

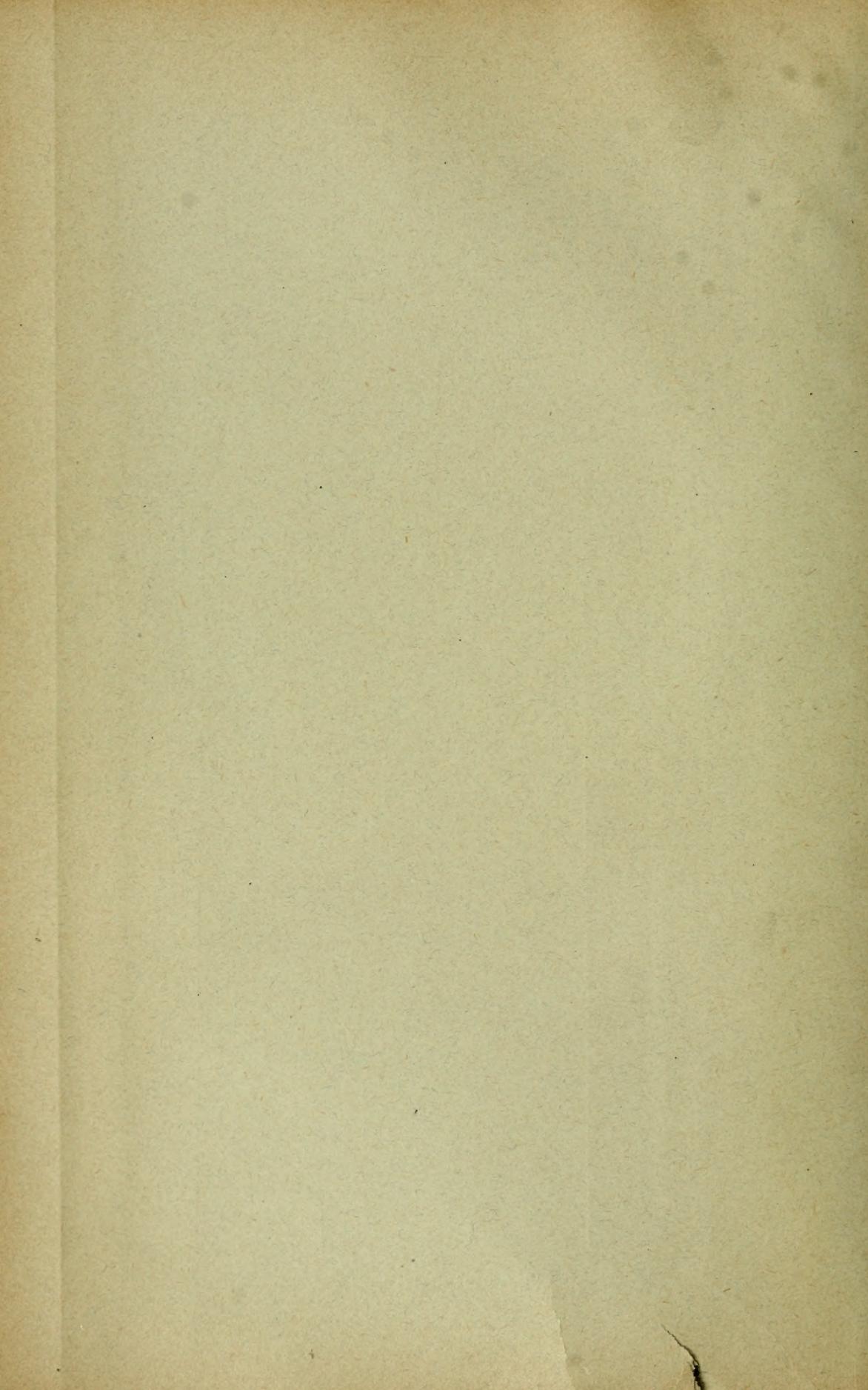
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PROCEEDINGS

OF THE

S E C T I O N O F S C I E N C E S .

— ❖ —

VOLUME VIII.

— ❖ —

AMSTERDAM,
JOHANNES MÜLLER.
June 1906.

YRZEEIJ
OF THE
MUSEUM HADISMA
YKOTER JARUTAN

(Translated from: Verslagen van de Gewone Vergaderingen der Wis- en Natuurkundige
Afdeeling van 27 Mei 1905 tot 27 April 1906. Dl. XIV.)

Koninklijke Akademie van Wetenschappen
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PROCEEDINGS

OF THE

SECTION OF SCIENCES.

—❧—
VOLUME VIII.

(1st PART)

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AMSTERDAM,
JOHANNES MÜLLER.
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KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM.

PROCEEDINGS OF THE MEETING
of Saturday May 27, 1905.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige
Afdeling van Zaterdag 27 Mei 1905, Dl. XIV).

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The following papers were read:

Anatomy. — "*On the development of the cerebellum in man.*"
(First part). By Prof. L. BOLK.

(Communicated in the meeting of March 25, 1905.)

On account of the fact that the lobulisation of the adult cerebellum of Primates generally and of man in particular, deviates in various respects from that of the remaining mammals, so that a homologisation of the lobes of the cerebellum of Primates occasionally presents difficulties, I undertook an investigation concerning the development of the grooves and lobes of the cerebellum in man, in order to try to elucidate certain obscure points in the anatomy of the Primate-cerebellum in this way. This investigation comprises some forty cerebella of human embryos, varying in length from crown to sole from 5 to 30 cm.

All the objects had been hardened in formol *in situ*; alcoholic material cannot be used for the study of this developmental process.

A complete systematic investigation of the formation of the lobes in the cerebellum of man has until now not been carried out. RETZIUS gives in his well-known standard work — *Das Menschenhirn* — a great number of pictures of developmental stages, also of the cerebellum, but a reasoned explanation to them is lacking. Of an earlier period we moreover mention the communications of KÖLLIKER and SCHWALBE, of more recent date those of KUITHAN, ELLIOT SMITH and CHARNOCK BRADLEY. In general, however, these investigations have been made with material which for this purpose was insufficient and as a consequence of this, opinions have become current which I have found to be wrong. This is more especially the case with the view concerning the way in which the sulcus horizontalis develops. Particularly with a view to the individual variations which arise especially in the later period of the lobulisation, it is essential to carry out the investigation with an extensive material, if we want to form a clear and continuous idea of the process and if we desire to distinguish well what is norm here and what exception.

In the morphogenetic process of the human cerebellum three periods may be distinguished, the first period is that of the development of the "cerebellar lamella" until the appearance of the first cortical groove; the second and third periods are those of the formation of grooves and lobes, during which, in the second period, those grooves appear which are generally characteristic for the cerebellum of mammals, in the third, the specific grooves and lobes of the Primate cerebellum. In this first communication only the first and second periods will be described.

Fig. 1, 2, 3 and 4 are sufficient to give an idea of the development of the "cerebellar lamella" until the time of appearance of the first groove. Fig. 1 has been taken from a foetus of 5 cm. length from crown to sole. The curvatures of the pons and neck have reached their maximum. The cerebellum appears as the already fairly thickened "cerebellar lamella" of MIHALCOVICS. It is remarkable that the thickening is turned intraventricularly in man whereas in the rabbit and pig (CHARNOCK BRADLEY) and the sheep (KUITHAN) it is exactly the extraventricular face which is most prominent.

From figs. 2*a* and 3*a* it appears that the convexity of the intraventricular plane becomes greater and greater, while the outer plane is only slightly vaulted. As a consequence of this, the cerebellum has in Fig. 3 acquired a triangular shape in the section with one extra- and two intraventricular planes; of these latter one faces

basalwards, the other caudalwards. The original caudal edge of the "Lamina cerebellaris" has consequently been shoved upward together with the insertion of the epithelial ventricular roof. Since in the mean time the plica-chorioidea has been formed, the peculiar condition has arisen, described by HIS for the human cerebellum, of which KUTHAN, however, denies the existence, since he could discover no trace of it in the sheep, although a complete developmental series was at his disposal. The anterior plait of the plica chorioidea, the so-called lamina chorioidea, is now stretched parallel to the intraventricular plane of the cerebellum which is turned backwards and this gives origin to a slit-shaped space between this plane and the lamella mentioned. HIS described this in this way that the lamina chorioidea partially encloses the cerebellum like a sac and how far this is the case appears from fig. 3*b* where the cerebellum is seen laterally. Now in fig. 4 nothing is found any longer of this condition, the plica chorioidea is now inserted at the edge of the cerebellum which now is turned to the back. Also in this respect I can confirm the observations of HIS against those of KUTHAN, that namely the lamina chorioidea lays itself upon the intraventricular plane and coalesces with this. Through this the latter has become an extraventricular plane and the plica chorioidea has obtained a new secondary line of insertion with the cerebellum. At the same time the outer plane has in this way become convex, the inner plane shows as a first indication of the "tent" in its posterior part a shallow groove which is to be distinguished as *Incisura fastigii*. The primitive line of insertion of the lamina chorioidea has to be sought in fig. 4 at the top of the extraventricular plane, laterally it lies more caudally, as follows from fig. 3*b*. This developmental stage of the cerebellum in man seems, by the peculiar way in which it thickens, to differ fundamentally from that of other mammals, where the cerebellar lamella retains in the section a more flattened lenticular shape.

At first the thickened lamina cerebellaris has the shape of a semi-ring, standing vertically on the anterior part of the longitudinal axis of the rhombencephalon and laterally passing into the still smooth regio pontis without a sharp border (fig. 2*b*). Soon the lateral parts of the lamina cerebellaris show a fairly strong clublike swelling (fig. 3*b*) by which a clear demarcation between cerebral base and cerebellum is formed. These lateral swellings remind us of the bilateral origin of the cerebellum in lower vertebrates (observed e.g. by SCHAPER in Teleosteans). Yet this lateral demarcation is only temporary; as soon as the pons begins to differentiate, it disappears again and arises

anew only at a much later stage when the cortex has already become amply lamellised.

In the mean time, during the thickening of the lamina cerebellaris, developmental phenomena have taken place in the bordering region between Mesencephalon and Rhombencephalon, giving rise to the formation of Plica encephali dorsalis (KUPFER), Isthmus rhombencephali and Velum medullare anterius. In the youngest stage represented (fig. 1) the anterior edge of the Lamina cerebellaris passes directly into the mesencephalic roof, only the posterior edge of this latter is a little inwardly invaginated. An Isthmus rhombencephali or Plica encephali dorsalis do not yet exist. In the next stage of development (fig. 2*a*) the mesencephalon has obtained a clearly defined posterior wall, vertical to the roof; the inward invagination of the posterior edge of the roof is still in existence and is partly visible in fig. 3, but has disappeared in fig. 4 on account of the thickening of the posterior wall of the mesencephalon. In fig. 2 the plica encephali dorsalis has developed, bordered in front by the posterior wall of the mesencephalon, at the back by the lamina cerebellaris. The formation of the Plica is accompanied by a rotation of the Lamina cerebellaris, the anterior edge of which is now no longer situated at the front but below and as a consequence of this the Isthmus rhombencephali is now also indicated in principle. Next the bottom of the plica encephali dorsalis becomes broader, there arises between the thickened lamina cerebellaris and the mesencephalon a thin middle plate (figs. 3*a* and 4), the first origin of the velum medullare anterius. The further details of this stage and the following stages will be extensively described elsewhere.

The lobulisation of the cerebellum in the second stage is characterised by the fact that the grooves which divide the surface of the cerebellum into several regions originate with a single exception in the median plane and from there extend laterally. These interlobular grooves are consequently unpaired with one exception and divide the foetal cerebellum of man into a number of lobes, which can be homologised without difficulty with those which I learnt to be typical for the adult mammalian cerebellum.

The median section of a cerebellum with indications of the grooves that appear first, is given in fig. 5. The incisura fastigii has been shifted more to the front compared with fig. 4. On the extraventricular plane two grooves can be clearly distinguished, one, a little rostrally from the top of the cerebellum, another at a short distance from the margo myelencephalicus. Which of these two arises first I have not been able to make out, evidently they both arise about simultaneously,

since in three cerebella of this stage I found both of them already present in each (total length of the foetus 8 to 10 cm.). The anterior groove is the sulcus primarius (1), the typical principal groove, easily recognised in every mammalian cerebellum, separating the two lobes of the cerebellum, the lobus anterior and lobus posterior. The posterior groove is the sulcus uvulo-nodularis (*mihl*) (sulcus postnodularis of ELLIOTT SMITH, sulcus praeuvularis of ZIEHEN, Fissure IV of CHARNOCK BRADLEY). It borders the nodulus in front, i. e. in the direction of the mesencephalon. Between these grooves a still shallow depression is visible on the upper part of the posterior plane, the first indication of the fissura secunda (ELLIOTT SMITH, *mihl*, sulcus inferior anterior of ZIEHEN, fissure *d* of CHARNOCK BRADLEY). The cerebellum, seen at this stage from behind, is somewhat biscuitshaped (fig. 6) and lies with the front planes of its lateral parts against the occipital poles of the hemispherical vesicles. Besides the two mentioned grooves, proceeding from the median line, the cerebellum possesses at this stage already a sulcus which is bilaterally symmetrical and lies at a short distance of the margo myelencephalicus. This groove (*p*), which develops in a latero-medial direction is the homologon of the groove which I have distinguished in the mammalian cerebellum as fissura para-floccularis. It borders in front the already slightly prominent so-called recessus lateralis. The anterior wall of this recessus lateralis has been distinguished by KÖLLIKER as gyrus chorioideus. It seems to me that the name "Gyrus floccularis" is more characteristic, since from this narrow cerebellar seam which is already marked out at so early a stage, the flocculi are later formed.

In a successive stage (Figs. 7 and 8) the sulcus primarius (1) has become deeper and the fissura secunda (2) has become a distinct groove; moreover a first secondary groove has arisen in the lobus anterior. Later this lobus is separated into four small lobes by three grooves; I have not been able, however, to make out which of these three is the first to appear. That the sulcus in the lobus anterior, seen in figs. 6 and 7, which is first in appearing, is really the groove, distinguished by ELLIOTT SMITH as sulcus praeulminatus, I have not been able to confirm, while also from a comparison of my human cerebella of this stage with corresponding figures given by CHARNOCK BRADLEY for the rabbit and pig, it appears that this first groove lies in the lobus anterior of man farther away from the sulcus primarius than with the two animals mentioned. So I cannot decide whether this first groove in the lobus anterior in man is homologous with the "Fissure 1" of CHARNOCK BRADLEY. Also in the lobus posterior a new groove has appeared in the median line, between

the sulcus primarius (1) and the fissura secunda (2). This groove, indicated in the following figures by 4, is the sulcus praepyramidalis (mihi) (sulcus inferior posterior of ZIEHEN, fissure suprapyramidalis of ELLIOTT SMITH, fissure III of CHARNOCK BRADLEY). This fissura praepyramidalis borders in front the pyramis and soon reaches the length of the fissura secunda. This latter can in its further development lengthen itself regularly in a lateral direction, or otherwise there independently arises (fig. 8*b* 2') in the hemisphere at a short distance above the fissura parafloccularis (ρ) a groove which soon becomes confluent with the fissura secunda. While at the same time the recessus laterales bend out further, the fissura parafloccularis (fig. 7*b*, 8*b*, ρ) becomes confluent with the sulcus uvulo-nodularis, by which the gyri flocculares form with the nodulus a part which is marked off from the remaining cerebellum. ELLIOTT SMITH mentions that the fissura parafloccularis can also flow together with the fissura secunda (2). This observation I can confirm for other mammals on account of the structure of the adult cerebellum; with the embryonic material of man I have not observed such a case. At a later stage the fissura secunda does terminate, above in the fissura parafloccularis.

In the cerebellum of a foetus of 13 cm. the hemispheres are no longer swollen balloonlike, but have, when seen from behind, obtained the more angular form which now is characteristic for them during a longer period of development (fig. 9*a*). The median zone is still a little depressed, even in the posterior part of the lobus anterior. The sulcus primarius (1) lies still relatively far at the back, the sulcus praepyramidalis (4) has already pretty far advanced into the hemispheres, but in such a way that the lateral parts with the transversally proceeding middle part form an obtuse angle, with the opening downwards. This peculiar shape forms during the successive stages of development, in which the interpretation of the grooves is not always easy, an excellent diagnostic for the sulcus praepyramidalis. The fissura secunda (2) has advanced as far as the lateral wall of the cerebellum so that the regio tonsillaris (fig. 9*a* *t*) is now bordered on all sides. This region is always more or less swollen in the shape of an egg. The gyrus floccularis is divided by a longitudinal groove into two small lobes. At this stage consequently the uvula with the appertaining lateral parts and so also the nodulus with its lateral regions are already differentiated in principle. This rapid developmental process contrasts strongly with the still very simple condition found in the remaining part of the lobus posterior and supports to some extent the opinion of ELLIOTT SMITH who looks upon the complex of uvula with tonsils, nodulus with flocculi, as a more independent

L. BOLK. "On th



Fig





Fig. 1.



Fig. 2a



Fig. 2b



Fig. 3a



Fig. 3b



Fig. 4



Fig. 5.



Fig. 6



Fig. 7a



Fig. 7b

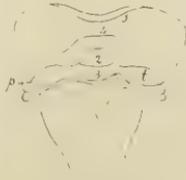


Fig. 9a



Fig. 9b.



Fig. 8a.



Fig. 8b



Fig. 8c



Fig. 10a



Fig. 10b.

lobe of the cerebellum. Then the peculiar surface division in the median line between sulcus primarius (1) and fissura secunda (2) deserves notice. The sulcus praepyramidalis (4), namely, at first always divides this region into two unequal parts; the lower half, the greater, situated between sulcus praepyramidalis (4) and fissura secunda is the origin of the pyramis, while from the very narrow upper half, situated between sulcus primarius (1) and sulcus praepyramidalis, must originate: declive, folium vermis and tuber vermis. In this respect a parallelism can be noticed between the phylogenetic and ontogenetic development of the cerebellum. For the narrow region between sulcus primarius and sulcus praepyramidalis is homologous with that lobulus which in the median section of the mammalian cerebellum I have distinguished as lobulus C_2 and which only in the Primates attains a very strong development.

The frontal plane and median section of the cerebellum of a foetus of 15 cm. are given in fig. 10. This stage of development is important because now the foetal human cerebellum shows the same lobulisation which I learnt to be the fundamental type of the mammalian cerebellum generally, a stage which only lasts a short time, since now soon the grooves appear that characterise the Primates generally or the Anthropoids and man more particularly and the homologa of which are missed with other mammals. For as will be seen from fig. 10*b*, now in the median section, as well the lobus anterior as the lobus posterior, is divided by three grooves into four lobuli. With the mammalian cerebellum I have distinguished the four lobuli of the lobulus anterior as lobulus 1, 2, 3 and 4, the latter being situated immediately before the sulcus primarius, the four lobuli of the lobus posterior I distinguished as lobulus *a* (homologous with the nodulus), lobulus *b* (homologous with the uvula), lobulus C_1 (homologous with the pyramis) and lobulus C_2 (homologous with the complex of declive, folium vermis and tuber vermis). It will be seen by a comparison with the investigations of CHARNOCK BRADLEY, that the stage with man, sketched in figs. 9 and 10, has a strong resemblance with a developmental stage which the cerebellum of other mammals (pig and rabbit) traverse before the final lobulisation of the cerebellum. However much the Primate cerebellum may in its final form differ from that of other mammals the groundplan of its lobulisation is, as is evident from the now sketched period of development, not different from that of other mammals. In the next following stage, however, it follows a development of its own, grooves occur, introductory to the lamellisation of the cortex, which are specific for the Primates and which will be described in the second communication.

Botany. — “*Some observations on the longitudinal growth of stems and flower-stalks*”. By Prof. E. VERSCHAFFELT. (Communicated by Prof. HUGO DE VRIES).

(Communicated in the meeting of March 25, 1905).

Superficial observation already shows that in many cases the growth of stems, leaf- and flower-stalks is greatly dependent on the organs which they bear: buds, leaf-lamina, flowers. When these latter are removed the growth of the axial parts is generally arrested and they even die after a shorter or longer time.

In literature I have not found any investigations mentioned, attempting to analyse this phenomenon more closely; e.g. in the case of flower-stalks, to find out whether excision of certain parts of the flower had as much influence on the growth of the stalk as the removal of the entire flower. I have now been able to make this out for some vernal plants by measurements of growth and I shall in what follows give a short account of the results.

I chose preferably flowers for this purpose, since here at the top of the same spindle organs of different physiological functions occur together and so the experiments admitted of greater variety. In one case, that of *Eranthis hiemalis* Salisb., I shall describe the course of the investigation and its results a little more in extenso; the other examples will be more briefly dealt with.

The stem of *Eranthis*, as will be known, bears at its top a single flower and close under it, united to a sort of broad collar, a whorl of three green sitting parted leaves. As long as the stem is still under the ground, its top is sharply bent downward and the still perfectly closed flower hangs down, protected by the three leaves, still yellow then, which envelop it. As soon as the top of the stem has come above the ground and also the flower has come free, this latter raises and soon unfolds itself; then the basal collar spreads out and turns green. The measurements of growth were made in the stage between the period when the stem is not yet visible above the ground and that, in which, after the petals and stamens have fallen off, only the fertilised pistils remain. About this time the longitudinal growth stops. Whether afterwards, during the ripening of the fruits, a new period of growth begins, as in other plants, I have not investigated.

The plants, serving for the investigation, were placed in a hothouse of the Botanical Garden at Amsterdam, in which the mean temperature was 20° C. and in which the specimens developed very rapidly and entirely normally.

I will first show by a few examples that the presence of the organs on the top is necessary in order to cause the stem to grow normally in length.

The stem of an *Eranthis* was on February 4, 1905, 40 mm. long, measured from the base near the rhizoma to the junction of the leaf-whorl. Placed in the hothouse the plant was at first measured daily, afterwards every other day; for briefness' sake I shall here only give the length reached by the stem after every four or five days.

Date	4.2.05	8.2	13.2	17.2	22.2	26.2
Length in mm.	40	89	135	154	162	162

In the same time the development of a stem on which leaves and flower had been cut away, was:

Date	4.2	8.2	13.2	17.2
Length	49	52	54	55

Another example of growth with a normal stem:

Date	5.2	9.2	13.2	17.2	22.2	26.2
Length	44	98	128	145	150	150

and of a stem, bereft of leaves and flowers:

Date	5.2	9.2	13.2	17.2
Length	97	103	104	104

Whereas with normal *Eranthis*-stems the top with the flower on it, had in the hothouse after a couple of days, entirely erected itself, on the other hand the hook-shaped curvature of the stem without flower or leaf-whorl, partially remained and it was only very slowly that its extremity raised itself to some extent. This need cause no wonder, if it is remembered that the disappearance of this curvature is caused by asymmetrical growth of the top of the stem.

Now in a series of *Eranthis* plants the organs on the top of the stem were only partly removed; e.g. the three green leaves, the petals, the stamens, the pistils. The length of the stems was measured from day to day. The result of these experiments has been very clear. As long as the green leaves remained undamaged, the growth of the stem might be called normal. At the utmost the stem remained a little below its normal length if the whole flower or certain parts

of it were cut away. On the other hand the growth was very considerably impeded by removing the whorl of green leaves. This will be seen from the following measurements.

Eranthis-stem, on which only the three leaves under the flower have been preserved, the flower itself having been removed:

Date	7.2	11.2	15.2	19.2	22.2	26.2
Length in mm.	51	107	134	141	141	141

Another example of the same case:

Date	6.2	10.2	13.2	17.2	22.2	26.2
Length in mm.	58	104	129	135	135	135

Eranthis-stem of which the basal whorl has been cut away, the flower remaining intact:

Date	6.2	10.2	13.2	17.2	19.2
Length in mm.	86	96	97	100	100

Another example of the same case:

Date	7.2	11.2	15.2	17.2
Length in mm.	59	72	74	74

Hence a stem which had been bereft of its flower grew in length in a period of twelve days 176 % in the first and 133 % in the second experiment, this increase in length being only 16 % and 25 % respectively in the same time with a stem on which the flower had been preserved but the whorl of leaves removed.

The influence which the presence of the leaf-whorl has on growth follows clearly enough from this. Also in the other cases which I investigated, the growth of stems that bore flowers only, may have been a little greater than of stems from which the leaf-whorl as well as the flower had been removed, it is certain, however, that the longitudinal growth is chiefly regulated by the presence of the green leaves.

A related fact is that after removal of the leaf-whorl the flower raises itself only very slowly and often only partly.

Although the supposition is not very probable, it might be presumed that the observed effect of the three leaves is caused by the circumstance that they have to provide the stem with food. That this

is not the case follows from the fact that the same results are obtained in the dark and that consequently the presence also of the non-assimilating leaves renders a strong longitudinal growth of the stem possible, which does not occur if only the flower is preserved on the top. It will be superfluous to mention figures in this respect.

No more does it appear necessary to give in extenso the measurements proving that removal of the pistils, the stamens or the petals has with *Eranthis* little or no influence on the longitudinal growth of the stem. On the other hand it is not superfluous to remark that the leaf-whorl must be pretty completely cut away if we want soon to arrest growth. The three green leaves namely show basal growth themselves and if their foot is not damaged, this latter may appreciably grow in size in the course of a few days; at the same time the stem continues growing in length.

Example: foot of the three green leaves kept; also the flower intact.

Date	8.2	11.2	15.2	20.2	26.2
Length in mm.	54	81	113	145	145

Already on the 13th the leaf-whorl had considerably grown out; at the edge nothing of the nature of a wound could be seen any more. In the same time a stem of 102 m.m. length on which the leaf-whorl had been completely cut away, the flower remaining intact, had only reached a length of 117 m.m.

If one should be inclined to think that not the presence of the whorl of green leaves but the intact condition of the junction of the leaves on the stalk is the principal point here, I must remark that of this junction zone a layer of tissue may be removed all round without the longitudinal growth being materially affected. Also from the somewhat vaulted receptacle a part may be removed or the middle part may be hollowed without any other consequences than would ensue on the plucking off of the floral parts situated on it.

Finally we remark that *Eranthis*-stems, cut off near the junction on the rhizoma can continue growing for days when they are put with their feet in water and then show the same behaviour as whole plantlets. Besides, the presence of one out of the three green leaves is sufficient to render a considerable growth in length of the stem possible; e.g. lengthening from 53 to 89 mm. in two weeks. That also with *Eranthis*-leaves the growth of the leaf-stalk depends on the presence of the leaf-disk will now be obvious; I have ascertained myself of it by measurements, however.

Galanthus nivalis L. enables us to observe phenomena of a different kind in this same respect. With this plant also, the stem terminates in a single flower which, however, when it is fully developed and unfolded, hangs on a thin, limp, flower-stalk. This is implanted on the top of the stem, where also two coalescent bracts are found which enveloped the flower-bud before its unfolding. Hence we must here investigate the influence of the terminal organs on the growth of the stem as well as on that of the flower-stalk.

Concerning the longitudinal growth of the stem, we find that it is completely independent of the presence of the flower. A single example will suffice to show this. The stem was measured from the point where it appears from the bulb to the implantation of the bracts; these latter still surrounded the flower-bud; in *a* the plant remained undamaged; in *b* bracts and flower were cut away to the foot.

Date	13.2	16.2	20.2	23.2	26.2
Length in mm. <i>a.</i>	90	133	157	161	162
<i>b.</i>	46	60	90	105	108

On the other hand, the growth of the flower-stalk stops as soon as the flower is removed. The influence of the flower on this organ is even so great that already after a couple of days the stalk of cut flowers turns yellow at the top and soon dies from above downward. The measurements show that the ovary plays if not a preponderant, yet a considerable part here. So the flower-stalks of flowers which already opened, grew from 28.2.05 to 6.3.05, in two cases from 16 and 14 mm. to 23 and 24 mm.; a flower of which the perianth was removed, in the same time from 17 to 21 mm., while two flower-stalks without their flowers measuring 20 and 14 mm. had reached 22 and 16 mm. the next day, but after that died off. Cutting the stamens has no great influence on growth; yet growth remains very small if stamens as well as perianth are removed, so that with *Galanthus* the ovary regulates the growth of the flower-stalk to a great extent but not exclusively. On the other hand the flower-stalk remains alive as long as the ovary is still present on its top.

Exactly the same behaviour is shown by *Narcissus Pseudo-Narcissus* L., where the stem continues growing when the flower is cut, but the flower-stalk stops growing and dies, if the ovary is wanting. I may add here that for the growth of the stem it makes no difference whether its top is cut above or below the

swelling occurring at the point where the bracts and flower-stalk are implanted, so that this zone also has no importance for the growth of the parts under it. Also stems of *Galanthus* and *Narcissus*, cut in the basal part and hence separated from the bulb, or even parts of them, if they were taken from plants with their flower-buds still closed, continue to grow vigorously whether the flower-bud be present or not.

Tulipa Gesneriana L. shows something different again. Here the flower is born by a leafed stem; the internodes which are placed near the base stop growing sensibly towards the time that the flower becomes visible from the outside and is about to open. At this stage, however, the upper internode with the flower at the top, still grows considerably in length. For this the presence of the flower is absolutely necessary. The upper portion of the stem is arrested in growth and gradually dies off as soon as the flower is cut off.

Example: *a.* flower present; *b.* flower removed. Only the upper internode measured.

	Data	6.3	8.3	13.3
Length in mm. <i>a.</i>		42	53	83
	<i>b.</i>	41	42	44

From the following measurements the significance of the various floral parts may be seen :

- a.* perianth removed.
- b.* stamens removed.
- c.* pistil removed.

	Date	6.3	8.3	13.3
Length in mm. <i>a.</i>		36	41	45
	<i>b.</i>	46	63	70
	<i>c.</i>	41	51	68

Although removal of each of the individual whorls of organs, partly suppresses the growth of the upper internode, yet it is seen that the petals have the greatest influence here. The above is only an example chosen from several concordant measurements.

Finally some observations were made with *Crocus vernus* All. Since the ovary lies fairly deep here, hidden in the tube formed by

the green leaves and the bracts round them, plants that had been cut open had to be used for the measurements, in which the flower was laid bare over its full length. For this purpose flowers were chosen which were still surrounded by bracts and entirely closed and the top of which became just visible above the ground. It appeared, however, that at this stage the stem on which the flower is situated, had reached about its full length and only grew a few millimetres more. The further longitudinal growth which is very considerable and brings the flower above the ground is nearly wholly caused by the corolline tube between the ovary and the loose slips of the perianth. Only to this stage I paid attention. Some measurements of the corolline tube may follow:

- a. flower undamaged.
- b. corolline lobes removed.
- c. corolline lobes, stamens and pistil cut away at the upper end of the coalescent corolline tube.

	Datum	8.3	9.3	11.3
Length in mm. a.		46	101	108
	b.	55	84	84
	c.	31	72	72

So removal of the terminal organs has not remained without influence on the growth of the corolline tube, but has not been able to check it to the same extent as in the preceding cases.

It deserves notice that removing the anthers and stigmas did not prevent the stamens and styles to reach about their normal length.

Summary. The investigation has shown that the normal longitudinal growth of the stem with *Eranthis hiemalis* is only possible when the whorl of leaves at the top is present, while the flower exercises no influence on it. This latter is also the case with the stem of *Galanthus nivalis* and *Narcissus Pseudo-Narcissus*; the flower-stalk however, in these two plants, is checked in growth as soon as the flower is cut, the ovary proving to be of especial importance. With *Tulipa Gesneriana* it is chiefly the perianth that rules the longitudinal growth of the upper internode; with *Crocus vernus*, finally, the growth of corolline tube, stamens and style is in a high degree independent of the presence of petal lobes as well as of anthers and stigmas.

Zoology. — “*On the Structure of some Siliceous Spicules of Sponges.*
 I. The styli of *Tethya lynceurium*, by Dr. G. C. J. VOSMAER
 and Dr. H. P. WIJSMAN, Professors at the Leiden University.

(Communicated in the meeting of April 22, 1905).

After SCHWEIGGER (1819) had demonstrated that the spicules of sponges in some cases do not consist of calcium carbonate, GRANT (1826) found them to contain silica, and BOWERBANK (1841 *a*) showed that, in addition to the silica some organic matter is present. He reached this conclusion through the fact that the spicula when heated, were partly carbonised. KÖLLIKER (1864) remarked that the brown or black colour, produced by heating, is certainly not only due to carbonised organic matter; examined in reflected light the heated spicula appear white, and the dark spots seen in transmitted light are, therefore, partly due to inclosed air. THOULET (1884) found no organic matter and concluded: “les spicules sont donc constitués par de la silice pure”, which he compares with opal. SOLLAS (1885) likewise finds that the silica resembles opal. It is now generally accepted that the spicules of siliceous sponges consist of some kind of opal; but that in some way or other, organic matter is also present. So far here is a general agreement of opinion but the chemical analyses which have been carried out show considerable differences as to the quantity of water, combined with the silica as a gel. The formulae, given for the composition vary from 2 (SiO_2) + H_2O to 5 (SiO_2) + H_2O , but must be considered as mere failures. F. E. SCHULZE (1904) comes to the result: “dass, entweder die Siphone keinen bestimmten konstanten Wassergehalt haben, oder dass die organischen Zwischenlamellen . . . einen je nach der vorgängigen stärkeren oder geringeren Austrocknung wechselnden Gehalt an Wasser haben”.

It is certain that even in the best cases, the quantity of organic matter is so little that it cannot well be ascertained. Its presence can, however, be proved by treating the spicules with hydrofluoric acid. But there is also some disagreement as to the nature of this matter and the exact place in the spicules where it is met with. We shall see that different kinds of spicules vary in this point.

In addition to the silica, which behaves like some kind of opal, and which we propose to call *spicopal*, and the organic matter which F. E. SCHULZE called *spiculine*, — modifying the original term used by HAECKEL — in some spicules there have been found traces of Na, K, Cl, Fe, Mg and Ca, but in such slight quantities that they can be left out of consideration for the moment.

As to the structure of the spicules, GRAY (1835) had found them in *Hyalonema* to consist of layers, which became conspicuous by heating. These layers concentrically surround a "central canal", which is filled out, as KÖLLIKER (1864) has shown, by an organic mass, the axial rod. CLAUS (1868) found that the silica which directly surrounds this central rod, is homogeneous; he called this homogeneous cylinder the axial cylinder. According to MAX SCHULTZE (1860) the longitudinal striae, which become conspicuous especially after heating, are due to the fact that layers of silica alternate with very thin layers of organic matter; the first are, after SCHULTZE, isotropic, the second anisotropic. The outer layer is generally found to be of organic nature.

In all these cases, the investigators described some special kind of spicule; naturally they have chosen very large spicules. GRAY, CLAUS and MAX SCHULTZE studied the large rods of Hexactinellida, such as *Hyalonema* and *Euplectella*. It may be asked, how far their results hold good for spicules of other sponges.

KÖLLIKER had already found that not in every case the axial thread is conspicuous. Also it has not been possible to demonstrate in every case alternating layers of spicopal and of organic matter, not even where longitudinal lines are evident. There is a great confusion with regard to the presence of a so-called spicular sheath. Any accurate determination of the refractive power of different spicules is likewise wanting.

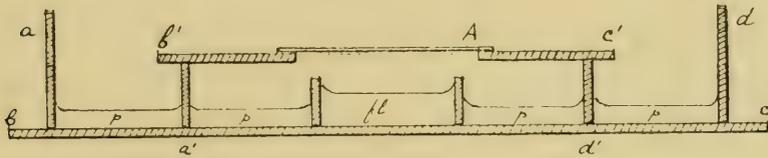
It seems, therefore, desirable to get some more information about these subjects. Since F. E. SCHULZE (1904) studied the enormous spicula of *Monorhaphis*, it appears useful to investigate, whether spicules from other groups agree with them as to their structure, and their chemical and physical properties.

We began our examination by the large styli of *Tethya lynceurium*. After bringing this point to some certainty, we have compared the results with those obtained from other species.

In the first place we tried to answer the question: Do the styli of *Tethya* contain other organic elements than the central rod, either as a sheath, or as layers between the spicopal, or as both of them.

Of course, the method which at first presents itself for the detection of organic matter, is the dissolution of the silica by means of hydrofluoric acid. Former investigators who applied this reagent, have omitted to give an accurate description of their experiments. SOLLAS (1888 p. XLIX) put the isolated spicules into a drop of water and added a drop of hydrofluoric acid. On doing this, one generally sees that the silica is dissolved and that the central rod remains.

Adding less hydrofluoric acid, the process does not go to the end. As it is necessary to cover the slide by means of Canada balsam (SOLLAS) in order to preserve the object glass from the disastrous influence of the vapours of hydrofluoric acid, it is difficult to vary the acidity of the fluid, in which the spicules are mounted. Also it is impossible in this way, to exclude the influence of the glass. We had therefore, to construct an apparatus allowing the concentration of the hydrofluoric acid to be varied without danger to the lenses of the microscope. At first we tried ebonite, in combination with glass, covered by a layer of celluloid, which is sold in solution under the name of zapon. But as this method did not satisfy our purposes, we tried another and we think that we have found a good and rather simple device. The adjoined figure needs little explanation. Out of a sheet of trans-



parent celluloid, 1 mm. thick, is constructed a case, $abcd$ ¹⁾; the bottom measures 6×10 cm., the height is 1.5 cm. In the midst of the case a circular rim of celluloid, high 5 mm., is joined to the bottom. Another case of celluloid $a'b'c'd'$ measures 4.5×6 cm. bottom and 8 mm. height. In the middle of the bottom a square of 2×2.5 cm. is cut out. This opening is covered by a sheet of thin celluloid, no more than 0.5 mm. thick, measuring 2.5×3.5 cm. This thin sheet A is joined with $b'c'$ air- and watertight by means of soft paraffin. The spicules under examination are placed on the bottom of the case $a'b'c'd'$, e. g. in a drop of water. To flatten this drop it is covered by a very thin film of celluloid. In the exterior part of the case $abcd$ is poured out some liquid paraffin p , in the interior commercial hydrofluoric acid (fl), diluted with 3 or 4 parts of water. Now the case $a'b'c'd'$ is reversed and put into $abcd$. As we have found that hydrofluoric acid in the gaseous state after some time

1) The carefully cut and cleaned sheets of celluloid are easily united by means of acetone. The parts that should be united are pressed together, and by means of a small brush a little drop of acetone is applied. The celluloid immediately sticks together. The corners are afterwards, to diminish the chance of leakage, cemented another time with zapon. Celluloid is got at the D. Celluloid Fabrik Leipzig.

1) Very thin films of celluloid are got by pouring out zapon on a glassplate, in the way that collodion plates are made, and tearing it off the glass after drying.

passes through thin strata of celluloid, it might be expected that the very thin layer of celluloid used in the above manner would be no obstacle for the acid to attain the spicules. Even the retaining of the reaction in this way is an advantage, as it may now be observed without the use of very dilute solutions.

In this way we have constructed a little apparatus which has answered to our purposes in several respects, viz: absence of glass, slow reaction, rather great security for the lenses of the microscope, and the possibility of interrupting the reaction at any moment.

As we found it unmaterial whether the spicules (obtained from sponges preserved in alcohol) were isolated by means of artificial gastric juice (after some days at 35° C) or by boiling with hydrochloric acid, we preferred the latter method. Such spicules, having been boiled with hydrochloric acid for some minutes, washed out repeatedly with water, either with the aid of a centrifuge or not, and dried afterwards at the ordinary temperature, are the objects investigated by us, if another treatment is not expressly mentioned. By placing some spicules in a drop of water, and covering them with the thin film of celluloid, one can first study under the microscope whether they are normal in their aspect, uninjured etc. Also, and *Tethya* is a proper object for this, which spicules are open, which closed. Then we expose the preparation to the vapours of the hydrofluoric acid. The commencement of the reaction is more or less retarded, depending upon the concentration of the acid, the quantity of water and the thickness of the film of celluloid; but at any rate the spicules begin to be dissolved after some 30 or 50 minutes.

It is best to give attention to the fractures, as the reaction is here to be seen at first.

BÜTSCHLI (1901) already remarked that the dissolution of the silica may occur in different ways. We can confirm this observation for the styli of *Tethya*. Observing what happens at the broken end of a spiculum, the opal surrounding the axial thread is seen to be hollowed out in the shape of a cone. The top of the cone is very sharp, and becomes still sharper if the reaction proceeds. BÜTSCHLI says (l. c. 258—259): "Man könnte wegen dieser so häufigen Bildung einer trichterförmigen Auflösungshöhle an den Enden auf die Vermuthung kommen, dass die Angreifbarkeit und Löslichkeit der Schichten von aussen nach innen, gegen den Achsenfaden successive zunehme. Eine solche Annahme scheint jedoch zur Erklärung der Erscheinung nicht nöthig, vielmehr dürfte sie sich schon daraus hinreichend erläutern, dass die Flusssäure allmählich in den geöffneten Achsenkanal eindringt und gleichzeitig auch in dem Masse

stärker wirkt, als der Achsenkanal durch Auflösung erweitert wird, indem dann eine grössere Menge der Säure zur Verfügung steht." We believe, on the contrary, that it really follows from the observation that the inner parts of the spicopal are more easily dissolved than the outer ones. For we see the sharp conical funnel long before any trace of reaction is to be seen on the rest of the fracture. The borders remain intact for a considerable time. And we get the same view by boiling in a solution of caustic potash. Only when the conical hole has attained a certain depth, the dissolution of the spiculum from the exterior commences. Finally there remains a kind of tube, formed of silica in which the axial thread is laying isolated, until all the spicopal has entirely passed into dissolution.

If we study the way in which the hydrofluoric acid acts on completely intact spicules, some difference may be seen, according as we have to do with sharply pointed needles or with those of which the apex is rounded off. Blunt styli, i. e. transitions to stronglyli, resist the acid for some time; but once the dissolution has begun from the exterior, the process proceeds regularly, the spiculum becomes thinner and thinner.

It seems that in pointed styli, the apices are first attacked; in such cases we see the axial thread gradually coming free by external dissolution of the spicopal. Sometimes it may be observed that, in addition to the dissolving process as described above, a hollowing out along the axial thread takes place. In other cases, however, this is not seen, and we get half dissolved spicules in which the axial thread is partly freed, partly enclosed in a coat of spicopal, thus strongly resembling whips; the more so as the thread is generally flexible, whereas the rest is still straight and rigid.

BÜRTSCHLI has already remarked that there are sometimes seen "durch lokale stärkere Auflösung der Kieselsubstanz zellenartige Vertiefungen der Nadeloberfläche". "Indem diese Vertiefungen schliesslich zu Löchern werden, die bis zum Achsenkanal reichen, wird dieser der Flusssäure zugänglich und nun beginnt von diesen Löchern des Kanals aus . . . die innere Auflösung der Kieselsubstanz unter Entwicklung zweier trichterförmiger Höhlen . . ." This observation we can confirm; we consider it another proof that the spicopal in the neighbourhood of the central thread is more easily dissolved than the peripheric mass; the observation can hardly be explained in another way.

Spicules, dissolved in the described way, show, that there remained not only after the dissolution of the spicopal an organic central thread, but also a very thin coat, which covered the exterior layer of the spicopal. This coat, which represents the true spicule sheath, is

extraordinarily delicate; consequently it is easily torn or shrunk. Still, we are convinced that it exists, but the examination must be carried out with the utmost care. In some preparations we found it in the greater part of the objects. That it is not always observed may partly be due to the treatment of the spicules with hydrochloric acid, partly by its being destroyed already during the life of the sponge. The axial thread is likewise not always visible, or at least not over the whole length of the spiculum. On carefully dissolving the spiculum it may be observed that, while the cylinder of silica gradually diminishes its diameter, a very thin line shows the dimensions it originally possessed.

When the spicules are observed in water, the limits show themselves as rather broad black bands, as the refractive index of the spicopal is considerably higher than that of water. When the dissolving process goes on, the black bands gradually approach each other, and the thin line, the optical section of the spicule sheath, becomes conspicuous. When the object is now studied in acid fuchsine, the central thread stains intensely red as it is set free, and the sheath becomes faintly reddish in the mean time. Organic layers, so called layers of spiculine, such as can easily be demonstrated in the large needles of Hexactinellida, are nowhere met with in *Tethya*. In some cases we saw something which resembled them, but in every case we could explain the phenomenon by a folding of the sheath. Consequently we conclude that layers of spiculine are absent in *Tethya*. And we cannot agree with MINCHIN (1900), who says about spicula in general (l. c. p. 40): "the mineral matter is deposited round it (viz. the axial thread) in concentric lamellae of colloid silica, alternating with lamellae of organic nature".

As to the spicule sheath, writers do not agree. What F. E. SCHULZE calls "Spiculascheide" in his last publication (1904) is not homologous with what we indicate with the name of sheath. That we notwithstanding use this term has historical reasons, as it seems to us that the word is originally used for formations belonging to the spicule itself, homologous to the product which is found in calcareous spicules, where its existence had been first demonstrated. In this sense MINCHIN applied the term, and he is the author of the newest and best general treatise on Porifera.

KÖLLIKER (1864) may be regarded as the discoverer of the spicule sheath. It seems to us beyond doubt what KÖLLIKER meant by it, although we acknowledge that his opinion is not always expressed with the utmost clearness, and that from the beginning there had existed some confusion of ideas about this organ.

KÖLLIKER says (l. c. p. 64—65), speaking about "*Nardoa spongiosa*": "Ausserdem finden sich dann noch nach der Auflösung der Spicula durch Essigsäure, zahlreiche Lücken, welche diese Bildungen enthalten, die allen von einer scharfen Linie begrenzt sind, wie bei *Dunstervilia*. Bei *Nardoa* glaube ich mich davon überzeugt zu haben, dass diese scharfe Linie der optische Ausdruck einer selbständigen Scheide der Spicula ist . . ." What KÖLLIKER means by the word "selbständig" becomes clear when we read that in every canal spicules project, in which, after treatment with acetic acid, "an der Stelle des in die Flimmercanäle hineinragenden Strahles der genannten Spicula zarte Scheiden leer zurück (bleiben)". These sheaths are, according to KÖLLIKER, perhaps a "Rest von Bildungszellen." However, he adds: "freie Spicula zeigen, der Einwirkung der Essigsäure ausgesetzt, keine solche Scheide...." What is meant here with "freie" spicula is not evident. It can hardly mean anything else than isolated spicules. If they be isolated mechanically, the sheath is as obvious as in spicules in situ; if they be isolated chemically, then of course the absence of a sheath is no proof at all.

It is easy enough to repeat KÖLLIKER'S experiments, especially in using specimens with thin walls, as e.g. *Leucosolenia*. If a fragment of a wide tube of *L. variabilis* which has been cut open, is spread out in water under the microscope, and carefully treated with acetic acid, the carbonate of lime is seen to be gradually dissolved, and soon the sheaths, with sharply defined outlines, exactly as described by KÖLLIKER, are visible. The sharp outlines are especially clear on spots where the spicules are wholly enclosed by parenchyma; in projecting spicules the conical sheath of spiculine is seen to remain as a homogeneous, extremely thin film; still more striking, perhaps, is the phenomenon if the sponge is stained on the object glass, e. g. with carmalum (GRÜBLER). The carmalum, which is generally somewhat acid, causes the calcite to dissolve, and stains the sheath purple; the sharply defined outlines (optical sections) appear dark-purple, while the projecting spicules are faintly purplish. If such preparations are examined in glycerine or in Canada balsam, the spots where the carbonate of lime has been dissolved, or where it is still present, are hardly to be discerned. When we use the polarising microscope, however, the presence of calcite becomes immediately visible. Consequently, there really exists a special layer of organic substance which tightly covers the spicule, which can be isolated with the spiculum, but which cannot be separated from it otherwise than by dissolving the carbonate of lime. Doubtless it is this organic layer which KÖLLIKER called "Scheide". In this sense also MINCHIN uses the word.

The question now arises how far siliceous spicules are likewise enclosed by such organic coats, homologous to the sheaths of the calcareous spicules. We are of opinion that this is actually the case; the delicate organic film which we found covering the spicules of *Tethya* we consider as the homologon of the spicule sheath of calcareous spicules. Such products have been already observed. NOLL (1888 p. 16-17) says: "Noch ist für die Spicula von *Desmacidon Bosei* eines Ueberzugs von organischer Substanz Erwähnung zu thun, Hauptsächlich nach Behandlung der Präparate mit einer Höllesteinlösung weniger deutlich mit Acidum pyrophosphoricum, manchmal auch mit Picrocarmin wurde derselbe sichtbar. Stifte, die isoliert, ohne Ueberzug von verkittendem Spongin, über die Hälfte frei aus dem Schwammgewebe hervorstanden oder auch solche, die ganz frei lagen, waren besonders nach der Silberfärbung gleichmässig mit einem lichtbraunen Ueberzuge versehen, der trotz seiner geringen Dicke doppelte Konturen erkennen liess und die Stifte gleichmässig überdeckte Die Spicula von *Desmacidon Bosei* besitzen also einen homogenen hautartigen Ueberzug von organischer Substanz, der verschiedene Farbstoffe aufnimmt. Wir wollen ihn als Spicula-Oberhaut bezeichnen . . ." Although NOLL sees in this coat something else than what KÖLLIKER found in calcareous spicules, we suppose them to be equivalent. Just as KÖLLIKER indicates that his "Scheide", is perhaps a "Rest von Bildungszellen", so NOLL writes that his "Oberhaut" may be "der Rest der die Nadeln bildenden Zellen".

SOLLAS described in the same year (1888) such a sheath, which became perceptible after treatment with hydrofluoric acid. Description and drawing (l. c. p. XLIX, Pl. XLIII, fig. 18), regarding the spicule of "*Dorypleres Dendyi*", leave nothing to be desired as to clearness. "Although at first sight the acid appears to remove all the substance of the spicule except the axial rod, careful observation will show that this is not the case, for a delicate film of organic matter also remains behind; it has the form of a hollow sheath, corresponding in form and position with the outermost boundary of the original spicule; between it and the axial rod the whole of the spicule is completely removed. The spicule thus consists of a central organic axis, surrounded by concentric layers of opal, the outermost of which is invested in a spicule sheath of organic matter or rather of organic matter in intimate association (chemical union?) with silica". Our results regarding the presence of such a sheath in spicules of other species we hope to give in a next publication; for the present we deal only with the spicules of *Tethya*.

It is evident, that if we are right in our conception of the spicule sheath, other coats which sometimes are found surrounding spicules, may not be called sheaths.

F. E. SCHULZE describes in his last paper with his well known accuracy such surroundings from the enormous needles of *Monorhaphis*. We regret not to agree with him in calling this formation "Scheide". As SCHULZE demonstrated it to be not only an investment of each spiculum for itself, but also a means of joining different spicules together, and as this is true for other spicules also, we propose to call it *periapt*¹⁾. SOLLAS (1880 p. 401²⁾) described a similar coat surrounding spicules from *Isops phlegraei*. BÜTSCHLI found it in *Tethya lyncurium*, a fact which we can confirm. The periapt is composed of connective tissue with conspicuous fibrils and cells; it has therefore, nothing to do with the spicules as such and may be left out of consideration here. Mutatis mutandis, the periapt behaves to the spicule sheath as a perimysium to the sarcolemma.

We have seen already that when the spicopal is dissolved first of all the axial rod appears. The presence of such an organic thread in macroscleres is no more doubted. Although we have no more doubt that the axial thread is normally present, it cannot be denied that in some cases it is wholly or partly absent. We consider such cases, however, to be pathological.

With regard to the shape of the rod BÜTSCHLI (1901 p. 253) writes: "eigenthümlich ist das Querschnittsbild des Fadens, das... stets deutlich dreieckig erscheint, gleichgültig ob der äussere Umriss des Nadelquerschnitts selbst etwas dreiseitig oder ganz kreisrund ist. Vielfach ist jedoch auf den Nadelquerschnitten zu erkennen, dass der Querschnitt des Achsenfadens sechseckig erscheint, indem die Ecken des dreiseitigen Umrisses regelmässig abgestumpft sind". Consequently, the central thread in such cases, e. g. in *Tethya*, would be a triangular rod and not a cylinder. Whereas already BOWERBANK (1864) apparently had seen something like this in *Geodia*, F. E. SCHULZE (1904) arrived at the conclusion that the axial threads in Hexactinellida are cylindric. In view of this contradiction we thought it necessary to submit the axial thread of *Tethya* to a careful investigation. In order to judge about the shape of a thread in transverse section, we followed the method of BÜTSCHLI by grinding spicules in an agate mortar. In the powder, procured in this way, there is found always a sufficient quantity of particles of approximately

¹⁾ περιέπτω I bind together.

²⁾ Not 1890; — apparently this is a misprint in SCHULZE (1904 p. 204), — also not p. 440—441 but 400—401.

cylindrical shape, although that the fracture is irregular. If these pieces are mounted in glycerine,¹⁾ it is possible, as the spicopal almost entirely disappears from the eye, to judge with certainty in which position the thread is seen, whether oblique or not. Paying attention only to those which are undoubtedly seen in transverse optical section, we found by careful focussing that they were really triangular with the angles cut off. In the second place we studied isolated axial threads. By moving somewhat the coverglass, a quantity of little pieces break off, generally almost transversely. At the same time it can be observed that the little fragments turn over, owing to the movement of the fluid. In this way we saw plenty of them from all sides. With high power (Zeiss, homog. imm.) we found that in this case also the transverse section is triangular. In spite of our astonishment that the axial rod in *Tethya* is triangular we cannot but agree with BÜTSCHLI's observations. We did not see varicosities nor sharp restrictions; normally the isolated rods are perfectly smooth. The diameter remains the same, with exception of the extremities; these are, in uninjured threads, either sharply pointed or rounded off, according to the well known shape of the styli themselves. Deviations of this rule seem to us to be pathological.

Not less strange than the shape appears to be, is the consistency. This may be the reason that previous authors so little agree. Whereas we find, after treatment with hydrofluoric acid, that the free axial threads on one hand are very flexible, so that they can form clews, we see on the other hand that in many cases they break off at once if touched with a needle. We remarked already that they generally break at right angles to the axis. In a certain sense BÜTSCHLI is right, therefore, if he calls them "spröde", but it is by no means the sort of brittleness of for example a thread of glass. The consistency of the axial thread can be best compared with agar-agar. Here a certain flexibility is likewise combined with the property of suddenly breaking. Similar phenomena are known of gels at a certain point of dehydration.

The axial rod in *Tethya* is, taken as a whole, *not* homogeneous. First of all we observe, especially in threads stained with iodine, a double contour. This is easily demonstrated on uninjured, isolated threads as well as in transverse sections; in the triangular figure, mentioned above, the wall is both inside and outside triangular. This wall is comparatively thick — about $\frac{1}{4}$ or $\frac{1}{5}$ of the total diameter. We may consider the axial thread as a tube, filled with something;

¹⁾ Refractive index $n = 1.4508$. Cf. infra.

whereas the wall seems to be homogeneous, the contents are homogeneous or rather granular, apparently of a softer consistency than the more rigid wall. This we conclude from the fact that curved or bent axial threads under the microscope resemble curved or bent indiarubber tubes, filled with a fluid or semi-fluid substance. Solid, flexible cylinders never show such abruptly bent figures.

