0.4
	0.020		7 × 0.36	
	0.023		7 × 0.71	
		0.024		4.7
	0.028		7 × 2.3	

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[1]) It amounted to only 12 microvolts, and this was compensated. The seat of these E. M. F. (up to 340 microvolts) is to be found principally in the portion above hydrogen temperature.

[2]) This means more precisely 0° 04 below the boiling point of helium.

within a fall of 0°.02, was again confirmed with a resistance of about 50 Ω (calculated for liquid mercury at 0° C.).

Concerning the threshold value of current and the potential differences appearing at higher currents, i.e. the phenomenon to which the investigations were especially directed this time (Dec. 1911) results were obtained which correspond pretty well with the previous ones (Oct. 1911) if we assume that the origin of the phenomenon is in the resistance itself, and at the same time make the natural assumption that the potential difference increases with the current density, and with conductors joined in series is equal to the sum of the potential differences in each of these conductors. This is shown in the table, in which both series of observations are combined, and holds both for the minimum value of the current at which the potential difference appears, and the value of the potential difference at a given excess value of current and a given temperature.

For we must remember that the previous resistance consisted of 7 U-shaped tubes not all precisely similar, averaging 37 Ω, and the present one of one U-shaped tube of 50 Ω, while the lengths of the tubes did not differ much. The appearance of the potential difference was therefore, on our supposition, to be expected in the last case at a slightly smaller current than in the first; on the other hand, the greater length which was partly compensated by a greater section, made it probable that in the October experiments the potential difference at the same temperature and current would be a few times larger, though not as much as seven times.

§ 4. *Questions to which the experiments give rise.* There were not sufficient data to make out whether the resistances used really differed as much as was thought as regards the opportunity of receiving heat through heat conduction from elsewhere, in particular Joule heat. It would however have to be regarded as a curious coincidence that this conduction of heat in conjunction with other causes had led to such a close correspondence in the phenomena observed. It seemed much more probable that the phenomena were to be accounted for not by disturbances from outside, but by resistance arising in the thread itself.

Where such a remarkable change in the condition of the mercury takes place as is shown by the disappearance of the ordinary resistance, the appearance of a "threshold value" dependent on the temperature naturally gave rise to the question, if we had to do with a deviation from Ohm's law[1] for mercury below 4°.19 K. The electron

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[1] I hope to return to the new and important theory of Wien, in a further comm.

theory, supplemented by the hypothesis in Comm. N°. 119, that the resistance is caused by PLANCK's vibrators [1]), and by the more special hypothesis that the electrons move freely through the atoms as long as they do not collide with the vibrators and are reflected as perfectly elastic bodies at the surface of the conductor, indicates causes which might work in that direction. The distance which the free electrons travel between two collisions at which they give off energy derived from the electric force, might become comparable to the dimensions of the conductor below 4°.19 K. (compare Comm. N°. 119 Feb. 1911 § 3, last note); the speed which they acquire in the electric current is perhaps no longer negligible compared with the velocity of the heat movement; for a certain current density at each temperature it might be just sufficient to bring the vibrators into motion, which otherwise below 4°.19 K. are stationary [2]). Considering all this, we may not take it as a matter of course, that OHM's law will still hold below 4°.19 K. and a further investigation of this will be interesting, if it only proves that this is actually the case.

As long as the contrary is not experimentally proved, we shall however adhere to this law, because we have first to try to refer the phenomena as much as possible to already known ones and so far on appropriate suppositions from the domain of known phenomena the results obtained did not seem incompatible with OHM's law.

Various possibilities presented themselves at once. A very small residual resistance evenly distributed throughout the whole thread might remain, which might be peculiar to the pure metal as such (§ 12*a*), or might be the consequence of an admixture (mixed crystals)

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[1]) LENARD has recently given two important papers on the conduction of electricity by free electrons and carriers, which intend with a third paper to make a whole of his highly interesting researches on the interaction of electrons and atoms and the theory of metallic conduction. This gives to the latter a new and very promising base. In the first paper Ann. d. Physik 40 p. 414, 1913 he comes to the result making use of the great conductivity of metals at helium temperatures (Comm. N°. 119) that OHM's law is only valid within narrow limits for metals at very low temperatures; comp. further VIII § 16 of this Series. (Note added in the translation).

[2]) At the great current densities that were attained in some of the experiments (see § 7), (they went up to 1000 Amp. per mm^2) the question arises if even the change in the resistance of the conductor through its own magnetic field of the current through the conductor should be considered, as it might be the case, that the resistance in the magnetic field for mercury in this condition was much greater, just as it alters with the temperature for some other substances, and has been found to increase for mercury at hydrogen temperatures (KAMERLINGH ONNES and BENGT BECKMAN, Leiden Comm. N°. 132*a*).

evenly distributed through the metal. It might also be that the pure metal in the particular condition in which it comes below 4°.19 K. and in which the atoms perhaps form one whole together, does not possess any resistance at all, but that somewhere (§ 11) in the thread through some peculiarity a section is sufficiently heated by great current density, to bring the temperature of the thread locally up to the vanishing point. In either way an ordinary resistance could be formed somewhere, which, when the strength of current is further increased, gives rise to an accelerated heat evolution and an increased development of resistance.

§ 5. *Further investigation of the potential difference phenomena, in particular at temperatures slightly below the vanishing point.* It was considered desirable in the first place, to investigate the influence of the thickness of the thread upon the temperature, at which the fall of resistance occurs, and also upon the more or less sudden disappearance of the resistance.

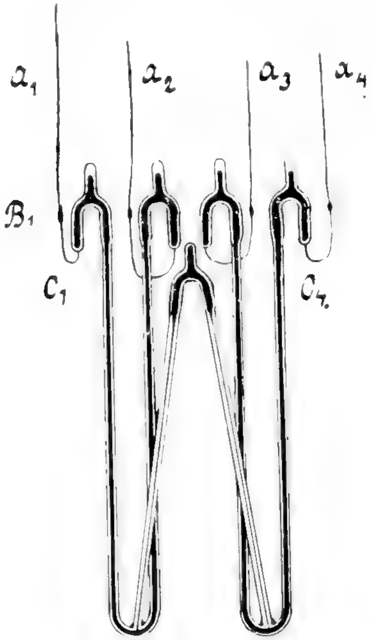

Fig. 3.

The resistance apparatus with which the experiments (Jan. 1912) for this purpose were made differed from those of Dec. 1911 only in this, that in the two pairs of mercury threads which serve for the measurement of the resistance of the mercury (two current leads and two potential threads) the pieces that were above helium temperature were replaced by copper wire, in this way that the mercury legs were cut off and sealed up, and in the sealed up ends, as in the resistances of Oct. 1911, platinum wires were sealed in, which were in their turn joined to copper leads [1]. During the experiments all these contacts were immersed in liquid helium, compare fig. 3. This change was made since

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[1] The wires were made comparatively fine, to prevent the liquid helium from evaporating too quickly from the conduction of heat. Besides the condition of heat from above the absorption of radiated heat by the metal in the transparent apparatus was avoided. Later on, when the various circumstances could be better surveyed, leads were constructed which could carry a strong current without causing too much evaporation.

it had been shown that the kind of lead had little influence on the phenomena, so as to be free from the troublesome thermocurrents in the potential wires, when these were of mercury, from the resistance which was immersed in helium to where the ordinary temperature began, and all four were replaced in order to be free in the choice of the pair of threads which were to be used as potential wires or as current leads. The thermopowers were now only about 10 microvolts.

The experiments of Jan. 1912 were made with two mercury threads, one with a resistance of about 50 Ω, the other of about 130 Ω. These resistances were joined up in a circuit with a milliammeter, which could be shunted, and to each of them one of the coils of a differential galvanometer was connected as a shunt. By using only one coil at a time the resistance of each of the mercury threads could be measured separately; by connecting the two coils in the opposite direction the change in the ratio of them with the temperature could be investigated as long as the difference was small.

The ratio

$$\left(\frac{W_{180}}{W_{50}}\right)_{T=290^\circ} = \frac{128,4}{50,4} = 2\ 55$$

became, through cooling to the boiling point of helium

$$\left(\frac{W_{180}}{W_{50}}\right)_{T=4^0,25} = \frac{0,0542}{0,0249} = 2,18.$$

The ratio changed, as had been found before, and as could be readily explained by a slightly different manner of freezing of the mercury in the two tubes.

On changing the current strength at 4°.25 K. we found

Current in Amp.	W_{130}	W_{50}
0,006	0,0545	0,0251
0,010		$0,0250^5$
0,016		0,0249
0,030	0,0549	0,0260 [1]).

Up to currents of 0.03 amp. therefore it is confirmed that there is no reason to assume a deviation from Ohm's law above the vanishing point.

On lowering the temperature from the boiling point to where the

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1) As regards the deviation at 0,03 amp. of W_{50}, we may perhaps conclude from the comparison of the ratio of the resistances at $T = 290°$ K and $T = 4°.25$ K. in the two resistances, that there is a thinner place in the thread W_{50} by which a greater heating takes place locally at temperatures above the vanishing point, than would be expected from the average section.

disappearance of the resistance begins, this ratio remained unchanged according to the observations with the differential galvanometer; from that point downwards the resistance in which the current density was smaller, disappeared more quickly.

Although the resistance in the experiments disappeared gradually, yet the way in which it disappears gives the impression that the change in resistance of the mercury with the temperature occurs suddenly and that the gradual disappearance of the potential is due to the fact that the thread is only gradually cooled over its whole length to below the vanishing point, and only that part which is below this temperature loses its resistance.

It was again confirmed that at temperatures some tenths of a degree below the vanishing point no resistance was found up to very high current densities. Table III may be compared with Table I. In W_{130} the current density could be raised to 400 amp. per sq. mm. without the least resistance being perceptible. The highest limit for the resistance is hereby put back at 3°.6 K. to $< 4.10^{-10}$ of

TABLE II.

Resistance of mercury threads carrying current in the neighbourhood of 4°.2 K.

T	3.7 amp./mm^2 W_{130}	1.6 amp./mm^2 W_{50}
4°.24 K.	0.0532	0.0244^5
4 .22	459	182
216	314	0.0069
214	264	34
213	190	13
210	128	0.0003
207	0.0087	1
205	50	1
201	46	0.0000
196	21	0.0000
190	0.0005	0.0000
180	0.0000	0.0000

the value at 0° C. (in the solid state) and reduced to about half of that to which we could go down in the January experiments.

TABLE III

Potential differences at the extremities of mercury threads carrying a current. $l = 20$ cm.
$\pi r^2 = 0{,}0016$ mm² for W_{130}
$= 0{,}004$ „ „ W_{50}

Temp.	Current density in amp. per mm².		Potential difference in microvolts	
	W_{130}	W_{50}	W_{130}	W_{50}
3°.6 K	375	160	0	0
	490		0.27	
	5(0		2.12	
	625	260	12.9	0

For W_{50} at a strength of current of 1 amp. the current density which in W_{130} appeared to be the threshold value was not yet reached. A stronger current was applied. But now a special disturbance arose: on raising the current to 1.5 amp. so much **Joule** heat was generated by the current in the platinum wires joining the mercury leg, that this reached the thin mercury thread and brought it up to a temperature above the vanishing point. All this was accompanied by a rapid boiling of the helium, while the ammeter showed a strong falling off of the main current corresponding to a decided rise in the resistance. From the readings it could be seen that the resistance of W_{50} had risen to that which it has at hydrogen temperature. This time it seemed most probable that the potential differences could be attributed entirely to heat introduced from outside, so that if this could be prevented it would be possible to bring at these lowest temperatures the highest limit for the possible residual resistance still nearer to zero.

§ 6. *Experiments with an apparatus arranged so as to be sure that no heat penetrates to the thread from places at a higher temperature than that of the vanishing point.*

A mercury resistance was made, suitable for observing the potential changes, when a current of 3 amp. went through the same mercury thread as in the last experiments, and to make certain that the disturbances which had occurred would be impossible. The mercury thread *C*, see fig. 4, at the ends of which the potential was to be measured was for this purpose lengthened at both ends by an auxiliary mercury thread of larger section. We will call these auxiliary threads *A* and *B*.

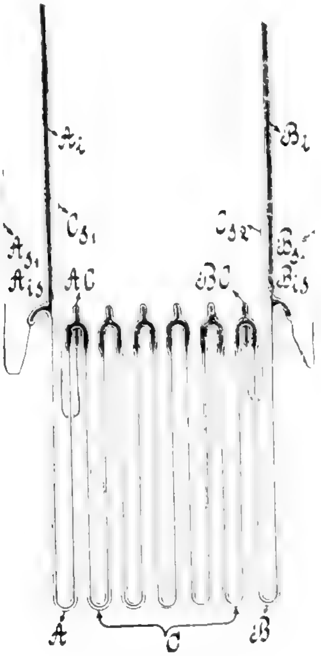

Fig. 4.

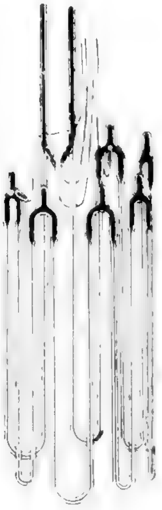

Fig. 5.

By measuring the potential difference at the extremities of both auxiliary threads it could be ascertained that any heating above the vanishing point could not be the consequence of the introduction of heat which had entered the extremities of the resistance *C* which was to be examined through conduction. For this heat could only enter through the sentinel wires, and these could only become dangerous to the experiment after betraying a heating above the vanishing point by showing a potential fall.

On the ground of the experience in the last experiments, the connecting wires carrying the current in to the resistance (compare the diagrammatical fig. 4 and the perspective fig. 5) were again of mercury, in order to prevent Joule heat being transported to the resistance, while sealed in platinum wires to which copper wires were soldered served as potential wires. The sentinel thread *A* had at the ordinary temperature about 35 Ω, the sentinel thread *B* about 36 Ω resistance, the resistance *C* consisted of five threads in series of about 80 Ω resistance each and with a combined resistance of about 390 Ω at ordinary tempe.ature.

At the boiling point of helium $W_{SA} = 0.01831\ \Omega$, $W_B = 1.01285\ \Omega$, $W_C = 0.1773\ \Omega$. The observations were as shown in Table IV.

We had therefore not succeeded, as had been our intention in giving a larger section to *A* and *B* than to *C*, in managing that if *C* should show potential difference, it would do so before *A* and *B* did it. Only if this had happened it would have been shown that the heat that brought *C* to a temperature above the vanishing point was developed inside *C*. And the potential which now appeared in *C* can again be ascribed to heat conduction through *A*. The experiment shows very clearly that accidental circumstances in the freezing of the mercury threads play a part in the determination of the "threshold value" of the current density, and that in calcu-

TABLE IV.
Resistance of a mercury thread
just below 4°.20 K.
$\pi r^2 = 0.0025$ mm² for W_C.

Temp.	W_{SA}	W_{SB}	W_C
	current density 2.5 Amp. p. mm² in W_C		
4°.24			0.163 Ω
4 .234			0.161
4 .230		0.011	0.158
4 .222		0.0078	0.0774
4 .208	0.0022	0.0025	0.00775
4 .192	0.000024		0.000024
4 .185	0.000012		$< 10^{-6}$
	current density 12 Amp. p. mm² in W_C		
4 .185	0.000071	0.000153	$< 10^{-6}$
	current density 20 Amp. p. mm² in W_C		
4 .185	0.000117		0.000048

lating with the average section of the tube in which the thread is frozen, only a lower limit can be given for this.

Possibly the mercury in A and B was only frozen in an unfavourable form, and therefore greater local current densities or worse exchange of heat had arisen than the average.

§ 7. *Repetition of the experiment with the same apparatus.* We obtained more favourable results from another freezing. First a few results may be given, which were obtained by measurements at different strengths of current at 4°.25 K., that is at a temperature above the vanishing point. These results gave an opportunity of judging to what degree heat can be given off by the mercury thread closed up in a glass capillary or flows off along the extremities.

From the increase of resistance at greater current strength, the rise of temperature was deduced on somewhat simplified suppositions, at which the equilibrium between the JOULE heat and the heat given off to the outside is established. The result for the resistance and the average rise of temperature of C was:

current		resistance	rise of temp.
0,006	amp	0,1928	0°,
0,006	,,	0,1932	0°,
0,356	,,	0,2149	0°,12
0,500	,,	0,2410	0°,25

The average rise of temperature was calculated by the formula got by separate determinations

$$W_T = W_S(1 + 0.9(T - T_s))\ ^{1)}$$

in which T_s represents the boiling point of helium.

It follows from these determinations that per degree of difference of temperature between mercury thread and bath 0.057 calorie is given off per second. If we assume that all the heat goes through the glass, that the mercury touches the glass everywhere, and that we only have to consider the narrow capillary, then we find with $d_i = 0.056$ mm, $d = 2.07$ mm, $l = 100$ cm, for the conductivity of glass $k = 0.00033$, while at ordinary temperature $k = 0.0022$.

The loss of heat through the glass must therefore by cooling to the boiling point of helium have become much less than at ordinary temperature, which might possibly be the consequence of the mercury only touching the glass at a few places besides in the bends.

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1) See the fig. in Comm. No. 124. Dec. 1911.

The application of the data obtained at temperatures below the vanishing point is in the nature of the matter uncertain, as we do not know whether, with the galvanic change in the mercury, there may not be another change in the thread, which would bring about a further change in the giving off of heat.

With regard to the appearance of potential differences at the extremities of the thread, we found the data contained in Table V.

At 3°.6 K. the current at which a potential difference would appear in the sentinel wires could not be measured, as, before the current had reached this value, the resistance *C* was heated to above the vanishing point along too great a length.

TABLE V.

Strength of current at which the potential difference appears at the extremities of a mercury wire carrying a current below 4°.2 K.
$\pi r^2 = 0{,}0025$ mm² for *C*.

Temp.	*A*	*B*	*C*
4°.18 K	0,0535	0,0615	0,034
4. 10	0,232	0,317	0,172
3. 60			1.068
3. 28			1,646
2. 45			2,56

What we were aiming at was however attained in these experiments of Feb. 1912. It is established that heat is produced in *C* by raising the strength of current sufficiently, and that the heat is not conducted to it from *A* and *B*, since *A* and *B* were at a lower temp. than the vanishing point as appeared by the absence of potential fall in them. It is developed in the thread itself.

Table VI may be subjoined concerning the experiment at 2°.45 K. corresponding to Tables I and III.

At the same moment that the galvanometer which measures the potential difference at the extremities of the thread is deflected, the strength of current in the main circuit falls from $i = 2.84$ amp. to $i = 1.04$ amp. which corresponds to an increase of resistance $\Delta W = 2.44\ \Omega$ in the circuit, from which it appears that the resistance is heated nearly to the temperature of hydrogen by the remaining current, of 1 amp. nearly.

If we take the last described experiments together, we have been able by them on the one hand to raise the current density to the enormous value of about 1000 amp. per mm², without any heat being developed in the wire. This threshold value for the current density brings the highest limit for the possible resistance of mercury in the peculiar condition into which it passes below 4°.19 K. and particularly when it is cooled to 2°.45 K. still further back, and the ratio of the resistance at 2°.25 K. to that of solid mercury at 273° K. becomes $\frac{W_{2^\circ.45\ K}}{W_{273^\circ\ K}} < 2.10^{-10}$.

TABLE VI.

Potential difference at the extremity of a mercury thread carrying a current below 4.°2 K.
$\pi r^2 = 0.0025\ mm^2$

Temp.	current density in amp. per mm.²	potential diff. in microvolts
2°.45 K.	944	< 0.03
»	1024	0.56
»	1064	1.5
»	1096	6.3
»	1120	very large

On the other hand it is proved that *the development of heat* which appears at a still higher strength of current, *has its origin in the thread itself.*

§ 8. *Influence of the current density upon the manner in which the resistance in mercury threads disappears.* What has been related above can all very well be reconciled with the view (see § 5) that the disappearance of the ordinary mercury resistance at 4°.19 K. occurs quite suddenly, and in a thread that has been cooled to below that temperature, as soon as the "threshold value" of the current density is exceeded, somewhere heating occurs which carries the thread at that place to above that temperature, at first over a scarcely perceptible length but at higher currents over a rapidly increasing distance, by which ordinary resistance is generated in this part of the wire. With these larger currents the thread then comes in a state on which there is no uncertainty, it assumes over its entire length the new temperature equilibrium of a thread carrying a current, which equilibrium is determined above the vanishing point in the usual way. In order to improve the comprehensive view that may be formed on the ground of Table IV combined with Table II in which latter the different current densities do not refer to the same wire, further experiments were made in June 1912, which show how with the same thread the resistance disappears at different current densities.

The thread had a section of about 0.003 mm²., at the boiling point of helium the resistance was 0.1287 Ω. The experiments were made with a falling temperature, with current densities of 1.3, 13 and 130 amp. per mm². (strength of current 4, 40 and 400 milliamp.). The phenomena are shown in the accompanying figs., upon which the numerical values are distinct enough to make it unnecessary to print a table. Fig. 6 allows a comparison between the phenomena at 0.004 amp. and 0.04 amp., fig. 7 at 0.004 amp. and 0.4 amp. The ordinates represent the potential fall in microvolts divided by the strength of the current, expressed in 0.004 amp., the abscissae the difference of the temp. T with that of the boiling point $T_s = 4°.25$ K. in thousandths of a degree. The unit of the scale of the abscissae in fig. 7 is five times as large as in fig. 6. At 0.04 amp. the curve continues with diminishing values of the ordinate to lower temperatures than are shown on the fig.; at 4°.11 K., when the experiment had to be stopped, the resistance was not quite 0, we found 0.2 . 10^{-6} V. The intersection with the

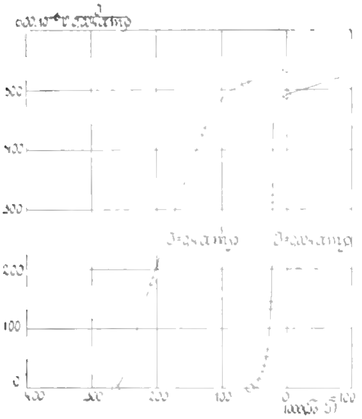

Fig. 6.

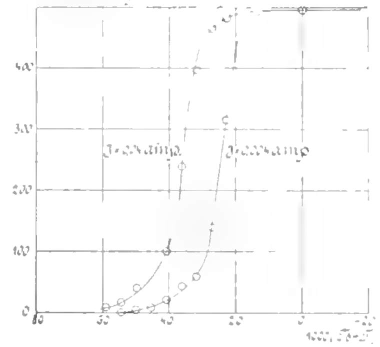

Fig. 7.

horizontal axis in fig. 7 is probably drawn too sharp; at 3°.96 K. the potential difference was $< 0.03 \,.\, 10^{-6}\, V$.

The whole gives one the impression that the lower temperature of the bath at greater strength of current is required (a comparison of 0.004 and 0.04 amp. shows that an almost constant shift of temperature would change the potential differences per unit of current in the one case into those of the other) to cool the part of the thread that has an ordinary resistance strongly enough to prevent it imparting its temperature to the part which is below the vanishing point, and to prevent the temperature in the latter part from being raised above the vanishing point by the greater local development of heat.

With the same thread in the manner of table III the results of table VII were found, in which experiments are included with a second thread with a section of about 0.012 mm².

It appears that in the thread W_I, to which the experiments just quoted refer, local heating takes place more easily at the same current density than in W_{180} (see § 5). The fact that the latter thread gives off heat more readily also explains why in W_{180} a greater current density checks the disappearance of the resistance less than in the case of W_I (June 1912).

As regards the threshold value of the current density for different temperatures with the same thread, it would seem from Table VII and Table V roughly speaking to change linearly with the temperature,

TABLE VII.

Potential differences at the extremities of mercury threads carrying current

Temp.	Current density in amp. per mm².		Potential difference in microvolts	
	W_I	W_{II}	W_I	W_{II}
3.°6 *K*		129		0.5
		141		very large
	363		0,3	
	412		3,8	
	429		12,1	
	431		very large	

if the fall below the vanishing point is not too small, and if we leave out of account a term for JOULE heat which only appears distinctly at a higher current strength. This naturally suggests that we are dealing with a PELTIER-effect raising the temperature to the vanishing point of resistance (e. g. connected with different forms of crystallisation or tensions); (the simultaneous cooling of the opposite contact has no effect on the resistance which is already practically zero and remains zero when further cooled). As regards the threshold value of the density at a given temperature for different threads this appears (comp. § 6 and Table IV) to be rendered uncertain by accidental circumstances. But it deserves notice that it was also found very high in very narrow capillaries.