A remarkable phenomenon is to be seen in broken spicules under the influence of hydrofluoric acid. As stated above, the spicopal is dissolved in a peculiar way, the central canal being hollowed out in the shape of a funnel. If we now only take into consideration the cases where the thread is broken at the same place as the spicopal, we see the thread gradually shrinking somewhat under the influence of the hydrofluoric acid. However, the wall and its contents do not shrink equally. The result is that the contents somewhat pour out beyond the wall. It is not improbable that BÜTSCHLI has seen this; at least his illustration (fig. 24 on pl. XXI) strongly resembles what we observed. But BÜTSCHLI explains it in another way; he believes the thread to be restricted "manschettenförmig".

According to BÜTSCHLI the axial thread consists of a proteid substance. With F. E. SCHULZE we can confirm this in the main points. Boiled in MILLON'S fluid the threads in ground spicules turn yellow. This staining is especially distinct in pieces where a part of the thread is lost, and where, consequently, the axis of the spicule is partly uncoloured, partly filled with a yellowish thread. Isolated axial threads or threads partly freed by solution of the spicopal are easily stained with iodine. Treated with nitric acid (25 %) they swell somewhat and acquire a faint yellow colour, which becomes darker by subsequent addition of ammonia. Heated with nitric acid the threads dissolve; likewise in caustic potash. We may conclude, therefore, that the central rod if not wholly, at least partly consists of some proteid. Observed under the polarisation microscope no trace of anisotropy could be seen.

With regard to the styles of *Tethya lyncurium* we thus arrived at the conclusion, that they are composed of an organic axial thread and an organic spicule-sheath, between which elements the spicopal is deposited. We failed in demonstrating any trace of organic (spiculine) lamellae. But still we found, that under special circumstances longitudinal, resp. concentric striae were distinctly seen. We have to look for an explanation of this fact.

In order to avoid a possible misunderstanding or confusion we wish at once to draw attention to the fact, hitherto rather neglected, that one has to distinguish the various *layers* of spicopal from their

limiting plains. We hope to show that the well-known stripes are nothing but the optic sections of such limiting plains, and that they are independent of eventual differences of the layers. It is easy enough to microscopically demonstrate such limiting plains in layers in artificial siliceous gels. If a coat of not yet coagulated siliceous gel is poured out over another one freshly coagulated, and if this is repeated, it becomes evident that the consecutive layers of gel in the beginning do not unite. Only in drying the layers become one mass; still, in section the limiting plains are very conspicuous. This experiment teaches us that in a siliceous gel a lamellar structure can appear, wherein the consecutive layers are separated by visible limits, without interference of another substance e. g. of an organic lamella. We will come back to this fact later.

Several ways are open to us for the study of the spicular structure, but they are not easy. Besides dissolving the spicopal by means of hydrofluoric acid and carefully watching the process, the method of heating has been applied since GRAY (1835) showed that this brings out more distinctly the lamellar structure. IJIMA (1901) was the first to point out the effect of different media. We shall see, that some spicules mounted either in Canada balsam or in glycerine, so widely differ in aspect that on first sight one believes that one has to deal with entirely different sorts of spicules. We thought it necessary, therefore, to begin by determining the refractive index of spicopal of various spicules somewhat more accurately than hitherto done. As far as we know of there exists no other information than given by SOLLAS (1885), who states in general that "the refractive index of sponge-silica is . . . that of opal or colloidal silica, and not of quartz", and that the spicules come nearest to invisibility when "mounted in chloroform, which possesses a refractive index of 1.449".

In determining the refractive index of the spicules we used the method, since SOLLAS generally used also in mineralogy, viz. to find in what fluid the spicule can no longer be seen. Perhaps there is a still better criterion to make out how much a spicule differs from its medium and in which direction, viz. the appearance of coloured borders. -- In order to avoid the effect of fluids which might influence the amount of water contained in the spicopal, but, on the other hand to demonstrate just this influence, we used fluids which do not mix with water as well as such which were diluted with water. The refractive indices were determined by the refractometer of ABBE, which has the great advantage of enabling us to work with ordinary daylight and to determine any number of indices, between the microscopical work. In spite of the apparatus of PULFRICH being more

accurate we used, therefore, an ABBE, the more so as it turned out to be sufficiently accurate for our purposes.

Among the fluids, not mixable with water, we took advantage of the series liquid paraffin ($n = 1.4759$), petroleum ($n = 1.4568$), benzin ($n = 1.3994$) and petroleum-ether ($n = 1.3780$).

We succeeded by using mixtures of petroleum and benzin in fixing the refractive index of the spicules at 1.4508--1.4510. In order to give an idea of the degree of accuracy that can be attained in this way, we may state that undoubtedly a difference is to be seen between spicules, mounted in a mixture of 20 cc. of petroleum with 3 cc. of benzin ($n = 1.4500$) and mounted in a mixture of 20 cc. of petroleum with 2.5 cc. of benzin ($n = 1.4510$). For a aqueous watery solution we used dilute glycerine, and found with this medium also a complete disappearance at $n = 1.4508$. In addition to these media we studied the influence of air, methylic alcohol, water, potassium acetate, creosote, oil of bergamot, venetian turpentine, oil of red cedar wood, oil of lemon, oil of thyme, firoil, oil of peppermint, oil of cloves (pure or mixed with alcohol), Canada balsam and monobrom-naphthaline. Practically however, we used more especially the two fluids mentioned above.

In glycerine with $n = 1.4508$ indeed the spicopal of some spicules disappears completely, and only the axial rod remains visible as a light bluish thread. In all styli, the central thread has a higher refractive index than the spicopal. By careful examination (Zeiss Apochr. 8.0c. 4) in most spicules a light, sharp line may be seen as border, and a system of longitudinal striae between the axial rod and the border. With low power the lamellar structure does not become conspicuous, though the borderline is still visible. Most probably this thin line, which exhibits double contours with high power, represents the organic spicule sheath.

By these experiments it becomes at the same time very evident, that the axial thread can be partly absent; on these spots the light bluish band (the central rod) abruptly ceased. If the glycerine has entered into the central canal, only an indication of the spicopal is visible; if air has entered, of course this is directly visible by the lower refraction. The aspect of styli isolated by means of boiling with hydrochloric acid, either with addition of potassium chlorate or without, or by digestion by means of artificial gastric juice, or by heating with sulphuric acid and potassium-bichromate, fundamentally agree.

Quite another aspect is shown by spicules which have been dried for some days in the presence of anhydrous phosphoric acid. We have

studied spicules which had been dried in this way for some days at an ordinary temperature, and also in VICTOR MEYER'S toluol bath at 104° . The heating, however, had no influence on the aspect. The determination of the refractive index is a little less accurate than with ordinary spicules, because on drying the lamellar structure had become somewhat more conspicuous, and therefore the disappearance in glycerine is a little less perfect. Still we could determine in petroleum-benzine the refractive index $n = 1.4052-1.4055$; with diluted glycerine the same results were obtained.

If the dried spicules, mounted in glycerine with $n = 1.4055$, and with the border of the coverglass well shut by means of vaseline, are left to themselves, gradually from the outside the refraction is seen to increase, and after one day the spicules become again highly refractive. If they are now as much as possible separated from adhering glycerine and transferred into glycerine of $n = 1.4508$, it is seen that they disappear in this medium, and consequently have absorbed again their original quantity of water. Spicules, which have been dried by P_2O_5 and are exposed to the air afterwards, behave in the same way. On the other hand we have examined the behaviour of spicules which, after being isolated and washed, were not dried in the air, but immediately after removing the adjacent water, were mounted in glycerine with $n = 1.4508$. We could indeed see a very slight difference with spicules which had been dried in the air at an ordinary temperature, more than corresponded with possibly adherent water, but too small to be measured. However, it appears that, even at the ordinary temperature, the spicopal gives off some water.

Consequently we have demonstrated that the spicopal is a form of hydrated siliceous acid, which may give off water in an atmosphere, dried by P_2O_5 , which diminishes hereby in refractive index, and which may again absorb the original quantity of water by immersion in a watery solution or by exposure to moist air. The spicopal also behaves with regard to the absorptive power for water just as a gel, as has been shown by the well known and intricate researches of VAN BEMMELEN.

(To be continued).

Mathematics. — “*On pencils of algebraic surfaces.*” By Prof. JAN DE VRIES.

1. Let a pencil (F^n) of surfaces F^n of order n be given, intersecting in the base-curve σ .

The principal tangents in a point S of σ to the surfaces of (F^n) form a cubic cone having the tangent s to σ for edge.

For, if (F^n) is indicated by

$$a_x^n + \lambda b_x^n = 0 \quad . \quad (1)$$

and if y_k are the coordinates of S , the substitution $x_k = y_k + \varrho z_k$ furnishes in connection with $a_y^n = 0$ and $b_y^n = 0$ for a point Z on a principal tangent the conditions

$$a_y^{n-1} a_z + \lambda b_y^{n-1} b_z = 0 \quad , \quad a_y^{n-2} a_z^2 + \lambda b_y^{n-2} b_z^2 = 0 ,$$

so that the locus of the principal tangents touching in S has as equation

$$a_y^{n-1} b_y^{n-2} a_z b_z^2 - a_y^{n-2} b_y^{n-1} a_z^2 b_z = 0 \quad . \quad . \quad . \quad (2)$$

If Z is a fixed point, Y a variable one, this equation represents a surface of order $(2n - 3)$ determining on σ the points S which are points of contact of principal tangents through Z .

The principal tangents in points of the base-curve form a congruence of order $n^2(2n - 3)$ and of class $3n^2$.

The inflexional tangents of a pencil of plane curves c^n enveloping a curve of class $3n(n - 2)$, the complex of rays of the principal tangents of F^n is of order $3n(n - 2)$.

2. A principal tangent t_3 in S becomes four-pointed tangent t_4 , if for a point Z lying on it the relation $a_y^{n-3} a_z^3 + \lambda b_y^{n-3} b_z^3 = 0$ holds good. So the tangents t_4 touching in S belong to the biquadratic cone

$$a_y^{n-1} b_y^{n-3} a_z b_z^3 - a_y^{n-3} b_y^{n-1} a_z^3 b_z = 0 \quad . \quad . \quad . \quad (3)$$

As the cones (2) and (3) have the tangent s represented by

$$a_y^{n-1} a_z = 0 \quad , \quad b_y^{n-1} b_z = 0 \quad , \quad . \quad . \quad . \quad . \quad (4)$$

in common, the point S will be the point of contact of *eleven four-pointed tangents*.

For $a_y^n = 0$ and $b_y^n = 0$ the equations (2) and (3) represent the figure formed by the surface of tangents (s) of σ and the scroll τ_4 of the right lines t_4 having their points of contact on σ .

To determine the order of τ_4 I search for the number of points

of intersection of the indicated figure with the right line $z_3 = 0$, $z_4 = 0$. Substitution in (2) and in (3) and elimination of z_1 and z_2 gives an equation containing the coefficients of (2) and (3) successively in the orders 4 and 3. Hence the resultant in the coordinates y is of order $4(2n - 3) + 3(2n - 4)$ or $14n - 24$.

So the number of points of intersection is $2n^2(7n - 12)$.

Applying the same treatment to (4) I find for the order of (s) the well-known number $2n^2(n - 1)$.

The four-pointed tangents having their points of contact on the base-curve σ form a scroll of order $2n^2(6n - 11)$, on which σ is elevenfold.

For $n = 3$ this scroll passes into the locus of the right lines on the surfaces of a pencil (F^3), thus into the scroll of the trisecants of σ^3 which is of order 42. For $2n^2(6n - 11)$ we now find 126, corresponding to the fact, that each trisecant does duty as right line t_4 for three points S .

On each surface F^n the points of contact P_4 of four-pointed tangents t_4 form a curve of order $n(11n - 24)$. As σ is evidently an elevenfold curve of the locus of the points of contact P_4 belonging to the F^n of the pencil this locus has in common with every F^n a locus of order $n(11n - 24) + 11n^2$.

The points of contact of four-pointed tangents form a surface of order $2(11n - 12)$.

For $n = 3$ we find the scroll of trisecants of order 42.

3. As the tangents t_3 passing through a point Z form a cone of order $3n(n - 2)$ and two principal tangents have their point of contact in Z the locus of the points of contact P_3 of the right lines t_3 containing Z is a curve of order $3n(n - 2) + 2$ with double point in Z .

Each of those right lines t_3 cuts the surface F^n osculated by it in $(n - 3)$ points Q more. The locus of the points Q is a curve of order $3n(n - 2)(n - 3) + (n^2 + 2)(n - 3)$ or $2(n - 3)(n - 1)(2n - 1)$. For, through Z pass $(n^2 + 2)(n - 3)$ tangents t_3 , osculating the surface indicated by Z in an other point ¹⁾.

To find the number ε of the coincidences of P_3 with Q , I make use of the well-known formula

$$\varepsilon = p + q - g,$$

which appears when the pairs of points P, Q are projected by a pencil of planes. Each point P belonging to $(n - 3)$ pairs we have

¹⁾ See CREMONA—CURTZE, Oberflächen, p. 66.

$p = (3n^2 - 6n + 2)(n - 3)$. Farther more $q = 2(n - 3)(n - 1)(2n - 1)$, whilst the number of right lines PQ resting on an axis is of course equal to $3n(n - 2)(n - 3)$. So $\varepsilon = 2(n - 3)(2n^2 - 3n + 2)$; this is also the number of four-pointed tangents through a given point a .

The number of right lines t_4 in a given plane is equal to the number of points of undulation on the curves c^n of a pencil; this number I have determined in a preceding paper¹⁾.

The four-pointed tangents form a congruence of order

$2(n - 3)(2n^2 - 3n + 2)$ and of class $\frac{9}{2}(n - 3)(n^3 + n^2 - 8n + 4)$.

4. If we wish to apply the above-mentioned formula of coincidence to the pairs of points of intersection Q, Q' on the right lines t_3 through Z we have to substitute $p = q = 2(n - 3)(n - 1)(2n - 1)(n - 4)$ and $g = 3n(n - 2)(n - 3)(n - 4)$. For each point Q belongs to $(n - 4)$ pairs and each right line t_3 bears $(n - 3)(n - 4)$ pairs. We then find $\varepsilon = (n - 3)(n - 4)(5n^2 - 6n + 4)$, i. e. the number of tangents $t_{3,2}$ through the point Z .

In the above-mentioned paper I have determined the number of right lines having with a curve of a pencil (c^n) a three-pointed and at the same time a two-pointed contact.

The two-three-pointed tangents form a congruence of order

$(n - 3)(n - 4)(5n^2 - 6n + 4)$ and of class

$$\frac{1}{2}(n - 4)(n - 3)^2(10n^4 + 35n^3 - 21n^2 - 80n + 20).$$

5. Each principal tangent t_3 having its point of osculation in a point S of the base-curve bears still $(n - 3)$ points of intersection Q with the surface F^n osculated by it. As S is point of contact of 11 four-pointed tangents the locus of the points Q will have an eleven-fold point in S . As an arbitrary plane through S evidently contains $3(n - 3)$ points Q (§ 1) the order of the curve (Q) is equal to $(3n + 2)$.

When applying the formula $\varepsilon = p + q - g$ to the pairs Q, Q' which the cubic cone with vertex S bears, we have to put $p = q = (3n + 2)(n - 4)$ and $g = 3(n - 3)(n - 4)$. Then we get $\varepsilon = (n - 4)(3n + 13)$. So this is the number of tangents $t_{3,2}$ for which the point of osculation lies in S .

In other words, σ is an $(n - 4)(3n + 13)$ -fold curve on the locus $[R_3]$ of the points of osculation of tangents $t_{3,2}$ to surfaces of (F^n). Now the points of osculation of the right lines $t_{3,2}$ of an F^n form a

¹⁾ "On linear systems of algebraic plane curves", (Proceedings, April 22, 1905.)

curve of order $n(n-4)(3n^2+5n-24)^1$. So $[R_3]$ has in common with an F^n of the pencil a curve of order

$$n(n-4)(3n^2+5n-24)+n^2(n-4)(3n+13)=n(n-4)(6n^2+18n-24).$$

The points of osculation of the three-two-pointed tangents of (F^n) form a surface of order $6(n-1)(n-4)(n+4)$.

6. To determine the order of the cone formed by the double tangents of (F^n) of which a point of contact in S lies on the base-curve σ , we notice that the tangent s in S to σ is intersected by a pencil in an involution of order $(n-2)$. Its $2(n-3)$ double points are points of contact of double tangents touching in S too. So s is a $2(n-3)$ -fold edge of the indicated cone.

In each plane ϕ through s we can draw out of S $n(n-1)-6$ tangents to the curve of intersection of ϕ with the surface F^n touching ϕ in S . From this ensues that the indicated cone is of order $(n-3)(n+4)$.

The locus of the second points of contact R_2 of the edges of this cone has evidently in S an elevenfold point, where it is touched by the eleven right lines t_4 . So the curve (R_2) is of order

$$(n-3)(n+4)+11=n^2+n-1.$$

Every edge of the cone intersects the surface doubly touched by it in $(n-4)$ points V more. The locus of these points passes $(n-4)(3n+13)$ times through S , where it is touched by the right lines $t_{3,2}$ osculating in S . As each plane through S bears moreover $(n^2+n-12)(n-4)$ points V , the curve (V) is of order

$$(n-4)(n^2+4n+1).$$

Now the number of coincidences of R_2 with V can be determined again by means of the formula $\varepsilon = p + q - g$. We find

$$\begin{aligned} \varepsilon &= (n^2+n-1)(n-4) + (n-4)(n^2+4n+1) - (n-3)(n+4)(n-4) = \\ &= (n-4)(n^2+4n+12). \end{aligned}$$

This is the number of tangents $t_{3,2}$, of which the point of contact lies in S , thus at the same time the multiplicity of the base-curve on the surface $[R_2]$ of the points of contact of surfaces of pencils with right lines $t_{3,2}$. Taking into consideration, that the points of contact R_2 form on the surface F^n a curve of order

$$n(n-2)(n-4)(n^2+2n+12)$$

we find that $[R_2]$ has with F^n an intersection of order

$$n(n-2)(n-4)(n^2+2n+12) + n^2(n-4)(n^2+4n+12).$$

¹⁾ See inter alia my paper: "Some characteristic numbers of an algebraic surface." Proceedings, April 22nd, 1905.

The points of contact of the three-pointed tangents of (F^n) form a surface of order $2(n-4)(n^2 + 2n^2 + 10n - 12)$.

7. Through the tangent s in S to σ we can make to pass four tangent planes to the cubic cone of the principal tangents (§ 1). So S is a parabolic point on four surfaces of the pencil. Therefore σ is a fourfold curve on the locus of the parabolic points.

As the parabolic points of an F^n lie on a curve of order $4n(n-2)$ the locus under consideration is cut by each of the surfaces F^n in a curve of order $4n(n-2) + 4n^2 = 8n(n-1)$.

The locus of the parabolic points of the surfaces of a pencil (F^n) is a surface of order $8(n-1)$.

Chemistry. — “On the shape of the plaitpoint curve for mixtures of normal substances.” (Second communication). By J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

1. In a previous paper¹⁾, starting from VAN DER WAALS' equation of state, in which b is assumed to be independent of v and T , I have found for the equation of the *spinodal curves* at successive temperatures (l. c. p. 690):

$$\underline{RT = \frac{2}{v^3} \left[x(1-x)\theta^2 + a(v-b)^2 \right]}, \quad \quad (1)$$

and for that of the plaitpoint curve in its v, x projection (l. c. p. 695):

$$\underline{x(1-x)\theta^3 \left[(1-2x)v - 3x(1-x)\beta \right] + \sqrt{a(v-b)^2} \left[3x(1-x)\theta(\theta - \beta\sqrt{a}) + a(v-b)(v-3b) \right]} = 0 \quad \quad (2)$$

In this $\theta = \pi + \alpha(v-b)$, $\pi = b_1\sqrt{a_2} - b_2\sqrt{a_1}$, $\alpha = \sqrt{a_2} - \sqrt{a_1}$, and $\beta = b_2 - b_1$.

The equations (1) and (2) hold for the so-called *symmetrical* case, where not only $b_{12} = \frac{1}{2}(b_1 + b_2)$ is assumed, but also $a_{12} = \sqrt{a_1 a_2}$. These hypotheses lead to:

$$b = (1-x)b_1 + xb_2 \quad ; \quad a = [(1-x)\sqrt{a_1} + x\sqrt{a_2}]^2.$$

The equation (1) had been given already before by VAN DER WAALS in implicit form²⁾, for after some reduction his general equation

1) These Proc. April 22, 1905, p. 646—657.

2) Cont. II, p. 45; Arch. Néerl. 24, p. 52 (1891).

passes really into (1) after substitution of the values of $\frac{da}{dx}$, $\frac{db}{dx}$, $\frac{d^2a}{dx^2}$ and $\frac{d^2b}{dx^2}$ in accordance with the above hypotheses.

But the equation (2) may be said to have been derived here for the first time in the above simple form. It is true that VAN DER WAALS gave a differential equation of this curve¹⁾, and derived an *approximate* rule for its shape²⁾, but he did not arrive at a general final expression. Nor has KORTEWEG arrived at it in his very important papers: "Sur les points de plissement" and "La théorie générale des plis, etc."³⁾ In his final equation (73) (l.c. p. 361) there occur, besides T , still several functions $\varphi(v)$, $\zeta(v)$, $\psi(v)$ and $\chi(v)$, which have been given respectively by the equations (37), (38), (40) and (74) (l.c. p. 350 and 361). KORTEWEG's equation is one of the 9th degree with respect to v , but it is easy to see that it may be reduced to one of the 8th degree (l.c. p. 361). It appears from our derivation that this degree may be reduced to the 4th. In a later paper⁴⁾ KORTEWEG confines himself to a full discussion of the plaitpoints in the neighbourhood of the borders of the ψ -surface.

I think that one of the reasons for failure in this direction is due to the intricate form of the differential equation of the plaitpoint curve, when we use the ψ -function. The ζ -function on the other hand leads to simpler expressions. Already the differential equation for the spinodal line at given temperature, viz. $\left(\frac{\partial^2 \zeta}{\partial x^2}\right)_{p,T} = 0$ or $\left(\frac{\partial \mu_1}{\partial x}\right)_{p,T} = 0$, is much simpler than the corresponding expression in ψ . And to get the plaitpoint curve, we have only to combine $\left(\frac{\partial \mu_1}{\partial x}\right)_{p,T} = 0$ with $\left(\frac{\partial^2 \mu_1}{\partial x^2}\right)_{p,T} = 0$.

2. We shall now examine the shape of the curves given by (1) and (2) more closely, and specially for the case that $\underline{\beta = 0}$, i. e. $\underline{b_1 = b_2 = b}$. The calculations are rendered very simple in this way, and it is obvious from the adjoined figs. 1—4, that when b_1 is not $= b_2$, so β not $= 0$, the results will be modified only quantitatively, but by no means qualitatively. We shall come back to this in a following paper.

¹⁾ Verslagen Kon. Akad. Amsterdam, 4, p. 20—30 en 82—93 (1896).

²⁾ Id. 6, p. 279—303 (1898).

³⁾ Arch. Néerl. 24, p. 57—98 en 295—368 (1891).

⁴⁾ These Proc. Jan. 31, 1903, p. 445.

As $\theta = \pi + \alpha(v - b) = \alpha v - \beta \sqrt{a}$ passes into αv for $\beta = 0$, we may write for (1):

$$RT = \frac{2}{v^3} \left[x(1-x)\alpha^2 v^2 + a(v-b)^2 \right], \quad \dots \quad (1a)$$

and (2) is reduced to:

$$x(1-x)\alpha^3 v^3 [(1-2x)v] + \sqrt{a}(v-b)^2 \left[3x(1-x)\alpha^2 v^2 + a(v-b)(v-3b) \right] = 0. \quad (2a)$$

Let us put these equations into a more homogeneous form.

As $a = [\sqrt{a_1} + x(\sqrt{a_2} - \sqrt{a_1})]^2 = (\sqrt{a_1} + x\alpha)^2$, we may write for (1a):

$$\begin{aligned} RT &= \frac{2}{v} \left[x(1-x)\alpha^2 + (\sqrt{a_1} + x\alpha)^2 \left(1 - \frac{b}{v}\right)^2 \right] \\ &= \frac{2\alpha^2}{v} \left[x(1-x) + \left(\frac{\sqrt{a_1}}{\alpha} + x\right)^2 \left(1 - \frac{b}{v}\right)^2 \right]. \end{aligned}$$

If we now put:

$$\frac{\sqrt{a_1}}{\alpha} = \varphi \quad ; \quad \frac{b}{v} = \omega,$$

this last equation becomes:

$$RT = \frac{2\alpha^2}{b} \omega \left[x(1-x) + (\varphi + x)^2 (1 - \omega)^2 \right].$$

Let us now introduce the "third" critical temperature T_0 . This temperature is the plaitpoint temperature at $v = b$, i. e. that at which the limiting curve lying in the limiting plane $v = b$ (see fig. 1 of my previous paper cited above) reaches its maximum, and is represented by ($\omega = 1$):

$$RT_0 = x_c(1-x_c) \frac{2\alpha^2}{b}.$$

But as in the case $b_1 = b_2$ for x_c the value $1/2$ is found (the maximum of the now parabolic curve), we get:

$$RT_0 = \frac{1/2 \alpha^2}{b}.$$

Our equation for RT becomes therefore:

$$RT = 4 RT_0 \omega \left[x(1-x) + (\varphi + x)^2 (1 - \omega)^2 \right].$$

And if henceforth all temperatures are expressed in multiples of T_0 , we have finally, putting

$$\frac{T}{T_0} = \tau,$$

$$\tau = 4 \omega \left[x(1-x) + (\varphi + x)^2 (1 - \omega)^2 \right] \quad \dots \quad (1b)$$

In this simple form the equation is very suitable for calculating successive spinodal curves. It is of the *second* degree with respect to x , of the *third* degree with respect to ω . For a given value of τ we have therefore only to put successively $\omega = 1, 0,9, 0,8$ etc. down to 0, and then we find the corresponding values of x by solution of ordinary quadratic equations.

The equation (2a) becomes after division by $x(1-x)\alpha^3v^4$:

$$(1-2x) + \frac{\sqrt{a}}{\alpha} \left(1 - \frac{b}{v}\right)^2 \left[3 + \frac{a/\alpha^2 (1-b/v)(1-3b/v)}{x(1-x)}\right] = 0,$$

i. e. as $\frac{\sqrt{a}}{\alpha} = \frac{\sqrt{a_1}}{\alpha} + x = \varphi + x$

$$(1-2x) + (\varphi+x)(1-\omega)^2 \left[3 + \frac{(\varphi+x)^2}{x(1-x)} (1-\omega)(1-3\omega)\right] = 0. \quad (2b)$$

This equation of the plaitpoint curve is of the *third* degree with respect to x , of the *fourth* degree with respect to ω .

3. Before discussing the equations (1b) and (2b) more fully, we shall first derive a few relations between T_0 , T_1 and T_2 .

As $RT_0 = \frac{1}{2} \alpha^2$ (see above) and $RT_1 = \frac{8}{27} \frac{a_1}{b}$, we find immediately:

$$\frac{T_1}{T_0} = \frac{16}{27} \frac{a_1}{\alpha^2} = \frac{16}{27} \varphi^2.$$

From this follows that for values of $\varphi < \sqrt[3]{3} (= 1,30)$ T_1 will be $< T_0$; i. e. the lower critical temperature of the two components will then be lower than the critical temperature of mixing of the two liquid phases at $v = b$.

As $\varphi = \frac{\sqrt{a_1}}{\sqrt{a_2} - \sqrt{a_1}}$, so $\frac{1}{\varphi} = \frac{\sqrt{a_2}}{\sqrt{a_1}} - 1$, and we have evidently:

$$\frac{T_2}{T_1} = \left(1 + \frac{1}{\varphi}\right)^2.$$

For $\varphi = 0$ is $T_2 = \infty \times T_1$; for $\varphi = \infty$ is $T_2 = T_1$. For $\varphi = \sqrt[3]{3}$ (see above) $T_2/T_1 = (1 + \sqrt[4]{3})^2 = \frac{1}{27} (43 + 24\sqrt{3}) = 3,13$.

It will also prove important to know the amount of the *pressure* for all points of the spinodal curves. For this purpose we reduce the equation:

$$p = \frac{RT}{v-b} - \frac{a}{v^2}$$

to

$$p = \frac{RT}{v(1-b/v)} - \frac{(V a_1 + x a)^2}{v^2} = \frac{RT}{v(1-\omega)} - \frac{\alpha^2}{v^2} (\varphi + x)^2.$$

This becomes on account of $\alpha^2 = 2bRT_0$ (see above) and $T/T_0 = \tau$:

$$p = \frac{RT_0}{b} \omega \left\{ \frac{\tau}{1-\omega} - 2\omega (\varphi + x)^2 \right\}.$$

Let us express p in the critical pressure p_1 . (As, namely, the pressure p_0 corresponding to T_0 ($v = b$) is evidently $= \infty$, p cannot be expressed in p_0). As $p_1 = 1/8 \frac{RT_1}{b}$ and $\frac{T_1}{T_0} = \frac{16}{27} \varphi^2$, $p_1 = \frac{2}{27} \frac{RT_0}{b} \varphi^2$, hence — when we put

$$\frac{p}{p_1} = \pi:$$

$$\pi = \frac{27}{2} \frac{\omega}{\varphi^2} \left[\frac{\tau}{1-\omega} - 2\omega (\varphi + x)^2 \right] (3)$$

This equation may be used, when τ is already known from (1b). If this value is, however, substituted, we get:

$$\pi = \frac{27}{\varphi^2} \frac{\omega^2}{1-\omega} \left[2x(1-x) + 2(\varphi+x)^2(1-\omega)^2 - (\varphi+x)^2(1-\omega) \right],$$

i. e.

$$\pi = \frac{27}{\varphi^2} \frac{\omega^2}{1-\omega} \left[2x(1-x) + (\varphi+x)^2(1-\omega)(1-2\omega) \right] (3a)$$

4. Better than descriptions and calculations the adjoined figures 1—4 represent the different relations which may present themselves in the discussion of (1b) and (2b), combined with 3 or (3a). We shall therefore confine ourselves in the following to what is strictly indispensable.

Two principal types occur, according as $\varphi < 1,43$ or $> 1,43$. Fig. 1 with $\varphi = 1$ is a representative of the one type, fig. 2 with $\varphi = 2$ of the other. The transition case $\varphi = 1,43$ is represented in fig. 4.

a. Description of the case $\varphi = 1$ (fig. 1 and 1a).

There are two plaitpoint curves, one of which extending from C_0 to C_2 , the other from C_1 to A . The latter, however, may only be realized down to a point between C_1 and R_1 , where it is touched by the spinodal line $\tau = 0,63$ ¹⁾.

¹⁾ See KORTEWEG, l. c. p. 305 (fig. 12) and plate F_1 to F_5 . (The plaitpoint : has already disappeared in the limiting line $v = b$ in our case). R_1 is a so-called point de plissement double hétérogène. Cf. also VAN DER WAALS, These Proc. V, 310, Oct. 25, 1902.

Beyond the point R_1 the temperature, and with it also the pressure, decreases, as is to be seen from the succession of the different spinodal curves, so that in the p, T -diagram (fig. 1a) the plaitpoint curve C_1R_1A shows a cusp at R_1 , and begins to run back.

It is known that this case is realized with mixtures of C_2H_6 and CH_3OH , ether and water (KUENEN), etc. It is the *principal type I*, as I have fully described it in one of my two preceding papers¹⁾.

Remarkable and quite unexpected is the fact that this type may be realized for mixtures of *normal* substances. It was formerly believed that such deviating plaitpoint curves were only possible when at least one of the two substances is anomalous. This, however, seems not to be the case; more and more the conviction gains ground with me that the anomaly of one or of both components only *accentuates* the phenomena *sharper* or brings them into *attainable* regions of temperature.

It is also striking in fig. 1a, that the curve C_0C_2 has the same appearance, viz. with an inflection in the middle part, as the typical curve as observed by KUENEN for $C_2H_6 + CH_3OH$ (see fig. 1 of my just cited paper). Only in our case there is not yet a pronounced maximum and minimum, as with the mixtures of C_2H_6 with the strongly *anomalous* substance CH_3OH .

The type of fig. 1 occurs for comparatively small values of φ . According to the equation given in § 3 the proportion $T_2/T_1 = 4$ corresponds with $\varphi = 1$. The critical temperatures of the two components must, therefore, lie comparatively far apart.

As $T_1/T_0 = \frac{16}{27}$, T_0 is considerably higher than T_1 . If we put $T_0 = 1$, as has been done in the figure, then $T_1 = 0,59$ and $T_2 = 2,37$.

b. Some mathematical and numerical details.

The plaitpoint curve C_0C_2 touches the line $x = 1/2$ in C_0 , the curve AC_1 touches the line $x = 0$ in A . Moreover the curve C_0C_2 touches the line $x = 1/2$ once more in D , and it does so at $\omega = 2/3$ ($v = 1,5 b$). In C_1 and C_2 no contact takes place.

When φ becomes < 1 , and approaches to 0 (T_2/T_1 then becomes larger and larger and approaches to ∞), then the curve C_1A approaches the straight line $x = 0$ more and more and the curve C_0C_2 the dotted curve in the figure, which continues to present a clearly

¹⁾ These Proc. VII p. 636–638, April 22, 1905.

pronounced inflection point up to the last ¹⁾). For values of $\varphi > 1$, the curve C_0C_2 lies partially on the left of the curve $x = 1/2$, and the point of contact at D passes into two points of intersection.

By an approximate solution of (2b) and substitution in (1^b) and (3) of the values found, the following points of the two plaitpoint curves are calculated. (The other values of ω or x are either imaginary or do not satisfy).

		<u>$\varphi = 1$</u>		
Curve C_0C_2			Curve C_1A	
$x = 0,5$	0,6 0,7 0,8 0,9 1	$\omega = 0,33$	0,4 0,5 ¹⁾	0,6 0,7 0,8 0,9 1
$\omega = 1$	0,49 0,43 0,39 0,36 0,33	$x = 0$	0,021 0,041 0,042 0,023	0,010 0,0017 0
$\tau = 1$	1,78 1,98 2,13 2,26 2,37	$\tau = 0,59$	0,63 0,62 0,51 0,33	0,16 0,042 0
$\pi = \infty$	6,4 5,75 5,05 4,51 4	$\tau = 1$	1,15 1,08 0	-3,09 -8,64 -16,9 -27

It is seen that the pressure begins to be *negative* for points in the neighbourhood of A . This is not remarkable; also for a simple substance the points of inflection in the ideal isotherms reach to within the region of the negative pressures. Though the pressures in some points on the *spinodal* curve are negative, this is no reason why those on the *connodal* curves should be so.

The limits of the region of negative pressures on the spinodal curves may be easily fixed (see the dotted curves in fig. 1) by solution of the equation (see (3a))

$$2x(1-x) = (\varphi + x)^2(1-\omega)(2\omega-1).$$

If we put here $(1-\omega)(2\omega-1) = \theta$, we find:

$$x = \frac{(1-\varphi\theta) \pm \sqrt{1-2\varphi(\varphi+1)\theta}}{2+\theta}.$$

In this way we calculate for $\varphi = 1$:

$$\omega = 1 \quad 0,9 \quad 0,8 \quad 0,7 \quad 0,6 \quad 0,5$$

$$x = \begin{cases} 0 & 0,04^5 & 0,07 & 0,07 & 0,04^5 & 0 \\ 1 & 0,84 & 0,75^5 & 0,75^5 & 0,84 & 1. \end{cases}$$

That π approaches to -27 for $x = 0$, $\omega = 1$, $\tau = 0$ follows immediately from (3). For as $\frac{\tau}{1-\omega}$ approaches to 0, as we shall prove presently, $\pi = \frac{27}{2} \frac{1}{\varphi^2} (-2\varphi^2) = -27$, independent of the value of φ .

1) For this plaitpoint curve $\varphi = 0$ the following points are easily calculated:

$$\omega = 0,9 \quad 0,8 \quad 0,7 \quad 0,6 \quad 0,5 \quad 0,4$$

$$x = 0,507 \quad 0,528 \quad 0,567 \quad 0,623 \quad 0,712 \quad 0,853$$

The equation (2b), viz., passes then into the following quadratic equation in $x\omega$:

$$x^2\omega^2(9-10\omega+3\omega^2) - 3x\omega(2-\omega) + 1 = 0.$$

The other value for x is always > 1 .

2) The maximum lies at $\omega = 0,54$; x is then about $= 0,043$.

In this we must notice that in the immediate neighbourhood of the point A , π increases with the utmost rapidity from -27 to $+\infty$, when we pass the above considered border curve; in the point A itself this transition takes of course place suddenly. For when $\omega = 1$, π approaches to $\frac{27}{\varphi^3} \frac{2x(1-x)}{1-\omega} = \infty$, according to (3a), *except* in the case that x is exactly $= 0$, when (see further) $\frac{2x(1-x)}{1-\omega} = 0$, the following term yielding then the finite value -27 . This follows also from the figure, because the border curve, which separates positive from negative pressures, passes *through* the point A .

That on the plaitpoint curve the expressions $\frac{x}{1-\omega}$ and $\frac{\tau}{1-\omega}$ approach to 0 for $x = 0$, $\omega = 1$, $\tau = 0$ at A , follows from (2b). For putting $x = \Delta$ and $1 - \omega = \sigma$, we get:

$$1 + \varphi \sigma^2 \left(3 - 2 \frac{\varphi^2}{\Delta} \sigma \right) = 0,$$

or as $3\varphi\sigma^2$ may be neutralized by 1, $1 - 2\varphi^3 \frac{\sigma^3}{\Delta} = 0$, from which follows, that at the point A $\frac{\Delta}{\sigma^3} = 2\varphi^3$, so remains finite. So Δ is of the order σ^3 , so that $\frac{x}{1-\omega} = \frac{\Delta}{\sigma}$ really approaches to 0 at A . From this follows also the *contact*. And as according to (1b) τ approaches to $4(\Delta + \varphi^2\sigma^2) = 4\varphi^2\sigma^2$ (Δ being of the order σ^3) for $x = 0$, $\omega = 1$, $\frac{\tau}{1-\omega}$ approaches to 0 at A .

In the same way the plaitpoint curve C_0C_2 touches the line $x = \frac{1}{2}$ for $x = \frac{1}{2}$, $\omega = 1$. For, for $x = \frac{1}{2}(1 + \Delta)$, $\omega = 1 - \sigma$ equation (2b) becomes:

$$-\Delta + (\varphi + \frac{1}{2}) \sigma^2 \left[3 - 8(\varphi + \frac{1}{2})^2 \sigma \right] = 0,$$

which approaches to $-\Delta + 3(\varphi + \frac{1}{2}) \sigma^2 = 0$, yielding $\frac{\Delta}{\sigma^2} = 3(\varphi + \frac{1}{2})$,

so again finite. So Δ is now of the order σ^2 , and so $\frac{\Delta}{\sigma}$ again $= 0$, which proves the contact at C_0 .

I call attention to the fact, that on account of the small values of Δ a large portion of the curve C_0C_2 from C_0 as far as beyond the point D may be calculated very accurately, by writing for (2b) ($\varphi = 1$):

$$-\Delta + \frac{3}{2}(1-\omega)^2 \left[3 - 9(1-\omega)(3\omega-1) \right],$$

so that
$$\Delta = \frac{9}{2}(1-\omega)^2 \left[1 - 3(1-\omega)(3\omega-1) \right],$$

From this follows e.g. for $\omega = 0,9, 0,8, 0,7, 0,6$ resp., for Δ 0,022, 0,029, 0,004, 0,029.

The contact at D . If we put in (2b) $x = \frac{1}{2}$, then $1 - 2x = 0$, and hence:

$$(\varphi + \frac{1}{2})(1-\omega)^2 \left[3 + 4(\varphi + \frac{1}{2})^2(1-\omega)(1-3\omega) \right] = 0.$$

This yields besides $\omega = 1$ (the point C_0), also:

$$(1-\omega)(3\omega-1) = \frac{3}{(2\varphi+1)^2},$$

hence:

$$\omega = \frac{2}{3} \pm \frac{1}{3} \sqrt{1 - \frac{9}{(2\varphi+1)^2}}.$$

For $\varphi = 1$ this yields two equal roots $\omega = \frac{2}{3}$, which proves the contact at D . For $\varphi < 1$ the roots become imaginary, so that then C_0C_2 no longer cuts the line $x = \frac{1}{2}$, but keeps continually on its right, whereas for $\varphi > 1$ two points of intersection are always found. So is e.g. for $\varphi = 2$ $\omega = \frac{14}{15}$ (close to C_0) and $\omega = \frac{2}{5}$ (lying on the other branch between C_1 and C_2 (see fig. 2)).

In order to facilitate the tracing of the different *spinodal* lines, it is to be recommended to fix the limiting values of τ for $x = 0$, $x = 1$, $\omega = 1$, $\omega = \frac{1}{3}$. Also for $x = \frac{1}{2}$ it is easy to calculate τ . From (1b) follows e.g. for $x = 0$, $\varphi = 1$:

$$\tau = 4\omega(1-\omega)^2.$$

This yields:

$\omega = 1$	0,9	0,8	0,7	0,6	0,5	0,4	0,333	0,3	0,2	0,1
$\tau = 0$	0,036	0,128	0,252	0,384	0,50	0,576	0,593	0,588	0,512	0,324

For $x = 1$ these values become simply 4 times larger, $(\varphi + x)^2$ then being = 4.

For $x = \frac{1}{2}$ we get,

$$\tau = \omega \{1 + 9(1-\omega)^2\},$$

yielding:

$\omega = 1$	0,95	0,9	0,8	0,7	0,6	0,5	0,4	0,33	0,3
$\tau = 1$	0,971	0,981	1,09	1,27	1,46	1,62 ⁵	1,70	1,67	1,62.

For $\omega = 1$ we get simply:

$$\tau = 4x(1-x),$$

from which follows:

$x = 0$	0,1	0,2	0,3	0,4	0,5	0,6	0,7	0,8	0,9	1
$\tau = 0$	0,36	0,64	0,84	0,96	1	0,96	0,84	0,64	0,36	0.

Finally we get for $\omega = 1/3$:

$$\tau = 1/3 \left[x(1-x) + 1/9(x+1)^2 \right],$$

yielding:

$x = 0$	0,1	0,2	0,3	0,4	0,5	0,6	0,7	0,8	0,9	1
$\tau = 0,593$	0,837	1,07	1,28	1,48	1,67	1,84	1,99	2,13	2,26	2,37.

It appears from the diagram (see also above for $x = 1/2$), that the temperature from C_0 to C_2 is not continually ascending, but that it shows a *minimum* very near C_0 . This causes the spinodal line $\tau = 1$ not to pass through C_0 , but to remain under it. The point C_0 , where τ is also $= 1$, is an isolated point belonging to that line. Just beyond C_0 the two branches of one and the same spinodal line intersect in a double point; beyond that place the course is normal; between C_0 and this intersection the spinodal line has two separate branches, one of which encloses the point C_0 . Now the question arises, whether this will be the case for every value of φ . If we solve x from (1b), we get:

$$x^2(2\omega - \omega^2) - x \left(1 + 2\varphi(1 - \omega)^2 \right) + \left(\frac{\tau}{4\omega} - \varphi^2(1 - \omega)^2 \right) = 0.$$

This gives for x two roots of the same value for given values of τ and ω , when

$$4\varphi(\varphi + 1)(1 - \omega)^2 + 1 - \tau(2 - \omega) = 0.$$

The value of x is then:

$$x = \frac{1/2 + \varphi(1 - \omega)^2}{\omega(2 - \omega)}.$$

Now it follows from the value of the above given discriminant, that it becomes $= 0$ for *two* values of ω . So two branches of a spinodal line intersect, when those values of ω become the same. From

$$4\varphi(\varphi + 1)\omega^2 - \omega \left(8\varphi(\varphi + 1) - \tau \right) + \left(4\varphi(\varphi + 1) + 1 - 2\tau \right) = 0$$

follows, that ω has two roots of the same value, when

$$\frac{\tau^2}{1 - \tau} = 16\varphi(\varphi + 1) ; \quad \omega = 1 - 1/8 \frac{\tau}{\varphi(\varphi + 1)}.$$

And τ being 1 at C_0 , the minimum disappears only, when τ becomes $= 1$ in the above expression. And this is evidently only the case for $\varphi = \infty$, i. e. when T_1 and T_2 should have the same value. Hence in general there will always be found a minimum in the neighbourhood of C_0 . For $\varphi = 1$ we find $\tau = 0,970$, $\omega = 0,94$, $x = 0,506$; for $\varphi = 2$ we find $\tau = 0,990$, $\omega = 0,98$, $x = 0,501$; etc. etc.

It may be easily demonstrated that in the neighbourhood of C_1 such a minimum never appears in our case. For from (1b) follows

$$\text{with } \tau = \frac{T_1}{T_0} = \frac{16}{27} \varphi^2 :$$

$$\frac{16}{27} \varphi^2 = 4\omega \left[x(1-x) + (\varphi + x)^2 (1-\omega)^2 \right].$$

After substitution of $x = \Delta$, $\omega = 1/3(1 + \delta)$, we get, neglecting Δ^2 , which is justified by the result:

$$(1 + \delta) \left[\frac{9}{4} \frac{\Delta}{\varphi^2} + \left(1 + \frac{2\Delta}{\varphi} \right) (1 - 1/2\delta)^2 \right] = 1,$$

$$\text{or as } \frac{1}{1+\delta} = 1 - \delta + \delta^2 - \dots, \text{ and so } \frac{1}{1+\delta} - (1 - 1/2\delta)^2 = 3/4\delta^2:$$

$$\frac{9}{4} \frac{\Delta}{\varphi^2} + \frac{2\Delta}{\varphi} (1 - 1/2\delta)^2 = 3/4\delta^2,$$

yielding :

$$\Delta = 3/4\delta^2 : \left(\frac{9}{4\varphi^2} + \frac{2}{\varphi} \right) = 3\delta^2 : \left(\frac{9}{\varphi^2} + \frac{8}{\varphi} \right).$$

The spinodal line $T = T_1$ touches, therefore, the axis $x = 0$ for every value of φ , and, at least on the assumptions made by us concerning a and b , a minimum can therefore never appear in the neighbourhood of C_1 , in consequence of which the spinodal lines in the immediate neighbourhood of C_1 would enclose this point.

Finally some corresponding values of x and ω are subjoined, which determine the shape of the spinodal line $\tau = 1$ ($T = T_0$). By solution of the quadratic equation

$$4\omega \left[x(1-x) + (1+x)^2 (1-\omega)^2 \right] = 1$$

follows immediately :

$\omega = 1$	0,8	0,7	0,6	0,5	0,4	0,33	0,3	0,2	0,1
$x = 0,5$	0,403	0,292	0,227	0,184	0,164	0,182	0,182	0,306	0,679
	0,743	1,004							

So this line cuts the axis $x = 1$ for $\omega = 0,7$, and henceforth only one solution satisfies. x becomes evidently 1 for $\omega(1-\omega)^2 = 1/16$, yielding about $\omega = 0,07$.

From the above derived equation $4\varphi(\varphi+1)(1-\omega)^2 + 1 - \tau(2-\omega) = 0$, which was the condition for two equal values of x , we find $\varphi = 1$, $\tau = 1$:

$$8\omega^2 - 15\omega + 7 = 0,$$

from which, besides $\omega = 1$, $\omega = 7/8$ follows. To this belongs then $x = 11/21 = 0,524$. Between $\omega = 1$ and $\omega = 0,875$ we find only imaginary values for x in the above table.

As to the spinodal line $T = T_1$ ($\tau = 0,59$), we calculate $x = 0,0019$ for $\omega = 0,30$, whereas $x = 0,006$ corresponds to $\omega = 0,40$.

As to the shape of the spinodal lines for great values of v (vapour branch) i. e. when τ and ω approach to 0, follows immediately from (1b):

$$\tau = 4\omega \left[x(1-x) + (\varphi + x)^2 \right] = 4\omega \left[\varphi^2 + (2\varphi + 1)x \right].$$

If we substitute $T/T_0 = T: \frac{1/2\alpha^2}{Rb}$ for τ , and $\frac{b}{v}$ for ω , we get:

$$RT = \frac{2\alpha^2}{v} \left[\varphi^2 + (2\varphi + 1)x \right].$$

After substitution of $\varphi = \frac{\sqrt{a_1}}{\alpha}$, this becomes:

$$v = \frac{2}{RT} \left[a_1 + (a_2 - a_1)x \right].$$

From this follows that the vapour branches of the spinodal lines in their v, x -projection will approach more and more to straight lines, which will cut the axes $x = 0$ and $x = 1$ at distances proportional to the quantities a_1 and a_2 .

5. Let us now consider the second type, which occurs for $\varphi = 2$.

a. Description of the case $\varphi = 2$ (fig. 2 and fig. 2a).

The two plaitpoint curves of fig. 1, viz. C_0C_2 and C_1A have met for φ about 1,43 (see fig. 4), after which two new ones have been formed, now C_1C_2 and C_0A . This case, which is found for comparatively large values of φ , for which the proportion $\frac{T_2}{T_1}$ approaches

more and more to unity, is the usual one or the normal one. It is the *principal type III*, as described in one of my two preceding papers¹⁾.

The region of negative pressures on the spinodal lines extends now all over the v, x -diagram, from $x = 0$ to $x = 1$, and is bounded by the two dotted curves (see fig. 2) above and below.

The spinodal line belonging to $\tau = 1,35$ touches now the curve C_0A in the point R_2 . Again the plaitpoints are not realisable from a point between R_2 and C_0 to A (see the footnote in § 4 at a.)

Beyond R_2 the temperature and with it the pressure decreases, so that in the p, T diagram (see fig. 2a) the curve C_0R_2A runs back

¹⁾ l. c. p. 642—644.

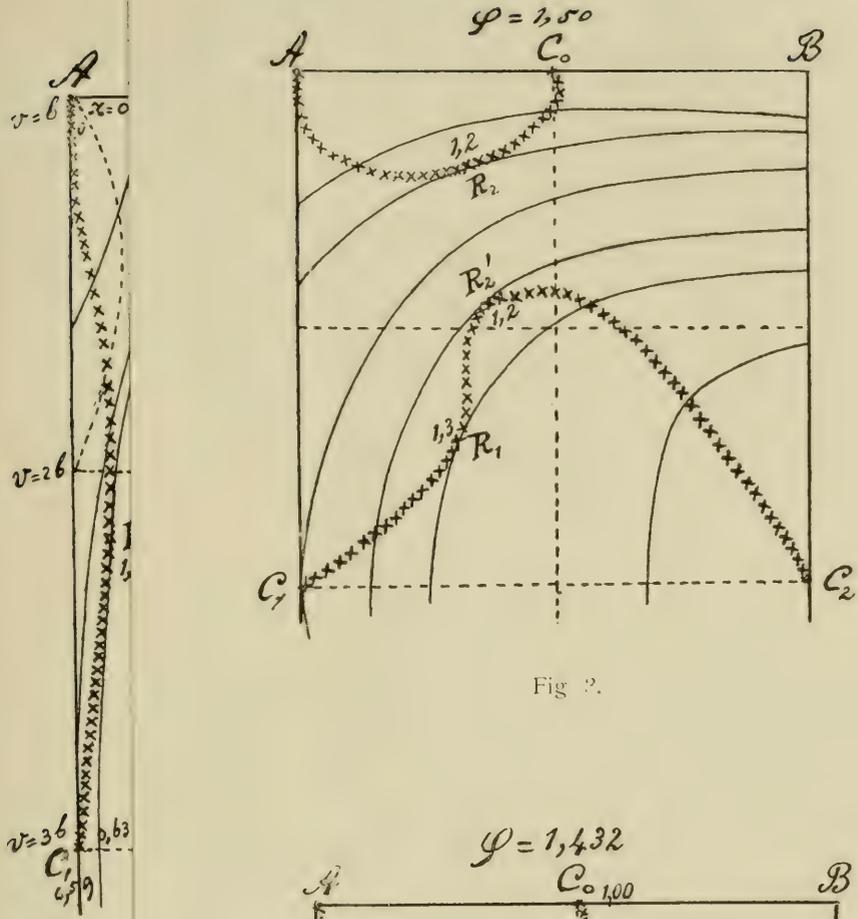


Fig. 2.