§ 9. *Experiments on impurities as a possible source of disturbances.* Although the greatest care was always bestowed upon the purification of the mercury, the explanation of the appearance of a residual resistance that offered itself the first for closer investigation was the influence of impurities. These may give an "additive mixture resistance" to the metal which changes little with the temperature and is proportional to the amount of impurity. To such an additive resistance I ascribed the fact (Comm. N°. 119 and Leiden Suppl. N°. 29) that the resistance of very pure platinum and very pure gold did not disappear at helium temperatures as I expected with absolutely pure metals. Now the experiments had realized the expectation, that mercury could be so far freed from impurities, as to make the resistance practically nothing. But if one may judge by the additive resistance which even very pure gold exhibits, then with the residual resistance of mercury which is only perceptible at the threshold value of current density for the lowest temperatures, it would be a question of an impurity of the order of a millionth of the trace that could possibly be present in the most carefully purified gold. And it was a priori doubtful if the mercury could be procured in so much greater a state of purity than gold.[1])

The experiment was therefore repeated with solid mercury in which I believed a very small quantity of an other metal to be present. After being distilled in a vacuum by means of liquid air, the mercury was in one case brought into contact with gold and the other time with cadmium, after which it was mixed with a larger quantity of pure mercury. To my surprise with the mercury

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[1]) For difficulties inherent in the supposition of a resistance equally distributed throughout the thread which apply also to our present case of additive mixture resistance see § 11.

that had been treated in this way, the resistance disappeared in the same way as with pure mercury[1]; much of the time spent on the preparation of pure mercury by distillation with liquid air, might therefore have been saved, without the experiments on the sudden disappearance of the resistance which were made with mercury prepared in the ordinary way with double distillation giving other results.

Even with the amalgam that is used for the backing of mirrors, the resistance was found 0 at helium temperatures. (Later Dec. 1912) it was found that it disappeared suddenly, as with the pure mercury but at a higher temperature.[2])

Where the influence of impurities, in the form of mixed crystals in the solid mercury, seems to retire into the back ground, the next most natural supposition is that less conductive particles, separated out of the mercury during the freezing, or coming amongst the mercury crystals in some other way, bring a resistance into the path of the current. But if we do not assume that a thread of perfectly pure mercury can possess a residual resistance itself, this theory of the origin of the potential differences is not very probable, because in a resistance-free path of current, only by a closing of the whole section by an ordinary conductor resistance is produced. Particles of the sort we mean, as also other casual circumstances, for instance the manner of freezing and small cracks, can influence the magnitude of the threshold value of the current density derived from the experiments, but the values found for this quantity, although they vary, differ so little, that in addition to the causes mentioned we must assume for a *thread* of pure mercury the existence of a residual resistance which we will call a "microresidual" resistance, to distinguish it from the "additive mixture" resistance to be attributed to impurities.

§ 10. *Experiments on the possible influence of contact with an ordinary conductor upon the superconductivity of mercury.* In the reasoning that we have just given it is assumed that the laws of current division between two conductors which touch each other also hold when one of the conductors consists of mercury below 4°.19 K. But this assumption might not be correct. In the line of

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[1]) Perhaps not even a quantity of the order of a thousand millionth of zinc or gold is absorbed in solid mercury. The application of the sensitive test of the disappearance of the resistance may be of value for the theory of solid solutions. Of course in our argument we only deal with absorption in a form which comes into consideration for the resistance (mixed crystals).

[2]) This part of the text is changed in accordance with the facts see § 13 γ in VIII of this series.

thought of § 4 and taking into account the heat motion which takes the electrons now to the inside and then to the surface of the conductor, a pushing forward of the electrons in the galvanic current through a super-conductor without performance of work seems only possible, when its surface only comes into contact with an insulator, which reflects the electrons with perfect elasticity. If the electrons can hit against the atoms (or more accurately the vibrators) of an ordinary conductor, they will of course give off work in this collision. Thus a thread of super-conducting mercury, if an ordinary conducting particle were present anywhere in the current path, could show resistance at that spot, even although the particle did not entirely bar the section which was otherwise free from resistance.

These considerations lead to the following experiment. A steel capillary tube, supplied with connecting pieces in which were platinum wires for measuring the resistance, was carefully filled with mercury at the air pump. The measuring wires were immersed in the mercury, without touching the current wires. According to the ordinary laws of current distribution the resistance of this composite conductor should disappear below 4°.19 K. Whether the mercury is in a glass or a metal capillary makes no difference to the conduction. Thus for instance, if one was to coil up such a steel capillary filled with mercury, and press the coils against each other without insulating them, the coil could still serve as a magnetic coil below 4°.19 K.; the coiled up mercury thread would be resistance-free, and the steel would take the part of the insulator, which otherwise separates the different windings of the current path in a magnetic coil. On the other hand if the above reasoning is correct, a mercury thread, that is provided with a close fitting steel covering should retain its resistance below 4°.19 K. though the current is lowered below the threshold value.

In several experiments with the above mentioned steel capillary, in accordance with the last conclusion, the resistance of the mercury thread did not disappear. Yet we must not conclude from this that the remaining resistance is given to the mercury by the contact with the steel. There only needs to be one little gap in the mercury which extends over the whole section, to cause the appearance of ordinary resistance of the amount according to the potential difference. If the resistance had disappeared in the experiments, there would on the other hand have been room for the question whether there had been contact between the steel and the mercury. With mercury in a steel capillary the result of the experiment remains always doubtful. We may therefore mention here, that afterwards

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when it was found that the resistance of tin disappeared suddenly too, we succeeded in making a less doubtful experiment than is possible with mercury, with a flattened out constantan wire, which was covered with a thin layer of tin[1]). The resistance of the layer of tin disappeared with a weak current and at a low temperature, while the constantan remains an ordinary conductor at that temperature.

Thus we may for the present adhere to the usual laws of current division, and in this extreme case continue to assume that in so far as the appearance of the potential difference is to be explained by a local heating in consequence of a local change in difference of the chemical nature of the conductor from pure mercury this disturbance must extend over the whole section of the current path. Thus the conclusion drawn in § 9 concerning the probability of the existence of a micro-resistance remains valid.

(*To be continued*).

Physics. — "*The radiation of Radium at the temperature of liquid hydrogen*". By Madame P. Curie and H. Kamerlingh Onnes. Communication N°. 135 from the Physical Laboratory at Leiden.

One of the most remarkable peculiarities of radio-active substances, is that the radiation is independent of the temperature. Neither do the radio-active constants change with the temperature. These two facts are related to each other; they prove that the radio-active transformations are not affected by the influence of temperature, which plays such an important part in the chemical transformation of the molecules.

According to the theory of radio-active transformations, the intensity of radiation of a simple substance is proportional to the rapidity of the transformation, so that a change in one of these quantities involves a change in the other.

The experimental investigations of the influence of temperature have been concerned with the measurement of the radio-active constants and the intensity of radiation of certain substances. P. Curie has shown that the law of transformation for the emanation does not change at a temperature of 450° C. nor at the temperature of liquid air[2]). Various observers have proved that the penetrating

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[1]) It is to be noted, however, that the current density in the thin layer had to be made very weak. Comp. the following part of this Communication VIII, § 16.

[2]) P. Curie, C. R. 1903.

radiation of radium and uranium have the same value at ordinary temperature and at the temperature of liquid air [1]. The influence of high temperatures on the radium emanation and its transformation products, particularly Radium *C*, has also been the subject of various investigations. The results have given rise to differences of opinion. Nevertheless it would seem to be justifiable to conclude that the dependence upon temperature which was observed in some cases must be attributed to secondary phenomena of less importance, and that the radioactive constants of the above substances are not appreciably altered when the temperature is raised to 1500° [2].

As the question is of great importance it was desirable to extend the results already obtained, by extending the experiments over a wider range of temperature and by increasing the accuracy of the measurements, which in the above mentioned investigations could not have been greater than 1 °/₀ at the most.

Our object was to descend to the temperature of liquid hydrogen. By using a compensation method we were able to determine very slight changes in the radiation intensity. Our measurements were concerned with the penetrating radiation of radium. The results, within the limits of accuracy which may be placed at 0.1 °/₀, do not confirm the existence of a quickly acting influence upon the radiation, in consequence of this strong decrease of temperature.

The investigations were made in the first part of 1911. The preliminary measurements were partly made in Paris, and partly in Leiden, while the final measurements took place in Leiden in July 1911. We intend to continue and extend the experiments, which is the reason of the publication having been postponed. But as the continuation of the work has been prevented so far by the long indisposition of one of us, we thought it best not to wait any longer in publishing our results.

Apparatus and arrangement of the measurements. After some preparatory experiments we decided to use the following apparatus. The apparatus consists of a vacuum glass *A*, in which a copper vessel *B* is placed, which contains the low temperature bath. The vacuum glass, which is fairly wide at the top (a_1) consists underneath of a tube-shaped portion, the length of which is about 16 cm. and the two diameters 8,5 and 13 mm. The copper vessel which fits into the vacuum glass, is also provided with a tube-

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[1] Becquerel, Curie, Dewar, Rutherford.

[2] Curie and Danne, C. R. 1904. Bronson, Phil. Mag. 1906. Makower and Russ, Le Radium, 1907. Engler, Ann. d. Phys. 1908. Schmidt, Phys. Zeitschr. 1908.

shaped portion, which is shorter than that of the vacuum glass. This copper tube is closed underneath (B_1) by a metal stopper C_1 to which a tube C_2 of thin aluminium is attached (thickness 0.3 mm.): this tube contains a sealed glass tube with the radium. The narrow space at the bottom of the vacuum glass in which this tube is placed, is cooled to a temperature that differs very little from that of the bath: the difference could hardly be established, when the copper vessel was filled with liquid air. This

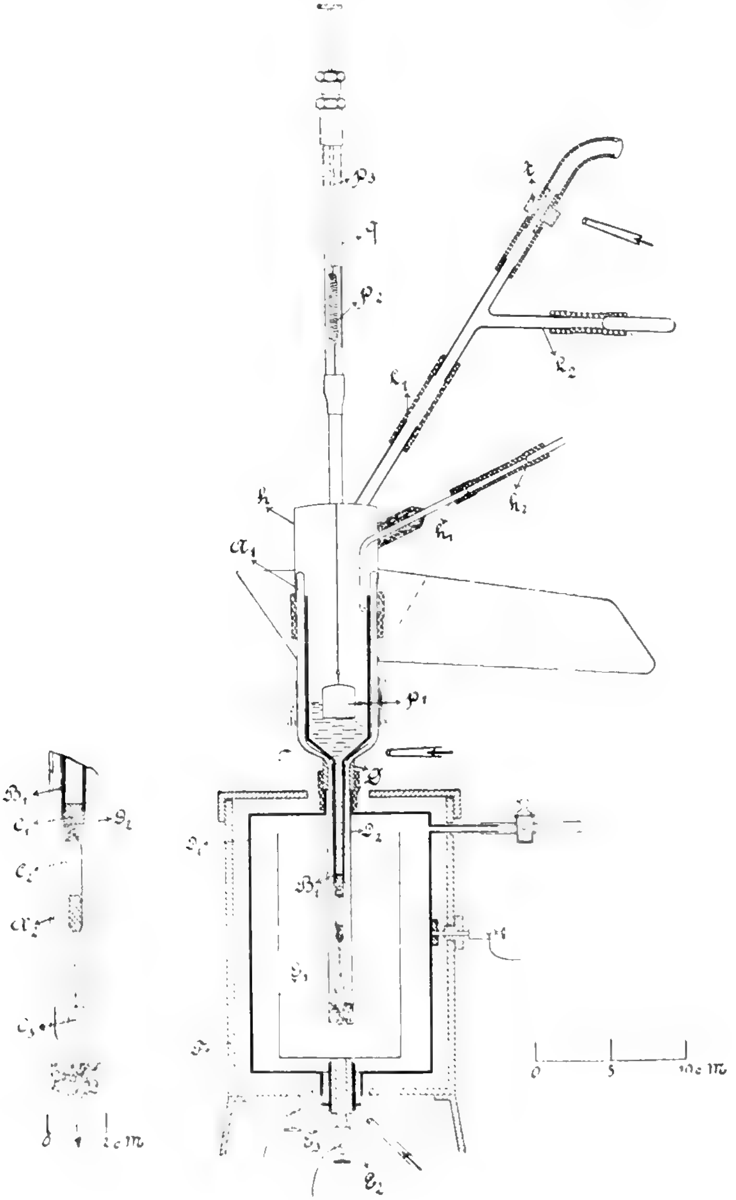


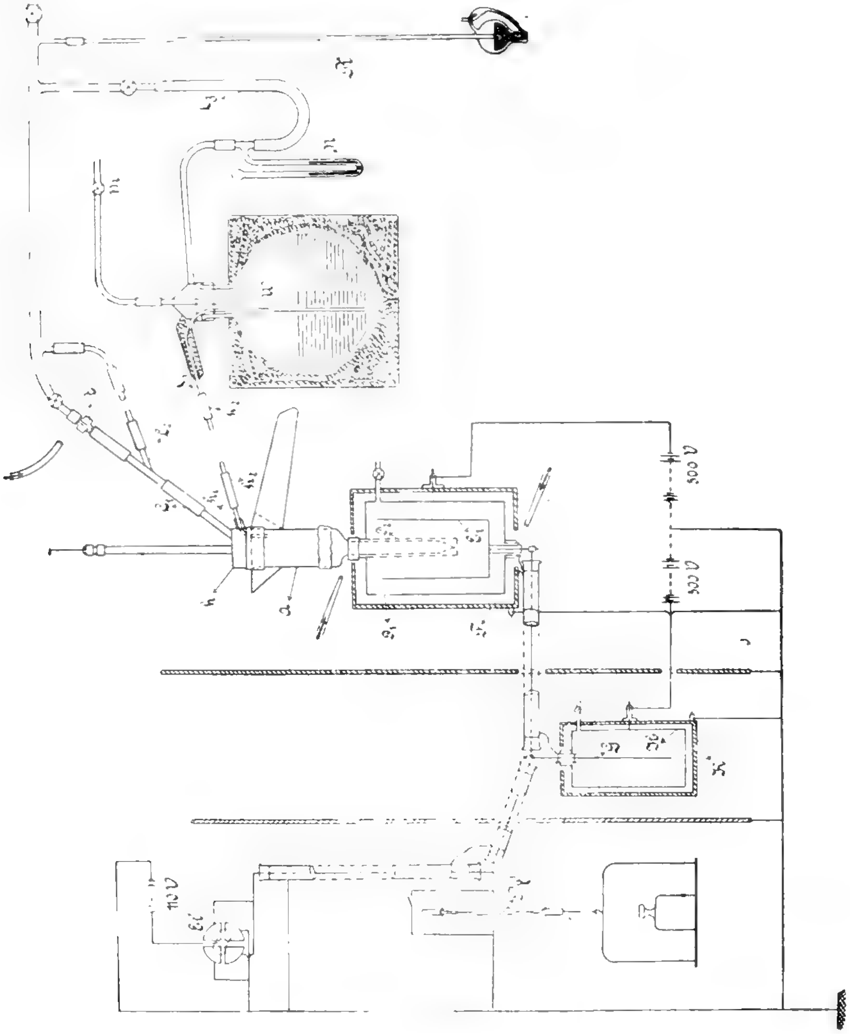
Fig. 1.

method of cooling seemed to us to be preferable to placing the tube itself into the liquid gas, which is always a little dangerous.

The rays that the radium in the tube sends out are partly of a penetrating nature. They go through the walls of the aluminium tube and those of the vacuum glass, and penetrate through a metal wall into the ionisation space. This consists of a cylindrical box D_1, which is connected to a battery; in the middle of the lid of this space a tube is soldered, which is closed at the lower end. The insulated electrode E_1 which is a hollow cylinder, is connected with the electrometer. The metal case F, which is connected to earth, serves for electrostatic protection. When the apparatus is mounted the tube-shaped portion of the vacuum glass is inside the tube D_2, which is placed centrally in the box D_1, while it is closed by a thick piece of india-rubber tubing round a piece of amber G which is sealed to the vacuum glass. When the tube containing the radium is in its place, ions are formed on both sides of the electrode E_1 in the air that fills the box D_1. The current that is taken up by this electrode is measured by an electrometer and a plate of piezoquartz.

The experiment consists in measuring the ionisation current generated by the rays of the radium: 1. when the radium is at the temperature of the room, and 2. when the radium is cooled to the temperature of liquid hydrogen. The ionisation chamber, which is outside the vacuum glass remains at about the temperature of the room. The chamber is airtight, and the quantity of gas that it contains does not alter during the experiments.

The accuracy of the measurements is greatly increased if instead of measuring the total current, a compensation method is used. This consists in compensating the current to be measured by a current in the opposite direction, which is generated in a second ionisation chamber by a tube containing radium, which is kept at constant temperature during the experiments. This current compensator is of a type which is greatly made use of in radioactive measurements. The insulated electrode G is in the form of a tube which is closed at the bottom; it is connected by means of copper wires (electrically protected in brass tubes filled with paraffin wax) with the electrometer and with the electrode E_1. This tube reaches into a cylindrical box H_1 which is connected to a battery and which forms an ionisation chamber. The outside case K serves for electrostatic protection. The electrodes G and E_1 are protected in the usual way by a protecting ring connected to earth. The tube G contains a sealed glass tube with radium salt. The boxes D_1 and H are kept at high potentials of opposite sign. Under these circumstances the difference of the two ionisation currents is measured which are generated in the two chambers. With sufficiently strong currents great accuracy can be attained in this way.



It is worth noticing, that the various small imperfections in the method of measuring, which are usually unnoticed, become apparent when the method described above is followed. E. g. when each current is measured separately, the saturation appears to be complete at a potential of about 500 volts. But when the difference between the currents was measured, which was usually under 5°/₀ of each current separately, it was found that the current under these circumstances increased with the voltage. When the potential increases from 500 to 800 volts, the current increases by 2 to 3 thousandths. Constant potentials must therefore be used.

The accuracy is limited by the stability of the apparatus and by the oscillations in the radio-active radiation.

The investigations were made with radium salts in the solid state, contained in sealed glass tubes; the salt was finely granular, and the tubes were not quite filled. When they are shaken the grains can move to a certain extent, which causes a slight change in the distribution of the radiation inside the ionisation chamber. The danger of this is lessened by giving the grains a definite arrangement beforehand by tapping the tube. But in spite of this, small perturbations of this nature remained in our experiments of not more than 1 in 1000 The very greatest care is, therefore, necessary in the manipulations which must be made during the experiments.

The radio-active oscillations of the ionisation current become apparent when the sensitivity of the measurements is raised sufficiently. They cause irregular deviations which can only be eliminated by a great number of measurements. They are least to be feared when gamma rays are used, as was the case in our experiments. In our case they could not do any harm to the determinations.

It is important that the ionisation chambers should contain an unchangeable quantity of air. When working with penetrating rays, the current is approximately proportional to the amount of ionised air. If one wishes to keep the current constant with great accuracy, we must, therefore, take care that the ionisation chambers are properly closed. Each chamber is supplied with a tap. By changing the amount of air in the compensation chamber, the current in the chamber could be so regulated as to get a compensation of the amount required. Both the compensation chambers are filled with dry air by a tube filled with cotton wool, which can be connected to the tap of the chambers by a ground joint, and to an air pump and a manometer to regulate the supply.

We had to take very great precautions to prevent the cryogene operations from causing insulation errors in consequence of the precipitation of moisture from the surrounding air on the strongly cooled parts of the apparatus. The cryogene apparatus used by us enabled us to avoid all difficulties of this sort. This instrument, which was arranged for working easily and safely with liquid hydrogen, had moreover the advantage that the radium tube could only come into contact with the gaseous phase of the liquified gas, so that when this was hydrogen there was no fear of solid air being deposited on the tube.

The cryogene apparatus is completely closed. The vacuum glass has a lid h of thin new silver, which is fastened air tight to the glass by means of an indiarubber ring, so that when the radium tube is in its place, the apparatus can be evacuated, and can be filled beforehand with pure, dry gaseous hydrogen (by L). A small hole in the stopper C_2, upon which the radium tube in the aluminium tube rests, ensures the pressure equilibrium, which establishes itself easily during these operations, so that the radium tube is not exposed to any danger.

The liquid hydrogen is poured into the vessel B through the new silver tube h_1 and through the india-rubber tube h_2. For this purpose the glass stopper is removed which closes the india-rubber tube, after the tube with the stopper K_2 has also been taken away, and the india-rubber tube is connected to the syphon K_1 of the large vacuum glass W, containing the liquid hydrogen that has been previously prepared. Before the syphon and the india-rubber tube are connected, the apparatus and the vacuum glass are connected to a gasometer with pure hydrogen, by the tubes L_1 and L_2. When the first mentioned connection has been made, the connection of the vacuum glass with the gasometer is broken, and the liquid hydrogen is poured into the apparatus by means of pressure from a cylinder with compressed hydrogen, admitted by the cork m, and controlled by the mercury manometer n. The supply-glass and the gasometer are then again connected. The syphon is taken off the inlet tube after the connection tube has been warmed, and this latter tube is immediately closed by a glass stopper.

To prevent these manipulations from shaking the apparatus, we made the indiarubber tube h_2, which is usually as short as possible, rather long; but as the great cold makes the india-rubber very brittle, and the breaking of it might cause great inconvenience, we used only a length of 7 c.m. In this way the shaking remained below the limits of stability in the apparatus which we used for these experiments. In a larger apparatus, intended for experiments that take longer, more than 24 hours, but with which we have only been able to make preliminary determinations so far, we were able to attain a greater amount of stability, and we were more independent of the shaking caused by the manipulations.

Care must be taken in filling the copper vessel B, that the liquid gas does not overflow, as it might penetrate into the cooling chamber, which would give rise to irregularities, and might injure the radium tube. On the other hand it is necessary to know when the liquid gas has evaporated, otherwise the experiments might be continued without our being certain of the temperature. The height of the surface of the liquid gas can be read by means of a float. This consists of a new-silver box p_1, suspended from a weak spring p_2, which spring is attached to a rod p_3. This rod is movable in a packing tube, which is fastened to the upper end of a glass tube q, carried by the lid h. Beside the spring and also hanging from the rod, is a flat rod which is provided with a scale at its lower end. In consideration of the very small density of the liquid hydrogen ($^1/_{14}$), the float is made very light. When the float reaches the surface of the liquid by the moving down of the spring, this is indicated by the shortening of the spring, and the height of the liquid can be read on the scale and on the rod.

Before pouring in the liquid gas, the float is regulated to the height to which the vessel is to be filled. Before beginning the measurements, the spring is pressed down as far as is necessary to make the lengthening of it show when the liquid is so far evaporated that the measurements must be stopped.

The evaporated hydrogen is carried off by L_1. The tube R, the extremity of which is placed in mercury, serves as a safety.

In order to be certain of the insulation of the vacuum glass, and to avoid currents which might be injurious to the constancy of the tension of the battery, a piece of amber is interposed in the tube L_1. To prevent the amber from being cooled too much by the filling, the cold vapours are carried off by a supplementary tube L_2, which is coupled off as soon as the filling is completed. When the evaporation of the bath has become stationary, a current of air a little warmer than that of the room directed upon the amber is sufficient to maintain the insulation. This current of air is given by a reservoir of compressed air, the air flows through a long tube, part of which is warmed by hot water.

The connection of the piece of amber, g, which is sealed to the vacuum glass, with the tube D_2 of the principal ionisation chamber, is very carefully made, to insure an airtight closing, and thereby to prevent the possibility of moisture penetrating to the space between the tube and the vacuum glass. The currents of cold air that come down are kept away by a paper screen. The water that runs down the glass from the lid must also be disposed of. The very low temperature of the vapours inside the lid causes frost to settle on it during the filling, which thaws afterwards. After the filling is finished, the condensation of water vapour out of the air continues; the water thus formed, is absorbed by cotton wool above the paper screen we mentioned, and below it by filter-paper. A current of dry slightly warmed air is directed upon the amber, which at the same time dries the lower part of the vacuum glass.

Finally, the cooling of the parts of the connection of the main electrode E_1 with the electrometer must be prevented. To attain this a current of dry and slightly warmed air is also directed upon the amber stopper between the stem E_2, and the protecting ring E_3 at the bottom of the main ionisation chamber.

The cold currents of air, which come down from the tubes that lead off the gases, are diverted from the apparatus by suitable screens, and large currents of air in the room are avoided as far as possible, so as to prevent the ionised air around the contacts from being displaced; these contacts were further protected by various lead protecting mantles (in the figure diagrammatically represented), by tin foil, etc. The influence of the warm currents of air already mentioned was tested at the temperature of the room: they did not cause any electrostatic phenomena.

Preparatory Experiments.

The experimental method was first studied in Paris, using liquid air as cooling bath.

The current in the main ionisation chamber was procured by using a tube with about 0.1 gr. of radium chloride. In the compensation chamber a tube with about 25 mgr. of radium chloride was used.

In the first experiments the first tube was contained in an aluminium tube with walls of 0.3 mm. thickness; the central tube D_2 in the chamber D_1 was also of aluminium, with walls of 0.5 mm. thickness. The rays, before penetrating into the ionisation chamber, passed through a layer of aluminium of about 0.8 mm. and moreover a glass layer about 2.5 mm. (wall of the radium tube and both walls of the vacuum glass).

During the cooling a diminution of the current in the main chamber could be observed. It was not very regular, and amounted to about 2 °/₀, it was perceptible immediately after the liquid air was poured into the copper vessel, and reached its maximum in about half an hour. When, however, the liquid air was quickly taken out of the vessel, and the temperature of the radium tube was followed with a thermoelement, it could be observed that while the temperature of the radium tube was still constant, the strength of current already began to rise, and reached about its original value, by the time the whole apparatus had returned to ordinary temperature. From this it was evident that the decrease of strength of current which we observed was not attributable to a change of radiation in the radium tube, but to some other cause.