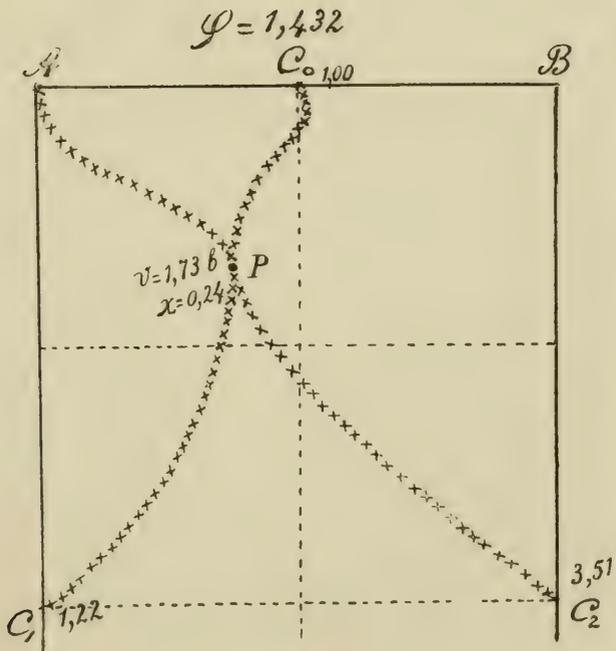
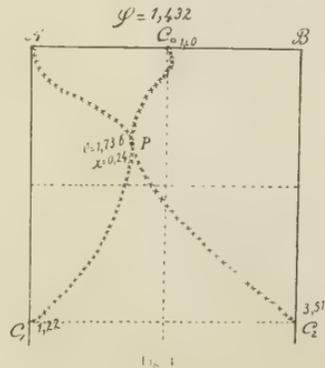
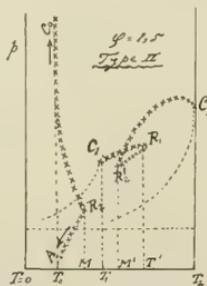
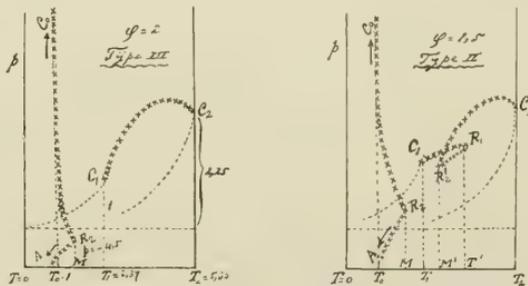
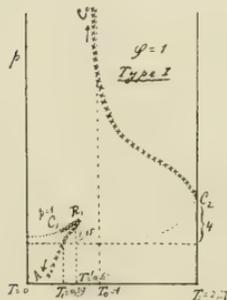
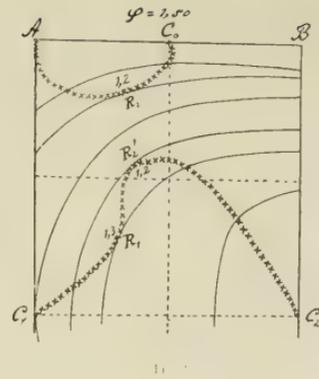
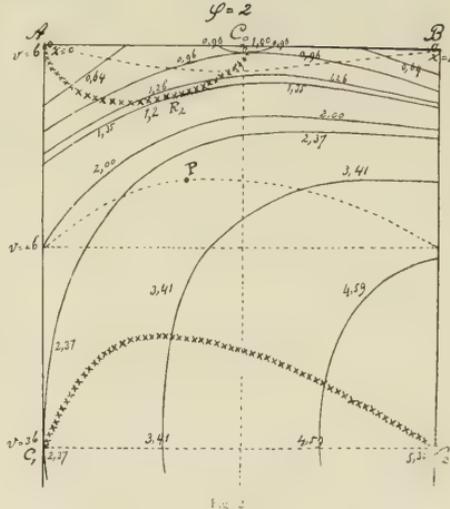
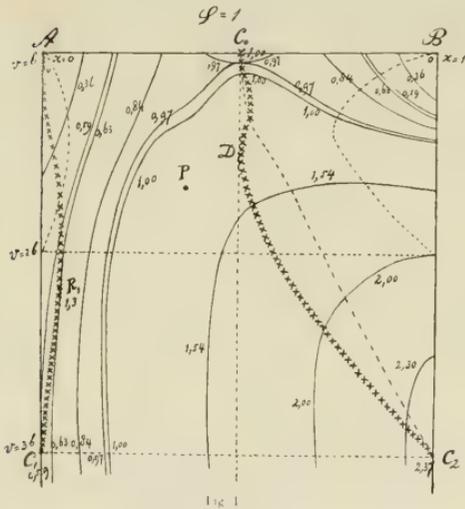


Fig. 4.



again from R_2 . In R_2 the pressure is already negative, and it becomes again $= -27 p_1$ in A . (See § 4 at b).

When $\varphi = 2$, we find easily from the equations derived in § 3, that then $T_2/T_1 = 2^{1/4}$ and $T_1/T_0 = 6^{1/27}$. So if T_0 is again $= 1$, then $T_1 = 2,37$ and $T_2 = 5,33$. Now T_1 is higher than T_0 .

b. Some mathematical and numerical details.

Much having already been derived in § 4, it will suffice to give some few values.

Of the two plaitpoint curves the following points were calculated

		<u>$\varphi = 2$</u>												
$x = 0$	0,15	0,2	0,3	0,4	0,5	0,6	0,7	0,8	0,9	1	}	Curve $C_1 C_2$		
$\omega = 0,33^3$	0,39 ⁵	0,40 ³	0,41 ⁺	0,41 ⁻	0,40	0,39 ⁺	0,37 ⁴	0,35 ⁹	0,34 ⁷	0,33 ³				
$\tau = 2,37$	2,87	3,04	3,38	3,70	4,00	4,28	4,60	4,87	5,10	5,33				
$\pi = 1$	1,46	1,62	1,90	2,11	2,25	2,32	2,37	2,36	2,33	2,25				
$x = 0$	0,01	0,1	0,2	0,3	0,4	0,5	}					Curve $C_0 A$.		
$\omega = 1$	0,91	0,81	0,78	0,80	0,85	0,933 and 1								
$\tau = 0$	0,15 ⁵	0,81	1,23	1,35	1,26	1,04 and 1								
$\pi = -27$	-17,3	-7,90	-5,16	-4,62	-3,98	49 and ∞								

The separation between the negative and positive pressures on the spinodal curves is given by

$$\omega = 1 \quad 0,9 \quad 0,894 \quad 0,606 \quad 0,6 \quad 0,5$$

$$x = \begin{cases} 0 & 0,31 & 0,40 & 0,40 & 0,31 & 0 \\ 1 & 0,50 & 0,40 & 0,40 & 0,50 & 1 \end{cases}$$

The places where x has here two equal values, are easily found from the value of x given in § 4. Evidently we must have then $\theta = (1 - \omega)(2\omega - 1) = 1/12$. This gives $\omega = 0,894$ and $0,606, = 1/4(3 \pm 1/3 \sqrt{3})$. For $\varphi = 1$ θ would have to be $1/4$, and there are no values of ω which satisfy this condition.

For the calculation of the different spinodal curves it is convenient to know the limiting values of τ again. We find for $x = 0$:

$$v/b = 1/\omega = 1 \quad 1,25 \quad 1,50 \quad 1,75 \quad 2 \quad 2,25 \quad 2,50 \quad 2,75 \quad 3$$

$$\tau = 0 \quad 0,51 \quad 1,19 \quad 1,68 \quad 2 \quad 2,20 \quad 2,30 \quad 2,36 \quad 2,37$$

For $x = 1$ these values are all $2^{1/4}$ times greater.

For $x = 1/2$ we find with the same values of ω :

$$\tau = 1 \quad 1,60 \quad 2,53 \quad 3,20 \quad 3,63 \quad 3,88 \quad 3,99 \quad 4,04 \quad 4,04$$

$\omega = 1$ yields the same values as in § 4 for $\varphi = 1$.

$\omega = 1/4$ yields:

$x = 0$	0,1	0,2	0,3	0,4	0,5	0,6	0,7	0,8	0,9	1
$\tau = 2,37$	2,73	3,08	3,41	3,73	4,03	4,33	4,59	4,86	5,10	5,33

6. We may now determine, where the transition represented in fig. 4, takes place. (The place of the point P is also drawn in figs. 1 and 2¹⁾).

If we put $1 - \omega = y$ in the equation (2b) of the plaitpoint curve, then

$$(1 - 2x) + (x + \varphi) y^2 \left(3 + (x + \varphi)^2 \frac{y(3y-2)}{x(1-x)} \right) = 0. \dots (a)$$

Now in the double point sought $\frac{\partial f}{\partial x}$ must be 0 and $\frac{\partial f}{\partial y}$ must be 0, when f denotes the first member of (a). This gives:

$$\begin{aligned} -2x(1-x) + (1-2x)^2 + 3y^2 \left\{ (1-2x)(x+\varphi) + x(1-x) \right\} + \\ + 3(x+\varphi)^2 y^3 (3y-2) = 0, \dots (b) \end{aligned}$$

and after division by $6y(x+\varphi)$:

$$x(1-x) + (x+\varphi)^2 y(2y-1) = 0 \dots (c)$$

Substitution of the value of $x(1-x)$ from (c) in (a) gives:

$$(1 - 2x) + (x + \varphi) y^2 \left(3 + \frac{3y - 2}{1 - 2y} \right) = 0,$$

or

$$(1 - 2x) + (x + \varphi) y^2 \frac{1 - 3y}{1 - 2y} = 0 \dots (a')$$

So we have to solve y , x and φ from (a'), (b) and (c). Substitution of $1 - 2x$ from (a'), and $x(1-x)$ from (c) in (b) gives, after division by $(x+\varphi)^2 y$:

$$\begin{aligned} -2(1-2y) + y^3 \left(\frac{1-3y}{1-2y} \right)^2 + \\ + 3y^2 \left\{ -y \frac{1-3y}{1-2y} + (1-2y) \right\} + 3y^2(3y-2) = 0, \end{aligned}$$

i. e. after multiplication by $(1-2y)^2$:

$$\begin{aligned} -2(1-2y)^3 + y^3(1-3y)^2 + \\ + 3y^2(1-2y) \left\{ -y(1-3y) + (1-2y)^2 \right\} + 3y^2(3y-2)(1-2y)^2 = 0, \end{aligned}$$

from which y may be solved. The above equation gives:

¹⁾ This point must be thought more to the left. In fig. 4 no contact but intersection takes place in the double point P .

$$-2(1-2y)^3 + y^3(1-3y)^2 + 3y^2(1-2y)(y^2+2y-1) = 0,$$

or $3y^5 - 15y^4 + 29y^3 - 27y^2 + 12y - 2 = 0,$

i. e. after division by $(y-1)^3$:

$$3y^2 - 6y + 2,$$

yielding :

$$y = 1 \pm \frac{1}{3} \sqrt{3}.$$

As it is obvious that y cannot be larger than 1, only :

$$\underline{y = 1 - \frac{1}{3} \sqrt{3} = 0,4226}$$

satisfies here.

If we substitute the value $x + \varphi$ from (a') into (c), we get:

$$x(1-x) - (1-2x)^2 \frac{(1-2y)^3}{y^3(1-3y)^2} = 0.$$

In this the last fraction passes into $\frac{1}{4}(1 + \sqrt{3})$, after substitution of $y = 1 - \frac{1}{3} \sqrt{3}$, so that we get for x :

$$x(1-x) - \frac{1}{4}(1 + \sqrt{3}) \left\{ 1 - 4x(1-x) \right\} = 0,$$

hence:

$$x(1-x) = \frac{1}{4}(-1 + \sqrt{3}),$$

giving:

$$x = \frac{1}{2} \left\{ 1 \pm \frac{1}{2} (\sqrt{6} - \sqrt{2}) \right\} = 0,2412 \text{ or } 0,7588.$$

It is obvious from the figure, that only the first value satisfies, viz.:

$$\underline{x = \frac{1}{2} \left\{ 1 - \frac{1}{2} (\sqrt{6} - \sqrt{2}) \right\} = 0,2412.}$$

The value of φ is finally found from (c):

$$(x + \varphi)^2 = \frac{x(1-x)}{y(1-2y)} = \frac{3}{4}(2 + \sqrt{3}),$$

giving $x + \varphi = \frac{1}{4}(3\sqrt{2} + \sqrt{6})$, hence $\underline{\varphi = \frac{1}{2}(-1 + \sqrt{2} + \sqrt{6}) = 1,432.}$

As $y = 1 - \frac{1}{3} \sqrt{3}$, $\omega = \frac{1}{3} \sqrt{3}$, i. e. the intersection takes place at $v = b \sqrt{3} = 1,732 b$.

As mentioned before $T_0 = T_1$ for $\varphi = 1,30$ (see § 3). For $\varphi = 1,43$ T_0 is already $< T_1$. For $T_1/T_0 = \frac{16}{27} \varphi^2$ we find easily the value 1,215, while 2,887 is found for $T_2/T_1 = (1 + 1/\varphi)^2$.

7. Besides the cases, given in figs. 1 and 2, representing the principal types I and III, there is another important type, viz. II, of which I also gave a full description in my previous paper, which I have already cited several times¹⁾. The p, T -diagram of this case

¹⁾ l. c. p. 663—667.

is given in fig. 4*a*. KUENEN met with it, among others, in the case of mixtures of C_2H_6 with ethyl- and some higher alcohols. Also triethylamine with water is a well-known instance.

This case is evidently found, when the plaitpoint curve C_1C_2 of fig. 2 assumes the shape drawn in fig. 3. We may namely imagine that when the two curves C_1C_2 and C_0A approach each other, a deviation from the straight course may be found on the left side of C_1C_2 , specially if b_1 should not be $= b_2$, by which the point C_0 would therefore be shifted to the left, to the side of the small volumes. At all events the anomaly of one of the two components can give rise to the occurrence of this second principal type, as I showed in a preceding paper.

From the shape of the different spinodal curves it is obvious that from C_1 the temperatures first increase, as far as the point of contact at R_1 . The temperature is then T' (see fig. 3*a*). But between R_1 and R_2' , where the plaitpoint curve is again touched by one of the spinodal curves, the temperature *decreases*, and so also the pressure, so that in the p, T -diagram of fig. 3*a* the line $R_1 R_2'$ runs back again, as in fig. 1*a* the line $R_1 A$ and in fig. 2*a* the line $R_2 A$, having in this case two *cusps* in R_1 and R_2' .

Here the points between R_1 and R_2' , and also those on C_1R_1 and C_2R_2' in the neighbourhood of R_1 and R_2' can again not be realized, and the consequence will be the occurrence of a three phase equilibrium¹).

As I already observed in one of my previous papers (l.c. p. 646), after the two liquid phases 1 and 2 have coincided in the neighbourhood of the point R_2' , here too, separation of the two liquid phases must take place again — provided the temperature be sufficiently lowered — and this will take place in the neighbourhood of the point, where one of the spinodal curves in R_2 touches the plaitpoint curve C_0A . This is also represented in the p, T -diagram of fig. 3*a*.

When comparing figs. 1, 2 and 3, we see clearly the connection between the three principal types and their transition into each other. The connection is given by the different course of the two plaitpoint curves in figs. 1 and 2, which (see fig. 3) may pass *continuously* into each other with changed circumstances of critical data of the two components.

¹) Cf. VAN DER WAALS, Continuität II, p. 187, and These Proceedings V, p. 307—11 Oct. 25, 1902.

Physics. — “Some remarks on Dr. PH. KOHNSTAMM’s last papers.”

By J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

1. With interest and full approval I read Dr. KOHNSTAMM’s three papers on the osmotic pressure¹⁾. From them it appeared to me that, practically, he perfectly agreed with me. Only with regard to a few points there are differences of opinion — only *in appearance*, however, as I shall show in what follows.

On pages 723—729 i. e., namely, KOHNSTAMM gives also a *thermodynamic* derivation of the osmotic pressure, which seems to lead to a somewhat different result from mine. He finds, namely, in the numerator finally the quantity $v_x - x \frac{db}{dx}$ instead of v_0 . [I use here my notation; v_0 is the molecular volume of the pure solvent (KOHNSTAMM’s v_g), v_x that of the solution, in which the dissolved substance is present with a concentration x (K.’s v_0)]. But here he overlooks that according to his approximations v_0 may be written for the latter. For on page 726 an integral is neglected, among others on the strength of the fact that $v_x - b$ approaches to 0. He puts therefore $v_x = b$, in consequence of which $v_x - x \frac{db}{dx} = b - x \frac{db}{dx} = b - x(b_2 - b_1) = b_1$. This however, is the value of b or v , when $x = 0$, so v_0 .

So KOHNSTAMM finds exactly the same thing as I found already in 1894 in a much simpler way. In my method no integral need be split into three parts, and we need not neglect anything but the compressibility of the liquid (which is of course also done by KOHNSTAMM), so that my result (the compressibility excepted) is *perfectly accurate*, which cannot be said of that of KOHNSTAMM.

2. The above mentioned method has been repeatedly published by me. [Z. f. Ph. Ch. XV, 1894; Arch. Teyler (Théorie générale), 1898; Lehrbuch der math. Chemie, 1901; Arch. Teyler (Quelques remarques sur la théorie des solutions non-diluées), 1903; and recently in the “Chemisch Weekblad”, 1905, N^o. 9]. The derivation may follow here once more.

If there is namely, equilibrium between the solution with the concentration x under a pressure p , with the pure solvent with a concentration 0 under the *arbitrary* pressure p_0 (e.g. that of the saturated vapour, or of the atmosphere etc.), the molecular potentials

1) These Proc. VII, 723—751.

of the solvent in the two liquid phases (separated by a semipermeable membrane only passable by the solvent) are the same. Hence:

$$\mu(0, p_0) = \mu(x, p) \dots \dots \dots (1)$$

But evidently we have the identity

$$\mu(0, p_0) = \mu(0, p) - \int_{p_0}^p \frac{\partial \mu_0}{\partial p} dp.$$

Here $\frac{\partial \mu_0}{\partial p} = v_0$ (for meaning of v_0 , see §1). So we have also:

$$\mu(0, p_0) = \mu(0, p) - \int_{p_0}^p v_0 dp.$$

If we now assume v_0 to be *independent of the pressure* — which KOHNSTAMM thinks perfectly permissible — we get:

$$\mu(0, p_0) = \mu(0, p) - v_0(p - p_0).$$

Substituting this in (1), we get at once:

$$\pi = p - p_0 = \frac{1}{v_0} (\mu_0 - \mu_x)_p, \dots \dots \dots (2)$$

by which the osmotic pressure is immediately brought into connection with the difference of the molecular potentials of the pure solvent and of that in the solution, *both under the same pressure* p .

Now we can in the usual way replace $\mu_0 - \mu_x$ by its value. We find then, as has been frequently derived:

$$- RT \log(1 - x) - \frac{ax^2}{(1 + rx)^2} + RT \log \frac{v_x - b}{v_0 - b_1} \text{ etc.}$$

in which the latter terms is often neglected, and a and r have the known meaning.

In this way the apparent deviation with regard to v_0 has been disproved. My statement, therefore, that in the numerator for v_0 no correction term need be applied (see KOHNSTAMM, p. 729), was by no means "too absolute".

3. When reading through KOHNSTAMM's paper, I was further struck by the following in my opinion inaccurate assertions.

On p. 739 it says: "It appears from the explanation convincingly, that VAN LAAR goes too far, when he states, that we cannot speak of osmotic pressure in an *isolated* solution."

I fully maintain this view. For in the kinetic explanation of

KOHNSTAMM the osmotic pressure in an isolated solution is established, *only when* he places semi-permeable walls or planes in it. But then it is of course no isolated solution any more! What I demonstrate is no more than this: Without semipermeable membrane no osmotic pressure. And to this KOHNSTAMM will certainly not have any objection, witness the cited question of PUPIN how it is possible, that e. g. a CaCl_2 -solution of no less than 53 atm. could be held in a thin glass vessel without bursting it! I do not see very well, what objection KOHNSTAMM can have to my assertion. For this is the *core* of the question, with regard to which he proves to be quite of my opinion in another place (cf. p. 742).

4. What KOHNSTAMM further observes on pages 742—4 with regard to the idea “thermodynamic potential”, and what he says on “palpable conceptions” may be very well left undiscussed here. For this is only a question of words, which does not affect the real nature of the affair at all. Every one who works with the thermodynamic potential, means with it the ζ -function of GIBBS, which perfectly determines the condition of equilibrium, as it must be *minimum* in this case.

Finally I may only be allowed to point out that Dr. KOHNSTAMM has evidently misunderstood me, where he says that he thinks the request to supply something “as a substitute” for the osmotic pressure and the kinetic conception of it less unreasonable than it seems to *me* (p. 746).

I, namely, spoke of the osmotic pressure in an *isolated* solution. And I very distinctly added: nothing can be put in the place for what *does not exist*. And I wrote further, that the *usual* (faulty) *kinetic* conception of the osmotic pressure (i. e. where there are semi-permeable membranes) must be replaced by a perfectly new kinetic explanation, in which inter alia, the process of diffusion at the membrane is put more into the foreground (Ch. Weekbl., 1905, N^o. 9).

And where KOHNSTAMM himself has made a very laudable attempt in this direction (l. c. p. 729—741) to explain the osmotic pressure, I have after all reasons for satisfaction, though he has wisely abandoned the idea of drawing up an equation for non-diluted solutions in *this* way.

And as to the *thermodynamic* derivation, in this KOHNSTAMM has been less fortunate in my opinion; where he has tried to substitute for my perfectly exact, and yet so simple derivation an indirect, elaborate derivation, the result of which on account of some neglects cannot even lay claim to perfect accuracy.

Mathematics. — “On the rank of the section of two algebraic surfaces.” By DR. W. A. VERSLUYS. (Communicated by Prof. P. H. SCHOUTE.

1. In this paper I intend to prove the relation new to me

$$r = m_1 n_2 + m_2 n_1 - 2\sigma - 3\chi, \dots \dots \dots (A)$$

where r is the rank of the curve of intersection s of two algebraic surfaces S_1 and S_2 , respectively of the degree n_1 and n_2 and of the class m_1 and m_2 and possessing in σ points an ordinary contact and in χ points a stationary contact. Some applications of this formula are given too.

Formerly I proved ¹⁾ the following extension of a well-known formula ²⁾

$$r = n_1 n_2 (n_1 + n_2 - 2) - 2(n_1 \xi_2 + n_2 \xi_1 + \sigma) - 3(n_1 v_2 + n_2 v_1 + \chi), \dots (B)$$

where ξ_1, ξ_2, v_1, v_2 represent the degrees of the nodal and cuspidal curves of the two surfaces S_1 and S_2 . Formula (A) shall first be proved for the case that S_1 and S_2 are developables. If we wish to apply formula (B) to developables the numbers of double generating lines ω_1 and ω_2 must be added to the orders ξ_1 and ξ_2 of the nodal curves and the numbers of stationary generating lines v_1 and v_2 to the orders v_1 and v_2 of the cuspidal curves.

Formula (B) becomes

$$r = n_1 n_2 (n_1 + n_2 - 2) - 2\{n_1 (\xi_2 + \omega_2) + n_2 (\xi_1 + \omega_1) + \sigma\} - 3\{n_1 (v_2 + v_2) + n_2 (v_1 + v_1) + \chi\} \dots \dots \dots (C)$$

2. Let $\Delta^2 S$ be the second polar surface of the degenerated surface $S_1 + S_2$ with respect to the arbitrary point P . This surface $\Delta^2 S$ is of the degree $(n_1 + n_2 - 2)$ and meets the curve of intersection s of S_1 and S_2 , this curve being of the degree $n_1 n_2$, in $n_1 n_2 (n_1 + n_2 - 2)$ points.

These points of intersection are 1st the triple points of $S_1 + S_2$ through which the curve s passes and 2nd the points of s for which the tangent plane to one of the two surfaces passes through P . The triple points of $S_1 + S_2$ through which the curve s passes are the points in which a double line of one of the two surfaces meets the other surface. So these triple points are:

1st. The $(n_1 v_2 + n_2 v_1)$ points in which a cuspidal curve of one of the surfaces meets the other one. These points are cusps on the curve of intersection s , they are indicated by CREMONA as points λ

¹⁾ VERSLUYS, Mémoires de Liège, 3me serie, t. VI. Sur les nombres Plückériens etc.

²⁾ E. PASCAL, Rep. di Mat. Sup. II, p. 325.

and must count according to him for three points of intersection of the nodal curve, thus here of the curve s with $\Delta^2 S^1$).

2nd. The $(n_1 v_2 + n_2 v_1)$ points in which a stationary generating line of one of the surfaces meets the other one. These points, also cusps on the curve s , are indicated by CREMONA as points r which must count according to him for three points of intersection of the nodal curve s with $\Delta^2 S^2$).

3rd. The $(n_1 \xi_2 + n_2 \xi_1)$ intersections of S_1 or S_2 with the nodal curve of the other surface. According to CREMONA each of the branches of the nodal curve meets $\Delta^2 S^3$) one time in a triple point τ . Through each of these points τ pass two branches of s , which is a nodal curve on $S_1 + S_2$; so each of these triple points counts for two points of intersection of s with $\Delta^2 S$.

4th. The $(n_1 \omega_2 + n_2 \omega_1)$ nodes of s in which a double generator of one of the surfaces S_1 or S_2 meets the other one. According to CREMONA the nodal curve s meets $\Delta^2 S^4$) two times in such a triple point r .

The surface $S_1 + S_2$ possesses still more triple points, among others the cusps β of the cuspidal curves; these points do lie on $\Delta^2 S$, but on the curve of intersection s they do not; so they do not belong to the points of intersection of s with $\Delta^2 S$.

3. Through P pass m_1 tangent planes of the surface S_1 . A generator of S_1 , along which one of the m_1 tangent planes through P touches S_1 , meets n_2 times the surface S_2 . Each of these points of intersection is a point on s also situated on $\Delta^2 S$. Such a point of s and of $\Delta^2 S$ counts for *one* point of intersection, according to CREMONA ⁵⁾. So $\Delta^2 S$ is met by the curve s in $(m_1 n_2 + m_2 n_1)$ points for which one of the tangent planes passes through P .

This gives the relation :

$$n_1 n_2 (n_1 + n_2 - 2) = m_1 n_2 + m_2 n_1 + 2 \{n_1 (\xi_2 + \omega_2) + n_2 (\xi_1 + \omega_1)\} + \\ + 3 \{n_1 (v_2 + v_2) + n_2 (v_1 + v_1)\} \quad . \quad . \quad . \quad . \quad (D)$$

Comparing the equations (C) and (D) we get immediately

$$r = m_1 n_2 + m_2 n_1 - 2\sigma - 3\chi. \quad . \quad . \quad . \quad . \quad (A)$$

The degree of a developable being the rank of its cuspidal curve, we can write for this formula :

$$r = m_1 r_2 + m_2 r_1 - 2\sigma - 3\chi.$$

1) CREMONA—CURTZE, Oberflächen § 108.

2) CREMONA—CURTZE, loc. cit. § 100.

3) CREMONA—CURTZE, loc. cit. § 109.

4) CREMONA—CURTZE, loc. cit. § 101.

5) CREMONA—CURTZE, loc. cit. § 99.

4. The formula (D) and hence also the formula (A), which is now proved for the case that the two surfaces are developables holds still good when S_1 and S_2 are arbitrary algebraic surfaces. Let ξ_1 and ν_1 represent the degree of the total nodal curve and total cuspidal curve of S_1 , likewise ξ_2 and ν_2 for S_2 . One of the formulae of PLÜCKER applied to an arbitrary plane section of S_1 gives

$$m_1 = n_1^2 - n_1 - 2\xi_1 - 3\nu_1,$$

or

$$0 = n_1^2 - n_1 - m_1 - 2\xi_1 - 3\nu_1.$$

In like manner an arbitrary plane section of S_2 gives

$$0 = n_2^2 - n_2 - m_2 - 2\xi_2 - 3\nu_2$$

hence

$$0 = n_2(n_1^2 - n_1 - m_1 - 2\xi_1 - 3\nu_1) + n_1(n_2^2 - n_2 - m_2 - 2\xi_2 - 3\nu_2)$$

or

$$n_1 n_2 (n_1 + n_2 - 2) = m_1 n_2 + m_2 n_1 + 2(n_1 \xi_2 + n_2 \xi_1) + 3(n_1 \nu_2 + n_2 \nu_1) \dots (D')$$

combining the formulae (D') and (B) we get the formula (A).

If S_2 is a plane, n_2 becomes equal to unity and m_2 equal to nought, whilst the curve s becomes a plane section and the rank r of s passes into the class of the plane section. So formula (A) gives for that class

$$r = m_1 - 2\sigma - 3\chi,$$

which is indeed the class of a section of S_1 with a plane, having with S_1 in σ points an ordinary contact and in χ points a stationary contact.

5. If S_2 is of the second degree and S_1 of the degree n and of the class m , the formula (A) gives for the rank of the curve of intersection

$$r = 2(m + n) - 2\sigma - 3\chi.$$

If S_2 is a quadratic cone K^2 this formula will be proved directly once more as follows for the sake of verification.

The rank of the curve of intersection s is the number of its tangents meeting an arbitrary right line, e.g. a generator l of K^2 . Each tangent of s , meeting the generator l has three points in common with the cone K^2 , in fact the two consecutive points it has in common with s and its point of intersection with l , unless the latter coincides with the point of contact to s . Each right line having three points in common with K^2 lies entirely on K^2 . The only tangents of s meeting l are thus the generating lines of K^2 which are at the same time tangents of s and the tangents to s at its points of intersection with l . The generator l of K^2 meets S_1 and therefore s too n times; through each of these points of intersection

pass two consecutive tangents of s : Whence already $2n$ tangents of s meeting l .

Tangents of s , being at the same time generating lines of K^2 , pass through the vertex T of K^2 and, being tangents of s , are also tangents of S_1 , and therefore situated on the tangent cone K of S_1 , having T for its vertex. Conversely every common generator of the two cones K^2 and K is a generator of K^2 having with S_1 , thus also with s , two coinciding points in common. A right line having with s two coinciding points in common is either a tangent of s or it passes through a double point of s . So the common generators of the cones K^2 and K are either tangents of s or they pass through double points of s . The order of the tangent cone K , being equal to the class m of S_1 , the number of common generators is $2m$. The number of tangents of s meeting l in the vertex T will be $2m$, diminished by a number still to be determined for the common generators passing through a double point of s .

If K^2 has in a point σ an ordinary contact with S_1 the common tangent plane π in σ is a tangent plane of S_1 passing through T . So π is also a tangent plane to the cone K along the line $T\sigma$. So the two cones K^2 and K have along the common generator $T\sigma$ a common tangent plane. The line $T\sigma$ must therefore count for two common generators of the cones K^2 and K . A point σ is a node of s and with the exception of very particular cases the two tangents of s in σ will not coincide with $T\sigma$. So for every point σ the number of tangents of s passing through T must be diminished by two.

The following example proves that for every point χ in which S_1 and K^2 have a stationary contact, the number of generators of K^2 touching s must be diminished by three. Let S_1 also be a quadratic surface and let the curve of intersection s be a not degenerated biquadratic curve R^4 with a cusp χ . Then the line $T\chi$ counts already at least for two common generators of the cones K^2 and K and is again not a tangent in χ to s or R^4 . If now $T\chi$ were to count only for two common generators the cones K^2 and K would have two more generators in common. These latter two cannot be two consecutive generators, for in that case R^4 would have two double points and so it would have to break up. Now it is easy to see that these two remaining generators are tangents to R^4 or s at points for which the osculating plane is a stationary plane. So R^4 would have to possess two stationary planes α whilst a R^4 with cusp possesses but one stationary plane α^1). The right line $T\chi$ must

¹⁾ E. PASCAL, loc. cit. p. 363.

therefore count for three common generators of K^2 and K . The number of tangents of s meeting the line l , thus the rank of s is consequently

$$r = 2n + 2m - 2\delta - 3\chi.$$

6. The reciprocal polar figure s' of the curve of intersection s of K^2 and S_1 is a developable circumscribed to a conic c^2 and to a surface S' of order m and of class n , whilst the conic c^2 touches δ times the surface S' and osculates it χ times. If we take for the conic c^2 the imaginary circle at infinity the developable s' becomes the developable focal surface of S' . The rank of s' is the same as that of s . So we find the theorem:

The rank of the focal developable of a surface of order m and of class n touching the imaginary circle at infinity δ times and osculating it χ times is

$$r = 2m + 2n - 2\delta - 3\chi.$$

If S_1 is a developable the point of contact of a common tangent plane that is an ordinary plane of S_1 is always a node of s ¹⁾. The developables K^2 and S_1 will only then have a stationary contact in a point χ , when the common tangent plane is a stationary plane a of S_1 . The line $T\chi$ counts thus for four lines of intersection of the cone K^2 with the tangent cone K which breaks up into m planes. It is easy to see that now the line $T\chi$ is at the same time tangent to s at the special cusp χ which is a singularity of order two, of rank unity and of class three²⁾. So a stationary contact χ gives rise to four lines of intersection of K^2 with K of which only one is an ordinary tangent of s lying on K^2 . Each point χ now also diminishes the rank of s by three. The reciprocal polar figure of S_1 is a curve S' of order m and of class n . Each common tangent plane of K^2 and S_1 is transformed in a common point of c^2 and S' . If the common plane is a stationary plane a of S_1 the common point is a cusp on the curve S' . So we find the theorem:

The rank of the focal developable of a plane curve or a twisted curve of the degree m and of the class n and of which δ ordinary points and χ cusps lie on the imaginary circle at infinity is

$$r = 2m + 2n - 2\delta - 3\chi.$$

7. If S'_1 and S'_2 are the reciprocal polar figures of the surfaces S_1 and S_2 , then S'_1 and S'_2 are respectively of the degree m_1 and m_2 and of the class n_1 and n_2 .

1) VERSLUYS, Mémoires de Liège, 3me série t. VI. loc. cit.

2) HALPHEN, Bull. de la Soc. Mat. de France, t. VI, p. 10.

If the surfaces S_1 and S_2 have an ordinary contact in σ points, the common tangent planes in these σ points are ordinary double tangent planes of the developable D circumscribing S_1 and S_2 ¹⁾. The surfaces S'_1 and S'_2 will also have in σ points an ordinary contact.

If the surfaces S_1 and S_2 have in χ points a stationary contact the tangent planes in these χ points are stationary tangent planes of the developable D ²⁾. The surfaces S'_1 and S'_2 have thus also in χ points a stationary contact.

So the rank of the curve of intersection d' of the surfaces S'_1 and S'_2 is according to formula (A), just as the rank of the curve s ,

$$r = m_1 n_2 + m_2 n_1 - 2\sigma - 3\chi.$$

The curve d' being the reciprocal polar figure of the circumscribing developable D , the rank of D is equal to the rank of d' . Whence the theorem:

For two arbitrary algebraic surfaces the rank of the curve of intersection is equal to the rank of the circumscribing developable.

Here we have supposed that the points of contact σ and χ are ordinary points on both surfaces and the tangent planes ordinary tangent planes in these points ³⁾.

1) VERSLUYS, Mém. de Liège. 3^{me} série t. VI. De l'influence d'un contact etc.

2) VERSLUYS, loc. cit.

3) VERSLUYS, loc. cit.

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday June 24, 1905.

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The following papers were read:

Physiology. — “*On the pressure of sound in Corti’s organ*”. By Prof. H. ZWAARDEMAKER.

(Communicated in the meeting of May 27, 1905).

According to the hypothesis of HELMHOLTZ-HENSEN the vibrations of sound, penetrating into the inner ear by way of the stapes, evoke a resonance in the transversely stretched fibres of the membrana basilaris. Strong vibrations are imparted to different fibres according to the pitch; these vibrations being communicated to the sensory epithelia of Corti’s organ and then becoming the stimulus for definite nerve-fibres. We recognise the tone by the nerve-fibres which are affected in this way.

That such short fibres as the transverse fibres of the membrana basilaris can resound to the relatively deep tones of the human scale is explained by HELMHOLTZ 1st by the resistance in the fluid and in the soft cell-masses (CLAUSIUS’ cells); 2nd, by their being loaded with Corti’s arches on which again a whole system of cells rests.

At first it was imagined that the fibre vibrates in its entire length as a freely stretched string. Later attention has been drawn to the fact that the pars arcuata (the part over which the Corti’s arches vault themselves) remains largely at rest while the pars pectinata (the remaining part of the string, not covered by the arches) makes the greatest excursions. But then the difference in length of the fibres is no longer sufficient to explain the difference in the pitch for which they are tuned, so that also a difference in tension and in load must be assumed. ¹⁾ Examining the proportions of microscopical preparations and bearing in mind that the arches are more or less rigid formations, one is soon convinced that the pars arcuata cannot possibly resound to the deep tones of the audible scale. It is not the bottom cells on their upper face that are an impediment to this, but the large vein on their lower surface. Moreover the transverse fibrous structure, which is so distinct in the pars pectinata is entirely absent in the pars arcuata. The property of resounding may on sufficient grounds be attributed to the stretched and loaded fibres of the pars pectinata only.

I have tried, as far as this is possible, to reproduce in a model the conditions prevailing in Corti’s organ. A horizontal steel string, $\frac{1}{2}$ millimetre thick and somewhat longer than a metre, represents a transversely stretched fibre of the membrana basilaris. On this rests, at one of the ends, a wooden imitation of Corti’s arches. The

¹⁾ A. A. GRAY, Journal of anat. and physiol. 1900, Vol. 34, p. 324.

other end is fastened, transversely to the direction of vibration, to the vibrating prong of an electrically driven tuning fork. Now, when the Corti's arches are sufficiently loaded (with sponges, or, for demonstrations, with a hollowed little board on which a drawing has been stuck), the tension of the string being at the same time regulated by means of a micrometer screw, it is possible to cause the system to resound to the tuning fork so that with small deflections of the fork the deflections of the *pars pectinata* become very large.

In the experiments for study proper, it deserves recommendation to attach pins to the wooden Corti's arches, on which smaller and larger sponges can be stuck in various positions. As long as the sponges are dry the whole system partakes in the vibrations. But when water is dropped on them, which is sucked in by the sponges and makes them heavier, the damping system is brought to rest and a node is formed at the base of the outer pillar. The string can be prevented from sinking down too much, by attaching the fixed extremity of the Corti's arch to a spring, which keeps it up. The free extremity of the arch is placed loose on the string. Sometimes it is a little difficult to obtain only vertical movements of the string, but by moving the fixed point of support of the string forward or backward, one always succeeds in this.

We find then :

1. broad deflections of the *pars pectinata*.
2. immovability of the *pars arcuata*.
3. immovability of the Corti's arches.
4. immovability of the loading mass.

This immovability is not absolute, of course ; on the contrary, the floor, the table, everything in the room vibrates under the influence of the tuning fork, but the movements are infinitely small compared with the excursions of the *pars pectinata* and are so insignificant, moreover, that a photograph of the parts, called immovable, shows absolutely sharp definition. On the same photograph the *pars pectinata* is seen in the extreme positions, which it reaches with broad amplitude.

The conditions of the model have purposely been so chosen that they correspond in general outlines to the conditions actually found in Corti's organ. A complete imitation is impossible, but within the limits of technical practicability we have reached here, without any preconceived opinion, what can be achieved with the ordinary means of the laboratory. Now if we may see in the described model a more or less happy imitation of reality and to this assumption we are especially entitled by the manner of loading, then it follows that

also in the organ itself as well the Corti's arches as the loading cells remain at rest. But then we must drop all the ideas, which have been broadly developed during a long time, about the impact of the ciliae of the hair-cells on the membrana tectoria, on the bending of the ciliae, etc. Rest prevails in the system of arches and a covibration of them is necessarily excluded.

Yet the imparting of stimuli, which was supposed to be explained by the co-vibration of the hairs, need not remain a mystery, if attention be paid to the effect of sound-pressure.

In a paper, entitled "the pressure of vibrations", Lord RAYLEIGH ¹⁾ has treated a simple case, which is nearly identical with ours. It is the case of a string, itself infinite, but vibrating between two rings, one fixed, the other sliding. When the string vibrates the sliding ring is pressed outward, towards the extremity, with an average force $F = \frac{E}{l}$; E being the energy of the vibration, l the length of the string.

The base of the outer pillar is in the case of the sliding ring. According to RETZIUS the pillar is one with the semi-solid cell-mass of the bottom-cell; from this cell it would originate and form a whole with it. In this way at the same time an attachment and a small movability in the cell-mass have been obtained.

But the pillar is not only in juxtaposition with the fibre, but also presses on it by the inertia of the large cell-masses with which it is connected, as soon as the fibre begins to execute movements. Hence the vibrating fibre will in this place present a node and the load itself will necessarily have a great influence on the conditions of tension during the vibration.

So the pillar has a double function: 1. that of the movable ring of RAYLEIGH, 2. that of carrier of the inertia of a damping and loading mass. In its first quality it receives a pressure in the direction of the modiolus, a pressure which can be perfectly measured by RAYLEIGH's formula.

In the model this pressure can even be demonstrated. For this purpose the pillars were removed and the base of the outer pillar, which imparts a node to the string, was replaced by a brass lamella, provided with a slit. The split lamella grips the string like a miniature fork. In this way the node is preserved. As the lamella is 19,5 cm. long and 0,1 cm. thick, it possesses a certain mass, which does not press on the string since the lamella is placed normally to it, but gives a distinct damping as soon as the string vibrates.

¹⁾ Lord RAYLEIGH, *Philosoph. Magazine* (6) III. 1902, p. 339.

Besides, at its place of attachment the lamella has been made considerably thinner (thickness 0,02 cm.) and consequently flexible over a length of 6 centimetres. The result is that the lamella, although accurately placed in the node of the vibrating string, will slightly deviate outward as soon as the excursions have become large enough. The force by which the little fork is driven outward is undoubtedly extremely small. Accordingly the deviation did not exceed 3 mm. with a semi-amplitude of the string of 0,4 cm. The new position can easily be fixed photographically and be compared with the position of rest which is assumed as soon as the string stops vibrating. This renders it possible to measure the force. But from a physiological point of view it has no meaning to perform the actual measurement on the model although it would be important if it could be performed under the actual conditions, *for this pressure must be the immediate cause of hearing*. This will be easily perceived with respect to the sensory elements at the modiulus side of the pillars.

The pressure of sound acting at the base of these outer pillars is in the direction of the string and hence of the modiulus. It has a component in the direction of the pillar itself. Through this the outer pillar, the upper end of which presses loosely against the capitulum of the inner pillar, is displaced parallel to itself and the cells at the modiulus side of the system must necessarily be compressed, although slightly. The pressure which they experience is either entirely continuous or periodically feebly variable. Beginning at the foot of the pillar the pressure varies from a maximum at the extreme deflection of the string to zero in the position of equilibrium. Higher up in the system these differences will probably for the greater part have disappeared, though they may remain to some extent. The pressure, however, is at all times positive; it never becomes negative, as would be the case if the Corti's arches and the loading cells followed the vibrations of the string. Since they are at rest, the pressure met with in the sensory cells at the modiulus side of the inner pillar must always act in the same sense, which is in the direction of the modiulus. It is quite possible that also the hairs of the hair-cells experience its influence, the effect of which will also be in one direction.

The matter is somewhat less simple for the sensory elements situated at the inner side of the outer pillar. These appear to me to experience no pressure at all from the outer pillar, which is retained in the soft cell-mass of the bottom cell. On the other hand such a pressure is present from the side of HENSEN's cells and also to some extent from the side of the supporting cells.

We are at liberty to consider this cell-group, situated at the exterior

of the directly sensory elements, also as a RAYLEIGH ring. We shall have to try this the sooner, since in birds the pillars are absent and so we cannot regard these formations as essential. If we try again to find in Corti's organ an analogon of RAYLEIGH's movable ring, and in abstracto it is always admissible to seek such an analogy, we may never restrict ourselves to the arches alone. For by doing this we should deny the essential meaning of analogy for the physiology of hearing.

So HENSEN's cells may also be regarded as a movable RAYLEIGH ring. They also rest with a relatively narrow foot on the fibres of the membrana basilaris, near the foot of the pillar, when the human organ of hearing is studied. They will also exert a damping and loading influence on the vibrating fibres by their inertia. They will also cause a relative node and be shifted laterally, in the direction of the modiolus, by the vibration. But if this is the case they also squeeze the sensory elements situated between them and the pillar¹).

Beside this lateral pressure, experienced by the cells themselves, it is not entirely impossible that also the hairs experience a pressure which they now receive through the agency of the lamina reticularis, which forms a whole with the capitula of the pillars. This pressure will then press them against the membrana tectoria with a somewhat varying force, but which is always in the positive direction.

All these reasonings can be simpler for the ear of birds than for that of man. The pillars are there absent and only the sensory elements and the supporting cells are found. Also this whole lies laterally on the fibres of the membrana basilaris and must experience a lateral pressure of sound.

The here developed conception, which deviates from the current one, has the important advantage that it reduces hearing to the perception of a pressure. The mechanical action of the vibration, which in the old form of the theory of HELMHOLTZ-HENSEN is vibratory, intermittently positive and negative, now becomes a permanent pressure of somewhat varying strength, to be sure, but at all times in the same direction, always positive. Hearing becomes the exact analogon of touching and all experience gathered for this latter sense we may try to find again *mutatis mutandis*, in the physiology of hearing.

Also small secondary advantages are gained by the new conception.

In the first place the simple juxtaposition of the heads of the

¹) For points inward of the node it can be shown in an elementary way that the masses there present and situated unilaterally, continually experience impulses having a permanent component in the direction of the node.

pillars (showing no joint like the auditory bones) finds an explanation. For a pressure which is always positive this is sufficient, not for a vibration. In the second place it explains the varying shapes and aspects presented by the membrana basilaris in the preparations. These are very obscure when they concern an integrating part of the organ, but are explained very easily if what we see in the preparations, is only a coagulated colloid or elastic mass.

Finally our conception is by no means bound to the theory of HELMHOLTZ-HENSEN. It is also acceptable to those who would exchange this theory for that of EWALD. For Lord RAYLEIGH treats in his paper also the case of a vibrating membrane: "but a membrane with a flexible and extensible boundary capable of slipping along the surface, provides for two dimensions. If the vibrations be equally distributed in the plane, the force outward per unit length of contour will be measured by one-half of the superficial density of the total energy".

So the theory of the pressure of sound might also be applied to a membrane such as is imagined by J. R. EWALD. But his membrane does not answer the conditions mentioned by RAYLEIGH, so that the quantitative relations are not so easily perceived as in the above developed case.

Finally, concerning the modern theories of hearing which I would call the pulsatory ones, since they only take into account the bulgings of the membrana basilaris, caused by the piston movement of the stapes, the hypothesis of the pressure of sound cannot be applied. For these theories purposely neglect the vibratory movements of the smallest parts and only take into account the mass-result. If however we lose sight of what is the essential thing in a vibration, we also lose the right of applying the properties of a vibration. In my opinion there can then be no question of pressure of sound.

The reader will have perceived that the starting-point of our reasoning was the probability of the fact that the arcuate zone and the arches vaulting over it remain perfectly at rest. On anatomical grounds this is very probable. Should it appear later that this rest is not absolute but only relative, the preceding reasoning is none the less valid.

Only one objection could then be raised, namely the small amount of the pressure of sound. This would then have to be placed against another small value, that of the possible movement of the hair-cells. Hence the question would be a quantitative one. But also in this case the two forces, the pressing force and the thrusting force, would by no means preclude each other. They would both have to be present. For the present we prefer, by assuming immovability, to neglect the thrusting force and only to retain the pressing force.

Chemistry. — “*The solubilities of the isomeric chromic chlorides*”.

By Prof. H. W. BAKHUIS ROOZEBOOM and J. OLIE Jr.

(Communicated in the meeting of May 27, 1905).

At the December meeting 1903, a communication was made by BAKHUIS ROOZEBOOM and ATEN as to the changes in form which may occur in the solubility-lines of binary mixtures in dependence on the quantities of the molecules of a compound which may be formed from the components in the liquid mixtures. This subject is only a part of a more extensive problem embracing the equilibria of phases in systems composed of three kinds of bodies between which a transformation is possible in liquid (or vapour). If that transformation takes place with greater velocity than the setting in of the equilibria of phases, the system will appear externally as a binary one, although it is in reality ternary, and in order to explain the course of the equilibria of phases we must take into account that ternary nature.

In those cases where the third kind of molecules consists of a combination of the two others no instance has, as yet, been noticed where a correct view could be formed with certainty as to the inner composition of the liquid phase.

We, however, came across an example where this is quite possible, namely in a case where two isomeric substances may be converted into each other by dissolving in a third substance. Similar cases may frequently occur with all kinds of organic isomers; but apart from the fact that their behaviour has been little investigated from the point of view of the equilibria of phases we often lack the means to determine the two kinds in solution. That possibility, however, presented itself with the isomeric chromic chlorides, which not only may be determined in each others' presence, but also require when in solution much more time to reach an equilibrium than is necessary to reach the equilibrium between solid matter and solution. This rendered it also possible to study the change of the solubility as a function of the progressive transformation in the solution. Finally, this research could also serve to elucidate the cause of the stability or instability of the isomers, and the most rational method of preparing the same from the solution.

It has long been known that all kinds of salts of trivalent chromium when in solution undergo molecular transformations depending on temperature and concentration which are shown by the change in colour of the solutions, which may vary from green to violet. Only of late this matter has been better understood when various

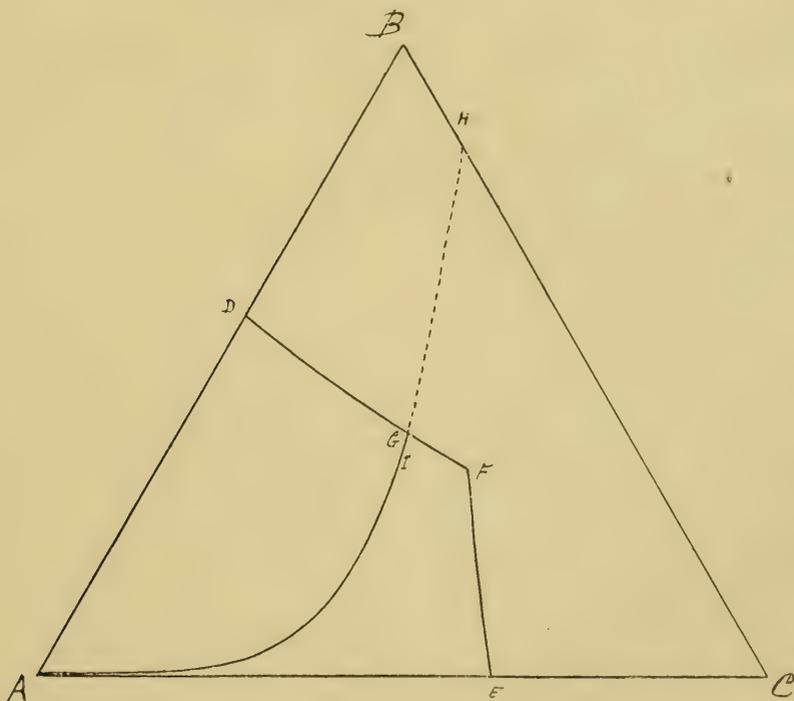
modifications of the same salt were successfully isolated in a solid condition.

In the case of chromic chloride two compounds were found to exist at the ordinary temperature with 6 H₂O. In connection with his theory on complex compounds, WERNER proposed the following structural formulae:



The first salt is violet, the second one green. In the first salt the three chlorine atoms should be capable of ionisation; in the latter only one. If only these are precipitable by silver solutions¹⁾ the amount of each salt in a mixed solution may thus be quantitatively determined.

First of all measurements were made at 25° as to the velocity of the transformation of solutions with different contents of chromic chloride and as to the final condition which they attain.



The result of these last investigations is indicated in the Figure by the line *AGH*.

In this figure *A* stands for the solvent H₂O, *B* for the green

¹⁾ We found this not to be absolutely correct but the precipitable chlorine could in any case be used as a measure for the two salts.

and C for the violet chromic chloride. Both are taken in the calculation as hydrates with $6\text{H}_2\text{O}$ so that the sum of H_2O and the two hydrates is always taken as 100 (percentage by weight).

The line AGH first runs close to the axis AC . This means that in weak solutions a final condition is reached in which the chromic chloride occurs nearly exclusively in the violet modification.

Strictly speaking this means in the condition in which the violet chromic chloride finds itself the moment it has dissolved. Briefly, we will call this the violet condition. If, therefore, we make a solution of the green chloride of the same concentration the green chloride will be almost completely changed into the violet salt. This process proceeds slowly enough to admit of its course being studied, also to show that both green and violet lead to the same final condition.

If the amount of hydrated chromic chloride exceeds 20% the line $AI G$ begins to run perceptibly upwards and consequently the final condition in the solution shifts more and more towards green.

In the point I the final equilibrium is situated near an equal amount of green and violet. This corresponds with a total of 65% of chloride¹⁾ of which 32.5% is green and 32.5% violet.

It will be noticed that we cannot go further than G because the solution there reaches its saturation. If crystallisation did not take place the prolongation of the line $AI G$ could be determined. If this may be represented by GH , the terminal point H would indicate the amount of green and of violet chloride in liquid hydrate of chromic chloride (without excess of water); this point would therefore lie at about 15% violet and 85% green. Its determination is however impossible as the green hydrate melts at 83° and the violet one at 92° . Although the melted hydrates crystallise very slowly still it is difficult to keep them liquid down to 25° .

The final condition of solutions of different concentrations thus being known, the solubility of the two-hydrates at 25° was studied. The saturation was very soon accomplished, D and E represent the concentrations of freshly prepared saturated solutions of green and violet chloride.

These, however, soon undergo a modification. In the green solution violet chloride is formed and conversely. This causes a change in the solubility which runs along the lines DI' and EI' respectively. These show that the total solubility of both green and violet increases as the transformation of green into violet or the reverse proceeds in the solution.

¹⁾ This total amount may be read off on AC or AB if we draw from I a line parallel with BC .

The solutions of the green chloride do not however run further than G , where the solution saturated with green also attains the inner composition corresponding with the equilibrium at the total concentration. Solutions on GF could only be made by rapidly dissolving a mixture of green and violet in the desired proportion and then introducing some solid green chloride. These solutions would then, however, recede towards G as the point of final equilibrium of the liquid saturated with green chloride.

The solutions saturated with violet chlorid run along the line EF . The solution F might be at the same time in equilibrium with green chloride, but as soon as this occurred the violet would be completely converted into the green and then the solution containing the green would again shift to G as a terminal point.

As the line of equilibrium AGH intersects the solubility line for the green but not that for the violet chlorid, the latter cannot be definitely in equilibrium at 25° with any solution, consequently at this temperature the green chloride is the only stable one. Even outside the solution the violet changes, therefore, after a lapse of time, into the green; in contact with the solution this takes place more rapidly. This is the reason why the line EF cannot always be followed up.

The question now arises how it is possible to separate violet chloride in the solid condition. This is done by leading gaseous HCl into solutions containing at most 30% of green chloride and which have been recently heated to 100° .

Addition of HCl at 25° diminishes in a high degree the solubility of both chlorides.

The two lines DF and EF are shifted towards the left about parallel to their original positions and about to the same extent. It will be easily seen that the point of intersection G will also move towards the left and might finally arrive in the liquid region to the left of the equilibrium line. In that case this line would no longer intersect DF but EF ; a saturated solution of violet chloride would then be in inner equilibrium and the violet chloride could be separated in a stable condition.

This, however, is not the case, because the line AG also moves strongly towards the left on addition of HCl and consequently the equilibrium in the solution shifts towards the green side. The investigation showed that the violet chloride is still metastable in contact with the solutions rich in HCl; the point of intersection F therefore remains, obviously, to the right of AG even on addition of HCl.

If, however, we heat to 100° before leading HCl, the line AG moves very considerably towards the violet side so that it now

intersects the solubility isotherm of the violet chloride at 25°. The receding of the solutions towards the green, on cooling, now proceeds with sufficient slowness to enable us to precipitate the violet chloride at 25° by means of a current of HCl, which diminishes its solubility.

Chemistry. — “*Nitration of symmetric nitrometaxylene.*” By Dr. J. J. BLANKSMA. (Communicated by Prof. A. F. HOLLEMAN).

(Communicated in the meeting of May 27, 1905).

If symmetric dinitrophenol or symmetric dinitromethylaniline is treated with mixed nitric and sulphuric acids, pentanitrophenol or pentanitrophenyl-methylnitramine is formed ¹⁾. Consequently the presence of the two nitro-groups, which are in the *meta*-position with regard to the OH or NHCH₃ group does not prevent the introduction of another three nitro-groups in the *para*-position and *ortho*-positions in the benzene core. Symmetric dinitroanisol and phenetol yield, however, on nitration tetranitroanisol or tetranitrophenetol ²⁾; the hydrogen atom in the *para*-position with regard to the oxyalkyl group is not replaced by NO₂ here. As the methyl group on substitution in the benzene core behaves in some respects analogous to the OH and NH₂ (or NH CH₃) groups it seemed of importance to investigate the conduct of symmetric dinitrotoluene on nitration in order to ascertain what influence is exercised here by the NO₂-groups in the *meta* position.