Various test experiments seemed to show that it was caused by change in the power of absorption of the screens, due to their contraction at low temperatures. It was therefore necessary to make use of heavier and thicker screens, to make sure that we only worked with the most penetrating rays, which are less susceptible to phenomena of this kind. After the radium tube had been inclosed in a copper tube of 1 mm. thickness, we found that the decrease of current when the liquid air was poured in was reduced to 0.1 °/₀. The decrease was completed in 10 minutes. Three successive experiments gave this result.

We found that we could make the circumstances even more favourable, by changing the arrangement of the apparatus in such a way that the screens in which the absorption of the rays took place were not cooled at all. In order to do this, the radium tube was once more put into the aluminium tube of 0.3 mm., while the central tube D_2 of the chamber D_1 was replaced by a brass tube of 2 mm. wall thickness. The decrease of the current became by this means less than 1 in 1000. This arrangement was used in the final experiments.

Final Experiments.

The experiments were made in Leiden from July 20th to 25th 1911.

The ionisation current in the main ionisation chamber was 1100, expressed in arbitrary units (about 10 electrostatic units). The strength of the compensation current was so regulated that it was a little larger. The difference was at most 20 units, about 2 °/₀ therefore. The rays used for the experiments were gamma rays.

We were able to make two experiments with liquid hydrogen. In the experiments the cold ionisation chamber, as we said above, was filled with dry gaseous hydrogen, and by this we made sure that no deposit could come on to the radium tube.

In the first experiment the current of originally 10.9 units, attained the value of 14.7 units after the pouring in of the liquid hydrogen, which took 15 minutes. This change corresponds to a change in the main current of 0.34 °/₀. In the second experiment the current measured had a strength of 18.3 units, and was very constant, the irregularities measured during an hour were less than 1/10000 of the main current. After the liquid hydrogen had been poured into the apparatus, measurements which agreed very well with each other gave for the value of the current during half an hour 18.5

units, and after an hour 18.2 units. We can thus assert that in this experiment, which was evidently conducted under very favourable circumstances the cooling had not caused a change in the main current of as much as 1 in 5000.

We made another experiment at the temperature of liquid oxygen. The current measured had a strength of 1.8 units. Measurements made during an hour at the temperature of liquid oxygen gave a value of 2.6 units for the current measured, which corresponds to a decrease of 0.7 in 1000 in the main current.

It would have been desirable to have made a greater number of experiments and to continue these during a greater length of time; nevertheless it would appear to be justifiable even now to state, that *cooling of radium down to the temperature of liquid hydrogen (about 20°.3 absolute) during a period of not more than* $1^1/_2$ *hours does not cause a change in the gamma radiation of* 1 *in* 1000 *and probably not even of* 1 *in* 5000.

It is thus probable paying due regard to the degree of accuracy attained, that this decrease of temperature has no immediate or quickly discernable influence upon the emanation or the active deposits of short period (radium *A*, *B* and *C*). But in these experiments there was no opportunity for detecting an eventual effect upon the radium itself, or a slowly developing effect upon its evolution products.

Experiments with polonium.

A few preliminary experiments on the influence of low temperatures upon the radiation of polonium have been made in Paris. The experiment which was made only with liquid air, gives rise to some difficulties. A plate on which was some deposit of polonium was placed at the bottom of a long glass tube, which could be immersed in liquid air. This plate radiated through a thin aluminium plate that closed the tube, into an airtight ionisation chamber, where the polonium rays were absorbed by the air. The polonium tube was as far as possible exhausted; and the vacuum was further improved by immersing a side tube containing a little charcoal in liquid air. The radiation was measured at ordinary temperature, and later, when the bottom of the tube was immersed in liquid air. In these experiments changes of current of inconstant amount were observed when cooling was applied. These changes were smaller in proportion as the vacuum was made more complete and kept more constant. It is thus highly probable that they were entirely due to the influence upon the polonium of the condensation of gases still present in the apparatus.

Experiments made in Leiden in liquid hydrogen with a provisional apparatus have convinced us that one might get rid of the condensations completely, even with liquid hydrogen, by using a ionisation chamber filled with pure gaseous hydrogen and a side tube with charcoal, immersed in liquid hydrogen.

Conclusions.

All these experiments which unfortunately are not so complete as we could have wished, confirm the independence of the radiation from the temperature, over a larger range of temperatures than had heretofore been done. Moreover these experiments have brought to light sources of error which must be taken into account, if one wants to make very accurate measurements at low temperatures.

Astronomy. — "*The periodic change in the sea level at Helder, in connection with the periodic change in the latitude*". By Prof. H. G. v. d. Sande Bakhuyzen.

At the meeting of the Academy in February 1894 I read a paper about the variation of the latitude, deduced from astronomical observations, and added to this a determination of the change in the mean water level in consequence of the variation of the latitude.

Roughly speaking, one may regard the variation of latitude, as consisting of two parts, a periodic variation which takes place in one year, probably due to meteorological influences, and a periodic variation which takes place in about 431 days, which depends amongst other things upon the coefficient of elasticity of the earth, its resistance to change of shape. As a consequence of these changes of position of the axis of the earth oscillations of the same periods must take place in the mean sea level and if we eliminate the annual oscillation, the periodic variation of 431 days remains.

For the determination of the latter variation, I had made use of the mean sea level during the different months of the years 1855—1892, taken by the tide gauge at Helder. The results attained then for the amplitude and the phase of the periodic variation confirmed the opinion that such variations actually existed in the water, but as the changes in question are very small, it was desirable to extend the investigation in order to increase the accuracy of the results. I resolved therefore to submit to the calculations all the tidal observations made at Helder in the years 1855—1912, and as the results of the years 1893—1912 were not at my disposal, Mr. GOCKINGA, Chief engineer Director of the "Waterstaat", was so good as to let me have the monthly averages of these years.

2. Before I give an account of how the monthly averages were used by me, it is desirable to explain the exact significance of the observation material. The tide curve of Helder, with its double maximum, has an asymmetrical form, which differs considerably from a sinecurve, so that to deduce the exact mean sea level during a day from the observations, one must either determine the area of the surface enclosed by the tide curve with a planimeter, or, as will also be sufficiently accurate, determine the average value of the 24 hourly heights. From the daily means one can then deduce the monthly means.

It will be clear that the work which is necessary to calculate all the observations in this way for the more than 21,000 days from 1855 to 1912 is very great; fortunately for our purpose we can use an easier way, as we do not need to know the actual mean heights, but only their mutual differences. If the tidal curve were symmetrical with respect to the mean sea level, the half of the sum of high and low water would correspond to the mean sea level of that day; but the form is not symmetrical, and even changes periodically, so that there is not only a difference between the half of the sum of high and low water, and the mean sea level, but this difference changes from day to day. If, however, we determine the average form of the tide curve during the period of a month, then we get a fairly constant shape, and for such a period one may assume, that the difference between the half sum of all the high and low waters and the mean sea level is almost constant. This assumption will differ even less from the truth, if we take the average of a great number of monthly means from different years, which is the case with my calculations.

On these grounds I have taken as the monthly means of the sea level the half of the sum of the high and low waters during these months, deduced from the registered tidal curves in the years 1855—1912.

These monthly means show rather marked deviations from the annual mean, due partly to the yearly and half-yearly sun tide, and partly to the regularly changing meteorological conditions. From 58 years, I found for Helder the following mean values for yearly means—monthly means in millimetres.

January,	February,	March,	April,	May,	June,	July,	August,
— 17.8	+ 28.5	+ 60.9	+ 102.4	+ 92.9	+ 48.0	1.6	38.4

September,	October,	November,	December.
— 42.6	— 85.2	75.1	72.5.

By the introduction of these corrections I have eliminated the influence of the yearly periodic variations in the water level.

In order to increase the accuracy of the values from which the results must be deduced and to remove entirely or partially the error that might arise, if the number of low waters in a month should be one less or more than the number of high waters, I have always taken the averages of two consecutive months: Jan. and Febr., Febr. and March, etc. The further calculations are based upon these two-monthly means.

Corrections for known tides are not introduced into these values. The influence of tides of short period is very slight upon the two-monthly means, and if, as is the case in my calculations, the average is taken of nearly 50 such means, it may be altogether neglected.

Of the tides of longer period we must mention, besides the yearly and half-yearly sun tide, the influence of which has been taken into account, the tide Mm, with a period of over 27 days. It appears from the calculations that the influence of this tide upon the two-monthly means can rise to about ± 6 mm. but as the amplitude and phase constant of this tide are very little known, we cannot calculate the exact value of the correction. We may, however, assume that in an average of about 50 of these values, for dates that correspond to very various phases of this tide, its influence may be neglected.

3. The length of the period of the latitude variation of about 431 days (Chandler's period) was deduced from long series of astronomical observations, by E. F. v. d. Sande Bakhuyzen, Dr. Zwiers and me; the results obtained by us differ very little, but I take as the most accurate that deduced by Dr. Zwiers in a paper in These Proceedings of June 24th, 1911, Vol. XIV, p. 111, that is 431,24 days.

In order to determine whether a variation in the sea level takes place in that period, I have, starting from the first bi-monthly mean for 31 Jan. 1855, determined the dates of the days, which fall 431,24 days later, or a multiple of that interval and then selected the bi-monthly means which are nearest to these dates, sometimes a little earlier and sometimes a little later, with a difference at most of 15 days. From all these mean sea levels, 49 in number, corresponding to the same phase of the latitude variation, an average is then formed. In a similar way the averages are taken from the series of sea levels which correspond to the phases of the latitude variation 1, 2, 3, . . . 13 months later than 31 January 1855. These 14 months contain over 426 days, almost the entire CHANDLER period therefore.

I found for the deviations of these 14 values from their general mean:

− 10.1 mm.
− 9.6
− 5.8
+ 1.7
+ 11.0
− 4.2
− 13.4
+ 2.9
+ 1.6
+ 1.2
+ 9.0
+ 7.4
+ 4.1
+ 3.3

These numbers with the exception of the 4th and 5th seem to show a periodic variation, and the assumption is permissible that the sea level at Helder undergoes a periodic change in the course of 431.24 days, and that the height, t days after the end of January 1855 is represented by

$$h = a \sin\left(\frac{t}{431.24} \times 360^\circ + \alpha_0\right) = a \sin(\varphi + \alpha_0) = a \cos\alpha_0 \sin\varphi + a \sin\alpha_0 \cos\varphi$$
$$= p \sin\varphi + q \cos\varphi .$$

The heights given in the above column are got by taking the average of the bi-monthly means; if at the beginning of the period $\varphi = \varphi_0$, and at the end $\varphi = \varphi_1$, then that average is

$$H = a \frac{\cos\varphi_0 - \cos\varphi_1}{\varphi_1 - \varphi_0} \cos\alpha_0 + a \frac{\sin\varphi_1 - \sin\varphi_0}{\varphi_1 - \varphi_0} \sin\alpha_0$$

or

$$H = p \frac{\cos\varphi_0 - \cos\varphi_1}{\varphi_1 - \varphi_0} + q \frac{\sin\varphi_1 - \sin\varphi_0}{\varphi_1 - \varphi_0} .$$

After the substitution of $\frac{\cos\varphi_0 - \cos\varphi_1}{\varphi_1 - \varphi_0}$ and $\frac{\sin\varphi_1 - \sin\varphi_0}{\varphi_1 - \varphi_0}$ in which $\varphi_1 - \varphi_0 = \frac{1}{1,1275}$, we get the following equations

$$\begin{array}{rrcr}
+0.415\,p & +0.874\,q & = & -10.1 \\
+0.750\,p & +0.611\,q & = & -9.6 \\
+0.940\,p & +0.230\,q & = & -5.8 \\
+0.948\,p & -0.195\,q & = & +1.7 \\
+0.772\,p & -0.529\,q & = & +11.0 \\
+0.447\,p & -0.858\,q & = & -4.2 \\
+0.036\,p & -0.967\,q & = & -13.4 \\
-0.382\,p & -0.889\,q & = & +2.9 \\
-0.727\,p & -0.639\,q & = & +1.6 \\
-0.930\,p & -0.265\,q & = & +1.2 \\
-0.954\,p & +0.160\,q & = & +9.0 \\
-0.793\,p & +0.554\,q & = & +7.4 \\
-0.479\,p & +0.841\,q & = & +4.1 \\
-0.072\,p & +0.965\,q & = & +3.3
\end{array}$$

Solving these by the method of least squares, we get

$$p = -4.40, \qquad q = +0.42,$$

therefore

$$h = 4.42 \sin(\varphi + 174^\circ 33').$$

The mean error of the unit of weight (mean of two consecutive months) is ± 51.5 mm., the mean errors of p and q are ± 2.86 and ± 2,89, and the probable errors ± 1.93 and ± 1.95 millimetres.