The symmetric dinitrotoluene was, therefore, heated with mixed nitric and sulphuric acid for two hours on the waterbath; the substance had not, however, undergone any change. The presence of the nitro-groups in the *meta*-position with regard to the CH₃ group consequently prevents the further introduction of nitro-groups in the positions 2, 4 and 6. If, however, one of the NO₂-groups in symmetric dinitrotoluene is replaced by bromine, this substance may be successfully nitrated. Symmetric bromonitrotoluene yields on treatment with mixed nitric and sulphuric acids three isomeric trinitrobromotoluenes which it is, however, difficult to isolate.

The question now arose what result is obtained when one of the NO₂-groups of symmetric dinitrotoluene is replaced by CH₃, in other words what is the behaviour of symmetric nitro-*m*-xylene on nitration? For it is known that *m*-xylene readily yields 2-4-6-trinitro-

¹⁾ Recueil **21**, 254.

²⁾ „ **23**, 111; **24**, 40.

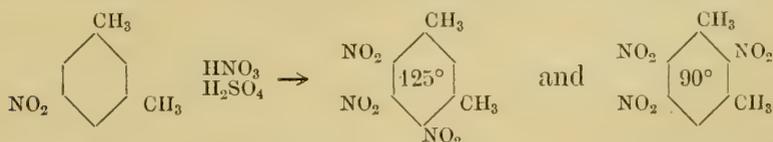
m-xylene. As in the symmetric nitro-m-xylene the NO_2 -group is placed in the meta-position with regard to the CH_3 -groups it did not seem impossible that this NO_2 -group (like the NO_2 -groups in symmetric dinitrophenol and symmetric dinitromethylaniline) would not prevent the further introduction of the NO_2 -groups in the positions 2, 4 and 6, so that we ought to arrive at tetranitro-m-xylene. On the other hand the nitration of m-nitrotoluene ¹⁾ and symmetric dinitrotoluene gave reason for believing that not four but at most three nitro-groups would be introduced.

The symmetric nitrometaxylene was prepared according to WROBLEWSKI'S directions ²⁾.

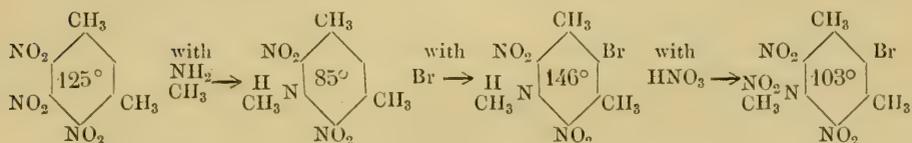
Two grams of this substance were treated for twenty minutes on the waterbath with mixed nitric and sulphuric acids; on cooling, long colorless needles were deposited. These were collected at the pump on glasswool and recrystallised from alcohol when long, colorless needles or rods were obtained, m. p. 125° .

The motherliquor of the acid solution was poured into water which caused a white flocculent precipitate. By recrystallising the product from alcohol fine four-sided crystals mixed with a few needles were obtained; the crystals melted at 90° and the needles at 125° . These crystals could be separated by recrystallisation from alcohol. From 2 grams of 5-nitro-m-xylene were obtained about 2 grams of the product melting at 125° and 0.5 gram of the product melting at 90° . The analysis showed that both substances had the composition of trinitroxylene.

In the trinitro-m-xylene (m. p. 182°) prepared by nitration of m-xylene the nitro-groups occupy the positions 2, 4 and 6. We had, therefore obtained the two as yet unknown trinitro-m-xylenes.

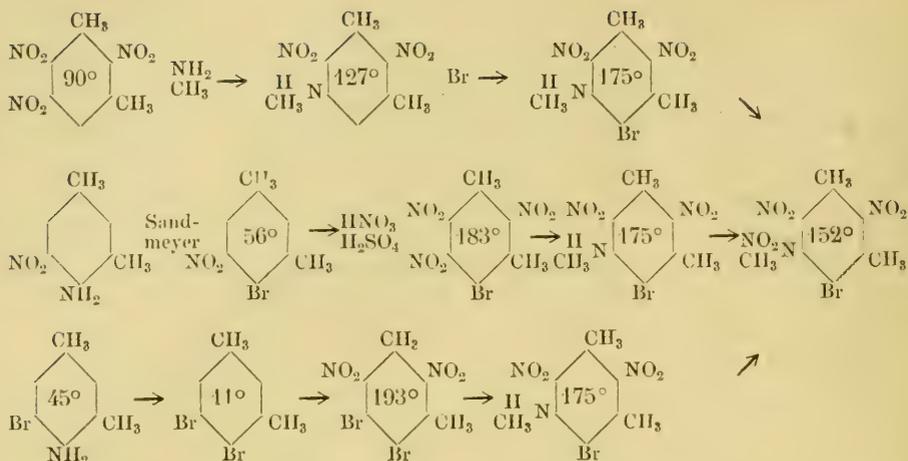


The constitution was determined according to the subjoined scheme.



¹⁾ HEPP. Ann. **215**. 366.

²⁾ Recently, WILLGERODT (Ber. **38**. 1473) has described more fully the preparation of symmetric nitro-m-xylene. I had then already made this preparation according to WROBLEWSKI'S directions. (Ann. der Chem. **207**. 94).

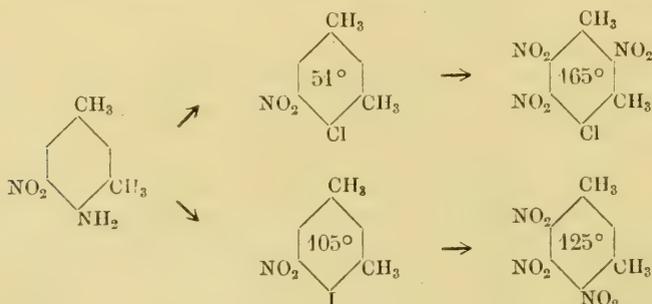


We therefore see that the substance melting at 90° is 2-5-6-trinitro-m-xylene; the compound melting at 125° must therefore be 4-5-6-trinitro-m-xylene.

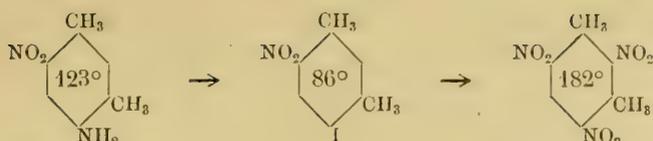
Both trinitroxylens contain a moveable NO₂-group; in the compound m.p. 90° the NO₂-group 5 is under the influence of an ortho- and a para-placed NO₂-group, whilst in the compound melting at 125°, the NO₂-group 5 stands between two ortho-placed groups. By the action of alcoholic ammonia or methylamine these groups are readily substituted by NH₂ or NHCH₃.

Of special interest is also the formation of 4-5-6-trinitro-m-xylene from 4-iodo-5-nitro-m-xylene.

While 4-bromo-5-nitro-m-xylene (see above scheme) and 4-chloro-5-nitro-m-xylene readily yield trinitrochloro(bromo)metaxylylene on treatment with a mixture of nitric acid (sp. gr. 1.52) and sulphuric acid, 4-iodo-5-nitro-m-xylene yields 4-5-6-trinitroxylene with elimination of the iodine atom from the benzene core:

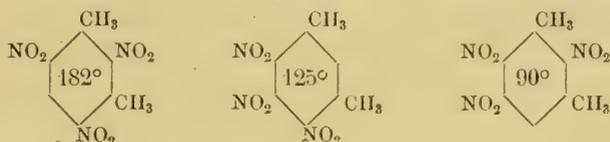


After this had been observed, the 4-iodo-6-nitro-m-xylene was also nitrated. Here the iodine atom was also replaced by NO₂ and 2-4-6-trinitro-m-xylene was formed m.p. 182°.



4-chloro(bromo)6-nitro-m.xylene yields, however, on subsequent nitration 4-chloro(bromo)2-6-dinitro-m.xylene¹⁾. This made two cases in which an iodine atom was replaced by a NO₂-group whilst it was shown at the same time that Br and Cl were not displaced by the NO₂-group under the same circumstances²⁾.

If we compare the melting points of the three trinitro-m-xylenes



we notice that these are situated the higher the more symmetrical the position of the nitro-groups in the core is; this consequently agrees with the rule that the melting point of isomeric substances is generally the more elevated the more symmetrically constructed the molecule is.

It was also found that the higher the melting point of the three isomers is situated the less their solubility in alcohol becomes³⁾.

Dr. JAEGER was kind enough to examine the crystals of the three trinitro-compounds and communicated to me his results.

2-5-6-Trinitro-1-3-xylene $t = 90^\circ$ crystallised from alcohol.

Triclinic pinacoidal. $a : b : c = 2.8359 : 1 : 0.8510$ with $A = 117^\circ.2\frac{1}{2}'$. $B = 114^\circ.38'$ $C = 120^\circ.22'$; $\alpha = 100^\circ.54'$ $\beta = 106^\circ.59'$ $\gamma = 117^\circ.51\frac{1}{2}'$.

Forms: $a = \{100\}$, $b = \{010\}$, $p = \{1\bar{1}0\}$ all very lustrous; $c = \{001\}$, striped parallel ($c : a$); $r = \{101\}$, $s = \{30\bar{1}\}$, $t = \{20\bar{1}\}$; finally $o = \{1\bar{1}1\}$ very narrow and dull.

4-5-6-Trinitro-1-3-xylene $t = 125^\circ$ crystallised from alcohol.

Monoklino prismatic. $a : b : c = 0.5950 : 1 : 0.2706$ with $\beta = 88^\circ.11'$. Large long-prismatic crystals. Forms $b = \{010\}$ broad; $m = \{110\}$ also; $a = \{100\}$ narrow; $c = \{001\}$ large; $r = \{101\}$ well developed $o = \{110\}$ very narrow. Cleaves well towards r .

2-4-6-Trinitro-1-3-xylene. $t = 182^\circ$ crystallised from benzene + alcohol. Large thick prismatic very lustrous crystals; well built.

Rhombic-bipyramidal. $a : b : c = 0.6587 : 1 : 0.5045$. Forms $a = \{100\}$,

1) Ber. 24. 2012.

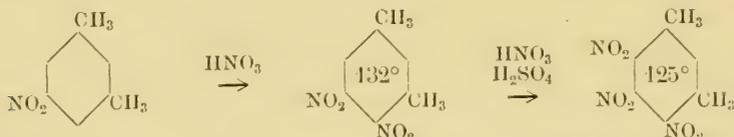
2) Many cases where COOH, SO₃H, I etc. is replaced by Br and this in turn by Cl or NO₂ have been described or referred to previously. Rec. 21, 283, 336. 23, 207.

3) Compare CARNELLEY and THOMSON, Journ. Chem. Soc. 53, 782. LOBRY DE BRUYN, Rec. 13. 116.

$m = \{110\}$, $b = \{010\}$ broad and lustrous; $o = \{122\}$ large; $r = \{102\}$ narrower; $q = \{012\}$ small very completely cleavable towards b , fairly so towards a . Optical axial plane is $\{001\}$; First diagonal is the a -axis. Faint dispersion, apparent axial angle in α monobromonaphthaline about 70° .

Dr. JAEGER intends publishing a more detailed examination later on.

If symmetric nitro-m-xylene is allowed to remain in contact for some time at the ordinary temperature with nitric acid of sp. gr. 1.52, the 4-5-dinitro-product is formed¹⁾. If the solution is poured into water a white flocculent precipitate is formed, which when recrystallised from alcohol yields fine, colorless needles m.p. 132° . As this substance on subsequent nitration with HNO_3 and H_2SO_4 yields chiefly trinitroxylene m.p. 125° the NO_2 -group must have been introduced into the position 4, for, if it had been introduced into position 2 the subsequent nitration would have formed exclusively trinitroxylene m.p. 90° .



An effort to prepare tetranitro-m-xylene from 4-5-6-trinitro-m-xylene ended in failure. The trinitro-xylene was treated at 150° with HNO_3 (sp. gr. 1.52) and H_2SO_4 . The substance was to a large extent destroyed but a small crop of colorless crystals was obtained m. p. 190° . These crystals were readily soluble in alcohol or warm water; the solutions had a strongly acid reaction so that probably one of the CH_3 groups was oxidised to COOH . Tetranitro-m-xylene which ought to have readily yielded trinitro-s.xylidine²⁾ on treatment with alcoholic ammonia was not found.

As the compound described by DROSSBACH³⁾ as trinitro-o-xylene has been found by NÖLTING⁴⁾ to be an impure trinitro-m-xylene, four of the possible six trinitro-xylenes (o. m. and p.) are now known, namely, the three trinitro-m-xylenes and also trinitro-p-xylene.

Summary. Symmetric nitro-m-xylene yields on treatment with nitric acid 4-5-dinitro-m-xylene; on nitration with HNO_3 (sp. gr. 1.52) and H_2SO_4 two isomeric trinitro-m-xylenes are formed being chiefly the 4-5-6-trinitro-1-3-xylene m. p. 125° besides a smaller quantity of 2-5-6-trinitro-1-3-xylene m. p. 90° .

Amsterdam, May 1905.

1) A perceptible amount of 2-5-dinitro-m-xylene was not found.

2) Ber. 28. 2047. Rec. 21. 329.

3) Ber. 19. 2519.

4) Ber. 35. 634.

Physics. — Communication N° 94^b I and II from the physical laboratory at Leiden by Prof. H. KAMERLINGH ONNES.

(Communicated in the meeting of May 27, 1905).

I. *Improvement to the open mercury manometer of reduced height with transference of pressure by means of compressed gas.*

In Comm. N° 44, Oct. '98, § 6, is described how the steel capillary tubes q were cemented on to the glass tubes m (see figs. 1 and 4 of the plate belonging to Comm. N° 44, of which the part that has been modified is reproduced here as fig. 2 of the annexed plate). It was also remarked that from time to time these connections became defective (they slipped off when soft cement was used, or leaked when hard cement was used), and that therefore we were trying to find a better method of connecting. Since that time we have succeeded in finding a way to make perfectly trustworthy joints. For the usefulness of the manometer this is of great importance.

Fig. 1 shows the connection as made now. It is based on the method of CAILLETET to solder glass on to metal, which method has been mentioned in Comm. N° 27, II, June '96, for similar purposes and as appears from Comms. N° 85, June '03, and N° 89, Nov. '03, has stood the proof in several cases where it was applied. The steel capillary q_{10} reaches as high as q_{11} in the glass tube b_1 , which has a wider part b_{11} , containing mercury which is separated from the junctures of b_{10} and p_1 by a layer of marine glue b_{13} in b_{10} . Following the above mentioned method, the end of b_{10} has been platinised, then coppered galvanically and soldered on to p_1 .

This connection has quite answered the expectations. With the former method when the manometer was put under pressure it sometimes appeared that minute cracks had come in the sealing wax, through which the compressed gas which transfers the pressure from one manometer column to the other escaped. In case it escaped rapidly, the mercury of one manometer tube flew into the other before the pressure could be removed and within a few moments the apparatus was defect and wanted a thorough rearrangement to become again fit for use. This has never occurred with the new connections, and yet they have been used for a long time. If a tiny opening should have remained in the marine glue, the mercury has first to pass through it and a mercury drop at p gives warning. Then the manometer can be freed in time from pressure and when the leak of the single tube is repaired it may be immediately used again.

Formerly the escape of the gas which transfers the pressure on the mercury with the above mentioned consequences was to be feared at the connecting pieces of the steel capillaries q with the cocks K and the \perp -pieces T (cf. fig. 1, Comm. N^o 44). This was especially dangerous as the place where it happened was often detected too late. As packing between the flat steel surfaces of the joints for cocks, flanged tubes, and \perp -pieces, we use now only a single sheet of parchment paper. Leaks rarely occur. Moreover in the new arrangement care is taken that each place where gas might escape is kept under vaselin oil, so that even the smallest leak betrays itself immediately by a gasbulb raising in the oil.

In order to attain this the mounting of T and K is modified as shown on the annexed plate. Fig. 2 is a part taken from the plate of Comm. N^o. 44 (front elevation). Fig. 3 is a top view of this part from a section $\zeta\zeta$. Figs. 4, 5 and 6 next to it show the present arrangement in front elevation, section, and top view. The drawings do not require much explanation. H_k is a wooden case (tinlined and protected from action of mercury by parchment paper), in which are placed the tube H (vide Comm. N^o. 44) with all the cocks K and the \perp -pieces T connected with it. (K_{10} is a loose key on the cock-needle, H_k is a tap; the contents of the case is about 0.8 hectoliter).

II. *Improvement in the transference of pressure by compressed gas especially for the determination of isothermals.*

The advantages of the transference of pressure from the experimental apparatus to the measuring apparatus by means of compressed gas caused this method to be repeatedly used for experiments at Leiden. The drawback of it is, however, that much care is required to make connections which are perfectly tight and that it is a very elaborate work to seek for leaks, especially when there are a great number of connections. It may happen that a whole series of experiments loses its value when the existence of a leak is not immediately detected. For some time, therefore, we have arranged those connections where the escape of gas is to be feared, (as explained in part I of this paper for the open manometer) so that they can be covered with vaselin oil and yet are easily reached. It has appeared that with the arrangements based upon this principle we can work so much more securely and rapidly that it more than balances the small complication which sometimes arises when we carry out the principle.

As an elucidation we have represented in fig. 7 of the annexed

H. KAMERLINGH ONNES. I. Improvement to the open mercury manometer of reduced height with transference of pressure by means of compressed gas.
 II. Improvement in the transference of pressure by compressed gas especially for the determination of isothermals.

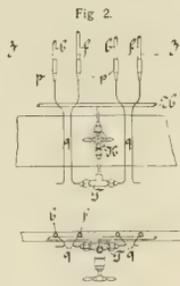
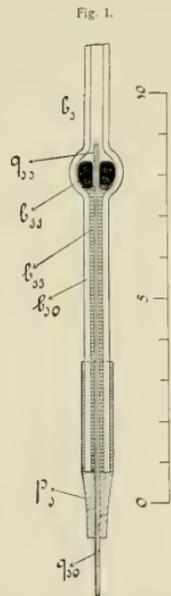


Fig. 3.

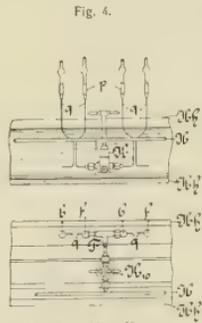
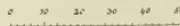


Fig. 5.

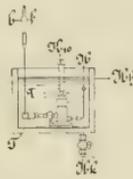


Fig. 6.

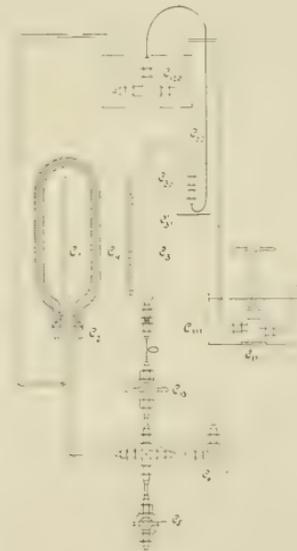


plate the way in which of late we have made the connections for the compression tube for piezometer determinations.

If we compare this figure with plate I, fig. 1, of Comm. N^o. 84, March '03, where the same parts are designated with the same letters, and also with the description of it given in Comm. N^o. 84, then no further explanation is required. The upper end of the level glass C'_3 is bent in order to immerse C'_{31} in the oil vessel C'_{33} . The cocks and connections which are not kept under oil, as for instance C_5 , are those where a leak must show itself by the outflow of mercury.

Physics. — Communication N^o. 94^c from the Physical Laboratory at Leiden by Prof. H. KAMERLING ONNES. "*Methods and apparatus used in the cryogenic laboratory. VII. A modified cryostat.*"

(Communicated in the Meeting of May 27, 1905)

§ 1. In several Communications I have described cryostats based on the use of baths of liquefied gas evaporating at ordinary or lower pressure. For those cryostats where, as described in Comm. N^o. 14, Dec. '94, I succeeded in maintaining during any desired time a bath of $\frac{1}{4}$ to $\frac{1}{2}$ liter of liquid oxygen for measurements at a constant low temperature by means of a circulation, no vacuum glass at all was used. The whole method had been worked out before DEWAR'S investigations showed that the vacuum glasses were fit above all for storing liquid gases.

Nor were any vacuum glasses used in the improved cryostats of large dimensions described in Comms. N^o. 51, Sept. '99, and N^o. 83, Feb. '03. When we started the measurements for which these cryostats were used, we could only obtain sufficiently trustworthy vacuum glasses which were blown to fit exactly when we were satisfied with small dimensions.

Since, however, excellent vacuum glasses which are also of large dimensions are made to fit, especially by R. BURGER at Berlin, it will be possible in many cases to find vacuum glasses of the proper size and the just mentioned methods of arranging will be especially reserved for those cases where we want vertical walls of plane parallel glass, or when the bath must be of excessively large dimensions¹⁾.

In Comm. N^o. 83 III § 6 we have already described a cryostat of small dimensions constructed by means of a vacuum glass. The

¹⁾ Comp. the end of VIII of this Series of Communications.

annexed plate shows such a cryostat in a vacuum glass of much larger dimensions (9 c.m. internal diameter) which during some years has satisfied high requirements.

The apparatus has served for measurements ¹⁾ with a differential thermometer of which one reservoir was filled with hydrogen the other with nitrogen, for a comparison of a thermoelement with the hydrogen thermometer (cf. Comm. N^o. 89) and for measurements on the isothermals of diatomic gases (cf. Comm. N^o. 69, April '01 and N^o. 98, April '02). If the plate is compared with Comm. N^o. 83 no much further explanation is wanted. The same letters designate the same parts. The connections of the cryostat with the regulating apparatus for *constant* temperature are the same as on Pls. I, V and VI of Comm. N^o. 83. The stirring apparatus to obtain a *uniform* temperature is moved by an electromotor as is the case with the cryostat represented there. During the measurements with the differential thermometer the temperature was regulated according to the indications of a thermoelement Θ (which is described in detail in Comm. N^o. 89 published lately). In the comparison of the thermoelement Θ with the hydrogen thermometer one of the thermometerreservoirs on the annexed plate was replaced by a resistance thermometer (double cylinder according to Comm. N^o. 93, Pl. I, fig. 2, with improvements which will be described later on). Moreover in the measurements of isothermals the piezometer (cf. Comm. N^o. 69, Pl. I) was put in the place of the second thermometerreservoir.

In order to secure a symmetrical distribution of the current in the bath mica screens, (which also serve for insulation) are used if necessary (for instance in the resistance thermometer), and a tube similar to the thermoelement Θ was mounted symmetrically with the latter.

The agreement between the mean temperatures of the measuring apparatus and the temperature indicator is further promoted by making the mean height of the two equal.

As with the cryostats of Comm. N^o. 83 we can reach by means of this one a constancy to within 0.01° C. For everything relating to this I refer to Comm. N^o. 83.

A silvered vacuumglass being used, there was arranged a float (not to be seen in the figure) to show the position of the level of the liquid.

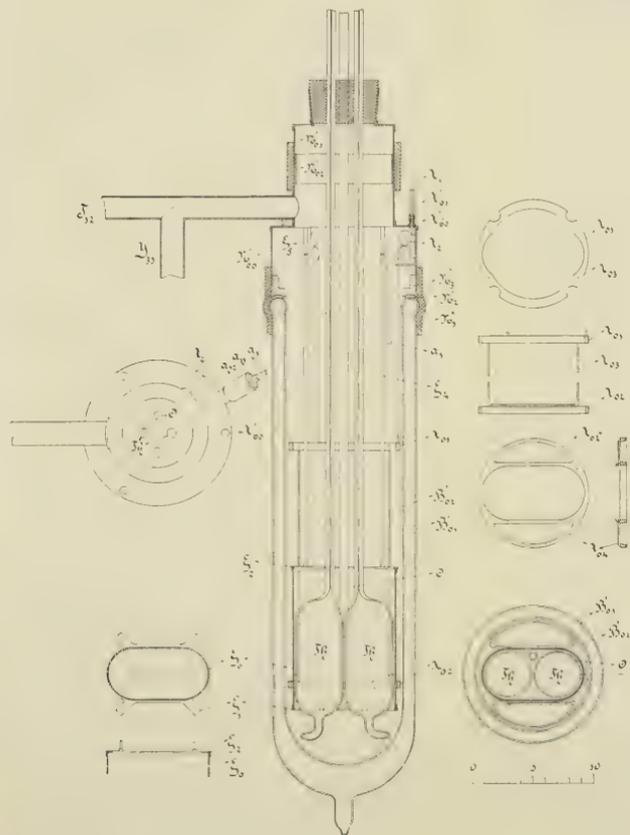
The stopper and the way in which the thermoelement is fixed

¹⁾ The completion of the calculations of these measurements, on the subject of which we shall soon publish a communication, requires some new determinations and the application of some corrections.

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H. KAMERLINGH ONNES. Methods and apparatus used in the cryogenic laboratory.
VII. A modified cryostat.



into it is given only schematically in the figure. In the same manner as the tube a_1 the thermoelement is easily introduced and moved up and down through a tube arranged for this end.

The controlling rod for determining the mean temperature of the capillary of the thermometer or piezometer could be omitted in these measurements.

§ 2. The working of the cryostats described in the last section and in former communications is based upon the cooling caused by evaporation at the surface of the liquid. Although the temperature in those apparatus is almost everywhere uniform there yet remains a colder layer at the surface and a warmer one at the bottom. In some measurements it is very disturbing that the temperature at the top of the bath is somewhat, though very little, lower than elsewhere. In a following communication I hope to be able to give drawings of a cryostat where the bath is surrounded from the bottom upwards by vapours of a lower temperature than that of the bath, so that if we regulate the pressure there is a continual heating instead of a continual cooling at the surface and the normal condition that the temperature of the upper part of the bath is higher, is reached.

Physics. — *“Methods and apparatus used in the cryogenic laboratory. VIII. Cryostat with liquid oxygen for temperatures below — 210° C.”* Communication N°. 94^d from the Physical Laboratory at Leiden by Prof. H. KAMERLINGH ONNES.

In Comm. N°. 83 IV (March '03) I have described how in one of my cryostats constant temperatures between — 195° C. and — 210° C. (in round numbers) are maintained by means of liquid nitrogen. Whereas between — 180° C. and — 195° C. (in round numbers) oxygen is the proper liquid for cryostats, for the range between — 195° C. and the freezing point of nitrogen the latter substance offers the advantage that its vapour pressure is several times larger than that of oxygen and that the quantity of it which evaporates at the same quantity of heat supplied, can be taken up by a vacuum pump of a much smaller capacity. Moreover if for evaporation purposes we are obliged to use the same vacuum pump which also serves for the methylchloride or ethylene, the difficulties are much less with nitrogen than with oxygen. All these reasons made us formerly prefer nitrogen for temperatures below — 195° C. For temperatures below the freezing-point of nitrogen, however, we are

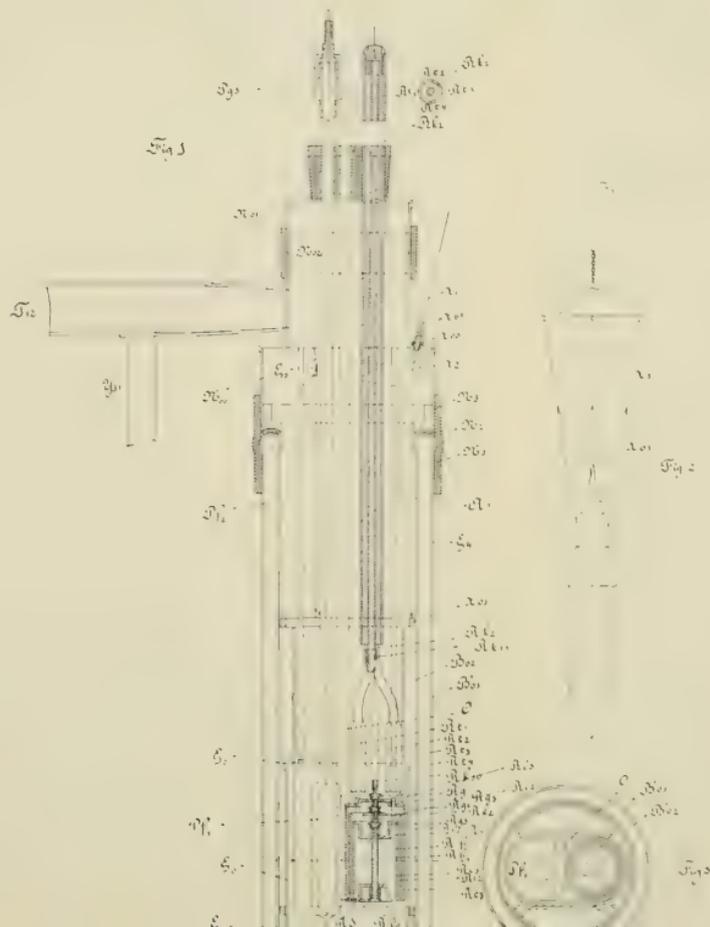
obliged to return to oxygen. Although in this case the volume of gas that must be displaced in order to allow the use of the cryostat described in the previous paper, becomes very large, still it may be controlled at -217° C. by a BURCKHARDT-WEISS vacuum pump, arranged as described in Comm. N^o. 83 V, which can displace 360 M³ an hour. Fortunately we could set an additional pump working to this end. Not only that in this way the BURCKHARDT-WEISS pump of the methylchloride circulation (Comm. N^o. 87, March '04) remains free, but now there is also little reason to use nitrogen for temperatures between -195° and -210° C. With the same cryostat with oxygen we can produce temperatures ranging from -180° to -217° C. The arrangement of the cryostat also admits of keeping the temperature constant to within $0^{\circ}.01$ à $0^{\circ}.02$ C.

On the annexed plate figs. 2, 3 represent a cryostat which is used for measurements at these low temperatures and which differs only in a few minor details from that of the last communication (N^o. 94c May '05) to which I refer for the rest (the same letters denote the same parts). In this cryostat the wires with which the valved stirrer is moved up and down do not pass over two pulleys χ_2 , so that they run parallel with each other outside the apparatus, but they leave the apparatus over a single pulley χ_2' diverging from each other (see fig. 2). Wearing and friction are lessened by this. In the india-rubber tubes surrounding these wires, at distances of 8 mm. small spirals, 3 mm. high and 3 mm. in diameter, are introduced, which prevent the compression of the tubes when the pressure in the cryostat is reduced. Tube $T_{1,2}$ is taken wider and had therefore (in order that we still might use the existing apparatus) to be flattened at the end where it passes into N_{o_2}' .

Fig. 1 represents the determination of the isothermals of hydrogen by means of the piezometers of Comms. N^o. 69, 78, 84 § 19, (general letter P) in this cryostat. The temperature is measured (cf. Comm. N^o. 83 III) with a thermoelement (Comm. N^o. 89), and regulated according to the indications of the resistance thermometer R (fig. 4 shows this in bottom view). As in the model given in Comm. N^o. 93, Oct. '04, (the small letters added to the general letter R have the same meaning as in Comm. N^o. 93 VIII, § 2), the resistance thermometer consists of naked platinum wires wound upon two glass cylinders and of one protecting cylinder. The improvements which are spoken of already in the previous paper, consist in using instead of the mica sheets i_0, i_1, i_2, i_3 (the form of the supporting ridges being modified) the glass tubes i_0', i_1', i_2', i_3' (hence in the figure R_{i_0}' etc.), so that short circuiting between the different parts

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 VIII. Cryostat with liquid oxygen for temperatures below -210° C.



of the resistance is better prevented. Moreover in the new construction the pins g_{01} (see fig. 4), which surrounded by glass tubes g_{02} , fit into the grooves g_{03} (see fig. 5, twice the dimensions of fig. 4), prevent the cylinders and the supporting ridges during the mounting from shifting against each other, which would cause the wires to break at the soldering places. Lastly, to prevent that (in consequence of being cooled conduction of heat) water vapour condenses at the place where the wires t_1, t_2, t_3, t_4 leave the apparatus, the upper part of the supporting rod k is made of glass. Therefore we have fastened the cap k_{11} to k_{10} by means of hard solder, and fixed according to CAILLETET's method (cf. Comm. N^o. 94b) the glass rod k_2 to this cap.

The connection of the cryostat with the auxiliary apparatus agrees in principle with that of Comm. N^o 83 (especially Pls. IV and VI) to which I refer for further details. The cryostat represented in this paper replaces Cr on Pl. IV. At the place of Exh' Pl. IV, the vacuum pump was exhausted by a smaller one, which displaces 20 M³ an hour. This forces the oxygen at normal pressure through a solution of caustic soda in order to keep back the oil carried along from the vacuum pumps. The small vacuum pump also replaces AC of Pl. IV (the lead Exh' terminates into it at Y_{34} , the tube with caustic soda replaces D_1 on Pl. IV). The oxygen, after having bubbled through the caustic soda solution, can without fear of explosion be compressed by a BROTHERHOOD compressor arranged as described in Comm. N^o. 51, Sept. '99, and lubricated with glycerine (cf. Comm. N^o 83 IV). It thus replaces HgC on Pl. IV of N^o. 83.

The admission of liquid oxygen is sometimes effected by directly syphoning over liquid oxygen from a vacuum glass into the cryostat. As a rule, however, compressed oxygen from a cylinder is used and as generally we have a large quantity of cylinders with compressed oxygen in store, it is supplied from another reservoir than that in which the sucked off oxygen is compressed (in that case the connection $RN-D_1$ of plate IV, Comm. N^o. 83, does not exist). The oxygen liquefies in a cooling tube immersed in liquid air (the nitrogen in CS of Pl. IV Comm. N^o. 83, is replaced by oxygen, the oxygen by air) and thence passes through a (see the annexed plate) to the cryostat.

As to the way to keep the temperature constant, the only alteration from what has been laid down in Comm. N^o. 83 is that with high vacua the oil manometer is no longer used and we regulate only by means of the cock Y_{37} (Comm. N^o. 83) being guided only by signals according to the readings of the resistance thermometer. The mean

temperature is determined exactly as described in Comm. N^o. 83.

The cryostat described could be relatively simple, because a vacuum-glass of large dimensions was used. Excellent though a vacuum-glass may be, it is still always to be feared that it bursts unexpectedly and so damages the measuring apparatus. Indeed, one of the series of measurements was put an end to in this way. Hence, when measuring apparatus are used to which we attach great value, because, for instance, many other measurements have been made with them, it is advisable when we want to bring them in baths of constant temperature below -210° C., to use the cryostat described in Comm. N^o. 83 III, where, though it is much more complicated than the one described here, no vacuum glasses are required, and in this the oxygen can be evaporated at a very low pressure, also with the aid of the above mentioned large vacuum-pump.

Physics. — *“Methods and apparatus used in the cryogenic laboratory.*

IX. *The purifying of gases by cooling combined with compression, especially the preparing of pure hydrogen.”* Communication N^o 94^c from the Physical Laboratory at Leiden by Prof. H. KAMERLINGH ONNES.

§ 1. To separate less volatile elements from a gaseous mixture by cooling with liquid air belongs now to the ordinary operations in laboratories. At Leiden it is applied on a fairly large scale to reobtain ethylene in its pure form after it has been mixed with air. In the experiments it repeatedly occurs that ethylene is contaminated with air; from time to time when in the ethylene cycle of the cascade process the condensation pressure of the ethylene increases, the gas which remains behind after the greatest part of the gas used in the cycle is liquefied, is blown off and replaced by pure ethylene, in order to reduce the condensation pressure to its ordinary amount. All such mixtures and remnants with a larger or smaller proportion of ethylene are collected in a large gasholder because of the expensiveness of this gas. The ethylene is afterwards frozen out from the collected gas in a vessel cooled by liquid air.

By cooling at a normal pressure we can from a mixture of gaseous substances which differ very much in volatility, separate a large portion of the least volatile substance when we go to temperatures which though lying above the boiling point of the one, reach far below that of the other substance. How much of the impurity is still in the remaining gas is then fairly well determined by the

vapour pressure of the less volatile element at the temperature of cooling. The separation will be much more perfect when we can also avail ourselves of compression, as it is the case, for instance, when the gas which we want to purify, at the lowest temperature to which we can cool, is still above its critical temperature.

If we do not take the pressure too high we may assume roughly that the degree of purity which we can reach with long continued cooling, is at the same temperature directly proportional to the pressure to which we compress. In cases where the gas flows through a cooled tube, other factors come into consideration, but even then compression offers a great advantage.

I have availed myself of this operation for a last and thorough purification of the electrolytic hydrogen (prepared as described in Comm. N^o. 27, May '96), which is used for piezometers and thermometers, when it appeared that notwithstanding it was led through drying tubes with phosphorus pentoxide, traces of water still occurred in the gas. This purification was effected by cooling hydrogen under strong pressure in liquid air.

A similar method may be recommended to free, for instance, helium from admixtures of neon and hydrogen. The degree of purity of the helium can be raised considerably by causing the bath (liquid hydrogen) to evaporate in vacuo; for this purpose an apparatus is being constructed ¹).

§ 2. *Pure hydrogen for thermometers and piezometers.*

Several improvements have been made to the apparatus for the preparation of pure hydrogen (described in Comm. N^o. 27). Some of them are described in Comm. N^o. 60, Sept. '00. Later the plate *f* of fig. 6, Pl. II, Comm. N^o. 27, was riveted to a platinum wire (instead of being soldered to the copper wire *e*) and melted in a glass tube which is bent down under the mercury on the bottom of the apparatus and is itself filled with mercury. Further the cock *d* was sealed to the bell-jar *c*, and the sealing place *k* is kept under mercury to be cooled by it; finally the shutting of the apparatus was made easier as the india rubber stoppers in the cover were replaced by cone-shaped ones which are pressed on to it by means of a small plate and tightening screws and as six tightening rods *t* instead of three as in the above mentioned figure have been made.

¹) After this had been written and published in the Dutch Proceedings of the Academy I found that DEWAR in his Bakerian Lecture, Proc. Roy. Soc. Vol. 68, 1901, recommended the method of adding compression to cooling for purifying helium.

The electrolytic hydrogen prepared under excess of pressure in the improved generating apparatus flows off through a fine regulating cock (see *R*, Pl. I, Comm. N^o. 27). It is, however, not directly admitted into the mercury airpump and the measuring apparatus which is to be filled, but is first led through a steel capillary to the piezometer in a pressure cylinder where pressure is exerted by compressed air, as was used in the experiments on the condensation of gaseous mixtures (see Comm. N^o. 92, Sept. '04, Pl. I, fig. 1). The stem of this piezometer carries a three way stopcock (Comm. N^o. 84, March '03 Pl. I figs. 2 and 3), to which are connected on the one side the above mentioned capillary, on the other side a copper cooling tube (a platinum cooling tube with platinum capillaries would still have been better), which at either extremity ends in steel capillaries with connections. A high pressure cock, which admits of a fine regulation, connects the cooling tube with the mercury air pump and the measuring apparatus. All the packings are made of cork, the gas itself has no contact with anything but the metal of the cooling tube and the capillaries, with glass, or with twice distilled mercury. After all parts between the generating apparatus and the mercury airpump have been carefully exhausted, the gas is admitted from the generating apparatus into the piezometer with the cooling tube, then the latter are shut off from the generating apparatus and the mercury in the piezometer is forced up until a pressure of 60 atm. is reached, the cooling tube being immersed in liquid air up to the steel capillaries. At the same pressure the gas is then led through the regulating cock into the measuring apparatus that are to be filled.

§ 3. *Hydrogen for the cycle with liquid hydrogen.* The commercial electrolytic hydrogen is as a rule too much contaminated with oxygen and air to serve for a circulation of hydrogen. In order to separate these admixtures we may compress it in a cooling tube immersed in oxygen, which evaporates in vacuo. The following operation is simpler still. The hydrogen is compressed and led through a cooling tube immersed in liquid air under normal pressure into the apparatus where liquid hydrogen is prepared by means of a regenerator spiral, which apparatus together with a gasholder, the compressors and drying apparatus forms a cycle. The pressure of compression is now regulated so that the compressed gas flows out without blocking the delivery cock of the regenerator spiral, at least not as long as this cock is opened and shut alternately. The pressure is gradually raised higher and higher, while the temperature of the outflowing gas falls, and this is continued until the cock is blocked, and the pause during

which we are waiting for the cock to be free again, is used to remove that which is deposited at the place intended for the liquid hydrogen. Thus it is not difficult to prepare from the commercial hydrogen large quantities of hydrogen with less than 1 pro mille of admixture.

Anatomy. — “*On the development of the Cerebellum in Man*”.
(Second Part). By Prof. L. BOLK.

In the first part of this communication the development of the Cerebellum is described until the stage in which the sulci appear typical for the mammalian cerebellum. In this stage it is divided by the sulcus primarius into an anterior and posterior lobe. The first of these lobes is separated by three grooves into four lobules, corresponding with the lobuli 1, 2, 3 and 4 of the mammalian cerebellum. The posterior lobe is also separated by three grooves (sulcus praepyramidalis, fissura secunda and sulcus uvulo-nodularis) in four lobules, corresponding with the lobuli A (nodulus), B (uvula), C₁, (pyramis) and C₂ (declive + folium vermis + tuber vermis), which, with a few exceptions, are to be found in the other mammals. In these exceptions the sulcus praepyramidalis, which separates the lobuli C₁ and C₂, is missing, as in *Erinaceus* (ARNBÄCK CHRISTIE LINDE), *Notoryctes* (ELLIOT SMITH), *Vesperugo* (CHARNOCK BRADLEY), *Chrysochloris* (LECHE). In this case the posterior lobe is only built up of three lobules. The missing of the sulcus praepyramidalis in these cerebella of extremely simple construction gives rise to the supposition that this fissure is phylogenetically the youngest of the primary sulci of the cerebellum. This supposition is corroborated by the fact that in man the sulcus praepyramidalis is ontogenetically the last that appears.

After the development of these primary sulci, grooves appear characteristic for the cerebellum of the primates, and whose homologa are wanting in other classes of mammals.

In embryos of a length from 16 to 22 c.M. arises a groove on the posterior surface of each of the hemispheres, the lateral part of which is directed to the obtuse angle of the lateral border of the cerebellum (Fig. 11 χ). The mesial ends of these grooves approaching each other, penetrate into the narrow lobule which is bordered by the sulcus primarius (1) and by the sulcus praepyramidalis (4); afterwards these grooves unite and divide the lobule in an upper and lower half. This differentiation however not always proceeds symmetrically, so that it may happen, that these grooves do not meet,

but that one of them unites with the sulcus præpyramidalis; in other cases they grow along of each other, causing in this way an asymmetry of the lobule, which influences the further lobulisation of this region; these cases however are rather exceptional. The appearance of these grooves is known in literature, and it is generally believed that they form the sulcus horizontalis. In the beginning I inclined to the same opinion, but the study of the abundant material which was at my disposition instructed me that this notion is wrong, and that this groove, which appears symmetrically, is the sulcus superior posterior which separates the lobulus lunatus posterior and the lobulus semilunaris superior. The sulcus horizontalis appears afterwards in a manner as illustrated in Fig. 12 and 13.

The fact that the sulcus superior posterior arises in an earlier period of human embryonic life than the sulcus horizontalis seems of interest in connection with other particulars of comparative anatomy. I found namely in my researches on the cerebellum of Primates the sulcus superior posterior appearing phylogenetically before the sulcus horizontalis. All Primates excepted the Arctopithecidae possess a sulcus superior posterior, whereas a sulcus horizontalis is only to be found in Anthropoids, although an indication is also to be found in Ateles. After the formation of the sulcus superior posterior, the lobule between the sulcus primarius and sulcus præpyramidalis quickly increases in size, the cerebellum becoming convex in its median zone. (Fig. 11 and 12. 1, 4 and γ).

In the same period in which the lobulus lunatus posterior — bordered by the sulcus primarius and the sulcus superior posterior — develops its secondary grooves, a short straight groove appears on the upperlip of the sulcus præpyramidalis. This groove is the sulcus horizontalis (Fig. 12 and 13, *h*), which, contrary to the general conception appears in the median portion as an unpaired groove. In the beginning therefore the region between sulcus horizontalis and sulcus præpyramidalis is extremely narrow in its median portion, the region however between the first sulcus and the sulcus superior posterior being relatively large. The first of these regions becomes the Tuber vermis, while the second forms the Folium vermis. If one compares the size of these regions with those of the Tuber and Folium vermis of the adult cerebellum it is evident that there must be a very unequal surface-expansion in these adjacent parts of the cerebellum and that the development of this organ in man is not as simple as it appears. And it may be concluded from the fact that the surface-expansion of the lobules takes place with very different intensity that the signification of the grooves and lobules is not merely a morpho-

logical one. The obvious difference in the extension of the cortex of the different lobules ought to have a physiological base.

In the stage of development in which the sulcus horizontalis forms a short straight groove in the forelip of the sulcus praepyramidalis, the Tuber vermis does not yet reach the surface, whereas the folium vermis, which in a later period is concealed, still appears broadly on the surface. This relation is modified by a lamella which mounts to the surface from the bottom of the sulcus praepyramidalis, and which pushing forwards the sulcus horizontalis, separates the latter from the sulcus praepyramidalis (Fig. 12 and 13. *h*, 4). This lamella, arising from the forewall of the sulcus praepyramidalis is the first "Anlage" of the Tuber vermis.

At the same time the sulcus horizontalis has lengthened and penetrates into the hemispheres, soon being equal in length to the sulcus superior posterior (Fig. 15*c*). These sulci include a cuneiform lobule with its top directed mesially, on the surface of which arise secondary furrows, even before the sulcus horizontalis has reached the lateral border of the cerebellum (Fig. 15*a b* and *c*). This wedge-shaped lobule is the lobulus semilunaris superior.

The sulcus praepyramidalis has also extended into the hemispheres (cf. Fig. 11 till 15. 4) and with that keeps its typical form for a long time: namely a median horizontal portion of which the lateral parts bend sharply down and back. This typical form enables us to recognize easily this groove. By this course of the sulcus a second cuneiform lobule is formed with its top directed mesially, bordered above by the sulcus horizontalis (*h*) below by the sulcus praepyramidalis (4). This region becomes the lobulus semilunaris inferior. It is remarkable that the first groove which subdivides this lobule also rises from the upperlip of the sulcus praepyramidalis from which again appears that here exists a focus of very intense surface-expansion. This groove penetrating into the lobulus semilunaris inferior can be seen in Fig. 13, 14 and 15 in different phases of development, whereas in Fig. 16*a* a second groove emerges from the underlip of the sulcus horizontalis, quite near the middleline, which grows out into the lobulus semilunaris inferior. By these two intralobular grooves is initiated the subdivision of the lobulus semilunaris inferior into three sublobuli, a fact, to which ZIEHEN has fixed attention.

The region between the sulcus praepyramidalis (4) and the fissura secunda (2) undergoes but fewer changes and takes part in a slighter degree in the surface-expansion. For a long while this area is broadest in its median zone (Fig. 11, 12, 13 and 14) and shows there one or two short grooves which are however limited to the middle

region and do not penetrate into the hemispheres; this broad middle-piece is the *Pyramis*. The parts of the hemispheres corresponding to the *Pyramis* are separated relatively late from the rest of the cerebellum. This separating is connected with other phenomena which are of importance for the topographical relation of the cerebellar lobules. The *fissura secunda* namely, which limits the regions of the *Uvula* and the *Tonsilla* on the upper side, extends originally from one lateral border of the cerebellum to the other (Fig. 11—14). The area however, situated above the transversal zone formed by *Uvula* and *Tonsilla*, increases more rapidly in transversal direction than the *Tonsilla* does and in this way the latter is enclosed. By this process the *fissura secunda* ends no longer at the lateral borders of the cerebellum, but, if observed from behind, at the myelencephalic border (Fig. 15). Now it is mainly that part of the hemispheres which gets situated at the side of the *Tonsillae*, which by a narrow lamella remains connected with the *Pyramis* and develops to the *lobulus biventer*.

The region of the *lobulus biventer* and *Pyramis* shows in its lamellisation a characteristic that indicates that the surface-expansions of the middle- and side-pieces are more or less independent of each other. Already I drew attention to the fact that in an early period of development one or two grooves appear in the *Pyramis* which do not extend into the hemispheres; figures 11—19 show these grooves at a number of two or three. Now we see, that the furrows of the *lobulus biventer* take their origin quite independently of those of the *Pyramis*. For according to my preparations the *lobulus biventer* is lamellised in two ways. From the underlip of the *sulcus praepyramidalis* arises a groove on some distance from the middleline. This groove lengthening itself in a lateral direction reaches the margin of the cerebellum and divides the *lobulus* into an upper and under part. In Figures 17, 18 and 19 this groove is indicated by a *b* and is identical with the *sulcus bipartiens* of ZIEHEN. The lamellisation of both parts of the *lobulus biventer* takes place in a different manner. The upper part of this lobule, which is cuneiform in shape develops new grooves, taking their origin from the underlip of the *sulcus praepyramidalis* or from the upperlip of the *sulcus bipartiens*, which grooves lengthen laterally; the grooves of the under part, which is a narrow lobule connected with the *Pyramis* arise from the margin of the cerebellum and grow out mesially. Especially figure 18 shows very clearly this difference in the folding of the cortex of both parts of the *lobulus biventer*, which difference gets more important when it is compared with the mode of folding in

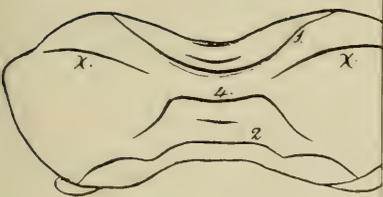


Fig. 11.

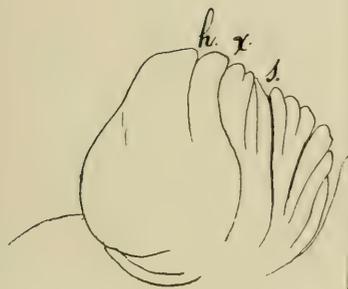




Fig. 11.



Fig. 12.



Fig. 13.



Fig. 14a.



Fig. 14b.



Fig. 14c.



Fig. 15a.



Fig. 15b.



Fig. 15c.



Fig. 15d.



Fig. 16a.



Fig. 16b.



Fig. 16c.



Fig. 17a.



Fig. 17b.

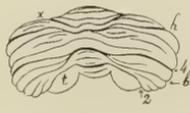


Fig. 18.



Fig. 19a.



Fig. 19b.



Fig. 19c.



Fig. 19d.

the Uvula and Tonsillae. Like the Pyramis the Uvula too very soon shows one or two transversal grooves, which do not penetrate into the Tonsillae. The surface of the last called lobules remains unfolded for a remarkably long time (Fig. 17 from a foetus of 29 c.M. and fig. 18 from one of 32 c.M.) and assumes an oval-shaped rounding. But, the folding of the cortex once commenced, it proceeds in the same way as in the under part of the lobulus biventer. For as can be observed in Fig. 16 and 19, the grooves begin on the margin of the lobules, i.e. laterally and grow out mesially. In connection with this last fact it must be recalled to mind that also the fissure which separates the Flocculus from the remainder of the cerebellum first appears at the lateral edge of the latter and lengthens afterwards in a mesial direction.

The Flocculi and Nodulus have undergone but little differentiation during the described stages of development; the Nodulus has increased in surface and in the number of its grooves; while the Flocculus in an foetus of 35 c.M. (Fig. 19c) shows only three lamellae.

A distinct differentiation between the cerebellum and pedunculi pontis is indicated sharply in foetus of 25 to 30 c.M. (Cf. 15c, 16b, 17a and 19c). In the foetus of 29 c.M. (Fig. 17a) the fossa lateralis is sharply bordered while the sulcus superior posterior (χ) ends in its fore border and the sulcus horizontalis in its top.

In the development of the human cerebellum some interesting phenomena may be observed, which are worth to be brought in the fore-ground and which may be summarised in the following way.

1st. In the grooving of the human cerebellum two stages may be observed; in the first stage those grooves arise that in general are characteristic for the mammalian cerebellum. By these primary grooves the organ is divided into an anterior lobus, which is subdivided into four lobules, and into a posterior lobus, which in the median plane is also subdivided into four lobules. All these grooves take their origin in the middleline. Besides these another groove appears, beginning at the lateral border of the cerebellum (Fissura parafloccularis). In the second stage those grooves become visible, that are typical for the cerebellum of the Primates.

2nd. After the primary grooves in the first stage having been formed the further lobulisation and lamellisation takes place in the second stage in a regular way. In the anterior lobe all the grooves take origin in the middleline and lengthen laterally; the same happens with the main grooves of the region between sulcus primarius and bipartiens, but in the last region there also arise grooves in the

hemispheres which are confined to the latter. Finally between the sulcus bipartiens and the margo myelencephalicus of the cerebellum the grooves begin at the border of the hemispheres and grow out mesially. The system of the grooves belonging to the Pyramis, Uvula and Nodus forms an independent system, which has no connection with the systems of grooves existing in the adjacent parts of the hemispheres. Consequently from a morphogenetic point of view three zones may be discerned. *Anterior zone*: all grooves arise in the middleline, grow out into the margin of the cerebellum or end at some distance of it. *In this zone the system of grooves is an unpaired one.* *Middle zone*: the grooves take their origin partly in the middleline and extend to the margin of the cerebellum, partly they arise in the middle of the hemispheres to which they are confined. *This system of grooves is a paired one.* *Posterior zone*: there arise grooves in the middleline which are confined to a narrow band, while independently of these a second system arises in the hemispheres. *In this zone the system of grooves possesses a threefold character.* The cerebellum of the Primates compared to that of the other Mammals is characterized by a progressive development of the anterior and middle zones and a regression of the posterior zone.

3rd. After the first stage of development having been passed there arise spheres of intense surface-expansion by the side of others, where this expansion is minimal. This is the case with: the most anterior part of the Lobus anterior, which develops into the Lingula; further with the Folium vermis, which at an early period of development reaches the surface as a relatively large lamelle, and the Flocculus, the surface of which enlarges very little. Spheres of intense surface-expansion are: the region in the middle line, immediately surrounding the sulcus primarius; the forelip of the sulcus praepyramidalis, from which arises the whole Tuber valvulae; the region between the sulcus horizontalis and sulcus praepyramidalis. Especially the human cerebellum is distinguished by the mighty development of this part.

The facts brought to notice in 2 and 3 lead to the conclusion that the cortex of the cerebellum is not an organ with a homogeneous distributed function, but a well organised entirety with localised functions.

4th. In general the anterior lobe keeps ahead of the posterior lobe in development, the lamellisation beginning latest in the caudal part of the cerebellum.