4. So far, we may deduce from this that the periodicity of the sea level in a period of 431.24 days is presumably real, although considering the small amount of this variation and the comparatively large value of the mean errors, a more detailed investigation as to the probability of the results is desirable.

For this purpose I have in the first place calculated the mean error of the unit of weight in another way, namely by taking the yearly means, and in the assumption of a small change in the sea level, proportional to the time, determining the mean error of a yearly mean and therefrom the mean error of the unit of weight; I found for the latter value ± 93.3 mm., much greater than the first value given. This shows that there are fairly large systematic errors in the sea levels, probably to a large extent caused by the circumstance, that the causes of deviations in the normal sea level are of lengthy duration, and thus can cause abnormally high or low sea levels during a long time.

In order to investigate this, I have taken the means of a series of 12 months in a different way, by combining the height in Jan. of the year a, with that in Feb. of the year $a+1$, in March of the year $a+2$ etc. From this follows for the mean error of the unit of weight ± 60.2 mm. which agrees much better with the value we found ± 51.5. The real mean errors of p and q therefore probably do not differ greatly from the values calculated.

5. A second way of judging of the reliability of the results obtained is the calculation of the same quantities from another combination of observations. For this purpose I chose the observations of 1855—1892, which I had calculated in 1894, but had now reduced to the yearly means with better values for the deviations of the monthly means and further the observations of 1893—1912. I found from both series of observations:

$$h = 4.50 \sin (q + 168^\circ.59) \quad . \; . \; . \quad (1855\text{—}1892)$$

and

$$h = 3{,}74 \sin (q + 176^\circ 13') \quad . \; . \; . \quad (1893\text{—}1912).$$

By the change in the reduction numbers and a more accurate calculation, the formula for the sea level during the period 1855—1892 differs somewhat from the formula found in 1894. The striking correspondence between the three formulas now found for the periods 1855—1892, 1893—1912 and 1855—1912 is certainly largely due to accident, but it confirms the view that the variation in the sea level is real.

6. In order to test the efficiency of the method that I had followed, I applied it to two cases in which one could not a priori expect a periodic variation, and to another case in which the existence of such a variation was certain.

First I arranged the bi-monthly means in a period of 13 months or 395.75 days which is not a multiple of any period of a sun or moon tide, and in which therefore we could not expect any periodic variation of level. For this purpose I used the observations of 1855—1892, and got the following deviations of the sea level from their general averages.

4.0 m.m.
— 14.8
4.1
+ 8.4
+ 5.1
+ 2.0
+ 9.3
2.8
+ 0.8
+ 2.9
— 9.8
— 4.6
+ 11.5

A periodicity looks less likely here than in the first case. Further I arranged the bi-monthly averages according to the period of 438.096 days, which, according to a paper by SCHUMANN from Vienna, should represent the length of the CHANDLER's period. This value differs very greatly from the results obtained in Leiden, and is a priori improbable as it is only theoretically deduced from the elements of the moon's orbit, without taking into account the elasticity of the earth, which certainly has a great influence upon this value. From all the observations from 1855 to 1912, arranged according to the phases of a periodic variation in 438.096 days, in distances of a month, I got the following figures for the sea level.

— 18.0 m.m.
— 4.8
+ 13.9
+ 8.6
— 4.4
— 0.7
— 5.3
— 2.9
+ 21.1
+ 17.1
— 5.6
— 0.9
— 1.6
— 16.7

In this series there is again little trace of a periodicity in a period of 438 days.

Finally I arranged the mean sea levels according to the phases of a period of 440.872 days, which is 16-times the period of the monthly moon tide Mm. the length of which is 27.5545 days. It is plain that the influence of this tide will only be felt to a very small degree in the bi-monthly means, as these are the means of two complete periods or 55.11 days and 5.7 days. The periodic variation in the bi-monthly means will be about $^1/_{16}$ of that which is due to the actual tide Mm.

After arranging and combining the bi-monthly means I got for the sea level at 14 different epochs with intervals of one month

— 2,6 mm.

7,2

— 7,3

+ 3,4

+ 7,2

+ 9,4

+ 7,1

+ 3,7

+ 12,2

+ 8,0

— 13,2

20,8

— 4,3

+ 4,3

The periodic character is here undeniable, and if we determine the amplitude of the Mm.-tide itself from these figures, we get for the amplitude 118.0 mm., whereas from the observations in 1892 I formerly got for the amplitude 83.4 mm. (Versl. Kon. Akad. v. Wet. Vol III, p. 197). The correspondence is satisfactory, if we consider that the error in the observations made in the above series appears in the amplitude multiplied by about 16

These different considerations give me reason to take the value found above for the periodic change of the mean water levels in the time of 431.24 days as correct within the limits of the probable errors.

The probable error of the amplitude 4.42 is ± 1.93, the probability that the amplitude lies between 0 and 8.84 mm. may therefore be put at 7.

7. We have next to discuss the question what the connection is

between this variation in the sea level and the change in the position of the pole. If the sea level always corresponded to the position of the pole, the lowest sea level at a given place would always correspond to the maximum of the latitude at that place.

In the formula for the periodic variation in the water level $\varphi = 0$ for 1 Jan. 1855 = 2398585 Julian date, and as the change of φ per day is 0°. 83478, we may represent the formula for the height of the sea level on a day for which the Julian date is t by

$$h = 4{,}42 \; Sin \; \{(t - 2398585 + 209{,}1) \; 0^{\circ}{,}83478\}$$

$$=$$

$$h = 4{,}42 \; Sin \; \{(t - 2398375{,}9) \; 0^{\circ} \; 83478\}.$$

The height of the sea level is a maximum when the expression under the sine is 90°; thus we find

Maximum height of sea level for $t = 2398483{,}7$.
Minimum ,, ,, ,, ,, ,, $t = 2398699{,}3$

and if we add to this $23 \times 431{,}25 = 9918{,}7$ we find

Minimum height of sea level for $t = 2408618{,}0$.

According to ZWIERS (These Proceedings XIV p. 211) the Julian date for the maximum latitude for Greenwich is 2408580, and if we reduce this for the difference of longitude between Greenwich and Helder, the date for the maximum latitude at Helder is 2408585,7 which gives a difference with the date of the minimum height of the sea level of only 32,3 days.

If the latitude variation is really the cause of the variation in the sea level, some time will elapse between the maximum latitude and the moment of the lowest sea level; how much this will be, cannot be theoretically determined: it depends upon the configuration of the continents, but the small difference which has been found is an argument in favour of the hypothesis that there is a connection between the two phenomena.

We will now investigate the relation between the amplitude of the 431-days tide and the magnitude of the latitude variation. The distance from a point of the ellipsoid of the earth to the centre of the earth is approximately expressed by

$$log \; \varrho = C + {}^1/_2 \; M \; \alpha \; Cos \; 2 \; \varphi$$

if α is the ellipticity of the earth, and the radius of the equator is taken equal to 1. If the pole moves through an angle $\Delta\varphi$ in the direction of the meridian of this point, so that the latitude becomes $\varphi + \Delta\varphi$, and the liquid and solid parts of the earth could immediately change so as to both acquire in relation to the new axis the same shape as they had to the original axis, then the distance from that point to the centre of the earth would vary by the amount $\Delta \varrho$, given by

$$\Delta \varrho = - \varrho \, \alpha \, Sin \, 2 \varphi \, \Delta \varphi$$

If we take for ϱ a mean value of 6367000 meters and for $\alpha \frac{1}{297}$ then expressing $\Delta \varphi$ in seconds:

$$\Delta \varrho = 104 \, Sin \, 2 \varphi \, \Delta \varphi \text{ mm.}$$

The amplitude $\Delta \varphi$ of the latitude variation seems to be variable, as shown by the investigations of Dr. ZWIERS; as mean value I take $\Delta \varphi = 0'',16$, then for Helder with a latitude of about 53°,

$$\Delta \varrho = 16 \text{ mm.}$$

The displacement of water that is necessary for this change in the surface of the sea will be lessened by the attraction of the earth; NEWCOMB in his paper (M. N. R. S. vol 52 p. 336) estimates that the displacement is only half as great: $\Delta \varrho$ would be in this case about 8 mm.

The sea level is measured with reference to the solid earth, so that, in order to determine the relative variation of the sea level, one must also know the variation in shape of the solid earth, which of course depends upon its rigidity. In my former publication of 1894 I had deduced from a very approximate theory and very rough estimates, that the amplitude of the water movement would be about 4.5 mm. I do not venture to give such a theoretical deduction any more, especially as so little is known about the rigidity of the earth; whereas SCHWEYDAR found by observations with a horizontal pendulum at Potsdam,

$$17.6 \times 10^{11},$$

for the coefficient of elasticity of the earth, HAID of Karlsruhe deduced a much smaller value in exactly the same way from observations with horizontal pendulums in Freiberg and Durlach, namely

$$3.2 \times 10^{11} \text{ and } 3.0 \times 10^{11}.$$

So long as this great uncertainty about the elasticity of the earth exists, estimations are of little value, and we can only state that the theoretical value of the amplitude of the variation of the sea level is of the same order as that which is deduced from the observations.

These various considerations confirm the opinion, that the periodic variation of the sea level in 431,24 days, as it is deduced from the observations, is real within the limits of the probable errors and that it is a consequence of the latitude variation.

I think it is of importance to apply similar calculations to other long series of sea levels, as they might contribute towards the determination of the coefficient of elasticity of the earth.

Astronomy. — *"The total solar radiation during the annular eclipse on April* 17th 1912. By Prof. W. H. Julius.

Scheme of the investigation.

The annular eclipse of the sun on April 17th, 1912, offered a rare opportunity for investigating the total amount of radiation due to the entire "solar atmosphere" i.e. to the complex of layers of the sun lying outside the level, generally indicated as surface of the photosphere.

Every part of the solar atmosphere emits some proper radiation and scatters some photospheric light, and it is only natural to suppose that the lowest layers bear the greatest share in that radiation and scattering. Now, at a total eclipse the base of the atmosphere is always wholly or partly screened by the moon; whereas during the annular phase of the eclipse of April 1912 even the lowest strata of the atmosphere all round the disk contributed to the remaining radiation. From the minimum value through which the remaining radiation passes at the instant of centrality one must be able to calculate an upper limit, which the radiation, emitted and scattered by the entire solar atmosphere, certainly does not exceed.

Since a reliable determination of such an upper limit would afford an important criterion for testing fundamental ideas regarding the nature of the photosphere, the principal aim kept in view in devising our actinometric apparatus was, that the minimum of the radiation curve should come out as sharply and definitely as possible.

On former occasions (during the eclipses of 1901 in Karang Sago, Sumatra and of 1905 near Burgos) we measured the march of the total radiation by means of a thermopile directly exposed to the sun's rays, without making use of any lenses or mirrors to concentrate the beam. If circumstances had then allowed us to find the true shape of the radiation curve, if would have been possible to calculate from those data trustworthy values for the radiating power of successive concentric zones of the solar disk. [1] Unfortunately the weather did not favour the Sumatra and Burgos observations; so we desired to make similar observations again. The apparatus had proved satisfactory, and sensitive enough to give measurable indications of heat even during totality; for at Burgos a break in the clouds had permitted us to state that at mid eclipse the unscreened part of the

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[1] W. H. Julius. A new method for determining the rate of decrease of the radiating power from the center toward the limb of the solar disk. Proc. Roy. Acad. Amst. **8**, 668, 1905; Astroph. Journal **23**, 312, 1906.

corona radiated less than $^1/_{200000}$ of the output of the uneclipsed sun or $^2/_3$ of that of the full moon. [1])

For observing the radiation during the annular eclipse we therefore decided to follow substantially the same plan, though with some alterations in the apparatus. This time the minimum would not be so low. From a close discussion of the Burgos results we presumed it to lie somewhere between $^1/_{10000}$ and $^1/_{1000}$. So the galvanometer could be taken less sensitive, but, on the other hand, the steadiness of the zero could be improved and the period of oscillation shortened.

Quickness of indication was, indeed, a very important condition, which not only the galvanometer but also the recipient of the radiation had to satisfy, if the minimum were to be observed exactly.

At the observing station near Maastricht [2]), selected by the Eclipse Commission of the Royal Academy of Amsterdam, the annular phase of the eclipse was expected to last less than one second. [3]) Our thermopile, used in Sumatra and Burgos, required 10 seconds for reaching a stationary temperature after being suddenly exposed to a constant source of radiation, and therefore would be too slow to catch the minimum, although quick enough to give the greater part of the radiation curve with sufficient accuracy.

Description of apparatus.

We determined on arranging two separate equipments: a rapidly working one, and a slower one, both suited for measuring the intensity of radiation from the first until the fourth contact, but in some respects complementing each other. The slower set of apparatus consisted of a *thermopile* (the same as used before), a moving-coil galvanometer of SIEMENS and HALSKE with accessories, and suitable resistances. The thermopile was very carefully protected against all disturbing influences; it reacted only upon the radiation that passed through a long tube fitted with diaphragms and mounted parallactically, so as to be easily kept pointing towards the sun by means of a finding arrangement [4]). We had ascertained by a special

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[1]) Proc. Roy. Acad. Amst. Vol. **8**, p. 503, 1905.

[2]) A preliminary account of the observations made by the Netherlands Expedition on April 17th 1912 is to be found in Proc. Roy. Acad. Amst. Vol. **14**, p. 1195 (1912). Cf also: NYLAND, "De eklips van 17 April 1912", Hemel en Dampkring **10**, 1, May 1912.

[3]) According to J. WEEDER, Proc. Roy. Acad Amst. **14**, 947, 1912.

[4]) A description of the instrument is given in: Total Eclipse of the Sun, May 18, 1901; Reports on the Dutch Expedition to Karang Sago, Sumatra, N⁰. 4, "Heat Radiation of the Sun during the Eclipse", by W. H. JULIUS (1905).

inquiry, that for temperature differences between the solderings not greater than those produced by full sunshine, the electromotive force of the thermopile could be considered strictly proportional to the intensity of irradiation. The deflections of the SIEMENS and HALSKE galvanometer were observed visually, by examining the positions of a bright index on a transparent scale. With a permanent shunt of 16 Ohms the instrument was just dead-beat; one millimeter deflection then corresponded to 10^{-8} Amp. The deflections were proportional to the current. The observer had the resistance box close at hand, in order to keep the image on the scale, and marked the epoch of each reading by means of a doublehanded chronometer, one hand of which could be stopped and made to catch up again (a "chronographe rattrapante"). Many readings were also made, in the course of the eclipse, with the thermopile screened; the zero proved very satisfactorily constant.

Our second actinometric set was especially intended to answer rapidly and to give a photographic record of the middle part of the radiation curve. It included a *bolometer* and a galvanometer with a moving coil of extremely small moment of inertia. Both instruments have been designed and constructed by Dr. W. J. H. MOLL, who also was in charge of this equipment on eclipse day. The bolometer consisted of many strips of very thin platinum (Wollaston sheet) coated with lampblack, and mounted so as to form two equal gratings, one of which received the radiation. A thick copper frame warranted quick equalization of temperature of all screened parts, while an envelope of non-conducting material protected it against rapid external changes. The whole was fastened to the end of a tube with diaphragms, which was directed toward the sun by an assistant.

As will appear from the photographic records, the galvanometer answered the purpose admirably (time of dead-beat swing less than one second; deflection 4 mm. for 1 microvolt; zero steady within 0.1 millimeter); but the instrument being only a temporary one, adapted to the requirements of this eclipse and not yet to general use, Dr. MOLL, who has since been improving the pattern, desires to publish full particulars at a later date.

In order to obtain reasonable bridge-currents within the very wide range of sensitivity imposed by the phenomenon, the observer varied the resistance of the principal bolometer circuit by steps, as the eclipse proceeded, and each time read the strength of the main current on a milliammeter; the resistance in the bridge being left unaltered. That the zero reading of the sensitive galvanometer was very little influenced thereby, was a proof of the symmetry of the arrangement.

Observations made with the bolometer.

During the greater part of the eclipse the galvanometer deflections were only visually observed, by noticing the motion of the reflected image of a slit on a transparent scale; but from 5 minutes before until 5 minutes after centrality the image was received on a photographic recording drum.

For a reproduction of the photogram we must refer to the *Astrophysical Journal* **37**, p. 229, Plate X, Fig. 1. On the same plate, Fig. 2 shows the central part of the curve on a larger scale [1]), and Fig. 3 gives on the same scale a control of the volt-sensitivity of the galvanometer, effected immediately after the eclipse was over. It shows well the qualities of the instrument.

The vertical lines are time-signals, produced by a small electric lamp flashing up at intervals of ten seconds in front of the slit of the recording apparatus; the first line following the minimum of the curve corresponds to $0^h34^m57^s$ Leiden M. T.

Two of the zero-readings, obtained by screening the bolometer, are visible on the curve (Fig. 1), one at 0^h30^m, another at 0^h37^m. A straight line joining them may quite safely be taken to represent the zero during the interval. The ordinate of the minimum thus comes out to be a quarter of a millimeter. At 11^h30^m (6 minutes after first contact) a deflection of 6.1 mm. [2]) was observed visually, the intensity of the main current at that time being $^1/_{195}$ of its value at the time of recording. Reduced to the latter value of the main current, the deflection corresponding to full sunshine would have been more than $195 \times 6.1 = 1190$ mm., or nearly 5000 times the deflection at minimum.

A few irregularities in the curve, especially at $0^h31^m20^s$ and at $0^h36^m40^s$, require explanation. They are not genuine, but simply due to an excusable negligence of the assistant who had to point the bolometer at the sun. The emotions of the event making him forget to keep the tube continuously in the right direction, he had twice suddenly to make up for the loss. Fortunately the minimum is unaffected.

Discussion of the bolometer results.

If the apparatus had followed the radiation instantaneously, the minimum would have been lower yet. We may therefore certainly

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[1]) The striped aspect of the curve is connected with the click of the recording apparatus.

[2]) As a basis for calculation we purposely select this *small* deflection, because the great deflections of the provisory galvanometer were not strictly proportional to the current.

conclude from these observations, that at the central phase of the annular eclipse the solar radiation fell below $^1/_{5000}$ of its ordinary value.

This remainder must in part be due to the unscreened ring of the disk. Assuming the apparent surface of that photospheric ring to be $^1/_{2500}$ of the surface of the disk (which certainly is a low estimate), and its apparent radiating power per unit of disk-surface to be $^1/_4$ of the average intrinsic radiating power of the disk, we may say that at the epoch of centrality the photosphere was still able to furnish us with at least $^1/_{10000}$ of the ordinary amount of radiation.

Consequently, less — and probably *much* less — than $^1/_{10000}$ of the sun's total radiation toward the earth is left as proceeding from the annular part of the *solar atmosphere* visible round the moon's edge.

So far, the inference is pretty sure, because it depends on the outcome of direct observations only.

What we want to deduce next, however, is an estimate of the radiation due to the entire solar atmosphere — or rather to the visible half of it. This we cannot do without making some simplyfying assumptions concerning the absolutely unknown conditions prevailing in the sun.

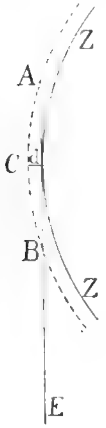

Fig. 1.

Let ZZ (fig. 1) be the photosphere (with radius r), ABE the direction toward the earth. If the radiating and scattering power of the solar atmosphere were distributed homogeneously through its whole depth d, the emission due to the hemispherical shell would bear approximately the same ratio to the atmospheric emission observed at mid-eclipse, that the volume of the hemispherical shell ($2\pi r^2 . d$) bears to the volume of the ring produced by the rotation of the segment ABC about the sun's diameter, which is parallel to AB, ($2\pi r$-segm. ABC).

That proportion is

$$p = \frac{rd}{segment\ ABC}.$$

For small values of d the surface of the segment is nearly $^2/_3\, d . AB$, and the ratio becomes

$$p = {}^3/_2\, \frac{r}{AB}.$$

Suppose we may replace the actual heterogeneous atmosphere by an ideal homogeneous one for which $d = 2000$ kilometers ($= {}^1/_{350}$ of the sun's radius). The corresponding value of AB is about $0{,}15\,r$, giving for the ratio

$$p = \frac{3}{2}\,\frac{r}{0{,}15r} = 10.$$

Our conclusion therefore is, that less than ${}^1/_{1000}$ of the sun's total radiation is emitted or scattered by parts of the celestial body lying outside the photospheric surface.

Even though we are free to admit an uncertainty of several hundreds percent in some of the estimates on which the above calculation is based, our result yet makes it impossible to maintain the current ideas on the nature of the photosphere.

Most solar theories, indeed, consider the photosphere to be a layer of incandescent clouds, whose decrease of luminosity from the centre toward the limb of the solar disk would be caused by absorption and scattering of light in an enveloping atmosphere ("the dusky veil"). According to calculations made by Pickering, Wilson, Schuster, Vogel, v. Seeliger, and others, such an atmosphere should intercept an important fraction (${}^3/_4$ to ${}^1/_2$) of the photospheric radiation. The atmosphere is of course in a stationary condition; receipts and expenses must balance each other. Now, what would become of that immense quantity of absorbed energy, of which only something of the order of magnitude ${}^1/_{1000}$ is emitted and scattered? So long as we have no evidence of any other form of solar output, especially proceeding from the atmospheric layers, and comparable in magnitude with the sun's total radiation, we are forced to reject the cloud-theory of the photosphere.

The radial variation of the brightness of the disk depends on the nature of the photosphere itself, not of its envelope. A new interpretation of the photosphere, agreeing with this result, will be proposed in a subsequent paper.

Observations made with the thermopile.

We now proceed to the discussion of the observations made for finding the shape of the entire radiation curve. In this part of the work our thermopile arrangement had the advantage of the bolometric apparatus in point of proportionality, within wide limits, between radiation and galvanometer deflection.

The total resistance of the thermopile circuit had to be varied in a few steps from 1300 for full sunshine to 100 for the central quarter of an hour, and back again. Table I contains the deflections

TABLE I.

Leiden mean time	Intensity of radiation	Leiden mean time	Intensity of radiation	Leiden mean time	Intensity of radiation
$23^h12^m23^s$	4960	$0^h21^m23^s$	849	$0^h44^m54^s$	612
13 52	(1ste contact)	23 42	680	46 37	733
15 35	4950	25 3	593	47 36	805
23 5	4725	28 1.4	410	48 37	872
25 16	4625	28 34.6	375	49 43	945
28 2	4460	29 10.4	335	50 22	993
29 40	4360	30 50.6	224	50 56	1034
31 28	4280	31 28.4	183	54 2	1222
37 15	3950	31 57.0	153	55 16	1313
38 52	3880	32 27.2	122	55 58	1386
40 27	3765	33 5.8	87	56 53	1453
46 23	3355	33 28.0	66.5	57 50	1550
48 31	3170	33 52.6	46	58 55	1640
50 20	3150	34 23.4	21	59 57	1738
51 43	3075	(minimum)	2.5	1 1 8	1839
0 3 36	2213	35 16.2	20	3 16	1962
5 8	2075	35 52.0	50	4 17	2010
6 41	1954	36 14.6	70	5 38	2095
8 7	1828	36 36.6	89	6 50	2190
9 45	1685	37 9.2	119	7 49	2325
11 38	1551	37 40.8	149	9 9	2382
13 39	1438	38 10.0	178	38 40	4340
14 53	1342	38 29.7	198	40 40	4380
16 52	1203	39 7.2	238	42 10	4425
17 49	1107	39 43.8	277	44 40	4520
18 38	1054	40 16.8	317	46 10	4600
19 28	978	40 50.6	356	52 10	4590
20 8	925	43 56	545	54 10	4660

all reduced to the lowest value of the resistance, and reckoned from zero-positions that were found by interpolation between a series of zero-readings, made in the course of the eclipse with the thermopile shaded. The shift of the zero was small and regular.

Plate XI 1) Fig. 1, is a reduced copy of the original mapping of the Table I. The deflections observed between $0^h28^m10^s$ and $0^h41^m30^s$, plotted on a ten times larger scale, are shown on Plate XI, Fig. 2. These latter observations give evidence of the exceptionally favourable condition of the sky especially during the middle part of the eclipse. When uniting the observational points by a curve, I was quite surprised to find it so perfectly smooth and symmetrical, for in our country a sky without even invisible haze is a rare occurrence.

The central part of this curve corroborates our conclusion drawn from the photographic curve, viz. that the minimum value of the radiation was $^1/_{5000}$ of the maximum. Indeed, the real minimum value could not be reached by the slow apparatus; but if we prolong the lower parts of the falling and the rising branch of the curve downward as nearly straight lines (beginning at points corresponding to 10 seconds before and 10 seconds after centrality), they meet at *one* millimeter above zero; and according to Plate XI Fig. 1, the maximum was represented by about 5000 millimeters.

The rest of the observations ran somewhat less regularly, both in the falling and in the rising phase of the radiation. From notes on sky-condition, made by other members of the party, we could afterwards state that the depressions in the series of points exactly corresponded to hazy cloudlets passing before the sun. Yet some arbitrariness was left in the process of tracing the radiation-curve so as to answer to an ideally constant degree of transparency of the sky. We simply made the curve pass through the *highest* points (because the observed values could only be too small), and for the rest took care that the curvature should vary as regularly as possible.