5th. In connection with the difference in the mode of lamellisation of the zones described in 2, sulci paramediani are wanting in

the anterior zone, in the middle zone they exist, but continuity between the lamellae of the hemispheres and of the vermis remains, and in the posterior zone they form a complete division between the lamellae of the hemispheres and of the vermis.

Anatomy. — “*On the sympathetic nervous system in Monotremes.*”

By A. J. P. v. D. BROEK. (Communicated by Prof. L. BOLK).

The following description contains the results of an investigation on the structure of the sympathetic nervous system in Monotremes.

For this investigation I had at my disposal a female specimen of *Echidna aculeata* and of *Ornithorhynchus paradoxus*. The sympathetic system of the two specimens resemble each other in many respects, i. e. in structure and ramification; in other respects they show important differences from placental mammals.

In the cervical sympathetic chord we find in *Echidna* one, in *Ornithorhynchus* two ganglia.

The ganglion cervicale of *Echidna* is (Fig. 1. g. c.) a rather large, oval-shaped body, situated close above the *Arteria subclavia*. Singular or double rami viscerales connect this ganglion with the first as far as the fifth cervical nerves included. The ramus visceralis of the first cervical nerve does not enter directly into the ganglion cervicale but is joined to a nerve that appears at the upper end of this ganglion and can be traced as far as the base of the skull (Fig. 1. a.) where it enters into a little foramen. Close to the base of the skull (Fig. 1. b.) two little twigs branch off this nerve, which go through the *M. longus colli* to the vertebral column. Anastomotical branches of this nerve with the *Nervus vagus* and the *ramus descendens hypoglossi* are under the base of the skull. (Fig. 1. c.)

In *Ornithorhynchus* a little part of the cervical ganglion, which should be considered as the fusion of the ganglion cervicale supremum and medium in placental mammals, is situated on the atlas as a ganglion cervicale supremum (Fig. 2 g. c. s.) and is connected with the first cervical nerve. A thick branch of the *Nervus vagus* enters into the ganglion from the lateral side; at the medial side the *Nervus laryngeus superior* (Fig. 2 l. s.) leaves it. In its course this nerve contains a little ganglion before dividing into *ramus externus* (Fig. 2 r. e. l. s.) and *internus*.

The rami viscerales parting from the second to the fifth cervical nerves included communicate in *Ornithorhynchus* with the ganglion

cervicale, which, as in *Echidna*, is situated close above the *Arteria subclavia*.

The communication between the ganglion cervicale and the ganglion stellatum is formed in *Echidna* by two nervestems, which form an *Ansa Vieussenii* round the *Arteria subclavia*; in *Ornithorhynchus* I only found one nervestem passing backwards round this artery. In both, the nerve that passes at the back of the artery is connected with the rami viscerales of the sixth and seventh cervical nerves, while that of the eighth cervical nerve passes directly into the ganglion stellatum. This ganglion also receives the rami viscerales of the first and second thoracic nerves. (The latter in *Echidna* partly).

The ganglion cervicale sends out some nerve branches to the heart, close to rami cardiaci of the vagus nerve (Fig. 1 and 2 r. c.). In *Echidna* these branches are also sent out from the anterior nervestem of the *Ansa Vieussenii*.

The cervical sympathetic system in Monotremes differs from that of the placental mammals not only by the composition and arrangement of the cervical ganglia, but also in the *nervus vertebralis*, which is wanting in Monotremes; in both *Echidna* and *Ornithorhynchus* the rami viscerales of the cervical nerves run extravertebral. If mechanical influences be the cause of the origin of the vertebral nerve (*cordon apophyso-vertebrale* of THÉBAULT¹⁾, it is important to point out the peculiarity of the cervical vertebrae in Monotremes, in which the rudiments of the ribs only confuse at a very late stage of development with the transverse processus of the vertebrae.

The visceral branches of the first and second thoracic nerves run to the ganglion stellatum; the third till twelfth intercostal nerves included are connected by very short rami viscerales with the top of triangular ganglia, situated in the spatia intercostalia.

From the seventh unto the eleventh spatium intercostale the sympathetic chord of *Echidna* is divided into two chords that run parallel, the lateral of which is much smaller than the medial one.

From the latter there goes a nerve in caudo-medial direction, which I could follow as far as the aorta. The rami viscerales of the ninth and tenth thoracic nerves of *Ornithorhynchus* divide into two rami and go to two sequent ganglia. With both animals the sympathetic chord, where it receives the ramus communicans of the thirteenth thoracic nerve, makes a curve in medial direction and penetrates the diaphragm in front of the vertebral column.

1) THÉBAULT. V. Etude sur les rapports qui existent entre le système pneumogastrique et sympathique chez les Oiseaux.

Annales des Sciences naturelles. Série 8. Tome VI, p. 1.

If one will call this part of the chord homologous to the Nervus splanchnicus major of placental mammals, it must be pointed out that in this group the Nervus splanchnicus is the entire sympathetic nerve. So the segmental caudal limit of this nerve falls in the region of the thirteenth or fourteenth thoracic nerve.

In the abdominal part some differences appear between *Echidna* and *Ornithorhynchus*. In the former the sympathetic nerve divides under the diaphragm into two branches of very unequal dimension. The larger of the two passes in medial direction and disappears in the corpus suprarenale (Fig. 1 g. s. r.) after having sent some small branches to the kidney. The second, much smaller branch passes in caudal direction and is the continuation of the sympathetic chord.

Into the latter first passes a branch, springing from the sympathetic ganglion of the fourteenth thoracic nerve, after that the rami viscerales of the succeeding thoracolumbar nerves.

In *Ornithorhynchus* the sympathetic chord passes under the diaphragm into an oblong ganglion. From the medial side of this some fibres arise, that pass to the suprarenal body (Fig. 2 g. s. r.) and the kidney (Fig. 2 n.). With this ganglion communicate moreover the rami viscerales of the sixteenth and partly that of the seventeenth thoracic nerve.

In *Ornithorhynchus* I did not find a ramus visceralis of the fifteenth thoracic nerve.

In *ECHIDNA* there were separated ganglia where the rami viscerales of the fifteenth and sixteenth thoracic nerves join the sympathetic nerve. A ganglion splanchnicum (ARNOLD), which occurs in mammals in the course of the Nervus splanchnicus major, *Monotremes* do not possess. Probably this ganglion is still contained in the corpus suprarenale; this organ we may therefore call in these animals "ganglion suprarenale".

Following the sympathetic nerve further in the abdomen we see that it receives the rami viscerales of the nerves in regularly arranged ganglia of which sometimes two are joined to a single one. (e. g. in *Ornithorhynchus* those of the seventeenth and eighteenth thoracolumbar nerve). Here and there I found double rami viscerales which then pass through the *M. psoas* in a curve.

On account of what I found in the lumbar part of the sympathetic chord in other mammals I am inclined to ascribe the splicing of the rami viscerales to mechanical influences, i. e. to the development of the processus transversi of the vertebrae and the *M. psoas*.

A division of the rami viscerales in grey and white rami, embracing

the intercostal arteries, is described by GASKELL¹⁾ from the second thoracic unto the second lumbar nerve in man. I did not observe a similar splicing in the Monotremes.

The most caudal branch of the sympathetic chord to the abdominal viscera leaves this chord in *Ornithorhynchus* at the level of the entrance of the ramus visceralis of the eighteenth thoraco-lumbar nerve, in *Echidna* at that of the nineteenth thoraco-lumbar nerve.

So the caudal limit of the visceral nerves in Monotremes is much lower than in man, in whom this limit is described by BISHOP HARMAN²⁾, in accordance with GASKELL at the level of the fifteenth thoraco-lumbar nerve.

In the caudal part of the sympathetic chord I found branches of it united with the pudendic nerve. In *Ornithorhynchus* these connecting branches arose from the chord at the level of the sacral and first caudal nerve, in *Echidna* at the level of the first till third caudal nerves. The plexus hypogastricus, which in mammals is found on the side of the caudal rectum end and the uro-genital canal, I found only slightly developed in Monotremes.

A few observations about the ramifications of the sympathetic branches to the abdominal viscera may be added here.

On the medial side of the suprarenal body two groups of nerve fibres appear (in the figures each of them is represented by one single line).

The topmost of the two groups is going to the origin of the Arteria coeliaca + mesenterica superior (Fig. 1 and 2 a. c. m.) and passes into the plexus coeliacus, in which in *Ornithorhynchus* two separate ganglia are to be distinguished. The plexus coeliacus also receives a branch of the Nervus vagus.

The second group of nerve fibres runs to a little quadrangular ganglion, situated in the peritoneum at the medial side of the kidney, which I will call ganglion renale (Fig. 1 and 2 g.r.). The ganglion renale sends off small nerve fibres to the kidney, to the plexus coeliacus (or in opposite direction) and continues at its caudal end into a nervestem, which runs parallel with the aorta.

In *Ornithorhynchus* this nervestem ends in a ganglion (Fig. 2 g.g.) which also receives the already described caudal limiting branch for the abdominal viscera.

1) W. GASKELL. The sympathetic nervous system. Nature 1895.

2) N. BISHOP HARMAN. The caudal limit of the lumbar visceral efferent nerves in man.



Fig. 1. Sym
ac

From this ganglion (Fig. 2 g.g.) nerve fibres pass to the Arteria mesenterica inferior and to the peritoneum in which they could be traced unto the urinary bladder. In Echidna I found two separate ganglia. In the topmost of the two enters the caudal limiting branch from the sympathetic chord, from the other the nerve fibres run in the same direction as I mentioned for Ornithorhynchus.

When we compare Echidna and Ornithorhynchus, it appears that Ornithorhynchus approaches a little more to the condition of placental mammals in so far as in this species we find a little ganglion cervicale supremum which is missing in Echidna and the sympathetic chord does not enter directly into the suprarenal body as is the case in Echidna.

Description of figures.

Fig. 1: Sympathetic chord and principal branches of Echidna aculeata ♀.

Fig. 2: Sympathetic chord and principal branches of Ornithorhynchus paradoxus ♀.

g. c. s. : ganglion cervicale supremum.

g. c. : ganglion cervicale.

n. l. s. : nervus laryngeus superior

r. e. n. l. : ramus externus nervi laryngei sup.

r. c. : rami cardiaci.

n. r. nervus recurrens vagi.

n. ph. nervus phrenicus.

a. s. d. : arteria subclavia dextra (too large in relation to the other arteries).

a. i. p. : arteria intercostalis prima.

a. c. m. : arteria coeliaca + mesenterica superior.

g. s. r. : corpus suprarenale.

n. : kidney.

g. r. : ganglion renale.

g. g. : ganglion at the origin of the art. mesenterica inferior.

a. m. i. : Arteria mesenterica inferior.

s. s. : left sympathetic chord.

Geology. — “*Some observations on the geological structure and origin of the Hondsrug*”. By Dr. H. G. JONKER. (Communicated by Prof. K. MARTIN).

For some years already I have been occupied in making observations on the structure of the Hondsrug. These are far from being complete yet and also for other reasons it will be impossible for me to examine that material with proper care for some time to come. Indeed, I should have had no reason for writing about it so soon, had it not been for an essay on this subject by Prof. E. DUBOIS at Haarlem published some years ago, in which a view is taken altogether differing from the opinion generally adopted till now. As his opinions seem to me to be wrong and yet have been propagated to an undue extent by their insertion into a little book *for the use of schools*¹⁾ — I have to thank Dr. J. LORIÉ for this information — I consider it my duty at once to develop in a somewhat detailed criticism, why I do not agree with him in his opinions.

EUG. DUBOIS: “*The geological structure of the Hondsrug in Drenthe and the origin of that ridge. (De geologische samenstelling en de wijze van ontstaan van den Hondsrug in Drenthe).*”

Roy. Acad. of Sc., Proceed. of the Sect. of Sc., Meeting of June 28, 1902; Vol. V, p. 93—103. (Versl. v. d. gew. Verg. d. Wis- en Nat. Afd. van 31 Mei en 28 Juni 1902; Dl. XI, 1, p. 43—50, 150—152.)

EUG. DUBOIS: “*La structure géologique et l'origine du Hondsrug dans la province de Drenthe.*”

Arch. néerl. d. Sc. exact. et natur., Sér. 2, T. VII, p. 484—496; 1902.

Further see:

J. LORIÉ: “*Beschrijving van eenige nieuwe grondboringen, V,*” p. 20—21.

Meded. omtr. d. geol. v. Nederland, verz. d. d. comm. v. h. geol. onderzoek, n^o. 33.

Verh. d. Kon. Ak. v. Wet., 2e Sectie, dl. X, n^o. 5; 1904.

EUG. DUBOIS: “*On the direction and the starting point of the diluvial ice motion over the Netherlands. (Richting en uitgangspunt der diluviale ijsbeweging over ons land).*”

Roy. Acad. of Sc., Proceed. of the Sect. of Sc., Meeting of May 28, 1904; Vol. VII, p. 40—41. (Versl. v. d. gew. Verg. d. Wis- en Nat. Afd. v. 28 Mei 1904; dl. XIII, 1, p. 44—45).

¹⁾ Overzicht van de geologie van Nederland (“*Outlines of the geology of the Netherlands*”), written by a teacher for his pupils.

H. G. JONKER: "*Bijdragen tot de kennis der sedimentaire zwerfsteenen in Nederland.*

I. De Hondsrug in de provincie Groningen.

1. Inleiding. Cambrische en ondersilurische zwerfsteenen."

Acad. Proefschrift, Groningen, 1904; Stelling XV.

First of all this remark. By the *Hondsrug* is usually meant a ridge extending from Groningen to Emmen in a nearly N. W.-S. E. direction. It should however not be thought that a perfectly continuous ridge even of but a small height is found here. He who goes by bicycle from Groningen by way of Zuidlaren, Gieten, Gasselte, Borger, Odoorn, to Emmen, will frequently find much difficulty in recognizing the ridge. As then the connection between the elevations which in many places are distinctly to be seen, is not always perceptible, and the examination of various of those parts has shown a great distinction in structure, it is advisable to be very careful in dealing with conclusions drawn from examinations of one part. Though it may be probable that the origin of the whole Hondsrug is attributable to a single factor, this cannot be adopted a priori and must be proved by comparison of the examination of the single parts. DUBOIS has examined the southern part of the Hondsrug between Buinen and Emmen, and has drawn conclusions from the observations there, which according to him hold good for the whole Hondsrug and even for the whole region of our Northern provinces. It might be expected therefore that the author had tested his new hypothesis by previous observations of the region not examined by him. This, however, has not been done; it seems to me that, if he had taken previous researches properly into account especially those made by VAN CALKER into the Groningen Hondsrug his opinions would no doubt have partially changed ¹⁾.

In the first communication — for particulars the reader is referred to the English text, to which the cited pages mentioned below also refer — the author demonstrates that the nucleus of the Hondsrug in South-Drente consists in diluvium of the Rhine, over which the glacial diluvium is pretty regularly spread; *on the ridge itself* in the shape of a bed of *boulder-sand*, seldom attaining a thickness of 1 M.; *on the sides* frequently as more or less thick banks of *boulder-clay*. These rather local observations suggest to him the hypothesis that all the land-ice has not reached our country in a direction nearly at right angles with the Hondsrug, but on the contrary

¹⁾ The essay does not mention a single source. It seems to me that this makes it difficult for the less expert reader to form an opinion.

has flowed *in the longitudinal direction* of the Hondsrug over our Northern provinces. In accordance with this was the mutual sliding of the parts of a split boulder of quartzite observed by DuBois.

That is all. To preclude all misunderstanding I shall quote the following passage (p. 100):

“The situation of the elevated ridge of preglacial sand side by side with the long and broad western ¹⁾ strip of boulder-clay makes us also suppose that the direction in which the ice moved was not, as is still generally admitted, from north-east to south-west or from north to south ²⁾, but the same as the extension of the Hondsrug, from north-west to south-east. Now with this supposition perfectly agrees the at first sight paradoxical direction of motion as derived from the shifted boulder of quartzite.”

After stating this hypothesis the author attempts to explain his observations more in particular by this. I need not enter into these explanations. Be it only said that he tries to support his hypothetical direction of the ice-flow by a second supposition about the possibility of the forcing back of the Scandinavian glacial flow by one coming from Scotland in the following words (p. 101):

“Now that it is known that the direction of ice-streams which ended in North-Germany has often been considerably modified by the form of the basin of the Baltic and also by the meeting with other ice streams, it is less surprising, that, notwithstanding the predominating or exclusive occurrence of Swedish, at least Scandinavian ³⁾ rock species in the bottom-moraine of our north-eastern provinces, these can nevertheless have arrived there in north-west-south-eastern direction. Suchlike factors, as supposed to have modified the direction of the North-German ice streams, may have been the cause of the deviations of an ice stream, which, coming from Sweden, *first took a south-western direction over Denmark* ⁴⁾, till it arrived in the North-Sea. We do not know how far the ice which came down from southern Scotland and northern England did progress south-eastward in the North-Sea; it might be possible, at least, that as a

¹⁾ The English text is here not perfectly corresponding with the Dutch (p. 49); see for this the note on p. 99.

²⁾ I do not know who ascribes the diluvium of our Northern provinces to a glacial flow directed from North to South.

³⁾ This addition again suggests that the author may think of *Norway* as the place of origin. Besides the greater part of the boulders in the ground-moraine of the *Hondsrug* is less of *Swedish* than of *Baltic* origin. More about this question below.

⁴⁾ The italics are mine.

very powerful stream it has met there with the ice stream coming from Sweden and has pushed this back south-eastward in the direction of Friesland, Groningen and Drenthe."

I wish to show first that the glacial cover of the Hondsrug in DUBOIS's sense does not exist. For this it is sufficient to prove that in various of the *highest* places of the Hondsrug boulder-clay occurs.

1st. Moreover DUBOIS himself, in his second communication, in which numerous observations of the occurrence of boulder-clay in South-Drenthe are enumerated, states its presence in various places in the Hondsrug between Buinen and Exlo, it is true very near the Eastern border but in the highest points of the Hondsrug (p. 102)¹). At a recent examination of the said section of the N. E. Local Railway this also proved to me to be the case.

2nd. Boulder-clay occurs further at the highest point of the Hondsrug near Gasselte. There the N. E. L. R. cuts the ground to a depth of 5 M. and at the same place where a bridge has been constructed over the new railway (about the highest point of the neighbourhood) a bed of boulder-clay 2 M. thick is found under a thin sandy layer of vegetable earth.

3rd. Moreover I wish just to make mention of a clay-pit near Zuidlaren, about $1\frac{3}{4}$ K.M. outside the village, about 300 M. north of the road from Zuidlaren to Vries. Though there the hilly character of the Hondsrug is less distinctly to be recognized, it is easy to see that the mentioned place is one of the highest of the surroundings. The clay-bed is 3 M. thick there.

4th. Finally I wish to remind the reader of the characteristics in Groningen and south of it. Though the Hondsrug is hardly noticed there, it is most characteristic as regards the shape. Well then, there, in numerous places, boulder-clay occurs very often at the highest places; on the borders there is usually more sand.

I am *not* of opinion that from these observations, rather regularly spread over the Hondsrug, it follows that boulder-clay, quite contrary to DUBOIS's opinion, should chiefly or exclusively occur at the highest points. For a conclusion a most accurate and extensive examination is required. I only wish, by the way, to call attention to an

¹) Still the author sees no reason in this to drop his hypothesis, though he says on p. 102:

"The origin of the Hondsrug according to the hypothesis indicated in the former communication can thus only be applied to that western strip of boulder-clay", but for the rest he maintains the opinion once pronounced as also appears from his answer to LORÉ's criticism cited before.

opinion already pronounced with regard to this question in the "Report of the Board of the Dutch Society for the Reclaiming of Heaths to the Provincial Government of Drente about an inquiry into the character of the waste land in that Province" ¹⁾, where may be read on p. 16—17 inter alia: "Red clay especially occurs on the Hondsrug and chiefly in its highest parts."

On the other hand I do think I am entitled to say that from what is said above appears sufficiently that a distinction between boulder-sand on the ridge itself and boulder-clay only along the sides is in reality wanting.

Moreover the author has, in my opinion, not satisfactorily proved that the boulder-sand of the elevations in South-Drente cannot have been originated by the wash-out of boulder-clay. He mentions the following reasons for this (p. 98—99):

1st. "The hard boulder-clay offers great resistance to eroding agencies. This appears amongst others from its forming steep and more or less projecting parts at the coast as the Roode Klif, the Mirdumer Klif and the Voorst, and even islands, as Urk and Wieringen."

Of course, there is no denying the truth of this statement, though something might be said against it as regards the difference in action between lateral and normal erosive agencies. But moreover may be argued against this that the boulder-clay of the ground-moraine has in a much greater number of places partially or altogether disappeared, no matter how this may have happened. Besides all kinds of intermediate stages between original boulder-clay (as original as we know of, at least) and altogether washed-out boulder-clay may be observed. In Drente e. g. boulder-clay is nearly everywhere washed-out so much, that all limestone has vanished from it. If we consider what important quantities of rock have been lost in this way, the powerful influence of such a solution and wash-out cannot be denied. In other places, on the contrary, the limestone is found preserved, but nearly all the finer parts of the clay washed away, so that the boulders lie in more or less clayish sand (which can also vary in many ways with boulder-clay which has remained more or less intact). I mention these examples to prove that a general appeal to the resistance of boulder-clay to erosive factors in this particular case is of no value.

¹⁾ "Rapport, uitgebracht door het Dagelijksch Bestuur der Nederlandsche Heidemaatschappij aan de Provinciale Staten van Drenthe omtrent een onderzoek naar den aard der woeste gronden in die provincie." (Tijdschr. d. Ned. Heidemaatsch., Jg. XII, 1900.

2nd. From his observations DUBOIS has calculated that about $\frac{1}{25}$ of the volume of the boulder-sand bed has consisted of boulders and as in that region boulder-clay is very poor in stones, boulder-clay of enormous thickness must have been washed out.

I have not repeated this computation, but have this objection that I have often observed that the percentage of stones in the boulder-clay — which indeed is very different in various places — *increases very much* towards the surface. The required thickness would decrease very much by it and as we know so little about the original thickness of the ground-moraine, this reasoning does not seem to me to settle the question.

3rd. “The boulder-sand contains very little flint, the boulder-clay very much, everywhere. Flint is the kind of rock most frequently occurring in the clay (Odoorn, Zwinderen, Nieuw-Amsterdam, Mirdumer Klif, Nicolaasga, Steenwijkerwold, Wieringen, etc.)”

First of all the remark that the places outside the Hondsrug, mentioned here had better not been taken into consideration. As regards the Hondsrug the decision that flint in boulder-clay is the prevailing rock is in its generality no doubt wrong. In clay of the Hondsrug in Groningen flint is very rare indeed. For example: When a pit, about $2\frac{1}{2}$ M. deep and a diameter of 3 M., was dug in the garden of “Klein-Zwitserland” near Harendermolen (the soil consists there chiefly of clayish sand and sandy clay, but with very much limestone), there was not a single flint among some thousands of boulders which were produced! This is, less strictly taken, everywhere the case there. In the Hondsrug in Drente I found some more flint in various clay-pits, but it was never predominant. Moreover through the disappearance of limestone the percentage is doubled. In this respect the Hondsrug differs very much from other parts of our glacial diluvium and this in my opinion very interesting characteristic will have to be explained satisfactorily. — To mention also some observations outside the Hondsrug which argue the reverse: the boulder-sand e. g. near Roden is exceedingly rich in flint, as it is in Steenbergen, etc.

This flint therefore does not prove anything.

4th. “Even the deepest and evidently *not* washed out parts of the boulder-sand, which rest immediately on the Rhine-sand, are as a rule poor in clay.”

I do not know what enables DUBOIS to state that they are not washed out. I beg to remind the reader of the vanished limestone it contained and the numerous brown veins sometimes as thick as an arm, which occur mostly under the boulder-sand in the white

river-diluvium and according to the author himself have come from the upper-stratum (p. 94—95).

5th. “Boulder-clay and boulder-sand are found jointly or the latter alone without this being expressed in the form of the surface.”

I cannot subscribe to this. My examination has not yet led to an established opinion, but in some places I can decidedly conclude from the relief whether we have to do with boulder-sand or with clay. I take for example the already mentioned hill near Gasselte, which runs nearly in the longitudinal direction of the Hondsrug. At the top we have a thick clay-bed there, which towards the sides passes into a thinner layer, at the deepest places altogether consisting of boulder-sand. Further observations in this direction are of course absolutely necessary before formulating this rule in general.

Taking all this into consideration, I am of opinion that, from the five mentioned reasons, it does not follow that the boulder-sand cannot be washed out from the clay. In my opinion the author has not taken either of the two ways in which this problem can possibly be solved :

1st the comparative mechanical analysis of boulder-sand and boulder-clay ;

2nd the study of the general petrographical nature and the characteristics of the surface of the enclosed stones. Nothing has been said about this, whereas it seems to me that only in this way it might *perhaps* be proved whether that is to be looked upon as inner-glacial-moraine and not as washed out ground-moraine.

Taking all this together it gives sufficient proof that the superficial structure of the Hondsrug does not correspond with DUBOIS's opinion. The direction of the glacial flow derived from this opinion is not supported by anything, apart from the piece of quartzite about which I have little to say. In my opinion only one observation like this has but very little value ; a greater number of course would be of great importance.

Moreover as regards the possibility of a deviation of the direction of the Scandinavian glacial flow owing to that of Scotland, I wish to make the following remark :

Not without some surprise have I noticed that DUBOIS represents the glacial flow from Sweden as moving first in a *South-western* direction to reach our country over Denmark, though one of the principal results of the examination of our boulders by K. MARTIN, VAN CALKER and SCHROEDER VAN DER KOLK is that the glacial flow which has produced the glacial diluvium in the North of the Netherlands has

been a *Baltic* one. This makes the author's opinion unexplainable, the more so as my own researches of the last years especially into the Groningen Hondsrug have completely confirmed this result. Though the examination of the diluvial boulders of Groningen will at least take one or two years more, yet I have got so far that I communicated part of the first results of my study at the 10th Physical and Medical Congress at Arnhem. I refer for this to the Proceedings which will no doubt soon be published and only mention here that the glacial flow which has created the Groningen diluvium originated somewhere in North-Sweden, passed the Ålands-islands through the Gulf of Bothnia to the South and South-*East* and further reached our country passing between Oesel and Gothland in the longitudinal direction of the Baltic. About the question whether the direction particularly derived as regards Groningen also applies to all the other parts of the Hondsrug, I will pronounce no opinion as yet. This must be examined more closely. Yet there is no denying the *prevailing Baltic* character of the glacial flow. Such a glacial flow then, would have to be supposed to be deviated about 90° through the one coming from Scotland. Perhaps after this elucidation DUBOIS, too, may abandon the supposition. Otherwise I should like to point out that, — from a parallelogram with the directions of those glacial flows being the conterminous sides and that of the Hondsrug the resultant, — it appears that for such a deviation a force must be ascribed to the Scotch flow much greater than that of the Baltic, a conclusion which is diametrically opposed to fact. It is the Scandinavian land-ice which has forced back the Scotch, witness the numerous Norwegian boulders on England's east coast, and not the reverse. Nothing has ever been heard about English erratics in the Netherlands. If I should find them this year in the Texel, I hope to communicate this at once. Till that moment this supposition is altogether unsupported and everything argues against it.

In the preceding pages I have made an attempt at refuting DUBOIS's supposed deviating glacial flow. This seems first of all necessary to me, because in case this conception is the right one a great number of researches into our "Scandinavian diluvium" would become doubtful and it would be advisable at once to begin a revision. Fortunately there is no reason for this yet.

As regards the remaining contents of the discussed essay, I wish to remark that I also object to looking upon the Hondsrug *as a whole* as being a terminal moraine by itself. It would carry me too far

here to trace how and on what grounds this name came to be general. I intend to explain this afterwards at some length.

Finally one remark more. The nucleus of the Hondsrug in South Drente is rightly said to be of a fluviatile nature. Yet it may be asked whether the boulder-sand, to keep to this, immediately rests on it and whether nothing can be observed there of formations known as stratified mixed and stratified glacial diluvium. This would indeed be very striking and in fact this is not always the case, though I must acknowledge that I have found in the discussed part of the Hondsrug only with great difficulty some profiles in which somewhat acute bounding lines may be observed. I must however put off this discussion. I have mentioned here only so much of my own observations as was strictly necessary; in a complete treatise of it I hope to have an opportunity to enter into the question of the origin of the Hondsrug more in particulars.

Groningen, Min.-Geol. Institute, June 6, 1905.

Astronomy. — *“Approximate formulae of a high degree of accuracy for the ratio of the triangles in the determination of an elliptic orbit from three observations II.”* By J. WEEDEK. (Communicated by Prof. H. G. VAN DE SANDE BAKHUYZEN).

In connection with my paper on the same subject read on 22 April 1905 I now intend to derive simple approximate formulae for the ratio of the triangles, which contain the 3 times of observation and the heliocentric distances belonging to them, and include the terms of the 5th order with respect to the intervals of time, it being easy to add, if necessary, those of the sixth order. The same problem has been treated by P. HARZER, and in the developments at which he arrived he attained a much higher degree of precision¹⁾. Nevertheless it appears to me that his publication does not render mine superfluous because of the different methods of the treatment and the conciseness of my results.

After the method, followed by GIBBS, to derive his fundamental equation, we find with satisfactory approximation a general relation between the values of a function $F(\tau)$ at the three instants, its second derivatives with regard to the time $\ddot{F}(\tau)$ at the same instants

¹⁾ P. HARZER, Ueber die Bestimmung und Verbesserung der Bahnen von Himmelskörpern nach drei Beobachtungen. Mit einem Anhang unter Mithilfe von F. RISTENPART und W. EBERT berechneter Tafeln. Leipzig 1901. Publication der Sternwarte Kiel XI.

and the two intervals of time τ_2 and τ_1 . The value namely, of the following expression

$$\tau_1 \left(F_1 + \ddot{F}_1 \frac{\tau_1^2 - \tau_2 \tau_3}{12} \right) - \tau_2 \left(F_2 + \ddot{F}_2 \frac{\tau_2^2 + \tau_1 \tau_3}{12} \right) + \tau_3 \left(F_3 + \ddot{F}_3 \frac{\tau_3^2 - \tau_1 \tau_2}{12} \right)$$

where $\tau_2 = \tau_1 + \tau_3$, is of the 6th order with respect to the intervals. I use the letters C_1 , C_2 and C_3 to designate the multipliers of the second derivatives in this expression and put

$$C_1 = \frac{\tau_1 \tau_2 \tau_3 - \tau_1^3}{12}, C_2 = \frac{\tau_1 \tau_2 \tau_3 + \tau_2^3}{12}, C_3 = \frac{\tau_1 \tau_2 \tau_3 - \tau_3^3}{12}.$$

Neglecting the terms of the 6th order we then have for an arbitrary function of the time, the relation

$$\tau_1 F_1 - C_1 \ddot{F}_1 - \tau_2 F_2 - C_2 \ddot{F}_2 + \tau_3 F_3 - C_3 \ddot{F}_3 = 0 \quad (IV)$$

provided this function and its first four derivatives be continuous and finite within the interval τ_2 .

Applying this formula to the heliocentric distance r and to r^2 , I obtain approximate expressions for the semi-parameter p , and the semi-axis major a of the elliptic orbit. By eliminating p , from the two well-known differential equations $\ddot{r} r^3 + r = p$ and $\dot{r}^2 = \frac{2}{r} - \frac{p}{r^2} - \frac{1}{a}$, I find a differential equation which may be easily reduced to $\frac{d^2}{d\tau^2}(r^2) = 2 \left(\frac{1}{r} - \frac{1}{a} \right)$. According to these relations $\ddot{F} = \frac{p-r}{r^3}$

belongs to $F = r$, and $\ddot{F} = 2 \left(\frac{1}{r} - \frac{1}{a} \right)$ to $F = r^2$.

If as before I put z for $1/r^3$, the substitution of $F = r$ in formula IV yields the following equation to determine p ,

$$\tau_1 r_1 - \tau_2 r_2 + \tau_3 r_3 - C_1 z_1 (p - r_1) - C_2 z_2 (p - r_2) - C_3 z_3 (p - r_3) = 0$$

whence :

$$p = \frac{(\tau_1 + C_1 z_1) r_1 - (\tau_2 - C_2 z_2) r_2 + (\tau_3 + C_3 z_3) r_3}{C_1 z_1 + C_2 z_2 + C_3 z_3} \quad (V)$$

Through the substitution of $F = r^2$ in IV I obtain the equation

$$\tau_1 r_1^2 - \tau_2 r_2^2 + \tau_3 r_3^2 - 2C_1 \left(\frac{1}{r_1} - \frac{1}{a} \right) - 2C_2 \left(\frac{1}{r_2} - \frac{1}{a} \right) - 2C_3 \left(\frac{1}{r_3} - \frac{1}{a} \right) = 0$$

whence

$$\frac{1}{a} = \frac{-\tau_1 r_1^2 + \tau_2 r_2^2 - \tau_3 r_3^2 + 2 \left(\frac{C_1}{r_1} + \frac{C_2}{r_2} + \frac{C_3}{r_3} \right)}{2(C_1 + C_2 + C_3)} \quad (VI)$$

The terms neglected in these expressions for p and $\frac{1}{a}$ are of the 3^d order with respect to the intervals of time.

I shall now proceed to show how we can avail ourselves of these values for p and $\frac{1}{a}$ for the calculation of the ratios of the triangles.

In my previous paper I have demonstrated that the area of the triangle PZP_1 considered as a function of $\tau = k(t-t_1)$ satisfies the differential equation $\ddot{F} + zF = 0$. The same differential equation is satisfied by the area of the triangle P_2ZP , considered as a function of $\tau = k(t_2-t)$. The two areas may, according to MAC LAURIN be expressed in series of the ascending powers of τ . If the variable τ takes the value $k(t_2-t_1) = \tau_3$, the two triangles become equal to P_2ZP_1 ; therefore it will be possible to obtain a new expansion in series for double the area ΔP_2ZP_1 , by putting in the sum of the two former series $\tau = \tau_3$. From this new series we can easily remove the terms with the even powers of τ .

According to this plan I give here first some higher derivatives of the function F , expressed in F, \dot{F}, z and derivatives of z with respect to the same variable.

$$F^{III} = -\dot{z}F - z\dot{F}$$

$$F^{IV} = (z^2 - \ddot{z})F - 2z\dot{F}$$

$$F^V = (4z\dot{z} - z^{III})F + (z^2 - 3\ddot{z})\dot{F}$$

$$F^{VI} = (-z^3 + 4z^2 + 7z\dot{z} - z^{IV})F + 2(3z\dot{z} - 2z^{III})\dot{F}$$

$$F^{VII} = (\dots)F + (13z\ddot{z} + 10z^2 - 5z^{IV} - z^3)\dot{F}$$

For $\tau=0$, the value of the function $\frac{\text{triangle } PZP_1}{\sqrt{p}} = F[k(t-t_1)] = F(\tau)$

and that of its first derivative is known, viz. $F_0 = 0$ and $\dot{F}_0 = +\frac{1}{2}$.

The above mentioned expansion in series for ΔPZP_1 is therefore :

$$\begin{aligned} \frac{\Delta PZP_1}{\sqrt{p}} &= \frac{1}{2} \frac{\tau}{1} - \frac{1}{2} z_1 \frac{\tau^3}{3!} - \dot{z}_1 \frac{\tau^4}{4!} + \frac{1}{2} (z_1^2 - 3\ddot{z}_1) \frac{\tau^5}{5!} + (3z_1\dot{z}_1 - 2z_1^{III}) \frac{\tau^6}{6!} + \\ &+ \frac{1}{2} (13z_1\ddot{z}_1 + 10\dot{z}_1^2 - 5z_1^{IV} - z_1^3) \frac{\tau^7}{7!} + \int_0^\tau \frac{u^7}{7!} F^{VIII}(\tau-u) du. \end{aligned}$$

The function $\frac{\Delta P_2ZP}{\sqrt{p}} = G[k(t_2-t)] = G(r)$ and its derivative also take for $t=t_2$ or $\tau=0$ the values $G_0 = 0$ and $\dot{G}_0 = +\frac{1}{2}$, and so

for this function, because it satisfies the differential equation $\ddot{G} + zG = 0$, the same expansion holds as for $F(\tau)$, but while in the series for ΔPZP_1 the derivatives are taken with regard to increasing time, those in that for ΔP_2ZP must be considered with regard to decreasing time. If we make use of the symbols $\dot{z}, \ddot{z}, z^{\text{III}}$ etc. to denote derivatives of z with regard to increasing time, the signs of the odd derivatives of z in the expansion for ΔP_2ZP must be reversed. Hence we obtain for ΔP_2ZP :

$$\frac{\Delta P_2ZP}{\sqrt{p}} = \frac{1}{2} \frac{\tau}{1} - \frac{1}{2} z_2 \frac{\tau^3}{3!} + \dot{z}_2 \frac{\tau^4}{4!} + \frac{1}{2} (z_2^2 - 3\ddot{z}_2) \frac{\tau^6}{5!} - (3z_2\dot{z}_2 - 2z_2^{\text{III}}) \frac{\tau^6}{6!} +$$

$$+ \frac{1}{2} (13z_2\ddot{z}_2 + 10\dot{z}_2^2 - 5z_2^{\text{IV}} - z_2^3) \frac{\tau^7}{7!} + \int_0^\tau \frac{u^7}{7!} G^{\text{VIII}}(\tau - u) du$$

and by summation of the two series, for $\tau = \tau_3$

$$2 \frac{\Delta P_2ZP_1}{\sqrt{p}} = \frac{\tau_3}{1} - \frac{z_1 + z_2}{2} \frac{\tau_3^3}{3!} + (\dot{z}_2 - \dot{z}_1) \frac{\tau_3^4}{4!} +$$

$$+ \left\{ \frac{1}{2} (z_2^2 - 3\ddot{z}_2) + \frac{1}{2} (z_1^2 - 3\ddot{z}_1) \right\} \frac{\tau_3^6}{5!} - \left\{ (3z_2\dot{z}_2 - 2z_2^{\text{III}}) - (3z_1\dot{z}_1 - 2z_1^{\text{III}}) \right\} \frac{\tau_3^6}{6!} +$$

$$+ \left[\frac{13z_2\ddot{z}_2 + 10\dot{z}_2^2 - 5z_2^{\text{IV}} - z_2^3}{2} + \frac{13z_1\ddot{z}_1 + 10\dot{z}_1^2 - 5z_1^{\text{IV}} - z_1^3}{2} \right] \frac{\tau_3^7}{7!} +$$

$$+ \int_0^{\tau_3} \frac{u^7}{7!} \{ F^{\text{VIII}}(\tau - u) + G^{\text{VIII}}(\tau - u) \} du.$$

It appears that in this formula the terms with even powers of τ_3 can be transformed into series of terms with the higher odd powers of τ_3 . In order to do this I derive an expansion in series by which this aim is reached in a general manner for the difference $f'(y) - f'(x)$, f being an arbitrary function which between x and y does not show singularities. Let here τ be put for $y - x$, and m for $\frac{y+x}{2}$ then

$$f(y) - f(x) = \int_{-\tau/2}^{+\tau/2} f'(m+u) du \text{ and after integration by parts:}$$

$$f(y) - f(x) = \frac{\tau}{2} [f'(y) + f'(x)] - \int_{-\tau/2}^{+\tau/2} u f''(m+u) du.$$

$$\text{As } \int_{-\tau/2}^{+\tau/2} u f''(m) du = 0 \text{ and } f''(m+u) - f''(m) = \int_0^u f'''(m+v) dv,$$

we may write instead of $\int_{-\tau/2}^{+\tau/2} u f''(m+u) du$, the double integral $\int_{-\tau/2}^{+\tau/2} u du \int_0^u f'''(m+v) dv$ which by reversing the order of integration is transformed into $\int_{-\tau/2}^{+\tau/2} f'''(m+v) dv \int_v^{+\tau/2} u du$.

I now proceed to integrate with respect to u , and so we obtain the following relation :

$$f(y) - f(x) = \frac{\tau}{2} [f'(y) + f'(x)] - \frac{1}{8} \int_{-\tau/2}^{+\tau/2} f'''(m+v) (\tau^2 - 4v^2) dv.$$

The operations may be repeated and by doing so we shall find :

$$f(y) - f(x) = \frac{\tau}{2} [f'(y) + f'(x)] - \frac{\tau^3}{24} [f'''(y) + f'''(x)] + \frac{1}{384} \int_{-\tau/2}^{+\tau/2} (\tau^2 - 4u^2) (5\tau^2 - 4u^2) f^{(V)}(m+u) du.$$

The expansion may be easily continued in the indicated manner, but for the end I have in view that deduced above goes far enough. If according to this formula we replace $\dot{z}_2 - \dot{z}_1$ by

$\frac{\tau_3}{2} (\ddot{z}_2 + \ddot{z}_1) - \frac{\tau_3^3}{24} (z_2^{IV} + z_1^{IV})$, terms of the fifth order are neglected, and if we replace $(3z_2\dot{z}_2 - 2z_2^{III}) - (3z_1\dot{z}_1 - 2z_1^{III})$ by

$$\frac{\tau_3}{2} (3\dot{z}_2^2 + 3z_2\ddot{z}_2 - 2z_2^{IV} + 3\dot{z}_1^2 + 3z_1\ddot{z}_1 - 2z_1^{IV}),$$

we neglect a quantity of the third order. I propose to terminate the expansion of $2 \frac{\Delta P_2 Z P_1}{\sqrt{P}}$ with the term in τ_3^7 , then the above mentioned substitutions will not alter the order of approximation. So we obtain the following approximate formula :

$$2 \frac{\Delta P_2 Z P_1}{\sqrt{p}} = \frac{\tau_3}{1} - \frac{z_1 + z_2}{2} \frac{\tau_3^3}{3!} + \left\{ \frac{1}{2} z_2^2 + \ddot{z}_2 + \frac{1}{2} z_1^2 + \ddot{z}_1 \right\} \frac{\tau_3^5}{5!} \\ - \left\{ (4z_2 \ddot{z}_2 + 5 \frac{1}{2} \dot{z}_2^2 + 4 \dot{z}_2^{IV} + \frac{1}{2} z_2^3) + (4z_1 \ddot{z}_1 + 5 \frac{1}{2} \dot{z}_1^2 + 4 \dot{z}_1^{IV} + \frac{1}{2} z_1^3) \right\} \frac{\tau_3^7}{7!}$$

The development is symmetrical with respect to z_1 and z_2 and their derivatives, and resolves itself into two parts, which have the same form, and which depend besides on τ_3 , only on the value of z and those of the derivatives of z at one point.

If the following series

$$\tau - z_1 \frac{\tau^3}{3!} + (z_1^2 + 2\ddot{z}_1) \frac{\tau^5}{5!} - (8z_1 \ddot{z}_1 + 11\dot{z}_1^2 + 8\frac{1}{2} z_1^{IV} + z_1^3) \frac{\tau^7}{7!} \dots$$

where only the odd powers of the variable τ occur, be denoted by $U_1(\tau)$ and the corresponding series for z_2 and its derivatives by $U_2(\tau)$, we get:

$$2 \frac{\Delta P_2 Z P_1}{\sqrt{p}} = \frac{1}{2} \{U_1(\tau_3) + U_2(\tau_3)\}$$

and the ratios of the triangles may be expressed in the following way in these functions U :

$$\frac{\Delta P_2 Z P_1}{\Delta P_3 Z P_1} = n_3 = \frac{U_1(\tau_3) + U_2(\tau_3)}{U_1(\tau_2) + U_3(\tau_2)} \dots \dots \dots \text{(VIIa)}$$

and

$$\frac{\Delta P_3 Z P_2}{\Delta P_3 Z P_1} = n_1 = \frac{U_2(\tau_1) + U_3(\tau_1)}{U_1(\tau_2) + U_3(\tau_2)} \dots \dots \dots \text{(VIIb)}$$

In the series $U(\tau)$ only such differential quotients occur as can be rationally expressed in p and $\frac{1}{a}$. By means of the known differential equations of the 1st and of the 2nd order for r

$$r^2 = \frac{2}{r} - \frac{1}{a} - \frac{p}{r^2} \text{ and } \ddot{r} = \frac{p}{r^3} - \frac{1}{r^2}$$

we obtain by differentiating $z = \frac{1}{r^3}$

$$\dot{z} = 9z^3 \left(2 - \frac{r}{a} - \frac{p}{r} \right)$$

$$\ddot{z} = 3z^2 \left(9 - 4\frac{r}{a} - 5\frac{p}{r} \right)$$

while from the differential equation $z^{\text{III}} = 5 \frac{\dot{z}\ddot{z}}{z} - \frac{40}{9} \frac{\dot{z}^3}{z^2} - z\dot{z}$ by differentiation with respect to τ and by elimination of z^{III} the following expression is found for z^{IV} .

$$z^{IV} = -z^3 \left(6 \frac{\dot{z}^2}{z^3} + \frac{\ddot{z}}{z^2} - 5 \frac{\ddot{z}^2}{z^4} - \frac{20}{3} \frac{\dot{z}}{z^2} \frac{\ddot{z}}{z^3} + \frac{40}{3} \frac{\dot{z}^4}{z^6} \right)$$

As $\frac{1}{a}$, p and the 3 heliocentric distances r are known, \dot{z}^2 , \ddot{z} and z^{IV} can be computed for each of the 3 points P_1 , P_2 and P_3 .

For a circular orbit all the derivatives of z are equal to zero and the function U becomes $\frac{\sin \tau \sqrt{z}}{\sqrt{z}}$. According to the preceding development we obtain for an elliptic orbit the following approximate formula for U , which still contains the 6th power of the interval :

$$U = \frac{\sin \tau \sqrt{z}}{\sqrt{z}} + \frac{\tau^5}{20} z^2 \left(9 - 4 \frac{r}{a} - 5 \frac{p}{r} \right). \quad \dots \quad (VIII)$$

By means of the values which take U_1 , U_2 and U_3 for the values τ_1 , τ_2 and τ_3 of the argument τ , we obtain for n_1 and n_3 values containing the terms of the 5th order with respect to the intervals; while the approximation may be extended to the 6th order, if we add to the above mentioned expression for U :

$$- \frac{\tau^7}{5040} z^3 (-\lambda - 120\mu + 170z^2 + 340\lambda\mu - 1020\mu^2).$$

where λ and μ denote :

$$\lambda = \frac{3}{2} \left(9 - 4 \frac{r}{a} - 5 \frac{p}{r} \right)$$

$$\mu = 3 \left(2 - \frac{r}{a} - \frac{p}{r} \right).$$

Astronomy. — “*Supplement to the account of the determination of the longitude of St. Denis (Island of Réunion), executed in 1874, containing also a general account of the observation of the transit of Venus*”. By Prof. J. A. C. OUDEMANS.

When I set about to correct the imperfections left in my first communication, I began by calculating for the times of observation of the occultations the correction of NEWCOMB'S parallactic correction, mentioned on p. 603 of my previous paper; as said there this correction amounts to

$$+ 0''67 \sin D + 0''05 \sin (D - g) - 0''09 \sin (D + g'),$$

where D stands for the mean elongation of the moon from the sun, g for the moon's mean anomaly, and g' for that of the sun.

D and g could be derived from Tables I and II at the end of NEWCOMB'S paper ¹⁾; there, however, in agreement with the method introduced by HANSEN in his tables of the moon, the unit is not a degree, but a mean day, so that the numbers derived from those tables must be multiplied by $12^{\circ},19$ and $13^{\circ},065$ respectively in order to be reduced to degrees. g' could be derived with a sufficient accuracy for our purpose from the tables of LARGETEAU in the *Conn. des Temps* for 1846.

The corrections found are, however, not to be applied to the true, but to the mean longitude, called by HANSEN $n \delta z$, and therefore must be reduced to corrections of the true longitude by multiplication by $(1 + 2e \cos g \dots)$, and these must again be reduced to corrections of right ascension and declination; for the latter reduction I used the moon's hourly motions in R. A. and declination from the *Nautical Almanac*, whence the direction of the moon's motion with regard to the parallel could be directly derived.

The corrections of the moon's ephemeris in the *Nautical Almanac*, given by NEWCOMB on p. 41 of his *Investigation* for each day from 1 Sept. 1874 to 31 January 1875, were corrected for the two first months by means of the values found; and in the calculation of the longitude from the occultations we have now applied these corrected corrections, instead of the corrections furnished by the meridian observations. It then would become evident which corrections were to be preferred, and it soon appeared that it was the former. The large corrections in declination found for 19 Sept. and 16 Oct. 1874, ($-4''.3$ and $-4''.1$) for instance, in consequence of which the second occultation observed on 19 Sept. was formerly rejected, were apparently due to the inaccuracy of the meridian observations.

I now shall give the details of my calculation. (see table p. 112).

These corrections were added to those given on p. 609 of my first account as being interpolated from NEWCOMB, and then the required alterations were made in all the calculations of the occultations.

Before I passed on to this second communication, I have once more thoroughly revised all the computations and thus was able to apply some corrections; some occultations which had been rejected, could now be retained after the error had been corrected.

1) S. NEWCOMB. *Investigation of corrections to HANSEN'S Tables of the Moon*; with tables for their application, forming Part III of papers published by the Commission on the Transit of Venus, Washington, Government Printing Office, 1876.

1874	M.T.Gr.	D	g	g'	$0^{h}07$ $\sin D$	$0^{h}05$ $\sin(D-g)$	$-0^{h}09$ $\sin(D+g)$	Sum $= \Delta n \delta z$	$\Delta \lambda$	$\Delta \alpha$	$\Delta \delta$	
Sept.	19	5 ^h 8	105°5	256°7	257°	+0 ^h 64	-0 ^h 02	0 ^h 00	+0 ^h 62	+0 ^h 60	+0 ^h 68 = +0 ^s 04	+0 ^h 01
	21	7.5	130.5	283.5	259	+0.51	-0.02	-0.05	+0.44	+0.45	+0.48 = +0.03	+0.11
	22	8.6	140.9	294.6	260	+0.42	-0.02	-0.06	+0.34	+0.35 ⁵	+0.34 = +0.02	+0.11
	22	10.3	144.1	298.1	260	+0.39	-0.02	-0.06	+0.31	+0.32 ⁵	+0.34 = +0.02	+0.11
	26	4.8	190.3	347.5	264	-0.12	-0.02	-0.09	-0.23	-0.26	-0.22 = -0.01 ⁵	-0.12
Oct.	2	41.5	267.1	69.8	270	-0.67	-0.01 ⁵	-0.00 ⁵	-0.69	-0.71	-0.79 = -0.05	+0.07
	4	41.6	291.5	95.9	272	-0.62	-0.01	+0.04	-0.59	-0.58	-0.60 = -0.04	+0.18
	15	3.8	61.7	283.3	283	+0.59	-0.01	+0.02	+0.60	+0.56	+0.63 = +0.04	-0.09
	16	5.0	74.3	248.8	284	+0.64	-0.00 ⁵	0.00	+0.64	+0.61	+0.70 = +0.05	-0.02
	17	7.2	87.7	263.2	285	+0.67	0.00	-0.02	+0.65	+0.64	+0.72 = +0.05	+0.06
48	8.3	100.3	276.7	286	+0.66	0.00	-0.04	+0.62	+0.62 ⁵	+0.68 = +0.04 ⁵	+0.13	
19	7.4	112.5	289.7	287	+0.62	0.00	-0.06	+0.56	+0.58	+0.60 = +0.04	+0.17	

I shall briefly record the modifications of my previous account ¹⁾.

The following are the numbers originally belonging to the observations mentioned there: 1, 3, 4, 7, 9, 10, 11, 12, 14, 16, 18, 20, 22, 23, 24, 25, 27, 28, 29, 30, 31, 32, 34, 35, 36, 37.

Hence were rejected the numbers: 2, 5, 6, 8, 13, 15, 17, 19, 21, 26, 33, 38, 39.

N^o. 2, disappearance of Arg. Z. 233, N^o. 77, observed by me on the ground of the harbour office on 19 Sept., yielded — 21^s.31 for the correction of the eastern longitude. It appeared that this large value was for the greater part due to the large correction (— 4''3) applied to the moon's declination as derived from the meridian observations. The corrected corrections of NEWCOMB were — 0^s.45 and + 0''.3 (that of the declination even with another sign), and the correction of the eastern longitude became — 6^s.85, not larger than several others.

N^{os}. 5 and 6, disappearances of Arg. Z. 311, N^{os}. 72 and 75 observed by me on the ground of the harbour office on 21 Sept. It appeared that in reducing these two observations the correction of the chronometer had been taken from the journal with a wrong sign. After rectification of this error the results were satisfactory.

N^o. 8, disappearance of a 9th magnitude star, observed by me on the ground of the harbour office on 22 Sept. at 7^h38^m25^s.07, hence 34^m9^s after that of 33 Capricorni. I have not succeeded in rectifying this observation. Judging from the map which by means of ARGELANDER'S *Zonae* had been constructed preliminary to the observations, it seemed that the star could be no other than N^o. 18 of A. Z. 255, but then the correction of the eastern longitude would have been + 58^s.24. Supposing that an error might have occurred in noting down the minute of the time of observation, I repeated the calculation adopting the time to be 1 minute later, but now I got: Corr. of the E. longitude + 20^s.07. The time of observation ought therefore to be taken another half minute later, but I did not hold myself justified to do so.

There still followed two occultations, which were missed through clouds, probably one of these two has been A. Z. 255 N^o. 18, and the star observed by me does not occur in A. Z. Neither SCHÖNFELD'S southern atlas, nor GILL'S catalogue could help me to arrive at a conclusion.

N^o. 13, disappearance of 73 Piscium on 26 September, N^o. 15, disappearance of 53 Geminorum and N^o. 17, disappearance of a star

¹⁾ In the 3rd column on p. 607 a few clerical or printing errors have crept in: for Cordoba III 1589 read Cordoba XVIII 1589 and for Cordoba XVIII 124 read Cordoba XVIII 1612.

of the $6\frac{1}{2}$ th magnitude, both on 2 October, were recorded as uncertain and besides the results were too discordant. Full moon had occurred on 25 September; so these disappearances took place at the bright limb of the moon, and it is well-known how uncertain their observation is then. In this case a sudden disappearance can only be observed with stars of the 1st or 2nd magnitude.

N^o. 19, disappearance of B. A. C. 5800 on 15 October, also yielded a large negative correction of the eastern longitude ($-13^s,14$), but there was no reason for rejecting it; the disappearance took place at the dark limb, the star was of the $6\frac{1}{2}$ th magnitude, hence very bright in the telescope, and in the journal of observation uncertainty is not mentioned.

N^o. 21, disappearance of A. Z. 223 N^o. 48, observed by Mr. E. F. VAN DE SANDE BAKHUYZEN on 16 October, yielded $+33^s,70$; N^o. 26 disappearance of a star of which the place was $20^h5^m16^s - 25^o10'46''$, gave $-120^s,6$. Both had therefore to be rejected.

Nor was I more fortunate with N^o. 33. The star as determined at Leyden gave an unsatisfactory result ($+21^m38^s$) and I could not find in the catalogues another star which fulfills the requirements.

I succeeded better with N^o. 38. N^o. 38 had been noted by Mr. BAKHUYZEN as disappearance of ζ Piscium on 28 October; it appears however that this star was not occulted and that the occulted star could be no other than 24 Piscium; assuming this, I arrived at a satisfactory conclusion.

In the case of N^o. 39, disappearance of 59 Geminorum at the dark limb on 26 November, we could only obtain a result, that was not wholly inadmissible, by assuming a combination of errors. Although each of these was in itself not quite improbable, it was thought necessary to reject also this observation.

About N^o. 27 I remark that on p. 607 I noted as observers S.B. i. e. that both Mr. SOETERS and Mr. BAKHUYZEN observed the occultation (disappearance at the dark limb); as the time recorded by Mr. BAKHUYZEN was 4 seconds *later* than that noted by Mr. SOETERS, I accepted the result of the former as the more probable one, the more so as it agreed better with the other results.

Generally, the endeavours to rectify the occultations, which at first seemed to have failed, have cost more work than those where nothing was wrong.

Finally I must remark that Mr. SOETERS himself had corrected a small error of computation in his reduction of the observations, made to determine the relative position of our different observing places, but had neglected to enter the corrected value in the final table of

his results. In consequence of this error we must read for the longitude east of Greenwich of the observing place on the ground of our dwelling house, as given on p. 604 $3^h41^m48^s.06$ instead of $48^s.11$.

Taking into account the corrections mentioned above, the list of results communicated in the Proceedings of March (p. 607 of the preceding volume) must be modified as given at the end of this paper; see tables *Ia* and *Ib*.

We then find as correction of Germain's longitude:

Using disapp. and reapp. indifferently . . . — $2^s.90 \pm 0^s.64$ (m.error)
 Treating them separately — 0.81 ± 1.22 (,, ,,)

It is much to be regretted we did not succeed in observing more reappearances. There is always a greater chance to observe the disappearances than the reappearances at the dark limb of the moon. A short time after new moon until a few days after first quarter we can easily see with a good telescope on the east side of the moon stars of the 8th, 9th or perhaps even the 9^{1/2}th magnitude, of which the disappearance may be easily observed; no preparation is required for this.

For the observation of reappearances at the dark limb, a preparation by means of star maps is necessary, which takes up much time. We must calculate from hour to hour the parallax of the moon in R. A. and declination and hence derive its apparent places, draw them on the map, and then derive geometrically the instants at which the stars considered must reappear. For the most southern declinations the star maps themselves had to be constructed first by means of ARGELANDER's southern *Zonae*. Moreover it is always desirable finally to derive more accurate results by a calculation according to the known formulae.

The operations described here have been executed as well for the days preceding full moon as for those following it, and it was our bad luck that in the latter part of the lunation the weather was always unfavourable.

After this revision of the calculations a small negative correction of the longitude of St. Denis according to Germain seems probable, although its exact amount is uncertain. We have however, still to consider what follows:

When in 1884 ATWERS wanted to determine a fundamental meridian for Australia¹⁾, for which purpose he chose that of SYDNEY, he used 78 occultations observed from 1873 to 1876 in Windsor (N.

¹⁾ Astron. Nachr. Vol. 110 p. 289—346.

S. Wales) by TEBBUTT and 18 occultations observed by ELLERY in 1874 and '75 at Melbourne. He applied to the ephemerides of the moon of the Nautical Almanac the corrections of NEWCOMB's *Investigation* and took for the relation between the moon's radius and the horizontal parallax the value $k = 0.27264$ found by me. (*Versl. en Meded. Akad. Amsterdam Afd. Nat. 1st Reeks, Vol. X p. 25*).

But as nevertheless a constant error might occur in the obtained results, he calculated, as a test, a large number of occultations, which had been observed either at Greenwich or at places of which the longitude had been determined by telegraph, viz: 31 observed at Greenwich, 25 at Washington, 40 at Nikolajef, 44 at Oxford, 30 at Luxor, 46 at Strassburg, 13 at Leipzig, 7 at Vienna, 2 at Königsberg, 2 at Moscow, 2 at Pulkowa and 1 at Kiel.

Thus he was able to derive the correction to be applied to a longitude determined by a disappearance at the dark limb, and found for this after a graphical compensation :

1873,0	+ 1,08,
1873,5	+ 1,63,
1874,0	+ 2,12,
1874,5	+ 2,52,
1875,0	+ 2,84,
1875,5	+ 3,11,
1876,0	+ 3,27,
1876,5	+ 3,38,
1877,0	+ 3,52.

I have on purpose given this table in full to show how constant is the positive sign of the correction. For the reappearances AUWERS found a correction which in the mean was larger by $+ 0^s,23$. (Although this value has been found having regard to weights, it yet seems to me rather uncertain; I find for its mean error $\pm 0^s,64$). It appears from this that this correction is due not to an erroneous value of the moon's radius, but to a slowly varying error still left in the tables of the moon.

Now if we want to apply this correction — and I consider this as quite justified — we must also take for the relation k between the apparent radius of the moon and the horizontal parallax the same value as AUWERS has used and hence apply the necessary corrections to our longitude.

The formulæ required for this could be easily derived. Let the difference in right ascension between the moon's centre and the place

of the star, after the moon's parallax, calculated for the point where the occultation took place, has been added to it with a contrary sign, be denoted by I ; let the geocentric radius of the moon (as it was used for this calculation) be $= R$, the horizontal parallax $= II$ and the difference in declination between the reduced place of the star and the moon's centre $= v$, then we have

$$I = \frac{1}{15} \text{ sec.} \frac{d' + D}{2} \sqrt{R^2 - v^2},$$

and hence

$$\partial I = \frac{I R}{R^2 - v^2} \partial R,$$

but as

$$R = II k$$

we have

$$\partial R = II \partial k$$

hence

$$\partial I = \frac{I R II}{R^2 - v^2} \partial k = \frac{I R^2}{R^2 - v^2} \cdot \frac{\partial k}{k}.$$

The reduction to be added to the star's R. A. to get that of the apparent moon's centre is $\mp I + II$, where the 2^d term is independent of k and the upper sign of the first is to be used for disappearances, the lower for reappearances.

If the hourly motion of the moon in R. A. is $\Delta\alpha$, the correction of the Greenwich mean time of an occultation is $\frac{\mp I + II}{\Delta\alpha} \times 3600^s$ and the correction of the eastern longitude derived from it: $\frac{\pm I - II}{\Delta\alpha} \times 3600^s$. Now as the assumed value of k was 0,272525 we have $\partial k = + 0,000115$:

$$\begin{aligned} \text{and} \quad \partial \text{ E. L.} &= \pm 3600 \times \frac{0,000115}{0,272525} \cdot \frac{I R^2}{(R^2 - v^2) \Delta\alpha} \\ &= \pm [0,1814] \frac{I R^2}{(R^2 - v^2) \Delta\alpha}, \end{aligned}$$

where the value in square brackets is a logarithm, and the logarithms of the other factors may be derived from the former calculation. The $+$ sign is to be used for disappearances, the $-$ sign for reappearances.

In this way I have found the corrections given in table II and thus obtained corrected values for the longitude. I think it best to use indistinctly the results from disappearances and reappearances.

We then find as mean correction of
 GERMAIN's longitude: $- 2^s,15 \pm 0^s,79$ (mean error)
 the supplementary correction according
 to AUWERS is for 1874,80: $+ 2^s,71 \pm 0^s,50$ ¹⁾
 and the final correction is $+ 0^s,56 \pm 0^s,93$.

Although our calculations were somewhat modified and a systematic correction was applied, which seems to be required, we arrive at the same conclusion as in our first paper, viz. that the correction of the longitude of St. Denis found by GERMAIN, in so far as we may judge from the occultations observed by us, is very small. If we pay attention to the mean error of our result, it is not even certain whether it is negative or positive, though there is a greater probability in favour of a small positive correction.

In my previous paper I have not mentioned that the reduction to 1874 of the places of the stars from all the available catalogues has been very carefully executed by Mr. H. KRESS, "amanuensis" at the Observatory at Utrecht. The derivation of the most probable places from the whole material I have made myself.

It will be interesting to record that the meridian observations of the moon, made at Leyden in Sept. and Oct. 1874 by Mr. H. HAGA, then assistant at the observatory (now professor of physics at the university of Groningen), has yielded the following corrections of the places in the Nautical Almanac, previously corrected according to NEWCOMB's *Investigation*: (see table p. 119)

¹⁾ This mean error has been estimated, and is based on the argument that the value of the correction, which was found by graphic compensation, rests on about 25 occultations, while AUWERS has arrived at the result (*A.N. Bd. 110, column 336*) that one disappearance at the dark limb yields a longitude, of which the mean error may be considered to be $\pm 2^s,5$.

1874	Limb.	Obs. — Comp.		Remarks.
		$\Delta \alpha$	$\Delta \delta$	
September 21	I upper	$-0^s 14$	$-4^m 7$	Very unsteady.
24	I upper	+0.07	+1.3	Clouds.
» 26	II lower	-0.28	+0.1	
» 27	II lower	-0.08	+1.9	
» 30	II lower	-0.04	-5.1	Clouds.
October 1	II	-0.07		
» 15	I	+0.35		Very faint, uncertain.
» 20	I upper	+0.22	-1.4	Very unsteady.
» 22	I upper	+0.13	+0.8	
» 24	I upper	+0.15	+1.8	
» 26	II lower	-0.08	+1.1	
» 27	II lower	-0.12	+1.3	
» 28	II lower	-0.14	+2.3	Clouds.
» 30	II upper	-0.14	-0.5	
Mean value :		$-0^s 01$	$-0^m 1$	

These results have not yet been published, but have been lately communicated to me by Dr. E. F. VAN DE SANDE BAKHUYZEN.

It will be desirable also to consider the other determinations of the longitude of St. Denis de la Réunion. Dr. E. F. VAN DE SANDE BAKHUYZEN kindly communicated them to me. These determinations, whose results only we shall mention for brevity, were made by Lord LINDSAY and Dr. COPELAND on the one side and by Messrs. LÖW and PECHÛLE on the other side, on their respective observing-stations Belmont and Solitude, both on the isle of Mauritius, the differences of longitude of those stations and St. Denis being determined by transportation of chronometers.

Lord LINDSAY and Dr. COPELAND¹⁾ found for Belmont:

¹⁾ Dun-Echt Observations. Vol. III. p. 171.

by means of 52 chronometers on the home voyage ¹⁾	3 ^h 50 ^m 40 ^s .03
from observations of the moon :	
from 11 occultations (7 disappearances and 4 reappearances at the dark limb)	3 ^h 50 ^m 40 ^s .60 ± 0 ^s .33
from 12 culminations of the moon	42 .6
Assigning to these two results weight 2 and 1, we get as mean result	3 ^h 50 ^m 41 ^s .27
Reduction on St. Denis flag-staff determined by transportation of chronometers	— 8 ^m 53 ^s .41
Hence longitude of St. Denis flag-staff E. of Gr. from the chronometers	3 ^h 41 ^m 46 ^s .62
from observations of the moon	47 .86

The German observers found for the longitude of Solitude ²⁾)	
from 6 culminations of the moon	3 ^h 50 ^m 39 ^s .52 ± 3 ^s .29
from 3 occultations	40 .33 ± 1 .91
whence in the mean	3 50 40 .13 ± 1 .65

Now Solitude is situated 0^s.89 west of Belmont,
Belmont 8^m53 ,41 east of St. Denis,
hence Solitude 8 52 ,52 „ „ „ „ .

Hence longitude of St. Denis (flag-staff) E. of Gr. 3^h41^m47^s.61

Combining all these results, omitting only that from the chronometers (comp. footnote) we have :

		Weight
by means of the longitude of BELMONT, (observations of the moon)	3 ^h 41 ^m 47 ^s .86 ± 0 ^s .90	1,25
by means of the longitude of SOLITUDE, (observations of the moon)	47 ,61 ± 2 ,00	0,25
determination by GERMAIN (culminations of the moon) :	47 ,40 ± 0 ,76	1,72
determination by OUDEMANS and BAK- HUYZEN, (occultations with corrections according to AUWERS) :	47 ,96 ± 0 ,93	1,16
Adopted longit. of St. Denis flag-staff	3 ^h 41 ^m 47 ^s .69 ± 0 ^s .44	4,38

¹⁾ Unfortunately the outward voyage has not yielded any result, because the rates of the chronometers after the landing could not be determined, as it had been neglected to wind them up. And this accident also takes off much of the value of the home voyage, because through this the difference between the rate at sea and that on land could not be eliminated. AUWERS has already made this remark in: Die Venus-Durchgänge 1874 und 1882. Bericht über die Deutschen Beobachtungen, Vol. VI p. 265, and therefore we shall also leave this result out of account.

²⁾ A. AUWERS. Die Venus-Durchgänge 1874 und 1882. Bericht über die Deutschen Beobachtungen Vol VI.

The longitude of our station now being determined as well as possible, I shall proceed to communicate our contact observations of Venus and the Sun during the Transit on December 9th.

Our place of observation was on the battery, in the immediate neighbourhood of the pavilion of the heliometer; its longitude must therefore be accepted to be $3^{\text{h}}41^{\text{m}}47^{\text{s}},81 + 0^{\text{s}},26 = 3^{\text{h}}41^{\text{m}}48^{\text{s}},07$.

The ingress took place very early in the morning, the sun being only five degrees above the horizon. Unfortunately at sunrise the sky was not quite clear. In the east, a few degrees above the horizon there was a dark stratus, and it was to be feared that at the instant of the second contact the sun would just be behind it. So it happened, and this was the more unfortunate as the station Réunion had expressly been chosen for the observation of that contact.

At the first contact the sun's limb was very unsteady. At $5^{\text{h}}38^{\text{m}}20^{\text{s}}$ mean time St. Denis, I thought that I saw an impression on the sun's limb, which I held to be made by Venus. A passing cloud, however, prevented me from seeing whether I had been right. When, after a minute the sun reappeared, I could not distinguish the impression on the limb any more. At $5^{\text{h}}41^{\text{m}}20^{\text{s}}$ it could however be seen plainly. The place where I then saw it was exactly the same as that where I had thought to see it 3 minutes earlier. However, as Venus had moved on $6''$ during those 3 minutes, the observation of the first contact must be considered as having failed. The mean between the two instants mentioned is no more than a very rough approximation.

As said already, the second contact was missed.

But both Mr. SOETERS and I observed the two last contacts.

The formulae, given in the Nautical Almanac of 1874 on p. 434 for the calculation of the contacts, are:

For the first external contact:

$$t = 13^{\text{h}}45^{\text{m}}58^{\text{s}} - [2,5773] \rho \sin l - [2,7049] \rho \cos l \cos (\lambda + 136^{\circ}39'.9),$$

for the first internal contact:

$$t = 14^{\text{h}}15^{\text{m}}24^{\text{s}} - [2,6992] \rho \sin l - [2,7462] \rho \cos l \cos (\lambda + 147^{\circ}55'.7),$$

for the second internal contact:

$$t = 17^{\text{h}}57^{\text{m}}26^{\text{s}} + [2,8253] \rho \sin l + [2,5265] \rho \cos l \cos (\lambda - 55^{\circ}37'.8),$$

for the second external contact:

$$t = 18^{\text{h}}26^{\text{m}}54^{\text{s}} + [2,7374] \rho \sin l + [2,5014] \rho \cos l \cos (\lambda - 37^{\circ}50'.9);$$

The times are given in Greenwich mean time; and ρ stands for the radius, l for the geocentric latitude and λ for the longitude east of Greenwich of the place of observation.

If in these formulae we substitute $\log \rho \sin l = 9.5488 (-)$, $\log \rho \cos l = 9.9707 (+)$; $\lambda = 55^{\circ}26'95$ and add to the obtained times the adopted longitude of the battery $3^{\text{h}}41^{\text{m}}48^{\text{s}}.1$, the error of which does probably not exceed one second, as appears from the preceding investigation, we obtain the following results.

Con- tact	M. T. Greenw. comp.	M. T. St. Denis comp.	Obs. O.	S,	Obs - Comp.	
					O.	S.
I	13 ^h 55 ^m 55 ^s .0	17 ^h 37 ^m 43 ^s .1	17 ^h 39 ^m 50 ^s ;		+4 ^m 17 ^s	
II	14 26 49, 3	18 8 7,4	missed			
III	17 58 43, 5	21 40 31,6	21 39 16,2	17 ^s .6	-1 15,4	-1 ^m 14 ^s .0
IV	18 28 23, 4	22 10 11,5	22 9 9,7	12,5	-1 1,8	-0 59,0

Neither Mr. SOETERS who observed with the telescope of the heliometer, nor myself who used the Fraunhofer telescope of Mr. DE BEAUFORT ¹⁾ have seen anything of the so-called black drop. The former telescope was provided with the strongest eyepiece, magnifying 86 times, the latter with one magnifying 121,5 times.

I shall say only a few words here on the observations with the heliometer and the photoheliograph.

The heliometer made by MERZ at Munich has caused me through its numerous imperfections much trouble and numerous investigations relative to the instrument proved later to be valueless. Only a few days before the transit took place we detected a defect in the construction of the instrument, which rendered the adjustment of the parallactic stand illusory, so that all the measured position angles were unreliable. Nevertheless I have made complete sets of observations with the heliometer, viz. distances of the "Perseus-stars", for the determination of the scale value and during the transit two sets of eight distances between the limbs of Venus and of the sun. This was as much as the cloudy state of the atmosphere prevailing during the whole transit would allow to do. The first set was made in the ordinary manner, the other along the most advantageous chord. (*Versl. en Meded. Kon. Akad. Amsterdam, Nat. Afd. 2^e Reeks, Vol. IX, p. 127*).

The division errors of the scales must still be determined; I hope to do this soon and then to revert to these measurements.

As to the observations with the photoheliograph, unfortunately the atmosphere, even in the moments that it allowed measurements with the heliometer, had a very bad effect on the clichés made. The

¹⁾ In my previous paper I have erroneously mentioned Mr. SROOP as the owner of this telescope; he possessed it in 1835, when KAISER used it for his observations of the comet Halley.

limbs of Venus are generally so ill defined that there is no question of making microscopic measurements. Dr. P.-J. KAISER, assisted by Mr. M. B. ROST VAN TONNINGEN, has done everything in his power to succeed, but specially in making photographic observations we are powerless against atmospheric conditions.

I cannot finish this paper without expressing our thanks to the Dutch and Dutch East Indian Government, who have assisted the expedition to Réunion as much as they could, also to the Teyler Society, the "Hollandsche Maatschappij der Wetenschappen", both at Haarlem, to the "Bataafsch Genootschap" at Rotterdam and to Mr. DE BEAUFORT, who contributed efficiently (the TEYLER Society and Mr. DE BEAUFORT by lending the photo-heliograph and a telescope) to procure the necessary means to the expedition. We have also cordially to thank the Governor of Réunion, (Mr. DE LORMEL)¹), the Maire of St. Denis, (Med. Dr. Le SINÈR), the director of the "Banque de la Réunion", (Mr. BRIDET), who often assisted and advised us, and further several other inhabitants of St. Denis, who opened their houses to us. Among these I mention MESSRS. BERTHO, HUGOT, DE TOURIS and PEZZANI. In Mr. CHAILLIEY, watchmaker, we fortunately found a clever instrumentmaker, who several times made the necessary reparations to our instruments.

I must also mention that Mr. SOETERS (engineer of the Geographical service at Java) during the passage from Batavia via Aden to Réunion suffered already from the first attacks of a liver-complaint, which a few years later, April 10th 1879 carried him to his grave. At St. Denis he was sometimes for several days unable to assist me at the heliometer, then Mr. BAKHUYZEN obligingly took his place. On these occasions he was looked after with the greatest care by the military surgeon Mr. MUIRCEC.

Lastly I mention the valuable assistance in several respects given by the "amanuensis" of the expedition Mr. T. F. BLANKEN.

¹) Scarcely had we cast anchor in the harbour of St. Denis, when the harbour-master arrived in a boat to offer us in the name of the Government his assistance to carry ashore the passengers, the luggage and the instruments,

TABLE 1b.

Results for the longitude of St. Denis de la Réunion, from disappearances and reappearances separately.

The 3 reappearances give $\Sigma G = 2.19$	$\Sigma G \Delta L = + 3.97$	hence $\Delta L_{Re} = + 1^s.81$
The total sum was	21.80	- 63.25
Hence the disappearances alone	19.51	- 67.22
		$\Delta L_{Dis} = - 3^s.43$
		Mean - 0^s.81

N ^o .	ε	G ²
------------------	---	----------------

Disappearances.

1	+ 5 ^s .07	17.99
2	- 3.42	7.02
3	+ 11.67	100.78
4	+ 11.99	86.26
5	- 2.59	6.04
6	- 3.32	10.96
7	+ 6.55	12.44
9	- 3.32	5.51
10	+ 3.01	5.71
11	+ 2.06	3.77
12	- 1.56	2.36
19	- 9.71	25.46
20	- 1.56	2.43
22	+ 3.56	5.07
23	- 0.66	0.42
24	- 0.60	0.19
25	- 0.16	0.01
27	- 2.40	4.37
28	+ 2.43	5.13
29	+ 3.45	2.26
30	- 3.52	7.19
31	+ 1.03	0.37
32	- 2.68	4.45
34	- 3.04	9.19
35	+ 0.64	0.40
36	- 1.03	1.03
37	- 6.66	30.12
38	+ 1.25	1.14

$$\begin{aligned}
 27 \ m^2 &= 358.07 \\
 m^2 &= 13.26 \\
 m &= \pm 3^s.64 \\
 &\text{(not used)}
 \end{aligned}$$

Together:

$$\begin{aligned}
 29 \ m^2 &= 363.87 \\
 m^2 &= 12.55 \\
 m &= \pm 3^s.54
 \end{aligned}$$

$$\frac{m^2}{19.61} = 0.64 \quad \checkmark = \pm 0^s.80$$

$$\frac{m^2}{2.19} = 5.27 \quad \checkmark = \pm 2^s.30$$

Reappearances.

14	+ 1.32	1.58
16	- 3.88	4.21
18	- 0.11	0.01

$$\begin{aligned}
 2 \ m^2 &= 5.80 \\
 m^2 &= 2.90 \\
 m &= \pm 1^s.70 \\
 &\text{(not used)}
 \end{aligned}$$

$$\begin{aligned}
 &5.91 \\
 &4 \frac{\quad}{\quad} \\
 &1.48 \quad \checkmark = \pm 1^s.22
 \end{aligned}$$

TABLE II.

Results for ΔL after the application of the correction for the radius, disappearances and reappearances together.

No.	ΔL	Corr.	ΔL corr.	G	$G \cdot \Delta L$	z	Gz^2
1	+1 ^s 64	+0 ^s 85	+2 ^s 49	0.70	+1.74	+4 ^s 64	16.07
2	-6.85	+1.13	-5.72	0.60	-3.43	-3.75	7.64
3	+8.24	+0.77	+9.01	0.74	+6.67	+11.16	92.17
4	+8.56	+0.81	+9.37	0.60	+5.62	+11.52	79.63
5	-6.02	+0.74	-5.28	0.90	-4.75	-3.13	8.82
6	-6.75	+0.80	-5.95	0.995	-5.92	-3.80	14.37
7	+3.12	+0.90	+4.02	0.29	+1.17	+6.17	11.04
9	-6.75	+3.75	-3.00	0.50	-1.50	-0.85	0.36
10	-0.42	+0.74	+0.32	0.63	+0.20	+2.47	3.84
11	-1.37	+1.12	-0.25	0.89	-0.22	+1.90	3.21
12	-4.99	+0.78	-4.21	0.97	-4.08	-2.06	4.11
14 R	+3.13	-1.24	+1.89	0.91	+1.72	+4.04	14.85
16 R	-2.07	-1.60	-3.67	0.28	-1.03	-1.52	0.65
18 R	+1.70	-0.77	+0.93	1.00	+0.93	+3.08	9.49
19	-13.14	+1.39	-11.75	0.27	-3.17	-9.60	24.88
20	-4.99	+0.75	-4.24	1.00	-4.24	-2.09	4.37
22	+0.13	+0.97	+1.10	0.40	+0.44	+3.25	4.22
23	-4.09	+0.81	-3.28	0.95	-3.12	-1.13	1.22
24	-4.03	+0.88	-3.15	0.515	-1.62	-1.00	0.51
25	-3.59	+0.90	-2.69	0.49	-1.32	-0.54	0.14
27	-5.53	+0.74	-4.79	0.99	-4.74	-2.64	6.90
28	-1.00	+0.84	-0.16	0.87	-0.14	+1.99	3.45
29	+0.02	+1.06	+1.08	0.19	+0.21	+3.23	1.98
30	-6.95	+0.80	-6.15	0.58	-3.57	-4.00	9.28
31	-2.40	+0.92	-1.48	0.35	-0.52	+0.67	0.16
32	-6.11	+0.79	-5.32	0.62	-3.30	-3.17	6.23
34	-6.47	+0.92	-5.55	0.95	-5.27	-3.40	10.98
35	-2.79	+1.06	-1.73	0.98	-1.69	+0.42	0.18
36	-4.46	+0.99 ^s	-3.46	0.97	-3.36	-1.31	1.67
37	-9.09	+1.05	-8.04	0.94	-7.56	-5.89	32.61
38	-2.18	+0.77	-1.41	0.73	-1.03	+0.74	0.40
				21.80	+18.70	30 $m^2 = 374.43$	
					-65.58	$m^2 = 12.48$	
					-46.88	$m = \pm 3^s 53$	
				21.80	-2 ^s 15	$\frac{m^2}{21.80} = 0.572, \sqrt{} = \pm 0^s 76$	

Utrecht, June 24, 1905.

Chemistry. — “On some derivatives of Phenylcarbamic acid.”

By Dr. F. M. JAEGER. (Communicated by Prof. P. VAN ROMBURGH).

The following contains a crystallographic description of some derivatives, chiefly nitroderivatives of phenylcarbamic acid $C_6H_5 \cdot NH \cdot COOH$ which have been kindly presented to me by Prof. VAN ROMBURGH. The substances belonging to this series, which have been investigated are:

Phenylcarbamic Methyl-ester.

Methylphenylcarbamic Methyl-ester.

1-4-Nitromethylphenylcarbamic Methyl-ester.

1-2-4-Dinitromethylphenylcarbamic Methyl-ester.

1-2-4-6-Trinitromethylphenylcarbamic Methyl-ester. (α -Modification).

1-2-4-6-Trinitromethylphenylcarbamic Methyl-ester. (β -Modification).

1-2-4-Dinitromethylphenylcarbamic Aethyl-ester.

1-2-4-6-Trinitromethylphenylcarbamic Aethyl-ester.

In addition, a description is given of *1-2-4-6-Methylphenylnitramine* m. p. $127^\circ C.$, which has been obtained from *1-2-4-Dinitromonomethyl-aniline* m. p. $178^\circ C.$ by means of fuming nitric acid, which aniline is the product of decomposition of the two *Dinitromethylphenylcarbamic esters* on heating with strong hydrochloric acid ¹⁾, and which has been already described by me in the *Zeits. f. Kryst. Bd. 40* (1905). p. 119.

1. Phenylcarbamic Methyl-ester.

$C_6H_5 \cdot NH \cdot CO \cdot O(CH_3)$; m. p. $47^\circ C.$

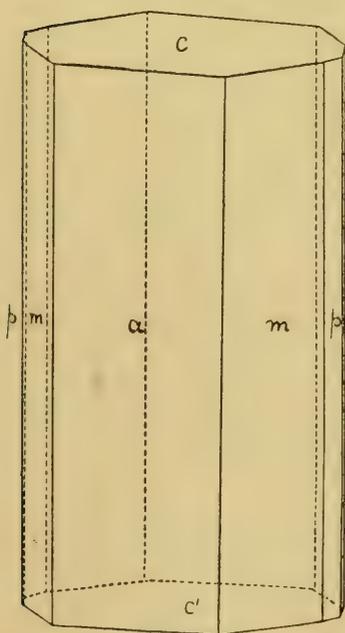


Fig. 1.

The compound crystallises best from alcohol and always in the form of colorless, elongated, rectangular little plates, which are very poor in combination forms.

Rhombic bipyramidal.

$$a : b = 1,5952 : 1.$$

The relation $b : c$ cannot be determined on account of the absence of planes from the zones of $(100,001)$, and of $(001,010)$.

Forms observed: $a = \{100\}$, strongly predominating often vertically striped; $p = \{110\}$, very lustrous; $m = \{120\}$, narrow or totally wanting and sometimes as strongly developed as p ; $b = \{010\}$, indicated only a few times; $c = \{001\}$, reflects well.

¹⁾ VAN ROMBURGH. On the action of nitric acid on the esters methylphenylaminoformic acid. *Proc.* 29 Dec. 1900, Vol. III. p. 451.

	<i>Measured :</i>	<i>Calculated :</i>
$a : p = (100) : (110) =$	$57^{\circ} 55'$	—
$a : m = (100) : (120) =$	38 31	$38^{\circ} 34\frac{1}{2}'$
$a : c = (100) : (001) =$	90 4	90 0
$m : p = (120) : (110) =$	19 34	19 24
$p : p = (110) : (\bar{1}10) =$	64 10	64 10
$p : b = (110) : (010) =$	32 10	32 5

Completely cleavable towards $\{001\}$ and towards $\{100\}$.

Orientated extinction on all planes in the vertical zone. The optical axial plane is $\{001\}$ with a as acute diagonal. The axial angle is small, the dispersion fair with $\rho > v$ around the a -axis.

The sp. gr. of the crystals is 1,251 at 19° ; the equivalent volume 120,7.

2. Methyl-Phenylcarbamic Methyl-ester.

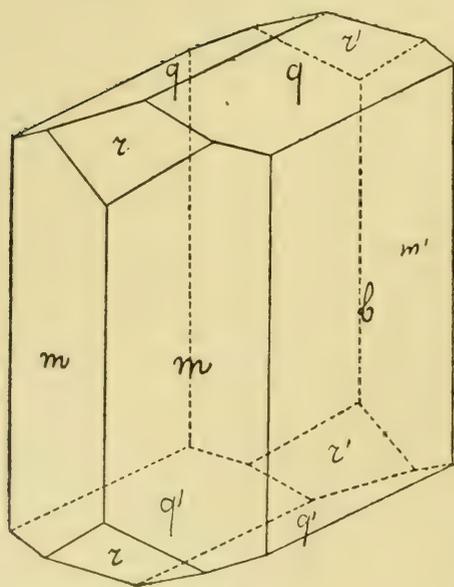
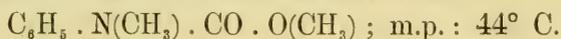


Fig. 2.

The compound crystallises from alcohol in large colourless crystals, which are frequently in clusters, often exhibit rather opaque planes and possess a peculiar camphor-like odour.

Rhombic-bipyramidal.

$$a : b : c = 0,8406 : 1 : 0,3320.$$

Forms observed :

$b = \{010\}$, strongly predominating; $m = \{110\}$, and $q = \{011\}$, both well developed and yielding sharp reflexes; $r = \{201\}$, fairly lustrous.

Different crystal-individuals exhibit not inconsiderable differences in the angular values.

	<i>Measured :</i>	<i>Calculated :</i>
$b : m = (010) : (110) =$	$49^{\circ} 57'$	—
$b : q = (010) : (011) =$	$71 38$	—
$r : r = (\bar{2}01) : (\bar{2}01) =$	103 25	$103^{\circ} 23'$
$r : m = (201) : (110) =$	61 54	$61 40\frac{1}{3}'$

Very completely cleavable towards b .

The optical axial plane $\{001\}$ whilst b is the first diagonal. The axial angle is small, the dispersion strong and perhaps abnormal. It was not possible to properly characterise it with the means at my disposal.

The sp. gr. of the crystals is 1,296, at 19° ; the equivalent volume 127,31.

Topical axes : $\chi : \psi : \omega = 5,1358 : 6,1099 : 4,0569$.

On account of the symbol $\{201\}$ the relation $b : c = 1 : 0,6640$ has been taken.

3. 1-4-Nitro-Methyl-Phenyl-Carbamic Methyl-ester.

$C_6H_4(NO_2) \cdot N(CH_3) \cdot CO \cdot O(CH_3)$; melting point : $108^\circ C$.
(4) (1)

This compound crystallises from alcohol or benzene in the form of small delicate needles, or large, pale-sherry coloured, somewhat

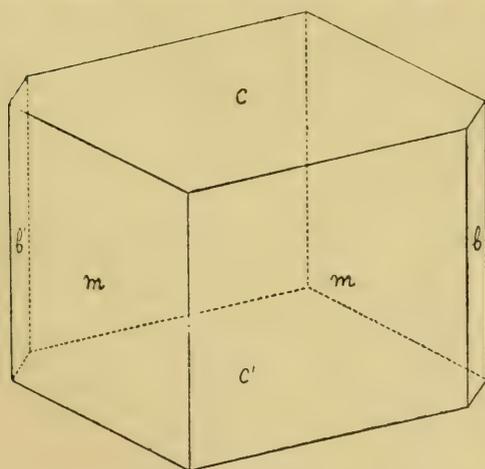


Fig. 3.

flat crystals, which, however, are very poor in planes, and, therefore, do not allow of a complete parameter-determination.

Monoclinic-prismatic.

$a : b = 0,6640 : 1$.

$\beta = 70^\circ 58'$.

Forms observed :

$c = \{001\}$ generally strongly predominating ; $m = \{110\}$ well developed ; $b = \{010\}$, narrow. Often the planes of m and b are curved and the crystals exhibit greater anomalies in the angular

values.

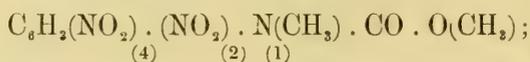
The habitus is mostly broadly flattened towards c , sometimes c and m are equally large and the habitus consequently becomes rhombohedral.

Very completely cleavable towards $\{001\}$.

The optical axial plane is probably $\{010\}$; on c one optical axis is visible on the border of the field of vision.

The sp. gr. of the crystals is 1,522 at 14° ; the equivalent-volume = 137,98.

4. 1-2-4-Dinitro-Methyl-Phenylcarbamic Methyl-ester.



m.p.: 98° C.

The best crystals are obtained from xylene. They are of a pale yellow colour and have the appearance of small, thick parallelogram-shaped crystals.

Monoclinic-prismatic.

$$a : b : c = 0,7597 : 1 : 1,0875.$$

$$\beta = 88^\circ 43\frac{1}{3}'.$$

Forms observed: $b = \{010\}$, predominating and very lustrous; $r = \{\bar{1}01\}$, broad and sharply reflecting; $\omega = \{111\}$, also broad and very lustrous; $o = \{\bar{1}\bar{1}1\}$, somewhat smaller than r but giving a good reflection; $q = \{011\}$, small and approximately measurable. The crystals are broadly flattened towards b .

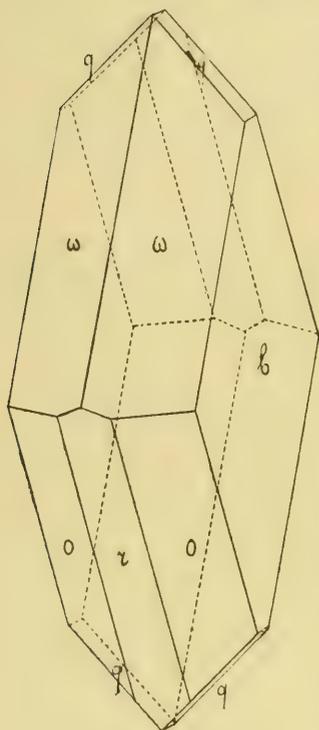


Fig. 4.

	<i>Measured:</i>	<i>Calculated:</i>
$o : r = (\bar{1}\bar{1}1) : (\bar{1}01) =^* 32^\circ 44'$		—
$\omega : \omega = (111) : (1\bar{1}\bar{1}) =^* 64^\circ 22\frac{1}{2}'$		—
$o : \omega = (\bar{1}\bar{1}1) : (111) =^* 86^\circ 37\frac{1}{2}'$		—
$b : \omega = (010) : (111) = 57^\circ 51'$		$57^\circ 49'$
$b : o = (010) : (\bar{1}\bar{1}1) = 57^\circ 0'$		$57^\circ 16'$
$\omega : q = (111) : (011) = 42^\circ 35' \text{ (about)}$		$42^\circ 54'$
$\omega : o = (\bar{1}\bar{1}1) : (\bar{1}\bar{1}\bar{1}) = 58^\circ 26'$		$58^\circ 12'$
$\omega : r = (\bar{1}\bar{1}\bar{1}) : (\bar{1}01) = 74^\circ 12'$		$74^\circ 24'$

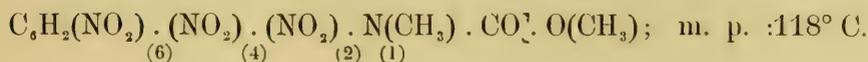
Cleavable towards $\{\bar{1}\bar{1}1\}$.

On $\{010\}$, the angle of extinction with regard to the side $b : \omega$ is 22° ; an axial image could not be observed.

The sp. gr. of the crystals is 1,506, at 14° ; the equivalent volume = 169,32.

Topical axes: $\chi : \psi : \omega = 4,4794 : 5,8963 : 6,4123$.

5. 1-2-4-6-Trinitro-Methyl-Phenylcarbamic Methyl-ester.



This compound occurs in two modifications.

α-Modification.

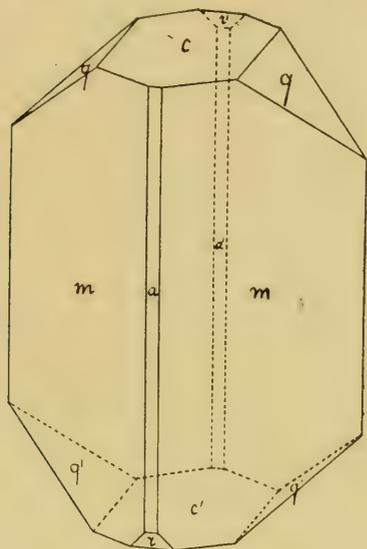


Fig. 5.

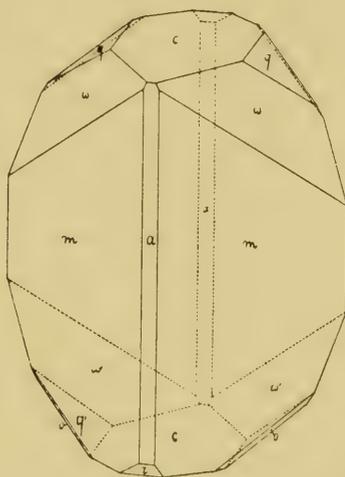


Fig. 6.

This *α*-modification is the one usually deposited from the ordinary solvents, alcohol, acetone, benzene etc. The crystals described here have been obtained from acetone. They are colourless or of a pale sherry colour and very lustrous.

Monoclinic-prismatic.

$$a : b : c = 0,5758 ; 1,08382.$$

$$\beta = 75^\circ 41'.$$

Forms observed: $m = \{110\}$, broad and very lustrous; $c = \{001\}$, ideal reflection; $q = \{011\}$, large and very lustrous; $w = \{121\}$, generally broader than q , sometimes also narrower or even completely wanting; $a = \{100\}$, lustrous but narrow; $r = \{\bar{1}01\}$ is often wanting but reflects well; $o = \{\bar{1}21\}$ very narrow and dull.

Measured: *Calculated:*

$a : c = (100) : (001) =$	$^* 75^\circ 41'$	—
$a : m = (100) : (110) =$	$^* 29 \ 9\frac{1}{2}$	—
$c : q = (001) : (011) =$	$^* 39 \ 5$	—

	<i>Measured:</i>	<i>Calculated:</i>
$m : c = (110) : (001) =$	$77\ 32\frac{1}{2}$	$77^{\circ}32'$
$m : q = (110) : (011) =$	$61\ 47$	$61\ 39$
$m : \omega = (110) : (121) =$	$26\ 30$	$26\ 27$
$a : \omega = (100) : (121) =$	$47\ 55\frac{1}{2}$	$48\ 0$
$\omega : c = (121) : (001) =$	$57\ 43$	$57\ 42$
$\omega : q = (121) : (011) =$	$35\ 16$	$35\ 12$
$m : q = (\bar{1}10) : (011) =$	$81\ 40$	$81\ 59$
$m : o = (\bar{1}10) : (\bar{1}21) =$	$34\ 39\frac{1}{2}$	$34\ 37\frac{1}{2}$
$o : q = (\bar{1}21) : (011) =$	$46\ 19\frac{1}{2}$	$46\ 22$
$c : r = (001) : (\bar{1}01) =$	$65\ 38\frac{1}{2}$	$65\ 36$
$a : r = (\bar{1}00) : (\bar{1}01) =$	$38\ 51\frac{1}{2}$	$38\ 43$
$m : r = (\bar{1}\bar{1}0) : (\bar{1}01) =$	$47\ 2$	$47\ 3$
$r : q = (\bar{1}01) : (011) =$	$70\ 59\frac{1}{2}$	$71\ 17\frac{3}{4}$

No distinct plane of cleavability was found; perhaps there is one present parallel to m .

The symmetric extinction on $\{110\}$ with regard to the side $(110) : (\bar{1}\bar{1}0)$, etc. amounts to about 18° ; on a and c it is normally orientated. The average refraction is a trifle greater than that of α -monobromo-naphthalene.

The sp. gr. gravity of the crystals is 1,612, at 19° ; the equivalent volume is 186,10.

Topical axes: $\chi : \psi : \omega = 4,2360 : 7,3555 : 6,1655$.

5b. Trinitro-Methyl-Phenylcarbamic Methylester.

β -Modification. When long kept, the crystals of the α -modification turn a little darker, somewhat more orange-yellow. The symmetry and all the angles of the α -modification are, however, preserved.

Sometimes, the alcohol deposits long needles together with crystals of the α -modification. These needles have an orange colour; at about 105° they again turn yellow and then melt just a little below 118° . Although it is not as yet quite clear in what relation these needles stand to the crystals, it is nevertheless certain, that they represent a second less stable modification of the compound. The meltingpoint of the crystals of the α -modification obtained from various solvents, or after heating in diffe-

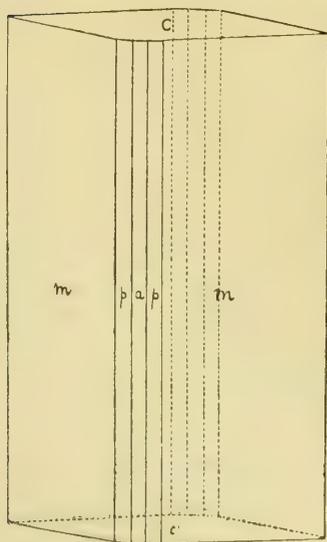


Fig. 7.

rent ways, fluctuates between 114° and 118° . A further investigation will be necessary to see what really takes place here.

Rhombic-bipyramidal.

$$a : b = 0,6596 : 1.$$

The relation $b : c$ cannot be determined, for want of the necessary terminal planes.

Forms observed: $m = \{110\}$, broad and lustrous; $c = \{001\}$, very sharply reflecting; $a = \{100\}$, narrow, well reflecting; $p = \{310\}$, very narrow and yielding bad reflexes.

	<i>Measured:</i>	<i>Calculated:</i>
$a : m = (100) : (110) =$	$33^\circ 24\frac{1}{2}'$	—
$m : m = (110) : (\bar{1}10) =$	$113 11\frac{1}{2}$	$113^\circ 11'$
$m : c = (110) : (001) =$	$90 1$	$90 0$
$m : p = (110) : (310) =$	$20 17$ (about)	$21 0$
$p : a = (310) : (100) =$	$13 2$ (about)	$12 24$

Perfectly cleavable towards $\{001\}$.

The optical axial plane is $\{001\}$; the first diagonal is the a -axis. The apparent axial angle is in α -monobromonaphthalene about 86° ; extraordinary strong dispersion with $\rho > v$, round the first bissectrix. Orientated extinction everywhere in the vertical zone.

The sp. gr. of the needles is 1,601, at 19° ; the equivalent volume = 187,32.

6. 1-2-4-Dinitro-Methyl-Phenylcarbamic Ethyl-ester.

$C_6 H_3 (NO_2)_{(4)} \cdot (NO_2)_{(2)} \cdot N_{(1)} (CH_3) \cdot CO \cdot O (C_2 H_5)$; m. p. $112^\circ C$.

This compound crystallises from a mixture of benzene and ligroine in the form of large, colourless, very lustrous crystals represented in fig 8.

Monoclinic-prismatic.

$$a : b : c = 0,6525 : 1 : 0,7035.$$

$$\beta = 69^\circ 59'.$$

Forms observed: $c = \{001\}$, predominating and very lustrous; $b = \{010\}$, about as broad as c and sharply reflecting; $m = \{110\}$, well reflecting and properly developed, sometimes with delicate striping parallel to $m : c$; $q = \{011\}$, narrower but readily measurable; $r = \{1\bar{0}1\}$, very distinctly developed and yielding

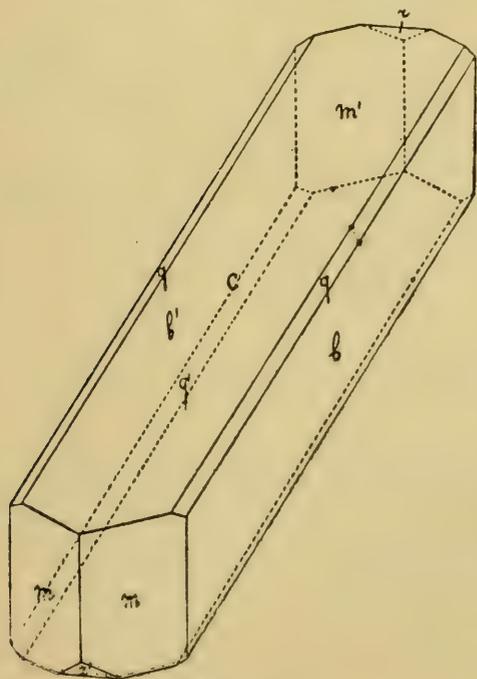


Fig. 8.

sharp reflexes; $\bar{p} = \{120\}$, very narrow and dull; often absent altogether.

	<i>Measured:</i>	<i>Calculated:</i>
$m : m = (100) \quad \bar{1}10 = *63^\circ 11\frac{1}{2}'$		—
$m : c = (110) : (001) = *73 \quad 2$		—
$q : c = (011) : (001) = *33 \quad 28$		—
$q : b = (011) : (010) = 56 \quad 32$		56° 32'
$m : b = (110) : (010) = 58 \quad 26\frac{1}{2}$		58 29
$m : p = (110) : (120) = 19 \quad 12$		19 17
$p : b = (120) : (010) = 39 \quad 23\frac{1}{2}$		39 12
$r : c = (\bar{1}01) : (001) = 58 \quad 10$		58 5
$r : m = (1\bar{0}\bar{1}) : (110) = 58 \quad 12$		58 18
$m : q = (110) : (01\bar{1}) = 57 \quad 58\frac{1}{2}$ (circa)		58 41
$q : r = (01\bar{1}) : (\bar{1}01) = 63 \quad 41\frac{1}{2}$ (circa)		63 22
$c : b = (001) : (010) = 89 \quad 58$		90 0

Very perfectly cleavable towards $\{001\}$; like "glimmer" the crystals may be reduced to very delicate lamellae.

On $\{001\}$ orientated extinction; on $\{110\}$ the inclination of the one elasticity-axis towards the vertical axis amounts to 19° ; on $\{010\}$: 27° with regard to the side $b : c$, in the acute angle β . The axial plane is, probably, situated perpendicularly to $\{010\}$. By means of α -monobromonaphthalene etched figures were obtained on m , c and b , which are in accordance with the indicated symmetry.

The sp. gr. of the crystals is 1,461 at 19° C.; the equivalent volume = 184,12.

Topical axes: $\chi : \psi : \omega = 4,9130 : 7,5296 : 5,2970$.

7. 1-2-4-6-Trinitromethylphenylcarbamic Ethyl-ester.

$C_6H_2(NO_2)_6 \cdot N(CH_3) \cdot CO \cdot O(C_2H_5)$; m.p. 65° C.
(6) (4) (2) (1)

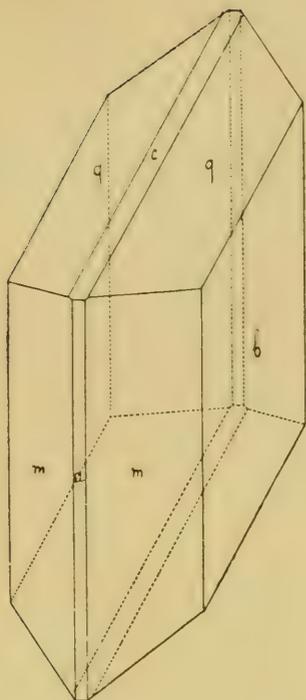


Fig. 9.

The crystals which have been measured are derived from a mixture of benzene and ligroine.

Delicate, very transparent, flat, pale sherry-coloured needles which possess a strong lustre.

Monoclinic-prismatic.

$$a : b : c = 0,9759 : 1 : 0,3929$$

$$\beta = 67^{\circ}7'.$$

Forms observed: $b = \{010\}$, yielding ideal reflexes and well developed: $o = \{\bar{1}21\}$, $a = \{100\}$, and $c = \{001\}$, very narrow and dull; $m = \{110\}$, broad and very lustrous; $q = \{011\}$, well developed and yielding sharp reflexes; an orthodome $\{h\ o\ k\}$ is indicated but not measurable. The needles are elongated towards the c -axis and somewhat flattened towards $\{010\}$.

	<i>Measured:</i>	<i>Calculated:</i>
$m : m = (110) : (110) =$	$*83^{\circ} 55'$	—
$m : q = (110) : (011) =$	$*60 \quad 2$	—
$q : q = (011) : (0\bar{1}1) =$	$*39 \quad 48$	—
$m : b = (110) : (010) =$	$48 \quad 3$	$48^{\circ} 1\frac{1}{2}'$
$b : q = (010) : (011) =$	$70 \quad 6$	$70 \quad 6$
$m : q = (\bar{1}10) : (\bar{0}11) =$	$119 \quad 58$	$119 \quad 58$
$m : o = (\bar{1}10) : (\bar{1}21) =$	$64 \quad 46$	$65 \quad 2$
$o : q = (\bar{1}21) : (011) =$	$27 \quad 32$	$27 \quad 29$
$q : m = (011) : (\bar{1}10) =$	$87 \quad 42$	$87 \quad 28$
$m : a = (110) : (100) =$	$41 \quad 57$	$41 \quad 57\frac{1}{2}$

A distinct cleavability was not observed.

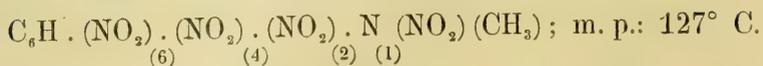
The angle of extinction on b is 9° with regard to the vertical axis, in the acute angle $a : c$; on m it is about $6\frac{1}{2}^{\circ}$.

In oil of cloves, solution figures were obtained as represented in fig. 8; they are in accordance with the found symmetry.

The sp. gr. of the crystals is $= 1,471$ at 14° ; the equivalent volume $= 194, \pm 2$.

Topical axes: $\chi = \psi : \omega = 7,9976 : 8,1950 : 3,2198$.

8. 1-2-4-6-Trinitrophenylmethylnitramine.



The compound is obtained from benzene + acetone in the shape of small, very strongly refracting, pale sherry-coloured needles, which possess a strong lustre and are, geometrically, very well built.

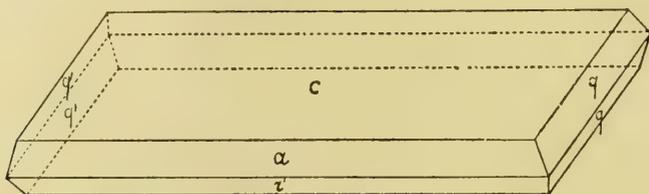


Fig. 10.

Monoclinic prismatic.

$$a : b : c = 2,7823 : 1 : 3,5242.$$

$$\beta = 75^\circ 31\frac{1}{2}'.$$

Forms observed: $c = \{001\}$, most strongly developed of all; $a = \{100\}$ and $r = \{\bar{1}01\}$, both strongly reflecting; $q = \{011\}$ somewhat more opaque.

	<i>Measured:</i>	<i>Calculated:</i>
$a : c = (100) : (001) =$	$* 75^\circ 31\frac{1}{2}'$	—
$a : r = (\bar{1}00) : (\bar{1}01) =$	$* 43 36\frac{1}{2}'$	—
$c : q = (001) : (011) =$	$* 73 40$	—
$c : r = (001) : (\bar{1}01) =$	60 53	$60^\circ 53'$
$q : q = (011) : (0\bar{1}1) =$	32 32	32 40
$a : q = (100) : (011) =$	85 54	85 58 $\frac{1}{2}'$

A distinct cleavability was not found.

Optical axial plane is $\{010\}$; on $\{001\}$ one axis is placed nearly perpendicular. The double refraction is moderate and negative; extraordinarily great dispersion with $q > v$.

The sp. gr. of the little crystals is: 1,570, at 19° ; the equivalent volume = 182,16.

$$\text{Topical axes: } \chi : \psi : \omega = 7,4485 : 2,6772 : 9,4347.$$

Chemistry. — “On the presence of lupeol in some kinds of gutta-percha.” By Prof. P. VAN ROMBURGH.

An investigation of the so-called resinous constituents of various authentic kinds of gutta-percha, made first in conjunction with Dr. SACK and afterwards with Dr. v. D. LINDEN, has shown that some of them contain various cinnamic esters of alcohols which seem related to cholesterol. One of these cinnamic esters, which appeared identical with TSCHIRCH's¹⁾ crystal-albane, and occurs as a beautifully crystallised compound m.p. 241° (corr.) I have submitted to a closer investigation, with Dr. v. D. LINDEN. On saponification, an alcohol was obtained melting at 210°, which on being treated with benzoyl chloride and pyridine yielded a benzoate melting at 264° (corr.). The melting points of these two last substances agree exactly with those of lupeol and its benzoate.

Lupeol has been discovered by E. SCHULZE²⁾ in the skins of lupines. At my request Prof. SCHULZE was kind enough to present me with a quantity of lupeol and its benzoate for the purpose of comparison, for which I wish here to express my best thanks. The alcohol being mixed with the lupeol, the melting point was not lowered; neither was this the case with the benzoates.