Special attention may be drawn to the points B (Plate XI Fig. 1), marked by small circlets. They are deduced from the Burgos observations of 1905 2) in the following way.

In the course of that eclipse the sun shone sometimes for a few minutes in a beautifully clear patch of sky between heavy clouds, and happened to do so during the phases in which the radiation passed through one-half of its maximum value. The exact epochs at which the intensity was $\frac{1794000}{2} = 897000$ occurred 33^m38^s before second

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1) Cf. *Astrophysical Journal*, **37**, p. 232, 1913.

2) *Astrophysical Journal* Vol. **23** p. 312, 1906.

contact and 33^m43^s after third contact; so, on the average, $33\,{}^2/_3$ minutes were required for the moon to cover the second effective half of the solar disk.

Now, at Burgos the moon's edge took $77\,{}^3/_4$ minutes to cross the whole solar disk; at Maastricht, in 1912, it took $80\,{}^3/_4$ minutes. If, therefore, the ratio of the radius of the moon's disk to the radius of the sun's disk had been the same in both cases, then the time necessary for covering the second effective half of the solar disk would have been, at Maastricht, $33\,{}^2/_3 \times \frac{80\,{}^3/_4}{77\,{}^3/_4} =$ very nearly 35 minutes.

But at Maastricht the moon's radius was practically equal to the sun's radius, whereas at Burgos the radii were in the proportion 132,8 : 126,8. This difference between the two cases implies that the interval of 35 minutes, calculated for Maastricht, is a little too great. Indeed, when drawing circles representing the sun and the moon in the right proportion and position, and taking the distribution of brightness on the disk into consideration, one easily concludes that the interval has to be taken about 25 seconds smaller say $34\,{}^1/_2$ minutes.

Consequently, the results obtained in 1905 required that in 1912, at the epochs $0^h0^m20^s$ and $1^h9^m20^s$ (i.e. $34\,{}^1/_2$ minutes before and after centrality), the radiation should have shown half its maximum intensity, or $\frac{4960}{2} = 2480$ scale divisions. This is indicated by the points B. The agreement with the actual observations of 1912 is indeed very satisfactory.

During the middle phase of the Burgos eclipse the conditions were, on the contrary, so unfavourable, that the central part of the radiation curve, there obtained, claims no confidence.

It was worth while, therefore, to found on our present eclipse-curve a renewed application of the method, formerly devised [1]), of determining the rate of decrease of the radiating power from the centre toward the limb of the solar disk.

Discussion of the thermopile results.

On a homogeneous piece of paper a circle of 40 centimeters in diameter, representing the sun, was drawn, and divided in the manner shown by the adjoined figure [2]). There are concentric zones,

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[1]) *Astrophysical Journal* **23**, 312, 1906.

[2]) The figure is not a copy of the original drawing, as this could not be so much reduced on account of the delicacy of the lines.

indicated by the numbers 1 to 12, and arcs representing the moon's limb in a series of positions. The width of the sickle-shaped strips bounded by these arcs, is $^1/_{20}$ of the sun's radius, excepting the strips *a*, *b*, *c*, *d*, for which it is $^1/_{40}$.

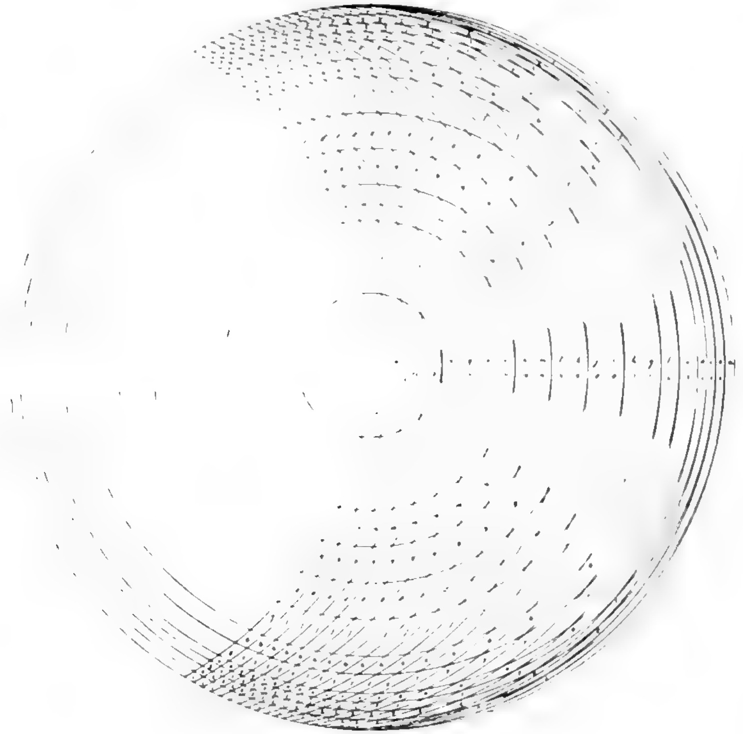

Fig. 2.

In $40^3/_8$ minutes the moon's limb accomplished a distance equal to the sun's apparent radius; so the strips *a*, *b*, *c*, *d*, required $^1/_{40} \times 40^3/_8$ minutes each for reappearing from behind the moon, the strips *e* to *u* took $^1/_{20} \times 40^3/_8$ minutes each. On our curve (Plate XI l. c.) we read the successive increments of the radiation, corresponding to the series of sickle-shaped strips. We shall denote these increments by the same letters as the strips.

The increment *a* is entirely due to radiation from zone 1; the increment *b* to radiation from the zones 1 and 2, etc.

Let us indicate by x_n the average intensity of the radiation with which a unit of disk-surface, belonging to zone *n*, supplies our thermopile. Then the increment *h*, for instance, will be composed as follows:

$$h = \theta_1 x_1 + \theta_2 x_2 + \ldots\ldots \theta_7 x_7 .$$

θ_1, θ_2 etc. being the surfaces of the parts that the corresponding zones contribute to the strip h. Though possible, it is extremely tedious to calculate these surfaces. We therefore determined them by cutting out and weighing the pieces of each strip. So the unit of area, adopted for measuring the surfaces, corresponds to a piece of our drawing-paper weighing 1 milligram. Expressed in that unit, the coëfficients $\theta_1, \theta_2 \ldots \theta_7$ were found to be 8,1, 11,9 . . . . . . 298. Table II contains all the coëfficients of $x_1, x_2, x_3 \ldots\ldots x_{12}$ thus

TABLE II.

Increments.	Coëfficients of:											
	x_1	x_2	x_3	x_4	x_5	x_6	x_7	x_8	x_9	x_{10}	x_{11}	x_{12}
$a =$ 47	251.0											
$b =$ 53.5	83.0	168.4										
$c =$ 58.5	25.5	88.5	137.5									
$d =$ 62	13.8	34.5	78.5	123.0								
$e =$ 130	15.7	37.5	59.6	113.0	264.0							
$f =$ 135	10.9	21.0	31.1	45.0	163.0	217.0						
$g =$ 140	8.5	15.0	19.5	27.0	80.0	146.0	192.0					
$h =$ 144	8.1	11.9	15.8	21.1	55.3	77.0	298.0					
$i =$ 147	7.7	10.3	12.3	15.9	42.0	55.5	198.0	146.5				
$j =$ 150	7.4	9.3	11.0	13.2	33.0	42.0	123.5	247.0				
$k =$ 152	7.1	8.4	9.2	11.9	28.7	34.8	93.5	168.5	120.0			
$l =$ 153	6.9	8.2	8.8	10.2	25.4	30.2	76.6	108.2	204.2			
$m =$ 154	6.9	8.1	8.5	9.8	22.4	27.5	66.0	86.5	142.0	93.2		
$n =$ 154.5	6.8	8.0	8.3	9.5	20.8	24.9	58.0	73.4	96.4	165.3		
$o =$ 154	6.8	7.7	8.1	9.2	19.8	22.6	52.5	63.6	77.8	119.7	77.7	
$p =$ 154	6.8	7.6	8.0	9.0	19.1	21.1	49.1	57.3	66.2	82.2	134.0	
$q =$ 154	6.7	7.5	7.8	8.8	18.3	19.7	44.9	53.0	57.7	68.9	164.7	
$r =$ 153.5	6.7	7.4	7.6	8.6	17.6	19.0	42.4	49.7	53.4	69.0	181.2	
$s =$ 152.5	6.8	7.5	7.6	8.4	17.0	18.2	40.3	45.5	49.2	54.5	143.0	50.3
$t =$ 151.5	6.8	7.5	7.5	8.2	16.7	17.5	39.2	42.9	45.5	51.1	115.3	83.6
$u =$ 149.5	6.8	7.4	7.5	8.1	16.5	17.1	38.0	41.7	45.1	48.3	102.0	97.0

obtained. The first column gives the values of the increments of the radiation as read on the eclipse-curve. Every horizontal row defines an equation. From the first equation we obtain x_1, from the second equation x_2, etc.

TABLE III.

Distance of Zone from Centre of Disk.	Average Radiating Power per Unit of Zone Surface: Found directly from the Equations	Average Radiating Power per Unit of Zone Surface: Reduced to value 100 at Centre	Found by graphical Interpolation	Distance from Centre of Disk.
0.9875	$x_1 = 0.18725$	48.6	40.0	1.0
0.9625	$x_2 = 0.2254$	58.5	61.0	0.95
0.9375	$x_3 = 0.2457$	63.9		
0.9125	$x_4 = 0.2631$	68.4	69.0	0.9
0.875	$x_5 = 0.2813$	73.0	74.2	0.85
0.825	$x_6 = 0.2900$	75.4		
			77.8	0.8
0.75	$x_7 = \begin{Bmatrix} 0.3038 \\ 0.3103 \end{Bmatrix} = 0.3071$	79.8		
			80.7	0.75
0.65	$x_8 = \begin{Bmatrix} 0.3221 \\ 9.3305 \end{Bmatrix} = 0.3263$	84.8		
			83.3	0.7
0.55	$x_9 = \begin{Bmatrix} 0.3463 \\ 0.3432 \end{Bmatrix} = 0.3447$	89.5	87.4	0.6
			91.0	0.5
0.45	$x_{10} = \begin{Bmatrix} 0.3519 \\ 0.3562 \end{Bmatrix} = 0.3540$	92.0		
			93.8	0.4
			96.5	0.3
0.3	$x_{11} = \begin{Bmatrix} 0.3656 \\ 0.3694 \\ 0.3681 \\ 0.3934 \end{Bmatrix} = 0.3691$	95.9		
			98.3	0.2
			99.5	0.1
0.125	$x_{12} = \begin{Bmatrix} 0.3817 \\ 0.3842 \\ 0.3860 \end{Bmatrix} = 0.3840$	99.8		
			100.0	0.0

The results are collected in the second column of Table III. The third column shows the same values converted into percentages of the intensity prevailing in the centre of the disk. After they had been plotted on millimeter paper, a smooth curve was drawn, fitting the points as well as possible. On this "distribution-curve" the numbers of the fourth column were read as ordinates, belonging to the places defined in the fifth column. Our results are thus made more easily comparable with those obtained by other observers.

It is not surprising to find the shape of our distribution-curve sensibly different from the shape of any of the curves that represent VOGEL's spectrophotometric measurements. Indeed, the latter show the distributions characteristic of special groups of rays, each covering a narrow part of the spectrum; they are germane, but yet vary considerably with the wave-length. The combined effect of *all* waves (invisible ones included), that are absorbed by our thermopile, must give a distribution-curve of another type, less simple than that to which VOGEL's curves for nearly monochromatic light belong.

Summary.

During the annular eclipse of the sun on April 17th 1912 the variation of the total radiation has been observed near Maastricht under exceptionally favourable sky-conditions, with two mutually independent sets of apparatus.

One set, comprising a bolometer and a short-period recording galvanometer, served the purpose of finding as accurately as possible the proportion of the minimum to the maximum radiation.

The ratio was found to be nearly $^1/_{5000}$. On this result we based an estimate of the total amount of energy radiated and scattered by the entire solar atmosphere; we thus obtained a very small fraction of the solar output (about $^1/_{1000}$).

It is impossible, therefore, to ascribe the fall of the sun's brightness from the centre toward the limb of the disk to absorption or scattering of the light by an atmosphere, enveloping a body that otherwise would appear uniformly luminous. The cloud-theory of the photosphere is not borne out by the facts.

With the other set of apparatus, consisting of a thermopile and accessories, we obtained a sufficient number of reliable readings for constructing the whole radiation-curve, from the first until the fourth contact, with a fair degree of exactness. Besides confirming the value of the minimum as found with the bolometer, this curve procured the data necessary for once more determining the rate of decrease of the radiating power from the centre to the limb of the solar disk.

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