In addition to its occurrence as a cinnamic ester, lupeol also seems to occur as an acetate in a substance related to gutta-percha, called “djelutung”, the product of the milky juice from some species of *Dyera*, which is known in European commerce under the name of “bresk” or Pontianak; this has been shown to be probable by Mr. COHEN, who is making a study of this article in my laboratory. In a consignment of “bresk” for which I have to thank Messrs. WEISE & Co., of Rotterdam, the amount of lupeol appeared to be rather considerable, thus enabling Mr. COHEN to make a study of this otherwise somewhat inaccessible product. On oxidation with chromic acid a beautifully crystallised ketone (m. p. 169°) has already been obtained, which also yields with hydroxylamine a crystalline substance.

Mr. COHEN, who intends to further investigate these substances, has also found in the “djelutung” the substance melting at 235°, which I had found previously in the gutta-percha from *Payena Leerii*, and which has been characterised as the acetic ester of an alcohol melting at 195°.

¹⁾ Arch. d. Pharm. 241, 653.

²⁾ Zeitschr. f. physiol. Chemie 15, 415; 41, 474.

Chemistry. — “*On the action of ammonia and amines on allyl formate*”. By Prof. P. VAN ROMBURGH.

The great ease with which allyl formate is saponified by alkalis induced me to try whether ammonia, which, as is well-known, acts upon esters of fatty acids but slowly at the ordinary temperature, would not react equally readily on this ester. The result surpassed my expectation.

If gaseous ammonia is passed into allyl formate still containing a little allyl alcohol, it is rapidly absorbed whilst the liquid gradually becomes so hot, that it is necessary to connect the flask with a reflux apparatus in order to prevent loss of ester. If the contents are heated to 120°, when the increase in weight slightly exceeds 1 mol. of ammonia to one mol. of ester, the excess of ammonia passes off with the allyl alcohol and if now the residue is distilled in vacuo, a fine yield of formamide is obtained (b.p.₁₀ 113°), which, after a single freezing, melts at 2°.4¹⁾.

If, however, dry ammonia is passed into *pure* allyl formate, hardly any action is noticed in the first hour. The ammonia is but slowly dissolved so that the concentration is only very small, but gradually as the reaction proceeds the gas is more eagerly absorbed and the temperature rises increasingly.

If, therefore, we wish to prepare in a short time large quantities of formamide by means of this method it is advisable to add to the allyl formate a few percents of allyl alcohol, although this may cause a slight diminution in the limit value²⁾, as happens, generally, in the formation of amides from esters.

I showed many years ago that allyl formate may be readily prepared by heating the diformine³⁾ of glycerol, obtained from glycerol and oxalic acid. As we can now obtain commercial formic acid of great concentration (99—100 %) at a very low price, large quan-

¹⁾ FRANCHIMONT (Rec. XVI, 137) found the melting point at 3°; other observers state a lower figure.

Pure formamide may be distilled by rapid heating without perceptible decomposition (b.p. 219°); at least with such a preparation I did not succeed in demonstrating the formation of ammonia and carbon monoxide, which are readily obtained from an impure product.

²⁾ BONZ, Zeitschr. phys. Chem. II, 865.

³⁾ I think it is not superfluous to point out that the theory recently defended by NEF (Ann. 335, 230) that the formation of allyl alcohol from glycerol and oxalic acid must be explained by a dissociation of diformine into formic acid and propargyl alcohol is based on an error. The main product of diformine on heating is allyl formate.

tities of allyl formate may be prepared in a still more convenient manner by heating equal parts by weight of glycerol and formic acid. The temperature is kept for some time at 125° , during which dilute formic acid distills over. Gradually it is raised to 240° and, with a quiet evolution of CO_2 , containing a little CO , a mixture passes over consisting of allyl formate, allyl alcohol and a very little formic acid. This is again submitted to distillation, the portion boiling up to 100° being collected. After treatment with dry potassium carbonate, the liquid is again distilled and the portion boiling below 85° , which mainly consists of allyl formate, is collected separately.

This ester may also be procured by distilling allyl alcohol with twice its weight of formic acid and collecting the portion passing over below 85° . The product is then treated with dry potassium carbonate and once more rectified.

After it had been ascertained that ammonia acts so very readily with allyl formate it was decided to try the action of amines also.

The investigation showed that amines of the fatty series, primary as well as secondary ones, readily react with the same. Benzylamine, phenylhydrazine and piperidine also seemed to react but no reaction could be observed with aniline.

If we mix one of these amines with allyl formate, in the majority of cases a rise in temperature does not necessarily take place immediately.

This rise rather varies in the different cases; whilst its maximum is sometimes reached fairly quickly, sometimes only after a lapse of about 20 minutes.

The reaction appears to be of such a nature that when working at a constant temperature we can ascertain its progress by means of a quantitative determination of the absorbed amine.

I intend making a series of experiments with different amines. The following contains a brief description of some qualitative experiments.

If methyl- or ethylamine is passed into allyl formate these substances are absorbed with great evolution of heat and the amides formed are left behind after distilling off the allyl alcohol.

5 grams of propylamine being mixed with 10 grams of allyl formate the temperature rapidly rose from 19° to 60° and propylformamide (b.p. 219° — 220°) was formed.

5 grams of isopropylamine being mixed with 10 grams of the ester the temperature slowly rose to 50° , whilst a good yield of isopropylformamide was obtained (b.p. 203° — 204°).

5 grams of isobutylamine being mixed with 7 grams of allyl formate the temperature rose to 75°. The — not as yet described — isobutylformamide boiled at 229°.

5 grams of allylamine being mixed with 10 grams of the ester the temperature rose to 65° and the allyl alcohol being removed by distillation, allylformamide was obtained (b.p. 220°.5).

With benzylamine (5 grams) and allyl formate (5 grams) the temperature rose from 19° to 55°. The alcohol being distilled off and allowed to cool to the ordinary temperature, there remained in the flask a solid mass, m. p. 62°. The melting point was not altered after recrystallisation the compound from petroleum ether, which is very suitable for this purpose.

Benzylformamide was first obtained by HOLLEMAN¹⁾, who described it as a substance melting at 49°. This statement is probably due to a clerical error, at least, a specimen prepared by Prof. HOLLEMAN and kindly presented to me by Dr. VERMEULEN of the Groningen Laboratory did not begin to soften until 59°. Boiling petroleum ether extracted a substance melting at 62°, which on being mixed with my own product did not alter its melting point.

Phenylhydrazine gives no rise of temperature with allyl formate, but on being kept for a day, an abundant quantity of formylphenylhydrazine forms, m. p. 145°.

With secondary aliphatic amines there is less heat evolved in the action on allyl formate.

Dimethylamine readily forms dimethylformamide. The action of 7 grams diethylamine on 10 grams of allyl formate causes (in about 20 minutes) a slow rise to 33°. Diaethylformamide was readily obtainable in a pure condition. Dipropylamine (5 grams) mixed in a WEINHOLD flask with 5 grams of the ester caused a slow rise to 35°.5. The dipropylformamide obtained boiled at 211° (corr.).

Judging from a preliminary experiment, diisopropylamine seems to react less readily; 3 grams of both compounds being mixed, only a slight elevation of temperature was noticed. This reaction deserves in particular a closer study.

With diisobutylamine the evolution of heat is also trifling; only 3° rise 10 grams of each substance being mixed. All the same, a good yield of diisobutylformamide was obtained, which boils at 227°—228° (corr.) and which, to my knowledge, has not yet been described.

Methylbenzylformamide (5 grams) with allyl formate (5 grams) gives a rise to 55°. The product formed has not yet been solidified.

¹⁾ Rec. 13. 415.

Piperidine (10 grams) with allyl formate (14 grams) gives a rise from 10° to 83°, and a very good yield of the formyl derivative, b. p. 220°.

The boiling points of the substituted formamides exhibit peculiar regularities to which I hope to refer later on.

The dialkylformamides and formylpiperidine have acquired some importance owing to the interesting researches of BOUVEAULT¹⁾, who used them as a starting point in the preparation of aldehydes; the above described simple methods of preparation may perhaps prove to be of service.

Chemistry. — “*On the action of hydrocyanic acid on ketones*”.

By A. J. ULTEE. (Communicated by Prof. P. VAN ROMBURGH).

Although it is stated in every textbook on organic chemistry that ketones may combine with hydrocyanic acid, the conditions under which this addition takes place have up to the present not been studied, and only those few cyanohydrins which are solid and may consequently be readily purified by recrystallisation have been isolated in a pure condition²⁾.

Three methods of formation of these substances are known:

1st. Action of dilute or anhydrous hydrocyanic acid on ketones, either by heating the mixture for some hours in sealed tubes at 100° or by simply leaving the two components in contact with each other at the ordinary temperature for several months.

2nd. Action of nascent hydrogen cyanide on ketones, for instance by very slowly dropping fuming hydrochloric acid on potassium cyanide covered with acetone.

3rd. By double decomposition of the so-called bisulphite compounds of the ketones with a solution of potassium cyanide.

A closer study of the nitriles of the oxy-acids was made in consequence of an observation made by Prof. VAN ROMBURGH³⁾ as to the action of solid potassium carbonate on a mixture of dry acetone and hydrocyanic acid; a small quantity of this salt caused the mass to boil and the temperature to rise to 70°.

The same phenomenon is caused by potassium hydroxide, potassium cyanide, ammonia, amines, in fact by all substances whose aqueous

¹⁾ Bull. Soc. chim. [3] **31**, 1322.

²⁾ Acetonecyanohydrin, obtained from Kalilbaum, seemed to contain much free hydrocyanic acid.

³⁾ Meeting 27 June 1896.

solutions possess hydroxyl ions; the presence of water greatly favours this catalysis.

If an attempt is made to isolate the evidently formed cyanohydrin by distillation under reduced pressure it is again resolved for the greater part into its components. If, however, the action of the potassium carbonate is stopped by means of a few drops of sulphuric acid, the mixture on being fractionated in vacuo first yields a distillate consisting of hydrocyanic acid and acetone and then the nitrile; by a second distillation this may be obtained in such a state of purity that silver nitrate with nitric acid no longer gives a precipitate of silver cyanide.

Traces of a base are, however, sufficient to again partially resolve the pure nitrile into its components, which in this case is, of course, accompanied by a fall in temperature.

Theory demands that the same equilibrium should be reached whether we start from one mol. of acetone plus one mol. of hydrogen cyanide or from pure cyanohydrin. In order to check this it is not necessary to determine the equilibrium both ways by analysis; the easiest plan is to measure some physical constant; for this I chose the refraction.

Found, starting from a mixture of acetone (1 mol.), hydrogen cyanide (1 mol.) and a trace of potassium hydroxide $n_D^{12} = 1,39721$.

Found, starting from the pure nitrile and a trace of potassium hydroxide $n_D^{12} = 1,39818$.

It having been thus ascertained that it makes no difference from what system we start, it became important to express the equilibrium in figures.

For practical reasons I always started from the nitriles; about one gram of the compound and 0,2 milligr. of potassium hydroxide (in a 10% solution) were introduced into a tube, which was then sealed and immersed in a beaker containing a solution of silver nitrate acidified with nitric acid, and the whole was then suspended in a thermostat for some hours.

If now the tube is broken the nitric acid at once neutralises the potassium hydroxide and the free hydrocyanic acid will be precipitated as silver cyanide. The liquid is decanted, the precipitate is dissolved in potassium cyanide and the silver deposited electrolytically in the usual manner. In this way it was found that one mol. of acetone and one mol. of hydrogen cyanide combine at 0° to the extent of 94,15%, at 25° to the extent of 88,60%.

For ethylmethylketone these values are, respectively 95,57% and 90,36%; for diethylketone 95,90% and 91,29%.

It is my intention to also determine this equilibrium in the case of other aliphatic and aromatic ketones and also aldehydes.

The investigation of URECH's diacetocyanohydrin and the products of the action of gaseous hydrochloric acid on oxynitriles quoted by PINNER ¹⁾ but as far as I know not further studied, has already been taken in hand.

In the light of the above results I have examined the different modes of preparation of the oxynitriles more closely.

Method 1. Dry hydrocyanic acid mixed with dry acetone and kept for six months in a well-closed steamed flask is still completely unchanged. On mixing, a slight rise in temperature took place. That, however, no trace of the addition product has been formed may be proved by first determining the total percentage of hydrocyanic acid by means of the well-known titration with silver nitrate and then by ascertaining the amount of free hydrocyanic acid in the same way as was done in the determination of the equilibria. We will then find the same figures. After six months the mixture still showed the same refraction, which also proves that no change had yet taken place.

The reason why previous investigators obtained cyanohydrin all the same may be safely attributed to the fact that there were still present traces of moisture and that minute traces of alkalis from the glass vessel considerably accelerate the reaction.

It is now also obvious why the methods 2 and 3 should lead to a good result as the alkaline potassium cyanide is always present in excess. It need hardly be said that the formation of nascent hydrogen cyanide previously looked upon as the most important factor in method 2 has nothing to do with the real reaction.

Although former investigators ²⁾ have not succeeded in preparing pure cyanohydrin by the second method, nothing is easier than the isolation of the pure nitrile by distillation under reduced pressure, if only care be taken to have a slight excess of hydrochloric acid present after the reaction has taken place.

The following are the chief properties of the nitriles, as yet investigated.

Dimethylketonecyanohydrin is a perfectly colourless liquid practically odourless. Sp. gr. at 18° 0,9342. Decomposes on distillation at the

¹⁾ B. B. 17, 2009.

²⁾ URECH, Ann. 164, 255.

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ordinary pressure, b.p. at 23 mm. 82° , m.p. — $19,5^\circ$, $n_D^{8,5} = 1,40526$.

Ethylmethylketonecyanohydrin, colourless liquid with a faint ketone-like odour. Sp. gr. at $18,5^\circ$ 0,9324. Boiling point at 20,5 m.m. 91° . Does not solidify in a paste of solid carbon dioxide and acetone. $n_D^{12,5} = 1,41775$.

Diethylketonecyanohydrin, colourless, a somewhat stronger odour than the former nitrile. Sp. gr. at $18,5^\circ$ 0,9300. Boiling point at 18,5 m.m. $97,5^\circ$, does not solidify in a paste of carbon dioxide and acetone. $n_D^{18} = 1,42585$.

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Chemistry. — “*The molecular rise of the lower critical temperature of a binary mixture of normal components.*” By J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

1. In the “*Chemisch Weekblad*” of April 8th 1905 (II, N^o. 14) I derived an expression for the so-called molecular rise of the lower critical temperature, viz:

$$\frac{1}{T_1} \left(\frac{dT_x}{dx} \right)_0 = 2\sqrt{\theta\psi} - (1 + \psi),$$

in which θ represents the ratio of the two critical temperatures $\frac{T_2}{T_1}$ and ψ the ratio $\frac{b_2}{b_1}$.

In this I started from the approximate assumption, that the critical temperature of a binary mixture may be represented by the simple expression

$$f R T_x = \frac{a_x}{b_x}.$$

The formula found is at any rate more accurate than that of VAN 'T HOFF, according to which the molecular rise would be *constant* (Chem. Weekbl. of Nov. 21st 1903 (I, N^o. 8)), and I adduced a few examples to show that the expression found by me represents the experimental results of CENTNERSZWER¹⁾ very accurately — provided the molecular weight of the solvent SO_2 is *doubled*.

BÜCHNER in his thesis for the doctorate²⁾ came to pretty much the same result with regard to CO_2 as solvent. He, too, had to double the molecular weight of CO_2 in order to get sufficient concordance

¹⁾ Z. f. Ph. Ch. **46**, 427—501 (1903).

²⁾ June 1905, p. 125—130.

with my formula for the substances examined by him (except for naphthaline and chloro-nitrobenzol).

Now BÜCHNER thinks the assumption of a $(\text{CO}_2)_2$ bimolecular at the critical temperature very doubtful, and KUENEN too recently called my attention to the fact that according to *his* measurements ¹⁾ of the vapour pressures of liquid CO_2 at different temperatures, the vapour pressure factor f presents a perfectly *normal course*, in opposition to what the measurements of REGNAULT at 0° and 10° C. , and those of CAILLETET at -50° to -80° give for it ²⁾.

Nor has the assumption of a bimolecular $(\text{SO}_2)_2$ really any foundation.

Now, just recently ³⁾ I have examined the accurate course of the plaitpoint curves for binary mixtures of normal substances, so that it is now possible to derive a more accurate expression than the above, in which the critical (plaitpoint) temperatures of the mixture were identified by approximation with the temperatures of the coincidence of the inflection points of the successive ψ -curves. That this was, of course, not true, was sufficiently known, and that the difference can be considerable has been more than once emphatically stated by VAN DER WAALS. One look at the plate adjoined to my paper mentioned above shows at once how perfectly different the course of the plaitpoint line — also at the beginning, at T_1 — can be.

It will appear from the following derivation that the values found from the above approximated formula should be *more than doubled* in many cases.

KESOM has already derived ⁴⁾ a general expression for the molecular rise $\frac{1}{T_1} \left(\frac{dT_x}{dx} \right)_0$, but as he used the law of the corresponding states, and as in his final expression, viz.

$$\frac{1}{T_1} \left(\frac{dT_x}{dx} \right)_0 = \alpha - \frac{\left\{ \beta - \alpha \left(\frac{\partial \pi}{\partial \tau} \right) \right\}^2}{C_4 \frac{\partial^2 \pi}{\partial \omega \partial \tau}},$$

there occur all kinds of quantities, which have either to be determined experimentally, or have to be calculated from the equation of state, I preferred to derive the required expression directly from the relation found by me for the course of the plaitpoint line for mixtures of *normal* substances.

¹⁾ Phil. Mag. **61**, Vol. 2.

²⁾ See my paper in the Arch. Teyler (2) **9**, 3^e Partie, p. 54.

³⁾ These Proc. of June 1905, p. 33 et. seq.

⁴⁾ These Proc.; Comm. Leiden N^o. 75, p. 6.

2. This relation was the following: ¹⁾

$$x(1-x)\theta^3 \left[(1-2x)v - 3x(1-x)\beta \right] + \sqrt{a(v-b)^2 \left[3x(1-x)\theta(\theta - \beta\sqrt{a}) + a(v-b)(v-3b) \right]} = 0 \dots \dots \dots (1)$$

In this $\theta = av - \beta\sqrt{a} = (b_1\sqrt{a_2} - b_2\sqrt{a_1}) + a(v-b)$; $a = \sqrt{a_2} - \sqrt{a_1}$ and $\beta = b_2 - b_1$.

In the derivation it was only assumed that $a_{12} = \sqrt{a_1 a_2}$ might be put, so that the quantity a may be represented by $\left\{ (1-x)\sqrt{a_1} + x\sqrt{a_2} \right\}^2$. This is the *only* simplifying assumption.

We now proceed to make the above given expression homogeneous in the way of p. 35 et. seq. of my last paper. (These Proc. June 1905). By considering only the case $b_1 = b_2$ more closely (which was sufficient for our purpose), we simplified this expression considerably in the paper mentioned, but now we shall put the quantity β not $= 0$, so that a new variable quantity must be introduced.

Let us put as before:

$$\frac{\sqrt{a_1}}{a} = \varphi \quad ; \quad \frac{b_1}{v} = \omega .$$

But now also:

$$\frac{b_2 - b_1}{v} = \frac{\beta}{v} = n\omega ,$$

then we get:

$$\frac{\sqrt{a}}{a} = \varphi + x \quad ; \quad \frac{b}{v} = \omega (1 + n\omega) .$$

Hence after division by $x(1-x)a^3v^4$ (1) passes successively into:

$$\left(1 - \frac{\beta\sqrt{a}}{v a} \right)^3 \left[(1-2x) - 3x(1-x)\frac{\beta}{v} \right] + \frac{\sqrt{a}}{a} \left(1 - \frac{b}{v} \right)^2 \left[3 \left(1 - \frac{\beta\sqrt{a}}{v a} \right) \left(1 - 2\frac{\beta\sqrt{a}}{v a} \right) + \frac{a}{a^2} \left(1 - \frac{b}{v} \right) \left(1 - 3\frac{b}{v} \right) \right] = 0 ,$$

and

$$\begin{aligned} & \left(1 - n\omega(\varphi + x) \right)^3 \left[(1-2x) - 3x(1-x)n\omega \right] + \\ & + (\varphi + x) \left(1 - \omega(1 + n\omega) \right)^2 \left[3 \left(1 - n\omega(\varphi + x) \right) \left(1 - 2n\omega(\varphi + x) \right) + \right. \\ & \left. + \frac{(\varphi + x)^2 \left(1 - \omega(1 + n\omega) \right) \left(1 - 3\omega(1 + n\omega) \right)}{x(1-x)} \right] = 0 . \end{aligned}$$

¹⁾ l. c. p. 33, formula (2). Cf. for the derivation: These Proc. of April 1905.

For small values of x this becomes:

$$(1-n\omega\varphi)^3 + \varphi(1-\omega)^2 \left[3(1-n\omega\varphi)(1-2n\omega\varphi) + \frac{\varphi^2(1-\omega)(1-3\omega(1+n\varphi))}{x} \right] = 0.$$

As viz. ω approaches then to $1/3$, $1-\omega(1+n\varphi)$ is replaced by $1-\omega$, but $1-3\omega(1+n\varphi)$ has been retained. Further introduction of $\omega = 1/3$ yields:

$$(1-1/3 n\varphi)^3 + 1/3 \varphi \left[3(1-1/3 n\varphi)(1-2/3 n\varphi) + \frac{2/3 \varphi^2 (1-3\omega(1+n\varphi))}{x} \right] = 0,$$

from which follows:

$$\frac{2/3 \varphi^2 (1-3\omega(1+n\varphi))}{x} = - \frac{(1-1/3 n\varphi)^3}{4/9 \varphi} - 3(1-1/3 n\varphi)(1-2/3 n\varphi),$$

or, after division by $-2/3 \varphi^2$:

$$\frac{3\omega-1}{x} + 3\omega n = \frac{(1-1/3 n\varphi)^3}{8/27 \varphi^3} + \frac{3}{2/3 \varphi^2} (1-1/3 n\varphi)(1-2/3 n\varphi).$$

If we now put $\omega = 1/3(1+\delta)$, we get:

$$\frac{\delta}{x} = \frac{(1-1/3 n\varphi)^3}{8/27 \varphi^3} + \frac{9}{2\varphi^2} (1-1/3 n\varphi)(1-2/3 n\varphi) - n, \quad (1a)$$

as we may put $3\omega n = n$. Thus we have separated in the first member the only term in which numerator and denominator approach to 0, whereas in the second member all infinitely small terms have been neglected by the side of those of finite value.

Formula (1a) indicates, in what way the volume v varies in the neighbourhood of $x=0$ with x , when we viz. vary the temperature in such a way that we remain in a plaitpoint.

3. Let us now introduce the temperature.

For this the relation holds: ¹⁾

$$\underline{RT = \frac{2}{v^3} \left[x(1-x)\theta^2 + a(v-b)^2 \right]}. \quad \dots \quad (2)$$

Here θ is again $= av - \beta\sqrt{a}$. Reduction gives successively:

$$RT = \frac{2\alpha^2}{v} \left[x(1-x) \left(1 - \frac{\beta\sqrt{a}}{v\alpha} \right)^2 + \frac{a}{\alpha^2} \left(1 - \frac{b}{v} \right)^2 \right],$$

and

$$\underline{RT = \frac{2\alpha^2}{b_1} \omega \left[x(1-x) \left(1 - n\omega(\varphi+x) \right)^2 + (\varphi+x)^2 \left(1 - \omega(1+n\varphi) \right)^2 \right]},$$

¹⁾ l. c. p. 33.

as $\frac{1}{v} = \frac{\omega}{b_1}$, while $\frac{\beta}{v}$ and $\frac{\sqrt{a}}{a}$ are replaced by their values (see § 2).

Now:

$$RT_1 = \frac{8 a_1}{27 b_1} = \frac{8 \alpha^2 \varphi^2}{27 b_1},$$

hence:

$$T = {}^{27/4} T_1 \frac{\omega}{\varphi^2} \left[x(1-x) \left(1 - n\omega(\varphi+x) \right)^2 + (\varphi+x)^2 \left(1 - \omega(1+nx) \right)^2 \right].$$

If we now put $T = T_1(1+\tau)$, $\omega = \frac{1}{3}(1+\delta)$, this becomes for small values of x :

$$1 + \tau = {}^{9/4} \frac{1+\delta}{\varphi^2} \left[x(1 - \frac{1}{3}n\varphi)^2 + \varphi^2 \left(1 + 2\frac{x}{\varphi} \right) (1-\omega)^2 \left(1 - 2\frac{\omega nx}{1-\omega} \right) \right],$$

in the second member of which only terms of finite value and those of the order x remain. We draw attention to the fact that according to (1a) δ is of the order x . Further substitution of $\omega = \frac{1}{3}(1+\delta)$ yields:

$$1 + \tau = {}^{9/4} \frac{1+\delta}{\varphi^2} \left[x(1 - \frac{1}{3}n\varphi)^2 + {}^{4/9} \varphi^2 \left(1 + 2\frac{x}{\varphi} \right) (1-\delta)(1-nx) \right],$$

as $1 - \omega = \frac{2}{3} - \frac{1}{3}\delta = \frac{2}{3}(1 - \frac{1}{2}\delta)$, so $(1-\omega)^2 = \frac{4}{9}(1-\delta)$

The last expression becomes now:

$$1 + \tau = (1 + \delta) \left[x \frac{(1 - \frac{1}{3}n\varphi)^2}{\frac{4}{9}\varphi^2} + \left(1 + 2\frac{x}{\varphi} - \delta - nx \right) \right],$$

or if we neglect terms of higher order than the first:

$$1 + \tau = \left(x \frac{(1 - \frac{1}{3}n\varphi)^2}{\frac{4}{9}\varphi^2} + 1 + 2\frac{x}{\varphi} - \delta - nx \right) + \delta.$$

And now it proves, that the terms with δ vanish, so that we *do not want* the value of $\frac{\delta}{x}$ from (1a) for the calculation of the limiting

value of the relation $\frac{\tau}{x}$. For the sake of completeness we have, however, calculated this value, as it may be of importance for some problems to know in what way v varies with x in the neighbourhood of the lower critical temperature (remaining on the plaitpoint curve).

¹⁾ This is, of course, in connection with the fact that at the critical temperature of the first component the spinodal line *touches* the line $x=0$, and — as the spinodal curve is *vertical* at that place (i.e. // to the v -axis) for very small values of x — a change of v will therefore only bring about a change of temperature (and so also of the plaitpoint temperature) infinitely smaller than the change of temperature, brought about by a change of x .

So we find finally:

$$\frac{\tau}{x} = \frac{(1 - \frac{1}{3}n\varphi)^2}{\frac{4}{9}\varphi^2} + \frac{2}{\varphi} - n, \dots \dots \dots (2a)$$

which is the required expression, by means of which the limiting value of $\frac{\tau}{x}$ at $x = 0$ may be calculated for every given value of φ and n .

4. Now it remains only to express the relations found in the ordinary variables.

These are viz. (see § 1):

$$\frac{T_2}{T_1} = \theta; \quad \frac{b_2}{b_1} = \psi.$$

Now the quantity φ introduced by us in § 2 and 3 is represented by :

$$\varphi = \frac{\sqrt{a_1}}{a} = \frac{\sqrt{a_1}}{\sqrt{a_2} - \sqrt{a_1}} = \frac{\sqrt{b_1 T_1}}{\sqrt{b_2 T_2} - \sqrt{b_1 T_1}} = \frac{1}{\sqrt{\theta\psi - 1}},$$

while n is given by :

$$n = \frac{\beta}{v} : \omega = \frac{\beta}{b_1} = \frac{b_2 - b_1}{b_1} = \psi - 1.$$

Formula (2a) passes therefore into :

$$\frac{\tau}{x} = \frac{\left(1 - \frac{1}{3} \frac{\psi - 1}{\sqrt{\theta\psi - 1}}\right)^2}{\frac{4}{9}(\sqrt{\theta\psi - 1})^{-2}} + 2(\sqrt{\theta\psi - 1}) - (\psi - 1),$$

or

$$\frac{\tau}{x} = \frac{9}{4} \left[(\sqrt{\theta\psi - 1}) - \frac{1}{3}(\psi - 1) \right]^2 + 2\sqrt{\theta\psi - 1} - (1 + \psi),$$

or finally, as $\tau = \frac{T - T_1}{T_1}$:

$$\frac{T - T_1}{T_1 x} = \frac{1}{T_1} \left(\frac{dT_x}{dx} \right)_0 = 2\sqrt{\theta\psi - 1} - (1 + \psi) + \frac{9}{4} \left\{ (\sqrt{\theta\psi - 1}) - \frac{1}{3}(\psi - 1) \right\}^2. \quad (3)$$

The original expression, derived on the assumption that fRT_x may be approximately represented by $\frac{a_x}{b_x}$, must therefore (see § 1) be *completed* by a term :

$$\frac{9}{4} \left\{ (\sqrt{\theta\psi - 1}) - \frac{1}{3}(\psi - 1) \right\}^2.$$

This is the correction which must be applied, and it is easy to see, that it can *considerably* modify the original approximated expression.

Let us now introduce the ratio of the *critical pressures* of the two components, viz.

$$\frac{p_2}{p_1} = \pi.$$

Evidently the relation $\psi = \frac{\theta}{\pi}$ exists, which changes (3) into:

$$\begin{aligned} \frac{1}{T_1} \left(\frac{dT_x}{dx} \right)_0 &= 2\theta \sqrt{\frac{1}{\pi}} - \left(1 + \frac{\theta}{\pi} \right) + \frac{3}{4} \left\{ \left(\theta \sqrt{\frac{1}{\pi}} - 1 \right) - \frac{1}{3} \left(\frac{\theta}{\pi} - 1 \right) \right\}^2 \\ &= 2\theta \sqrt{\frac{1}{\pi}} - \left(1 + \frac{\theta}{\pi} \right) + \left\{ \frac{3}{2} \theta \sqrt{\frac{1}{\pi}} \left(1 - \frac{1}{2} \sqrt{\frac{1}{\pi}} \right) - 1 \right\}^2 \\ &= 2\theta \sqrt{\frac{1}{\pi}} - \frac{\theta}{\pi} + \frac{\theta^2}{\pi} \left(\frac{3}{2} - \frac{1}{2} \sqrt{\frac{1}{\pi}} \right)^2 - 2\theta \sqrt{\frac{1}{\pi}} \left(\frac{3}{2} - \frac{1}{2} \sqrt{\frac{1}{\pi}} \right) \\ &= -\theta \sqrt{\frac{1}{\pi}} + \frac{\theta^2}{\pi} \left(\frac{3}{2} - \frac{1}{2} \sqrt{\frac{1}{\pi}} \right)^2, \end{aligned}$$

or

$$\frac{1}{T_1} \left(\frac{dT_x}{dx} \right)_0 = \Delta = \theta \sqrt{\frac{1}{\pi}} \left\{ \theta \sqrt{\frac{1}{\pi}} \left(\frac{3}{2} - \frac{1}{2} \sqrt{\frac{1}{\pi}} \right)^2 - 1 \right\}, \quad \dots \quad (3a)$$

being the final expression for the molecular rise of the critical temperature on the side of the lower critical temperature.

Now a case of frequent occurrence is, that the *critical pressures* of the two components *differ little*. If these pressures are the same, $\pi = 1$, and (3a) becomes:

$$\Delta = \theta (\theta - 1), \quad \dots \dots \dots (3b)$$

whereas the former, approximated expression (see § 1) for this case would yield: (ψ is then $= \theta$) $\Delta = \theta - 1 = \frac{T_2 - T_1}{T_1}$.

So for the case $\pi = 1$ the former expression must be multiplied by $\theta = \frac{T_2}{T_1}$, in order to yield the correct expression.

A few instances will prove that it is *no longer necessary* now to *double* the molecular formula of the solvent.

As π is near 1 in most cases, and the formula (3b) varies very little with changes in the value of π , we shall use the formula $\Delta = \theta (\theta - 1)$ for convenience, the sooner as the values of T_2 (the critical temperature of the dissolved substance) are all unknown, and can be given only by approximation.

Let us first take the four substances which CENTNERSZWER's experiments induced me to calculate in the "Chemisch Weekbl." (l.c. p. 227—228). We shall now calculate the values of T_2 from the values

of Δ found experimentally, and see if the values found in this way are about the double of those of the (absolute) melting temperatures ¹⁾.

	Δ found	θ calculated	T_2 calculated	Melting point	Quotient
Anthraquinone	3,58	2,46	1060°	560°	1,9
Resorcine	2,36	2,12	910°	480°	1,9
Campher	1,53	1,83	790°	450°	1,8
Naphtaline	1,45	1,80	770°	350°	2,2

1,95 average

The values of T_2 are calculated from $T_2 = \theta \times T_1$, where $T_1 = 430^\circ$, being the critical temperature of the solvent SO_2 .

So we find really a value in the neighbourhood of 2 for the ratio between critical temperature and melting temperature. We call attention to the fact that 2,0 is found as mean value for this ratio for bi- and tri-atomic substances; for multi-atomic-substances this mean value rises to 2,3. There are, however, substances, where the ratio mentioned falls to 1,4 or rises to 3,5. The values calculated by means of the formula $\Delta = \theta(\theta - 1)$ are therefore in any case not in contradiction with what experience teaches us.

In the second place we shall consider in the same way five substances, which have been examined by BÜCHNER only recently. (See Thesis for the doctorate, p. 128—129). The solvent was CO_2 , of which $T_1 = 304^\circ$.

	Δ found	θ calculated	T_2 calculated	Melting point	Quotient
Naphtaline	2,39	2,13	650°	350°	1,9 (in the preceding table 2,2)
$\text{C}_6\text{H}_4\text{Cl}_2$	2,65	2,20	670°	325°	2,1
$\text{C}_6\text{H}_4\text{Br}_2$	2,87	2,27	690°	360°	1,9
CHBr_3	2,32	2,10	640°	280°	2,3
$\text{o-C}_6\text{H}_5\text{ClNO}_2$	3,87	2,53	770°	305°	2,5

2,14 average

¹⁾ See my paper in the BOLTZMANN-Festschrift (1904), p. 322—324.

Here too, we find therefore values for the ratio in question, which are not in contradiction with its empirical value.

Doubling the molecular formula of the solvent is therefore no longer necessary, and we may, therefore, say that the formula found by us (3*a*) or approximated (3*b*) represents the molecular rise of the lower critical temperature very satisfactorily.

Finally I may point out, that the experiments — of CENTNERSZWER as well as those of BÜCHNER — are not so accurate that the difference between 1,9 and 2,2 for naphthaline is of much importance.

The reason of this is easy to see; it is exceedingly difficult to observe the critical *plaitpoint* temperature accurately. For it is required for this purpose, that the corresponding *volume* be accurately known beforehand, and that the volume of the tubes used be chosen accordingly. Else, of course, not the plaitpoint temperature sought, is found, but another temperature, situated more or less in its neighbourhood. And this too can be a source of inaccuracies¹⁾.

From all that precedes it sufficiently appears that VAN 'T HOFF'S assertion that the value of Δ is constant, and equal to about 3, is altogether incorrect. For the value of Δ is quite determined by the ratio θ of the critical temperatures.

If θ should happen to be in the neighbourhood of 2,3, then $\Delta = \theta(\theta - 1)$ will lie in the neighbourhood of $2,3 \times 1,3 = 3$. And now it has been very misleading, that really for the examined substances the values of θ lie nearly all near 2,3. (For the five substances mentioned examined by BÜCHNER the mean value of θ is 2,25, for the substances investigated by CENTNERSZWER this is also the case). If $\theta = 3$, we should find about 6 for Δ , so this is twice as much! Hence there is no question of constancy.

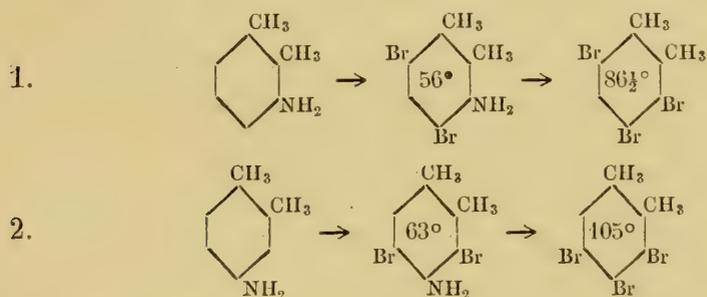
¹⁾ Also CENTNERSZWER calls attention to this in his paper (Z. f. Ph. Ch. 46, p. 427—501 (1903). See specially p. 446, 459, 464—466, 469—470, 489—492 and 497—499. It appears from these passages, how much trouble he has taken to determine the exact "Füllungsgrad", and in this way to get as near as possible to the critical plaitpoint temperature. As the determination of the rise of the critical temperature was only of minor importance to BÜCHNER, the values given by him, cannot — as he himself states — lay claim to the accuracy reached by CENTNERSZWER.

Chemistry. — “On the six isomeric tribromoxylenes.” By Dr. F. M. JAEGER and J. J. BLANKSMA. (Communicated by Prof. A. F. HOLLEMAN).

The six isomeric tribromotoluenes were prepared in 1880 by NEVILE and WINTHER¹⁾ and again in 1903 in a different manner by JAEGER²⁾ with the object of studying the connection between molecular and crystallographic symmetry with isomeric benzene derivatives. In order to be able to extend this study to another series of compounds with an analogous chemical character we have now prepared the isomeric tribromoxylenes and give a short review of the mode of formation of these substances; we intend publishing a more extended report later on in the “Recueil”.

Tribromo-*o*-xylenes.

These substances are prepared by starting from the orthoxylidines 1-2-3 and 1-2-4 according to the subjoined scheme:

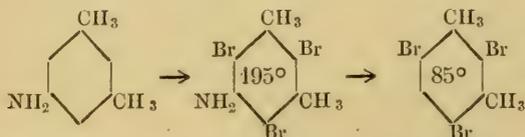


The orthoxylidines were treated in glacial acetic acid with the calculated amount of bromine and in the dibromoxylidines thus obtained the NH_2 -group was replaced by Br according to SANDMEYER'S method. The tribromoxylenes thus obtained were purified by distillation in steam.

Tribromo-*m*-xylenes.

3. 2-4-6-tribromo-*m*-xylene was prepared in different ways.

a. Starting from symmetrical xylylidine,



The sym. xylylidine was converted into tribromo-sym.-xylylidine and

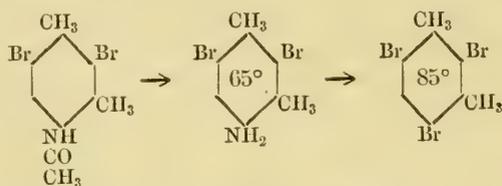
1) Ber. 13. 974.

2) Dissertation, Leiden, 1903.

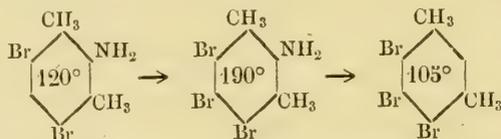
the NH_2 -group was then eliminated by means of amylnitrite with addition of finely divided copper.

b. Starting from 4-6-dibromo-2-amido-*m*-xylene prepared according to AUWERS¹⁾, we also obtain 2-4-6-tribromo-*m*-xylene m.p. 85° by replacing the NH_2 by Br according to SANDMEYER.

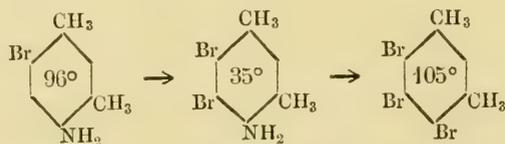
c. Acetoxylicide 1-3-4 yields on treatment with bromine and water dibromoacetoxylicide²⁾. If this is boiled with hydrochloric acid, so that the acetyl group is eliminated and if in the dibromoxylicidine so obtained the NH_2 -group is replaced by bromine 2-4-6-tribromo-*m*-xylene is also obtained.



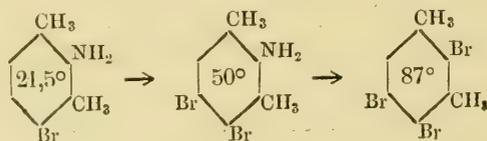
4. a. In order to arrive at 4-5-6-tribromo-*m*-xylene 4-6-dibromo-2-amido-*m*-xylene was converted by means of bromine into 4-5-6-tribromo-*m*-xylicidine and from this substance the NH_2 -group was eliminated by diazotation and boiling with alcohol.



b. Starting from 6-bromo-4-amido-*m*-xylene m.p. 96° we obtain by bromination 5-6-dibromo-4-amido-*m*-xylene m. p. 35° , which is converted by means of the SANDMEYER reaction into 4-5-6-tribromo-*m*-xylene.



5. After many failures to prepare it differently, 2-4-5-tribromo-*m*-xylene was finally made in the following manner.

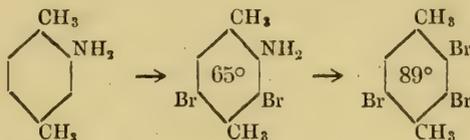


1) Ber. 32. 3313.

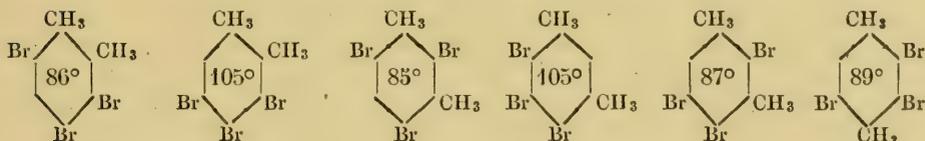
2) GENZ. Ber. 3 225.

Starting from 4-bromo-2-amido-*m*-xylene prepared according to NÖLTING¹⁾, we obtained 4-5-dibromo-2-amido-*m*-xylene by bromination and from this 2-4-5-tribromo-*m*-xylene was prepared according to SANDMEYER.

6. Finally, tribromo-*p*-xylene was prepared according to the sub-joined scheme.



Consequently all six tribromoxylenes had been obtained.



We wish here to express our thanks to Prof. FRANCHIMONT, who kindly presented us with the specimens for this research.

Zaandam, Juni 1905.
Amsterdam,

Meteorology. — “*Oscillations of the solar activity and the climate*”.
(Second communication²⁾). By Dr. C. EASTON. (Communicated by Prof. C. H. WIND.)

(Communicated in the meeting of May 27, 1905).

At the end of the first communication on this subject the supposition was started, that the 11-year oscillation of temperature with regard to the eleven-year cycle of the sun's activity generally was accelerated in the cold, retarded in the warm part of the larger oscillation. In order to investigate this matter more thoroughly, I proceeded as follows:

¹⁾ Ber. **34**, 2261.

²⁾ See for the First Communication: Proceedings of Nov. 26, 1904, p. 368. In that paper p. 372 read 89-years instead of 178-years. Furthermore strike out what has been said on p. 369 about the experiment of SAVÉLIEF.

The *observed* maxima of the eleven-year cycle were placed one beneath the other, beginning with the greatest positive deviation of the observed Maximum and ending with the greatest negative one.

Afterwards the cold-factors found for these periods were put in their places on both sides of that line of the Maxima, the dates being recorded accurate within a quarter of a year. Of the series thus obtained those before 1750 were provisionally left out of consideration: they are much less reliable, according to Wolf and Newcomb. The rest was divided into three groups (taking as limits the deviations ± 0.4 and -0.4 years): group A showing as a rule a strongly positive deviation from the maximum, group B containing small deviations in both directions, in group C the deviation being on the whole strongly negative. The mean deviation in group A (3 eleven-year cycles) is ± 1.5 years, that in group B (3 cycles) 0, that in group C (6 cycles) -1.7 years. For each group the cold-periods which fell in the same vertical column, were combined and the three rows of numbers thus obtained were smoothed.

The following rows (Table I) show the result; *M* means the place of the observed maximum, *m* and *m*₁ the calculated normal minima on both sides.

TABLE I.

Acceleration or retardation of the cold wave with regard to the sun wave.																			
A	8	10	4	0	0	3	7	5	2	6	9	5	3	5	7	6	2	4	10
B	8	3	6	9	7	6	3	0	1	2	0	0	5	10	5	3	6	6	8
C	4	7	9	10	21	26	15	6	5	13	17	7	3	11	19	17	8	7	12
						<i>m</i>				<i>M</i>									<i>m</i> ₁

No conclusions can be derived with any certainty from this table. Here again we find some indication of a distribution of the winter-cold, within the 11-year cycle, different for the warmer and the colder periods. Still however the curves B and C rather suggest a correlation of the minimum of the sun wave with the Maximum of the cold-wave. An other investigation seems to point in the same direction. It was made by the method explained on p. 372 of our First Communication¹⁾; it merely differs in so far that only the cold-factors since 1615 were included. We thus obtain the following table as a counterpart of Table II of the First Communication:

¹⁾ Table II of the First Communication is based on a 356-year period; of such periods, 3 are available. Each value given in that table represents therefore a frequency for 3 years. The values that follow hereafter represent a yearly frequency.

TABLE II.

Wintercold and phases of the 11-year sun-cycle since 1615.
(Groups from cold to warm).

	A	B	C	D
m	4.33	0.44	0.21	—
ap	0.77	0.25	0.44	0.26
M	0.42	0.36	0.21	—
d_{P_1}	0.27	0.46	0.21	0.20
d_{P_2}	0.32	0.53	0.21	0.43

There is, it is true, a strong elevation about the time of the minimum in the coldest group and a small elevation at ap in the warm one, but nothing is left of a curve corresponding with the 11-year one. This table does not confirm Table II of the First Communication. For the rest its value is only small, because the material, though purer, is so scanty: in 26 eleven-year cycles only 51 observed cases of severe or very severe winters are available.

The telluric perturbations thus seem to be so strong that, though they cannot cause the disappearance of the greater fluctuation, they practically abolish here the 11-year cycle, such at least is the case for the data at present under discussion. With regard to the supposition at the end of the First Communication, our conclusion therefore must be that the result of a more thorough investigation of all the available data is negative.

We have already remarked that there appears only a very incomplete correlation between the frequency of the sun spots and the oscillation of the temperature. The correspondence became only somewhat more apparent if, for the cold winters, we combined four 89-y. periods in one of 356 years. However the indication of parallelism obtained between the periodicity of the severe winters and that of the quantity $M-m$ of the sun's oscillation, leads us to consider more closely the other elements of the sun's oscillation. For a long time it has been well known that the maximum of an eleven-year cycle as a rule succeeds the minimum the faster, the higher the wave.

As the amplitude of the sun's period must be restricted within certain limits, this might be supposed to mean that the steepness of the ascending phase represents the only variable element in the sun's oscillation and that the minimum thus would remain constant, at

least would not be displaced systematically. In that case indeed a very high wave of the sun spot curve would have to coincide with an abbreviation of the normal ascending phase. When we examine the oscillation more closely, however, it soon appears that the place of the minimum varies systematically. We are thus led to inquire, whether for a comparison with telluric oscillations just this acceleration and retardation do not present real advantages over the other elements of the sun's activity. As by no means the observed deviations of the maxima and minima always agree in amount and direction, I investigated separately :

1. the deviations of the maximum,
2. those of the minimum,
3. those cases in which the deviations of M and m have the same sign. Where such is not the case, we should not attribute it to errors of observation without additional proof. However, case 3 will show the most pronounced deviations of the oscillations. The investigation was made *first* using the whole of the available materials; *second* excluding all periods before 1750 (that is of the least reliable observations). As the result did not deviate very strongly, only those of the last mentioned investigation are here communicated.

Meanwhile it seemed desirable to use not only NEWCOMB's list, but also the data as given by Prof. A. WOLFER¹⁾, because relatively small deviations in the observed values may already have an appreciable influence. In this case also the difference of the results was fairly small.

For the following tables I used WOLFER's data as a basis; only in the IVth it was deemed necessary to communicate also (in parentheses) the result obtained from NEWCOMB's data.

In the tables III and IV, column 1 shows the groups of the periods, arranged according to the amount of the deviations beginning with those that are largest positive; column 2 contains the numbers of 11-year cycles; 3 the mean amount of the deviations; 4 the quantity $M-m$; 5 the length of the period; 6 the mean of the Relativ-Zahlen (according to the smoothed table of WOLFER), in parentheses I placed the means of the highest elevations of the curve; 7 the cold-factors (yearly frequency). Table V column 3 shows the mean deviation as computed from the two phases.

1) A. WOLFER, *Astron. Mitteilungen*, XCIII, 1902.

TABLE III.

11-year periods, arranged according to the deviat. of the max.

1	2	3 <i>M</i>	4 <i>M-m</i>	5 <i>L</i>	6 <i>R.-Z.</i>	7 <i>Cf.</i>
A	4	+ 1.4	5.9	11.3	32.8 (64)	0.33
B	4	- 0.4	4.4	11.2	47.7 (103)	0.31
C	4	- 3.2	3.5	11.1	60.3 (128)	0.59

TABLE IV.

11-year periods, arranged according to the deviat. of the min.

1	2	3 <i>m</i>	4 <i>M-m</i>	5 <i>L</i>	6 <i>R.-Z.</i>	7 <i>Cf.</i>
A	4	+ 0.8 (+ 0.7)	4.7 (4.5)	10.5 (10.9)	46.5 (91) [43.2 (90)]	0.27 (0.29)
B	4	- 0.1 (0)	4.7 (4.3)	11.2 (10.7)	41.8 (90) [54.1 (111)]	0.38 (0.40)
C	4	- 2.2 (- 2.0)	4.4 (4.9)	11.9 (11.8)	52.5 (114) [43.6 (94)]	0.57 (0.51)

TABLE V.

11-year periods, arranged according to mean deviat. of both min. and max.

1	2	3 <i>m. and M.</i>	4 <i>M-m.</i>	5 <i>L</i>	6 <i>R.-Z.</i>	7 <i>Cf.</i>
A	2	+ 1.6	5.8	10.6	35.4 (66)	0.35
B	2	- 1.0	3.9	10.7	54.2 (114)	0.50
C	2	- 4.0	3.1	11.4	66.3 (142)	0.70

These tables show that the variation is least apparent in the length of the period, furthermore that the deviations in the position of the maximum of the period (as was to be expected) agree well with those of the Relativ-Zahlen and of the quantity $M-m$; finally that this correspondence is less satisfactory for the deviations in the position of the minimum, which however agree well with the modification in the cold factors. In Table III, it is true, the largest cold factors coincide with the largest deviations of the other elements of the

sun's activity, but the course is irregular (the list which also contains the periods before 1750 shows the same peculiarity).

It appears from Table IV that the correlation of the course of the coldfactors with the deviations of the minima is evident according to NEWCOMB's data as well as to those of WOLFER.

When we consider only those periods however, where the deviations of m and M are of the same sign, we find correlation between *all* the elements of the sun's activity and the cold factors. (That the extension is so small, proves that the acceleration of M and m is rather to be explained as an acceleration of the whole period). Unfortunately, if we leave out of consideration, as in Table V, the data which must be considered insufficiently reliable, the materials becomes so limited that the result can prove but little, and can only be considered as a strong indication.

In the preceding investigation the periods have not been chronologically arranged; it was not possible therefore to find any evidence of a periodic modification in the deviations of the sun's oscillation. According to our former results, however, we may expect that these deviations will generally correspond with the great periodic wave. To test this point the 11-year cycles have been arranged according to the adopted 89-year period; the deviations have been compared with the cold factors found for each period. An arrangement corresponding with the computed maxima seemed preferable to an arrangement corresponding with the minima, because of the previously indicated acceleration of the strong cold waves, beyond the observed solar minimum.

In Table VIA the vertical columns represent the eight 11-year cycles contained in the 89-year period; the first begins in 1648; in the 23^d and 24th square however I placed the periods 1626—1637 and 1637—1648, the periods since 1894 being of course not yet available. In each square the uppermost number represents the deviation of the maximum, the second the deviation of the following minimum according to NEWCOMB. Where the sign + or — follows the number, the deviation amounts to at least half a year, either in the positive or the negative direction. A 0 indicates a smaller deviation. The lower number gives the total of the cold factors between two consecutive maxima. Those phases to which NEWCOMB assigned a weight smaller than 3, have been placed in parentheses.

Table VIB contains the same data according to WOLFER; however, in the last square but one I have here written down the observed phases 1894 and 1900.

TABLE VI.

Deviations of M and m and cold factors in the 11-year cycles, arranged according to the 89-year period.

A. Newcomb.

I	II	III	IV	V	VI	VII	VIII
(+0.2) 0 (-0.3) 0	(+0.1) 0 (-0.4) 0	(+4.0) + (+1.9) +	(+2.9) + (+0.8) +	(-0.3) 0 -1.8 -	+1.1 + +1.0 +	+2.7 + +1.4 +	+0.8 + +0.8 +
4	10	2	3	4	3	4	1
+0.9 + +0.6 +	+1.1 + 0 0	+1.4 + -0.1 0	-1.3 - -1.9 -	-2.8 - -4.1 -	-4.4 - -1.5 -	-0.6 - -0.6 -	+1.1 + +0.9 +
4	3	7	3	9	5	6	1
+1.9 + +0.4 0	-0.8 - -0.5 -	-0.5 - +0.6 +	0 0 +0.4 0	+0.2 0 +0.1 0	+0.2 0 +0.2 0	-0.5 - +1.0 +	+1.9 + +0.8 +
4	5	4	3	6	3	1	1

B. Wolfers.

(-0.6) - (-0.1) 0	(-0.6) - (-0.2) 0	(+3.3) + (+2.1) +	(+2.2) + (+1.0) +	(-0.9) - (-1.7) -	+0.5 + +1.2 +	+2.1 + (+1.6) +	+0.3 0 (+0.9) +
(+0.4) 0 (+0.8) +	+0.9 + -0.2 0	+1.0 + 0 0	-1.9 - -2.1 -	-4.2 - -4.1 -	-5.6 - -1.6 -	+0.4 0 -0.5 -	+0.5 + +1.1 +
+2.9 + +0.6 +	-0.9 - -1.0 -	-1.1 - +0.4 0	-0.2 0 +0.4 0	-0.8 - +1.0 +	+1.4 + +0.5 +	+0.5 + +1.3 +	(+1.0) + +1.0 +

In order to bring into greater evidence those cases, in which the deviations are most decidedly indicated, I give in table VIIa, for the whole of the three last 89-year periods, the numbers of + or — (following the amounts) which remain, when I take together the signs of the same vertical column.

Furthermore I computed the sum of the amounts in each vertical column, both excluding and including the values in parentheses, taking then the mean amount for each phase (VII, b^a and b^b).

Table VIIc gives the elevations of the Relativ-Zahlen-curve computed from WOLFER'S table in the following way: the mean was taken of the three highest yearly means on both sides of the Maximum; the series of numbers thus obtained (nearly two complete series since 1750) were placed one beneath the other; then the means of these values were again computed.

The curve c^a was then obtained by placing against the rotation

number of the period the means of the last mentioned numbers taken in pairs (viz. the means of the maximum at the beginning and at the end). For the curve *c^b* the preceding maximum value was written down in the same place.

In table VII^d have been inserted cold factors as combined in each column for the three last 89-year periods.

Table VII^{e^a} shows the sum of the cold factors between the computed maxima of the 11-year cycles, obtained by addition of all the 89-year periods elapsed since 848. They are nothing else than the totals of Table I in my first communication about this subject (in ^{e^b} I gave a greater weight to the most recent data, see p. 163).

Figure I is a graphical representation of the curves of Table VII.

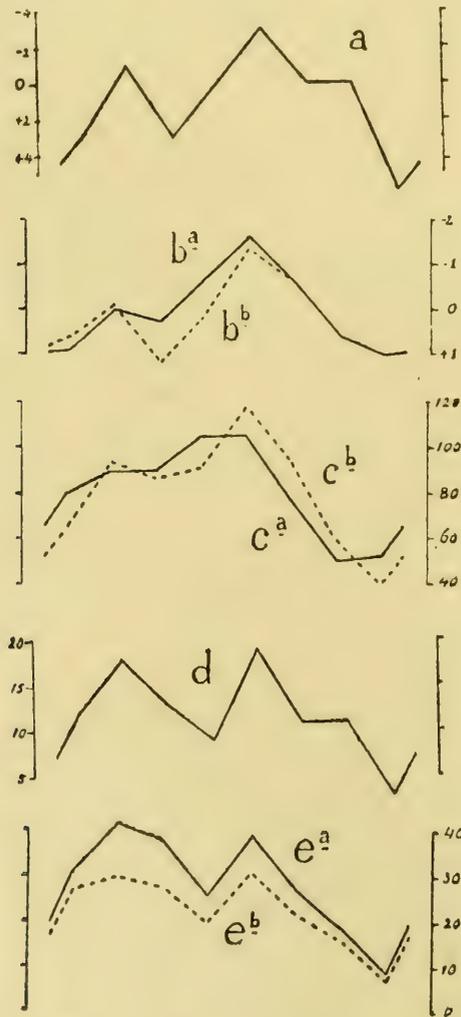


Fig. I. 89-year period.
a—c: Sun's activity.
d—e: Climate.

TABLE VII.

Deviation in the elements of the sun's activity, and 89-year oscillation of the climate.

	I	II	III	IV	V	VI	VII	VIII
a Direction of deviation.	3 +	1 -	3 +	0	3 -	0	0	6 +
b _b ^a Amount of deviation.	{ + 0.9 + 0.6	0 - 0.1	+ 0.3 + 1.2	- 0.7 + 0.4	- 1.6 - 1.4	- 0.6 - 0.6	+ 0.6 + 0.6	+ 1.0 + 1.0
c _b ^a Rel. Zahlen.	{ 79 65	90 94	89 87	105 92	106 118	77 94	50 61	52 40
d Cold factors 3 Per. of 89 years.	12	18	13	9	49	11	11	3?
e _b ^a Cold factors All the 89-year Per.	{ 31 27	41 ^s 30	38 28	26 20	39 31	27 22	19 16	9? 7?

All the curves show a corresponding course; the correspondence of the curve of the cold factors with that of the deviations *in time* of the sun waves is certainly as well indicated as that with the deviations in height. As was to be expected the correspondence does not extend to details, but the strong depression in an interval of 8 eleven-year sun cycles is apparent in all the curves.

In conclusion a few words on the apparent general increase of the coldfactors during the last centuries, which might be inferred from table I in my First Communication. Does it justify us in assuming a secular refrigeration?

In my opinion there is no reason for such a conclusion; it seems more probable that it must be explained provisionally at least by the incompleteness of the data for the earlier centuries. The numbers of winters which have a weight 5 according to KÖPPEN are distributed as follows over the different centuries (the material for the XIXth century is not homogeneous with that for the preceding ones).

Before the year 800	4	winters.
In the IX century	7	„
„ „ X „	5	„
„ „ XI „	7	„
„ „ XII „	7	„
„ „ XIII „	10	„
„ „ XIV „	6	„
„ „ XV „	15	„
„ „ XVI „	16	„
„ „ XVII „	21	„
„ „ XVIII „	19	„
„ „ (XIX) „	(16)	„

There is no evidence of a smooth course, but rather a sudden increase about the XIVth or XVth century. If there was any question of slowly increasing refrigeration, this would appear most clearly between the XVth and XIXth century, the material being more complete during this time.

For the three 356-year periods treated in Table I, First Communication, the numbers are: 25, 37 and 66. When treating this table with the weights 4, 6, 10 for the 1st, 2nd and 3rd "great period" we obtain for the totals (see Table VII and fig. 1, f b):

I (848—1203)	1.6	4.8	2.0	2.4	2.8	2.0	0	0.8
II (1204—1560)	1.8	6.9	10.8	3.6	5.4	3.6	4.8	1.8
III (1561—1916)	24.0	18.0	15.0	14.0	23.0	16.0	11.0	4.0
Total	27	30	28	20	31	22	16	7

In the recent material the depression about the middle of the 89-year period is pretty evident; we must remark however that it is not to be found in the even 89-year periods of Table I; the totals for the even periods separately become:

14, 17, 11, 12, 11, 10, 4, 3.

This may be attributed of course to a 356-year period, in which, as appears from the table, the third 89-year subperiod is strongly anomalous.

I will now try to summarise the main results of the investigation contained in these two communications.

We have seen — particularly when investigating the 11-year cycles, leaving out of account their connection with any longer period — that the purer our data the more evident the correlation between modifications of the sun's activity and the deviations of the climate. In the same degree however these data become more scanty and the accidental deviations might perhaps have a predominant influence for this reason.

In these circumstances the first of our final conclusions must be this : our data are insufficient for any rigid proof. In regard to each several part of the investigation, we can at most qualify them as strong indications.

For some points, however, these indications *taken together* are so strong that they may be considered convincing. Such is to my opinion first, the existence of a fluctuation, both in the activity of the sun and in the climate, larger than the well known 11-year cycle of the sun spots.

This conclusion, though very probable, would not seem to be demon-

strated, if it rested exclusively on the data about cold winters. (Table I First Communication).

A purely accidental coincidence becomes inadmissible however, now that we have found a similar fluctuation in different elements of the sun's activity, the more so, where the possibility — nay probability — of a causal connection between the two phenomena is obvious. This conclusion is strengthened by the correlation between the sun's activity and the temperature in tropical regions, found by KÖPPEN and NORDMANN.

On the other hand the exact nature of these fluctuations cannot yet be established.

The parallelism of the frequency of cold winters and the Relativ-Zahlen is most strongly marked, if we take as a basis the period of 356 years=32 eleven-year cycles (see fig. I of our First Communication).

Moreover we find both in the sun's activity and in the climate indications of a shorter period. Meanwhile it is only the 89-year periodicity which appears clearly in our data.

The matter may perhaps be cleared up by hypotheses about the physical cause of the oscillations (hypotheses into which I have not entered here). Therefore, what may be considered sufficiently demonstrated about the nature and the length of the periodicity, comes to this: Retardation and weakening of the 11-year suns' oscillation together with a diminution of the number of cold winters every 89 years.

Moreover it seems sufficiently certain that strong deviations from the "normal" 89-year oscillation occur at the same time in the sun's activity and in the climate. They are perhaps caused by the existence of a still longer period (see for instance the considerable acceleration and increase of the sun's oscillation in the latter half of the 11th 89-year period — second half of the 18th century — and the exceptionally high cold factors of that time).

Finally we may conclude from the whole of our investigation, and this is perhaps the most important conclusion: that in connection with meteorological phenomena, not only the frequency of the sun spots, but also other elements of the sun's activity curve deserve our attention.

Of course the possibility of a prediction of certain characteristics of the weather, long in advance, with a considerable degree of probability, is contained in our result.

Also its importance for explaining geographical and geological phenomena is obvious. I do not now wish to enter into details about these matters.

Chemistry. — “*On colorimetry and a colorimetric method for determining the dissociation constant of acids.*” By Mr. F. H. EIJDMAN JR. (Communicated by Prof. S. HOOGWERFF).

On colorimetry.

During the last few years I have been obliged to undertake a large number of colorimetric determinations, which had to be made as accurately as possible.

The impossibility of making really accurate colorimetric determinations without taking a number of precautions, made KNECHT¹⁾ utterly reject this method of working. As KNECHT's method (titration of the colouring matters by means of titanous chloride) is not applicable in all cases, it was thought that an effort to improve the colorimetric method, would not be undesirable.

PRINCIPLE OF THE COLORIMETRIC METHOD.

Starting from the supposition that *on diluting a solution of a colouring matter, neither the amount, nor the nature of the colouring matter present, undergoes a change*, the principle of the colorimetric method is as a rule indicated as follows:

If we examine in transmitted light two solutions, containing the same colouring matter, the concentrations will be inversely proportional to the heights of the layers of the same colour.

This formulation will be found in OSTWALD, *Handbuch für Physiko-Chemische Messungen*²⁾ and in HEERMANN, *Coloristische und Textilchemische Untersuchungen*³⁾.

The first supposition cannot at all be accepted as being generally correct; in fact, in the practice of colorimetry the circumstances, in which it is correct, occur but rarely.

In future those solutions of colouring matters, where these suppositions are permissible and which may, therefore, be determined colorimetrically without precautionary measures, will be styled *directly measurable*.

If the colouring matters under examination are not electrolytes, their nature and amount will suffer no change by dilution. Such colouring matters are, therefore, directly measurable.

But with acid, or basic colours, or their salts the case is different, as these can but rarely be determined directly. The cause may be found sometimes in the electrolytic dissociation, in other cases in a

¹⁾ Journal of the Society of Dyers & Colorists 1904, p. 242.

²⁾ Ibid. p. 179.

³⁾ Ibid. p. 63.

hydrolic phenomenon, which plays its part. If we have a solution containing acid colours, whose anions possess a different colour from the undissociated acid, the solution will exhibit a mixed colour composed of the colour of the anions and that of the undivided acid. This phenomenon may be readily demonstrated by means of the acids of the following colouring matters: *Methylorange*, *metanilyellow* and *benzopurpurin 4 B*.

That the change in colour, which these acids undergo when their solution is diluted, must really be explained in this manner, is proved in the second part of this paper, where an application is made of the fact that such dilute solutions may be restored to their original colour by addition of dilute acids¹⁾.

This explanation disposes of the theory of KÜSTER²⁾ and of that of GLASER³⁾ as to the indicator methylorange and it appears indeed that the methylorange-acid is, for an indicator, a fairly strong acid.

This phenomenon also occurs with salts of acid colours, therefore when testing the so-called acid and directly-dyeing technical colours.

Such a case has been mentioned by C. H. SLUITER⁴⁾, who noticed it when testing solutions of *isonitrosoacetophenonsodium*. He found that these solutions assumed an increasing yellow colour on increased dilution and he rightly attributes this to the more powerful electrolytic dissociation caused by the dilution. In this case the ionisation in *N/10* solutions had proceeded so far that a further dilution caused no further visible change in colour.

If however we want to measure solutions of *benzo-pure-blue*, *benzo-azurin* or allied colouring matters, it will be noticed that in solutions containing from 0.1—0.05 gram in a Liter (approximately *N/3000*—*N/6000*) the phenomenon is still of such an interfering nature, owing to the great difference in shade of colour, that a direct measurement is impossible. SLUITER's dissertation only reached me when my researches had already been brought to a close.

In theory, analogous phenomena are possible with basis colours and their salts, but I have not as yet met with any such instances and in fact, have not searched for them.

When salts of very weak acid colours are tested, the hydrolysis proves very troublesome, if the colour of the anions and that of the acids

1) Compare A. A. NOYES and A. A. BLANCHARD Journ. Americ. Chem. Soc. 22 p. 726 and Central Blatt 1901. I. p. 11 n^o 15.

2) KÜSTER, Zeitschrift für Anorganische Chemie 8 p. 127.

3) GLASER, die Indicatoren.

4) C. H. SLUITER. Het mechanisme van eenige organische reacties. Academisch Proefschrift. Scheltema en Holkema. 1905.

should be different. As the solutions get more diluted, they exhibit colours approaching the shade of the colour-acid.

A very striking example, which lends itself well for practical demonstration, is furnished by sodium carminate. Sodium alizarate may be also used, only the solutions, on being diluted, soon become turbid, owing to the slight solubility of alizarine.

From these examples it follows that the fundamental principle of colorimetry ought to be expressed as follows:

Solutions of the same colouring matter, when tested colorimetrically, exhibit in layers of the same thickness the same intensity of colour if they possess the same concentration.

THE COLORIMETER.

This apparatus must be so constructed that the liquid under examination may be brought to practically the same concentration as the standard liquid.

The apparatus best suited for this purpose is that of SALLERON¹⁾, modified by KOPPESCHAAR²⁾. In this colorimeter the most concentrated of the two solutions is diluted with water until it has the same colour as the weaker solution. From the amount of water added, the desired concentration is calculated. It is a matter of indifference whether the most concentrated or the most diluted solution is used as the standard liquid.

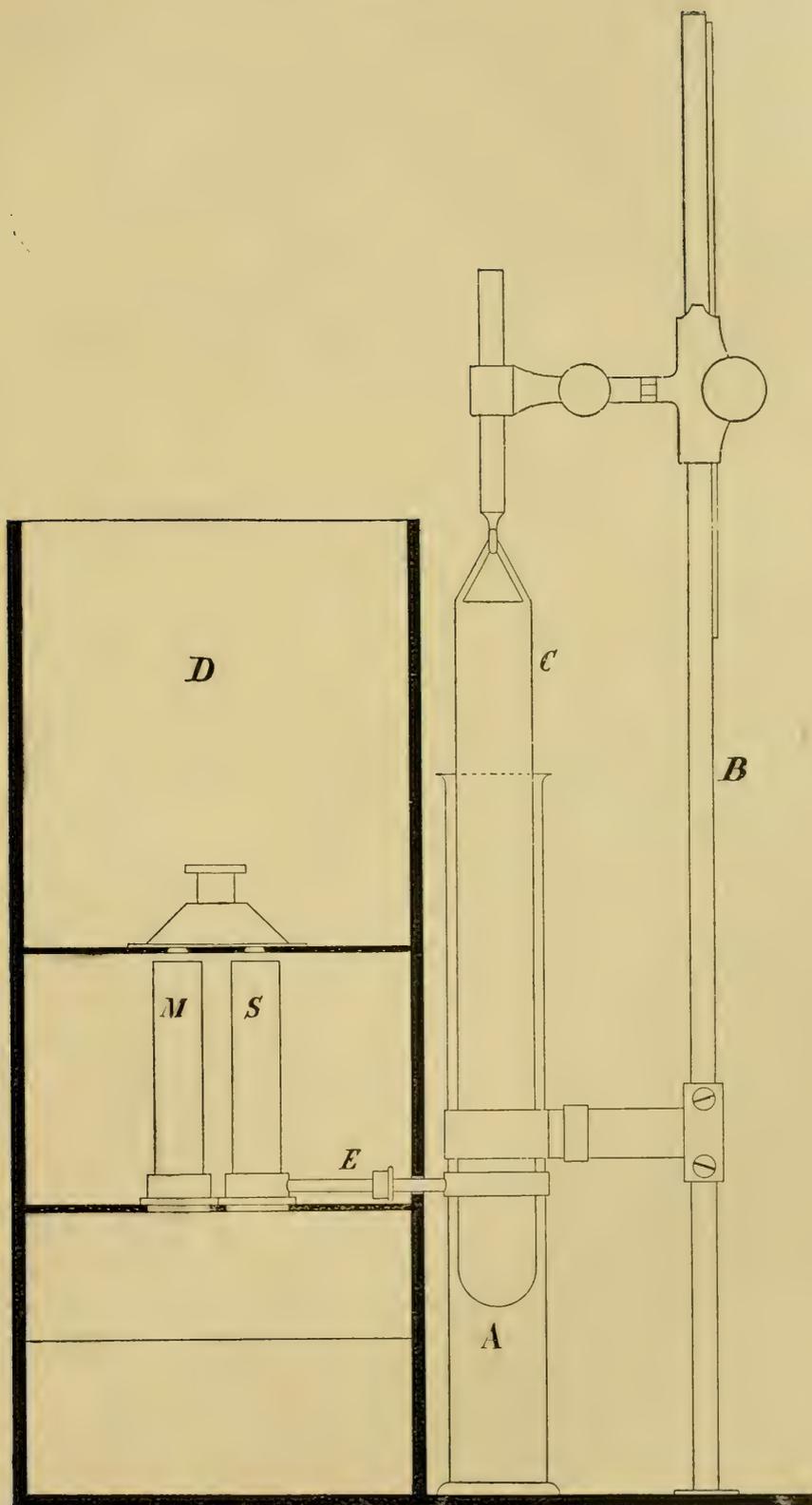
As it is not possible, when using the colorimeter of SALLERON-KOPPESCHAAR, to make rapidly successive readings of a quantity of solution to be measured, the apparatus, which I am now using and which is represented in the annexed drawing, is perhaps to be preferred. It is constructed from a colorimeter of C. H. WOLFF³⁾. The tube containing the standard liquid, the *standard tube S* is connected by means of a small horizontal tube *E* with the glass cylinder *A* in which a plunger *C* is suspended. This plunger can be moved up and down by means of a cog-wheel device along the standard *B*. In this way the level of the standard solution may be raised or lowered: by providing *B* with a scale, the position of the liquid may be read off on the same.

The actual colorimeter stands in the dark chamber *D*. It consists of the standard tube *S* and the tube containing the liquid to be measured, the *measuring tube M*.

1) Zeitschrift für Anal. Chemie 11 p. 302.

2) Zeitschrift für Anal. Chemie 38 p. 8.

3) Dingl. 236. 71.



The illumination of such a colorimeter is generally effected by means of a mirror placed below the tubes, which reflects the light from the sky. Owing to the clouds, this illumination may be very irregular, therefore artificial light is preferable. Incandescent light is very satisfactory. With artificial light, however, a mirror cannot be used, as small displacements of the lamp greatly affect the illumination of the two colorimeter tubes; instead of a mirror, a piece of ground milky-glass is then employed.

Above the tubes is placed the optical arrangement, which serves to create a field of vision, which is divided into two parts, one of which is illuminated by the rays, which have traversed the standard tube and the other by those, which have traversed the measuring tube.

In principle, it is preferable to make both halves of the field of vision exactly the same shape, as they are then observed under exactly the same conditions. These conditions are not satisfied by the prism-system of LUMMER and BRODHUN, which has been applied by H. KRÜSS to the WOLFF-colorimeter¹⁾. The field of vision is here a circle surrounded by a ring. This may, perhaps, partly explain the less favorable report of the Photometer Committee of the Netherland Society of Gasmanufacturers²⁾.

The prism-system of FRESNEL, generally met with in colorimeters, suffers from the drawback that it is liable to give way, when being cleaned, and cannot then be again properly joined together. This creates in the field a heavy black line of junction, which greatly impedes an accurate observation. A prism made from milky-glass³⁾ is not advisable on account of the transparency which causes the two halves to illuminate each other in the neighbourhood of the line of junction. An equality of colour is then noticed before it is really a fact.

I use a prism of polished telescope-metal with angles of 45° illuminated by two little mirrors also at angles of 45° placed above the tubes. The line of junction is then hardly visible and the prism is proof against the influences of a laboratory atmosphere.

The apparatus is now used as follows: The standard tube and the vessel *A* are provided with standard liquid, and fixed in such a manner that the height indicated on the rod *B* really corresponds with the position of the liquid in *S*. The standard liquid would have to be more diluted than the solution to be measured. A known

1) Zeitschrift für Instrumentenkunde 14. 102.

2) Report of the said committee 1893.

3) Ostwald l.c. p. 180.

quantity of the latter is then introduced into the measuring tube M and when the colours are equal, a reading is taken. In many cases it is not possible to take a reading, owing to the difference in shade of colour of the two liquids, but still we are able to see at which heights of the standard liquid this is decidedly darker or lighter than the measuring liquid.

The measuring tube is then filled with water up to the average of those heights and definitive determinations are now made. The difference in concentration between the two liquids is now in most cases so slight, that a difference in shade is no longer perceptible.

In any case it is desirable to dilute the contents of the measuring tube up to the height found and to take a fresh reading, even when determinations may be readily made without dilution.

In the case of acid colours this mode of working can sometimes not be applied. The measuring liquid should then be gradually diluted until, the colours being equal, the height of the measuring liquid is about the same as that of the standard liquid.

In the case of such small differences in the concentration it may be safely assumed that the concentrations are inversely proportional to the height of equally-coloured layers.

The great advantage of this method of working is this, that at the final determination a series of readings can be taken, also that the standard liquid can be alternately changed from darker to equality of colour and from lighter to equality, as is done in polarisation. This renders each determination very certain.

The readings may be rendered much more delicate by placing a coloured piece of glass on the ocular. It is necessary to choose such a colour that the rays of light, transmitted through the measuring liquids are also transmitted through the coloured glass. A trial with a pocket spectroscope or a consultation of FORMÁNEK'S work "*Der spectralanalytische Nachweis künstlicher organischer Farbstoffe*", renders the choice easy.

These glasses are readily made by dyeing old photographic plates with basic colours, which is easily done in the cold.

A colorimetric method for determining the dissociation constant of acids.

Acid colours whose anions possess a colour different from that of the acid itself, and which we will call *indicator-acids*, may be used to determine the dissociation constant of the indicator-acids themselves in the first place, and also of all other colourless acids, if we have

at our disposal a colourless acid the dissociation constant of which is known with certainty.

PRINCIPLE OF THE METHOD.

If the aqueous solution of an indicator-acid is diluted with water the colour will change in the direction of the colour of the anions. If for the dilution of an indicator-acid solution an isohydric solution of a colourless acid is used, the degree of dissociation will not alter and the colour of the solution will remain the same.

If the solution of the indicator-acid is diluted with water, we may titrate back with an acid of which the concentration of the H-ions is larger than that of the solution of the indicator-acid, until the original-colour is restored. We have then prepared from the water and the acid solution a mixture, which is isohydric with the solution of the indicator acid.

Starting from an acid with a known dissociation constant — *standard acid* — and an arbitrary solution of an indicator-acid we may in the same manner determine the dissociation constant of a second colourless acid, by preparing as directed, from the standard acid as well as from the unknown acid solutions, which are isohydric with the same solution of the indicator-acid. The acid solutions are then mutually isohydric and the calculation of the dissociation constant is readily made from the above data.

THE OPERATION.

The above described colorimeter is best suited for this method. The solution of the indicator-acid is introduced both in the standard tube and the measuring tube. The amount of indicator-acid does not matter, provided the quantity of it, in both tubes, is exactly the same. After most carefully adjusting the colours, the contents of the measuring tube are diluted with an accurately known volume of water, say, a cc. If now of a standard acid the dissociation constant is K_A and if from this is prepared a solution of a dilution v_A , we then titrate with this solution the contents of the measuring tube until the colours are again the same. If this should require b cc the dilution at which the solution of the standard acid is isohydric with the given solution of the indicator-acid is :

$$\frac{a + b}{b} \times v_A = V_A.$$

If now the dilution of the indicator-acid is known, or if we have found in the same way the dilution at which an unknown dissociation constant yields an isohydric solution, then, calling both dilutions

V_B , the unknown dissociation constant K_B is found by the following calculation:

If in the solution of the standard acid we call the dissociated part α then

$$\frac{\alpha}{V_A} = C_H,$$

the concentration of the H -ions, therefore,

$$C_H = \frac{K_A}{2} \left[-1 + \sqrt{1 + \left(\frac{4}{K_A V_A} + 1 \right)} \right].$$

For the acid with an unknown dissociation constant K_B , we may calculate the same from

$$C_H = \frac{K_B}{2} \left[-1 + \sqrt{1 + \left(\frac{4}{K_B V_B} + 1 \right)} \right],$$

as C_H and V_B are known. It is, however, simpler to make the calculation as follows:

From

$$\frac{\alpha^2}{1 - \alpha} = K V \quad \text{and} \quad \frac{\alpha}{V} = C$$

we find:

$$C^2 = \frac{K}{V} - C K.$$

As both acids are isohydric in dilutions of, respectively, V_A and V_B , C_H will be the same in both, therefore

$$\frac{K_A}{V_A} - C_H K_A = \frac{K_B}{V_B} - C_H K_B$$

from which

$$K_A = K_B \cdot \frac{V_A}{V_B} \cdot \frac{1 - C_H V_B}{1 - C_H V_A}.$$

TEST EXPERIMENTS.

In order to show the accuracy of the process, I have made three determinations. In the first one I have determined the dissociation constant of benzoic acid, taking the constant of salicylic acid as known. In the second experiment I have determined the dissociation constant of anthranilic acid, using the figure obtained for benzoic acid. In a third experiment, the dissociation constant of propionic acid has been also determined with the aid of benzoic acid.

Determination of the dissociation constant of benzoic acid.

Given:

$$K_s = 0.00102 \qquad v_s = 150 \\ v_b = 100$$

Indicator : metanilyellow-acid. The change in colour of this indicator on dilution was not strong enough. Therefore, the solution was mixed before use, with a few drops of hydrochloric acid, which caused the difference in colour to be more decided and more readily observable. This addition may be made without fear, for the colour is used as the indicator for the concentration of the hydrogen-ions and an equal concentration of the hydrogen-ions always gives the same colour. Only we must take care to use the same indicator solution for the whole series of determinations.

Found :

15 cc of indicator + 50 cc of water. Colour again restored with 9 cc salicylic acid solution, therefore :

$$\frac{50 + 9}{9} \times 150 = 983.5 = V_s$$

15 cc of indicator + 10 cc of water. Colour again restored with average 22.5 cc of benzoic acid solution, therefore

$$\frac{10 + 22.5}{22.5} \times 100 = 144 = V_b$$

from which :

$$C_{II} = \frac{0.00102}{2} \left[-1 + \sqrt{\left(\frac{4}{0.00102 \times 983.5} + 1 \right)} \right] = 0.0006294$$

and :

$$K_b = 0.00102 \cdot \frac{144}{983.5} \cdot \frac{1 - 0.0006294 \times 983.5}{1 - 0.0006294 \times 144} = \mathbf{0.000063.}$$

By the electrolytic process the value of $K_b = \mathbf{0.00006.}^1)$

Determination of the dissociation constant of anthranilic acid.

Given : $K_b = 0.00006$ $v_b = 200$

$v_a = 100$

Indicator : methylorange-acid.

Found :

15 cc of the indicator in both cases diluted with 50 cc were titrated back to the original colour.

For this was required

Benzoic acid : 0.87 cc

Anthranilic acid : 1.56 ,,

¹⁾ NERNST. Theoretische Chemie, p. 404.

From which :

$$V_b = \frac{50 + 0.87}{0.87} \times 200 = 11690$$

$$V_d = \frac{50 + 1.56}{1.56} \times 100 = 3306$$

$$C_H = \frac{0.00006}{2} \left[-1 + \sqrt{\left(\frac{4}{0.00006 \times 11690} + 1 \right)} \right] = 0.00004749$$

and

$$K_a = 0.00006 \cdot \frac{3306}{11690} \cdot \frac{1 - 11690 \times 0.00004749}{1 - 3306 \times 0.00004749} = \mathbf{0.0000089}.$$

The electrolytic process gave **0.0000096**.¹⁾

Determination of the dissociation constant of propionic acid.

Given : $K_b = 0.00006$ $v_b = 442.5$

$v_p = 1020$

Indicator: methylorange acid.

Found:

15 cc of indicator were diluted with 25 cc of water; the colour was restored on adding 1.5 cc solution of benzoic acid.

$$V_b = \frac{25 + 1.5}{1.5} \times 442.5 = 7816$$

15 cc of indicator were diluted with 10 cc of water; the colour was restored on adding 6 cc solution of propionic acid.

$$V_p = \frac{10 + 6}{6} \times 1020 = 2720$$

$$C_H = \frac{0.00006}{2} \left[-1 + \sqrt{\left(\frac{4}{0.00006 \times 7816} + 1 \right)} \right] = 0.00006261$$

and

$$K_p = 0.00006 \times \frac{2720}{7816} \times \frac{1 - 7816 \times 0.00006261}{1 - 2720 \times 0.00006261} = \mathbf{0.0000128} \text{ } ^2).$$

Found by the electrolytic process: **0.0000134**.

This method may, perhaps, prove useful in cases where the electrolytic method meets with difficulties, for instance in the determination of very small concentrations of hydrogen-ions or in the determination of the concentration of hydrogen-ions in presence of other cathions. I intend making further experiments in that direction.

Laboratory, Netherland Technical School.

Enschede, 15 May 1905.

1) OSTWALD. Zeitschr. für Physik. Chemie 1889, p. 261.

2) OSTWALD. Zeitschr. für Physik. Chemie 1889.

Mathematics. — “On the number of common tangents of a curve and a surface.” By Dr. W. A. VERSLUYS. (Communicated by Prof. D. J. KORTEWEG).

§ 1. Let C_1 be a plane algebraic curve of class r_1 and S_2 an algebraic surface of class m_2 . Every tangent of C_1 touching S_2 is a tangent of the section s of the surface S_2 with the plane V of C_1 . Conversely, each common tangent of C_1 and s is a common tangent of C_1 and S_2 . The curves C_1 and s being of the class r_1 and m_2 respectively, they have $r_1 m_2$ common tangents. Hence, S_2 and C_1 have $r_1 m_2$ common tangents too.

Let the plane V of C_1 occupy the particular position of touching S_2 in σ points of ordinary contact and in χ points of stationary contact, the class of the section s is now

$$m_2 - 2\sigma - 3\chi^1).$$

Hence, the curves s and C_1 have now

$$r_1 (m_2 - 2\sigma - 3\chi)$$

common tangents. Every tangent of C_1 passing through one of the points of contact σ and χ is a common tangent of C_1 and S_2 , without being a common tangent of C_1 and s . In § 8 will be proved, that, if D_1 be the developable formed by the tangents of C_1 , each generating line of D_1 touching S_2 in a point σ counts for two common tangents of C_1 and S_2 and each generator of D_1 touching S_2 in a point χ counts for three common tangents of C_1 and S_2 . If C_1 be a plane curve, the developable D_1 is the plane V counted r_1 times. Every ordinary contact σ gives thus $2r_1$ common tangents of C_1 and S_2 , and every stationary contact χ gives $3r_1$ common tangents of C_1 and S_2 . Thus, the total number of common tangents is

$$r_1 (m_2 - 2\sigma - 3\chi) + 2\sigma r_1 + 3\chi r_1 = r_1 m_2.$$

If the plane V of C_1 and the surface S_2 touch along a line, then every tangent of C_1 touches S_2 and the number of common tangents becomes infinite. This case presents itself if S_2 be a developable and V one of its tangent planes. Every tangent of C_1 touches S_2 twice, if S_2 be a torus and V be one of the planes touching S_2 along a circle.

If C_1 be a curve in space the number of common tangents of C_1 and S_2 is still $r_1 m_2$, where r_1 is the rank of C_1 . This will be proved first for some special curves and surfaces and afterwards for the general case.

§ 2. Let S_2 be a cone with vertex T ; the projection of a common

¹⁾ VERSLUYS, These Proceedings. May 27, 1905.

tangent of C_1 and S_2 on an arbitrary plane V , not passing through the centre of projection T , is a common tangent of the projection p_1 of C_1 and of the section s of S_2 with V . The converse is equally true. The class of p_1 and s being r_1 and m_2 respectively, the number of common tangents of p_1 and s and thus of C_1 and S_2 is $r_1 m_2$.

If S_2 be a developable D_2 , a tangent t of C_1 touches D_2 if a tangent plane of D_2 pass through t , and conversely. Let D'_1 and C'_2 be the polar reciprocals of C_1 and D_2 . To a plane of D_2 passing through a tangent t of C_1 corresponds a point of C'_2 on a generator t' of D'_1 , and conversely. The number of these intersections of C'_2 and D'_1 is $r_1 m_2$, for the curve C'_2 is of order m_2 and the developable D'_1 of order r_1 . Then, since there are $r_1 m_2$ planes of D_2 passing through tangents of C_1 , these are $r_1 m_2$ common tangents of C_1 and S_2 .

We can show in a very simple way, that if the curve C_1 be an arbitrary algebraic curve of rank r_1 , and the surface S_2 be an arbitrary algebraic surface of class m_2 , the number of common tangents is still $r_1 m_2$. For the tangents to S_2 form a complex of order m_2 , and the tangents of C_1 form a ruled surface of order r_1 . Now according to a theorem due to HALPHEN¹⁾ the number of their common rays is $r_1 m_2$, which proves the proposition.

§ 3. Some theorems concerning the contact of a developable with an arbitrary surface will be deduced from the theorem proved above.

Let C_1 be a twisted cubic C^3 and D^4 the developable formed by its tangents. Let S_2 be an arbitrary surface of order n_2 , having a cuspidal and a nodal curve respectively of order r_2 and ξ_2 and let D^4 and S_2 have an ordinary contact in σ and a stationary contact in χ points, whilst none of the tangents of C^3 is an inflexional tangent of S_2 and C^3 does not touch S_2 . The number of common tangents of C^3 and S_2 is now also for this particular position $r_1 m_2$ or $4 m_2$. These common tangents of C^3 and S_2 are: 1st the tangents of C^3 touching the curve of intersection s of D^4 and S_2 and 2nd the tangents of C^3 touching S_2 in the points σ and χ where the surfaces D^4 and S_2 touch. Let every common tangent of C^3 and S_2 passing through an ordinary point of contact σ count for x common tangents and let every common tangent through a stationary point of contact χ count y times.

The number of common tangents of C^3 and s will be

$$4 m_2 - x \sigma - y \chi.$$

¹⁾ R. STURM, Linien Geometrie, I p. 44.

Let K be the developable formed by the tangents of s . Let l be a common tangent of C^3 and S_2 , touching C^3 in R and s in P . One of the tangents of C^3 consecutive to l meets S_2 in two real points of s , consecutive to P , as l is supposed to be no principal tangent of S_2 . The osculating plane V of C^3 in R contains therefore four consecutive points of s , so it is a stationary plane α of s in P . Consequently the plane V is also a stationary tangent plane of K along the generating line l . So C^3 has in K three consecutive points in common with K and no more.

The $3n_2$ points where C^3 meets S_2 are cusps β of s^1), so they are triple points on the developable K .

Each of these $3n_2$ points β counts at least for three points of intersection of C^3 with K . Each of these points β counts for not more than three points of intersection, as we have assumed that C^3 does not touch S_2 , and the tangent in β to C^3 does not lie in the triple tangent plane of K in β , which triple tangent plane coincides with the osculating plane of s in β , i. e. with the tangent plane of S_2 in β .

The curve C^3 meets K only in the $4m_2 - x\sigma - y\chi$ points R and in the $3n_2$ points β , as every tangent to s lies in an osculating plane of C^3 , and through a point of C^3 no plane can pass osculating C^3 still elsewhere. The order of K or the rank of s is

$$r = 4m_2 + 3n_2 - 2\sigma - 3\chi^2).$$

So the number of points of intersection of C^3 and K is

$$3(4m_2 + 3n_2 - 2\sigma - 3\chi).$$

As the only points of intersection of C^3 and K are the points R and β counted three times, we find the relation

$$3(4m_2 + 3n_2 - 2\sigma - 3\chi) = 3 \times 3n_2 + 3(4m_2 - x\sigma - y\chi)$$

from which ensues

$$x = 2, \quad y = 3,$$

or in words:

If the developable D^4 and an arbitrary surface S_2 have an ordinary contact, two consecutive generating lines of D^4 touch S_2 .

If the developable D^4 and an ordinary surface S_2 have a stationary contact, three consecutive generating lines of D^4 touch S_2 .

These theorems hold good too in the case that the developable is a cone ²⁾).

¹⁾ VERSLUYS, Mém. de Liège. 3me série, T. VI, 1905. Sur les nombres Plückeriens etc.

²⁾ VERSLUYS, These Proceedings May 27, 1905.

³⁾ VERSLUYS, These Proceedings May 27, 1905.

The two theorems mentioned above and their reciprocals and some special cases will now be treated algebraically.

§ 4. Let C_1 be a rational twisted curve of rank r_1 and S a surface of order n , possessing no multiple curves. Let

$$ax + by + cz + d = 0$$

represent the osculating plane of C_1 , a, b, c, d being integer rational algebraic functions of t . Differentiating we find for an arbitrary tangent of C_1 equations of the form

$$a_1 x + b_1 y + c_1 z + d_1 = 0,$$

$$a_2 x + b_2 y + c_2 z + d_2 = 0.$$

Solving y and z in function of x and t we find:

$$y = \frac{Ax + B}{C}, z = \frac{Dx + E}{C}, \dots \dots \dots (A)$$

in which A, B, C, D and E are functions in t of order r_1 . If we substitute the values (A) in the equation of the surface S , we arrive at an equation (B), which is in x of order n and in t of order $n r_1$. For every value of t this equation (B) furnishes the n values of x belonging to the points of intersection of a tangent l to C_1 . If two of these values become equal, the tangent l will meet the surface S in two consecutive points and as S is supposed to have no multiple curves the tangent l will also be a tangent of S . Those tangents of C_1 are excluded which are at right angles with the X -axis, all points of intersection with S possessing the same x ; so all roots x coincide, without the points of intersection coinciding. Every line being at right angles with the X -axis meets the line at infinity in the plane $x = 0$. So the number of these particular tangents of C_1 is r_1 .

The equation (B) has two equal roots in x for a certain value of t , when this value of t causes the discriminant of (B) to vanish. The discriminant is in the coefficients of (B) of order $2(n-1)$ and as the coefficients of (B) are of order $r_1 n$ in t , the discriminant is of order $2 r_1 n (n-1)$ in t .

By a parallel displacement of the axes the plane $x = 0$ can be made to pass through one of the tangents of C_1 which is at right angles with the X -axis.

Writing $t + q$ for t , we can take q in such a way that this tangent of C_1 lying in $x = 0$ corresponds to the value $t = 0$. The equation (B) has then passed into an equation (B') where for $t = 0$ all roots x vanish.

The first equation (A)

$$y = \frac{Ax + B}{C} \quad \text{or} \quad x = \frac{Cy - B}{A}$$

must now pass into $x = 0$ for $t = 0$, so that C and B must contain, after the change of variables, t as a factor, A not being divisible by t . As the projection on the plane $x = 0$ of the tangent lying in this plane can be any arbitrary line and as C vanishes for $t = 0$, D and E must also vanish for $t = 0$. In the equation (B') the coefficient of x^n will be divisible by t and the coefficient of x^i divisible by t^{n-i} .

According to SALMON¹⁾ the discriminant of equation (B') will be divisible by $t^{n(n-1)}$. For each one of the r_1 particular tangents of C_1 which are at right angles with the X -axis $n(n-1)$ roots of the discriminant of equation (B) become equal. That discriminant possessing $2r_1 n(n-1)$ roots, there are left $r_1 n(n-1)$ roots, to each of which corresponds an equation (B) , possessing two equal roots. So there are $r_1 n(n-1)$ tangents of C_1 which also touch S . As S possesses no multiple curves the class m is $n(n-1)$. The number of common tangents of C_1 and S is thus as before mentioned

$$r_1 m.$$

§ 5. So far we have supposed that C_1 occupies no particular position with respect to S . For particular positions of C_1 two or more of the common tangents of C_1 and S can become consecutive tangents of C_1 . Let t be a tangent of C_1 touching S in P , and let a tangent of C_1 consecutive to t be also a tangent of S . The developable D_1 formed by the tangents of C_1 and the surface S will touch in P . We shall now investigate when the contact is ordinary and when stationary.

For simplification I assume for C_1 the twisted cubic C^3

$$(x = p + t, y = t^2, z = t^3).$$

The equation of the developable D_1 or D^4 is now :

$$z^2 - 6(x + p)yz + 4y^3 + 4(x + p)^3z - 3(x + p)^2y^2 = 0,$$

or

$$0 = z - \frac{3}{4p}y^2 + \text{etc.} \quad . \quad . \quad . \quad . \quad . \quad (A)$$

If we choose for point P where the surface S touches D^4 the origin of the coordinates the equation of S is

$$0 = z + ax^2 + 2hxy + by^2 + \text{etc.} \quad . \quad . \quad . \quad . \quad (B)$$

The surfaces D^4 and S have stationary contact in the origin when

¹⁾ Modern Higher Algebra, § 111, note.

plane determined by the X -axis and the point where C^3 touches $x = 0$. When $h = 0$ the terms of the lowest order in t in the coefficients a_0 , a_1 and a_2 are respectively of order 2, 2 and 0.

The terms of the lowest order in t of the discriminant appear in the first term of the equation (E) at the end of the preceding §, namely in the term $2na_0a_1\varphi_1$. So the terms of the lowest order in t are

$$Ca(3p + 4bp^2)t^2$$

where C represents a constant. The discriminant possesses three roots $t = 0$ or the X -axis counts for three common tangents of C^3 and S , if

$$a(3p + 4bp^2) = 0$$

or if

$$a = 0, \quad 3 + 4bp = 0, \quad p = 0.$$

If $9 + 4bp = 0$, the surfaces D^4 and S have according to (C) a stationary contact, as h is also equal to nought. The origin P is now an ordinary point (not a parabolic or double point) on the surface S and the common tangent (the X -axis) does not coincide with one of the inflexional tangents of S in P .

This furnishes the theorem :

If an arbitrary surface S and a developable D^4 have a stationary contact in an ordinary point P of both surfaces and the generating line l of D^4 through P is neither of the two inflexional tangents of S in P , then l counts for three common tangents of the cuspidal curve C^3 and of S .

If $a = 0$ the surfaces D^4 and S have according to (C) still a stationary contact, as still $h = 0$. The origin P is now a parabolic point of S whilst the X -axis is the only inflexional tangent. The coefficients a_0 , a_1 and a_2 all contain the factor t^2 . So the discriminant possesses the factor t^4 , so that now the discriminant has four roots $t = 0$. So the X -axis now counts for four common tangents of C^3 and S .

If $p = 0$, then C^3 touches S in the origin P , whilst the osculating plane of C^3 in P coincides with the tangent plane of S in P . The terms of the lowest order in t in the coefficients a_0 , a_1 and a_2 are now respectively of order 3, 2 and 0. So the discriminant (E) is divisible by t^3 , so that C^3 and S now have in the origin P three common tangents. Writing in the equation (B) of the surface S for the coordinates of a point on C^3 the expressions $x = t$, $y = t^2$, $z = t^3$, we obtain an equation in t , containing t^2 as a factor. The curve C^3 has thus in the origin only two points, but three tangents in common with S .

If $h = a = p = 0$, then C^3 touches the surface S in a parabolic

point P , the tangent in P to C^3 coincides with the principal tangent in P of S , whilst the osculating plane of C^3 in P coincides with the tangent plane of S in P . From the expressions (D) for a_0, a_1 and a_2 follows that the discriminant (E) is divisible by t^4 , so that C^3 and S have now four common tangents in common in the point P .

If $h = b = p = 0$ then C^3 touches S still in a parabolic point; the only difference to the preceding case is that C^3 no longer touches the principal tangent. From the equations (D) and (E) ensues that C^3 and S possess only three common tangents.

If $h = b = 0$ and $p \gtrless 0$, then P is a parabolic point for which the principal tangent does not coincide with the tangent to C^3 . From (D) and (E) ensues now readily that the X -axis counts but for two common tangents of C^3 and S .

§ 7. When the X -axis coincides with one of the principal tangents of S in P then the axes cannot be taken in such a way that $h = 0$; but we have now $a = 0$. The terms of the lowest order in t in the coefficients a_0, a_1, a_2 (D) are now respectively of degree 2, 1, 1. So the discriminant (E) is only divisible by t^2 , so that now the X -axis counts for two common tangents of C^3 and S . The X -axis itself has now with S in P three consecutive points in common, so it counts already for two common tangents. A tangent of C^3 following the X -axis does not touch S any more.

The term of the second degree in t of the discriminant (E) has now for coefficient $16Ch^2p^2$, where C is a constant. So the discriminant has three roots $t = 0$, when $h = 0$ or $p = 0$. The case $h = 0$ is just the one treated in § 6.

If $p = a = 0$ then C^3 touches in P one of the principal tangents of S in P , whilst the osculating plane of C^3 in P still coincides with the tangent plane of S in P . Out of the expressions (D) for a_0, a_1 and a_2 it is evident that these coefficients are respectively divisible by t^3, t^2 and t . So the discriminant (E) is divisible by t^4 or it has four roots $t = 0$. The X -axis counts thus for four common tangents of C^3 and S . By substitution of $x = t, y = t^2, z = t^3$ in the equation (B) of the surface S we find that C^3 and S now have in the origin three consecutive points in common.

§ 8. Let C_1 now be an arbitrary twisted curve and D_1 the developable formed by its tangents and let D_1 touch the arbitrary surface S in P . Let l be the generating line of D_1 touching S in P and let R be the point, in which it touches C_1 . Let V be the

osculating plane of C_1 in R . Through R and five points of C_1 consecutive to R a twisted cubic C^3 can be brought, on the condition that R , l and V are an ordinary point, an ordinary tangent and an ordinary osculating plane of C_1 . The developable D^4 formed by the tangents to C^3 and the developable D_1 have in common the line l and four consecutive generating lines.

If l must count for 2, 3 or 4 common tangents of C^3 and S , this is also the case for C_1 and S . The theorems proved in § 6 and 7 for C^3 hold good for any twisted curve. This gives rise to the following theorems:

If the developable D_1 corresponding to curve C_1 touches any surface S in point P whilst the generating line l of D_1 through P is no inflexional tangent of S , the line l counts for two or for three common tangents to C_1 and S according to the surfaces having in P an ordinary or a stationary contact.

If the point of contact P of D_1 and S be a parabolic point on S , then l counts for four or for two common tangents of C_1 and S according as the inflexional tangent of S in P coinciding with l or not.

If the point of contact P of D_1 and S be a hyperbolic point on S and if the tangent l of C_1 coincides with an inflexional tangent in the point P of S , then l counts for four or for two common tangents of C_1 and O according to R coinciding with P or not.

If C_1 touches S in P , whilst the osculating plane of C_1 in P coincides with the tangent plane of S in P , then the tangent l in P to C_1 counts for four or for three common tangents of C_1 and O , according to l being an inflexional tangent of O in P or not.

The theorems proved here for curves in space hold with a slight modification (see § 1) still for plane curves. They can be easily proved by taking for C_1 first a parabola p^2 after which they can be directly extended to an arbitrary conic section and after this to an arbitrary plane curve.

Delft, June 1905.

Physics. — *The shape of the sections of the surface of saturation normal to the x -axis, in case of a three phase pressure between two temperatures.”* By Prof. J. D. VAN DER WAALS.

In these Proceedings of March 1905 I have (fig. 4, 5 and 6) represented in a diagram some sections of the (p, T, v) -surface normal to the T -axis for three temperatures, at which three phases can exist simultaneously. The three temperatures chosen were: 1st the

temperature which we might call the transformation temperature and which I shall indicate by T_w (fig. 5), 2nd a temperature a little below the transformation temperature (fig. 4) and 3rd one a little above T_w .

In the case that these sections are known for all possible temperatures, the saturation surface is of course quite determined and known, and so all other sections e.g. those normal to the x -axis, are also determined. But it appears from the given figures, that though the realizable part of the saturation surface has a comparatively simple shape, the non-realizable part has a fairly intricate course — and that it is necessary to know also that intricate portion if we wish to get an insight into the course of the part that is to be realized.

To the intricacy of the hidden part it is due that though all the sections normal to the x -axis are given by those normal to the T -axis, the shape of the $(p, T)_x$ -sections will not always be easy to derive. Now that I for myself have obtained an insight into the course of these sections I have thought it not devoid of interest to try and make clear the properties of this curve by means of a series of successive figures.

If we wish to represent these $(p, T)_x$ figures in a diagram, all the surface must of course be known — in other words according to the course of our derivation from the $(p, x)_T$ sections — *all* the $(p, x)_T$ sections must be known.

Between two temperatures which are known by experiment, see fig. 4, 5 and 6 l.c., such a $(p, x)_T$ section has two tops, viz. P and Q . If T is raised, the part that has P as top, is narrowed, and the part that has Q as top widens, and the reverse. This property is perhaps not quite fulfilled in the schematical figures of the paper mentioned, but it follows immediately from the fact that with continued rise of temperature the top P vanishes, whereas with sufficient lowering of T the top Q vanishes. Let us call the temperature at which P vanishes T_e and that at which Q disappears T_a . I choose these symbols T_e and T_a , because I think of the mixture of ethane and alcohol as an example for the shape of the (p, T, x) -surface discussed here. Of these mixture the plaitpoint circumstances have been determined by KUENEN and ROBSON. At T_e the whole top the plaitpoint of which is P , will have contracted, and the only trace left on the outline of the (p, x) -figure of the complication found at lower values of T , is a point, at which the tangent is horizontal, while at that place there must be an inflection point in the (p, x) -curve, which has for the rest a continuous course. For T equal to T_a this is the

case for the point Q vanishing on the outline. Just as experiment yields the values of T'_e and T'_a , it also gives us the values of x_c and x_a at which the tops P and Q will disappear. For temperatures higher than T'_e and lower than T'_a the $(p, x)_T$ -curves have lost the complications which they had for values of T between T'_e and T'_a . Only at temperatures which lie little above T'_e or little below T'_a , there is still a deviation to be found from the well-known looplike shape of these figures, as there are inflection points to be found. So at T'_e and T'_a the complications which I shall call externally visible complications, have disappeared. But before we can say we know all the particularities of the whole (p, T, x) -surface, among which I also reckon the *hidden* complications, the question is to be settled whether the disappearance of the external complications involves the disappearance of the hidden complications, whether perhaps the hidden complications may continue to exist long after the external complications have disappeared. Figures (1) and (2) make clear between which two alternatives a choice must be made. According to fig. (1) the disappearance of the external complications would involve the disappearance of the hidden ones. According to fig. (2) the hidden ones continue to exist when the external ones have disappeared. And even when T rises above T'_e , they are still there. At higher values of T the hidden complication gets detached from the outline. The spinodal curve — — — retains its maximum and minimum, and there are still two plaitpoints, viz. at this maximum and minimum. And only at a certain value of T lying above T'_e that maximum and minimum have coincided to a double point and the hidden complication is about to disappear.

For the point Q a similar question occurs. Have all the complications disappeared at T'_a , or is it required that T descends below T'_a before the hidden complications have also disappeared on this side?

I must own that I have long been in doubt on this point, as will appear when we compare the answer I shall now give to this question with remarks I made previously on the experiments of KUENEN and ROBSON.

According to KORTEWEG's result a double plaitpoint will always originate on the spinodal curve. But in itself this does not seem decisive. For according to both figures, to fig. 1 as well as to fig. 2, a double plaitpoint disappears or appears on an existing spinodal curve. But in fig. 1 this takes also place on an existing binodal curve. And now it is KORTEWEG's opinion, that such an appearance of a double point, viz. on an existing binodal curve, would be such a special case that we must not conclude to it but in the utmost

necessity. This is in fact an argument that speaks for fig. 2, but which did not seem to me perfectly conclusive. For who warrants us, that these very special circumstances do not occur here? It is chiefly to decide this point, that I have also examined the course of the $(p, T)_x$ -lines. And this examination has taught me, that the particularities which occur in these lines, do not clash with the assumption which leads to fig. 2 — whereas we should be confronted with difficulties, when we concluded to fig. 1.

Then fig. 3 is drawn up on the supposition that there are still hidden complications beyond the values of T_e and T_a . In this figure is drawn in the first place the projection on the (T, x) -plane of the phases coexisting at the three phase pressure, viz. the continuous curve $DEAC$. So this line represents the locus for the points $A'AA''$ of the figs. 4, 5, 6 of the paper of March 1905. The value of T for the point E is therefore T_e , and for the point A , T has the value of T_a . That this broken line consists of three almost straight pieces is not essential, but it *has* been assumed that it does not change its direction continuously at the points E and A .

In the second place the projection of the plaitpoint line has been given by: — . — . It consists of a piece which may be considered as the projection of the points P of the figures of March 1905, i.e. the left part up to the point E . The part lying on the right from the point A represents then the projection of the points Q of the figures l. c. Every part of this line lying between E and A is projection of the hidden plaitpoints.

As we make one double plaitpoint disappear at $T > T_e$, and the other at $T < T_a$, this middle part starts on the left still running to higher values of T , (the piece EM) and on the right there is a piece mA , that also runs to higher values of T . The remaining part of this plaitpoint projection curve, viz. the piece Mm descends therefore with increasing value of x . That this plaitpoint curve possesses a maximum and a minimum value will be shown presently. This middle piece is the locus of the plaitpoints R of the figs. 4, 5, 6 l. c. The part between E and M , and also the part between A and m is the projection of the higher plaitpoint of the hidden complication in the cases that this complication still exists either above T_e or below T_a .

In the third place the three phase pressure is traced. In the points of the line DE thinner lines have been drawn parallel to the p -axis, increasing in length as we reach the point E . The three phase pressure itself is denoted by — — — —. We must, of course, take care that points of the branch of the three phase pressure lying

above EA , and also of the branch lying above AC must fulfil the condition that for the same value of T the pressure must have the same value for the three branches.

In the fourth place for some values of T sections parallel to the (p,x) -plane are given and those parts of these sections are drawn which correspond to the pieces $A'PA$ and AQA'' of the figs. 4, 5, 6 l. c. We must then, of course, take care that the maxima of the curves fall above the projection of the plaitpoint curve. It is hardly necessary to remark that at any rate as long as T lies between T_e and T_a the plaitpoint pressure for the left-hand branch, and also for the right-hand branch is greater than the three phase pressure. But if we want to compare the value of the plaitpoint pressure and that of the three phase pressure *at the same value of x* , we have to carry out another construction. Let G be a point of the projection of the three phase pressure. Let us draw the line GH parallel to the T -axis, then H (a point of the projection of the plaitpoint curve) has the same value of x , and so above H a point must be sought of the plaitpoint curve itself. How high this point lies depends on the value which the plaitpoint pressure has for this value of x . In the point H a somewhat thicker line has been drawn parallel to the p -axis, whose length would have to denote the value of this plaitpoint pressure. This length is left undetermined in the figure — but is clear that it will be smaller than the amount of the three phase pressure for the same value of x . For at the value of T , as it is for the point G , the pressure above G in the section for the chosen value of x is equal to the three phase pressure. The value of T for the point H is smaller than that for G . Between these two values of T the $(p,T)_x$ -section of the (p,T,x) -surface has a continuous course, and in such a $(p,T)_x$ -curve the pressure rises with the temperature. Only in the case that a maximum in the $(p,x)T$ -curve occurred, the pressure above H , so the plaitpoint pressure could be smaller than that above G . But in our diagrams we shall assume the more general case. Themodifications which would ensue from the assumption that in the region discussed here a maximum pressure occurs, would render numerous new figures necessary, and it will not be difficult to give them when the more common case has been understood.

According to fig. 3 there is in our case a maximum and a minimum for T_{pl} , so that there are values of x for which $\frac{dT_{pl}}{dx} = 0$.

For a plaitpoint $\left(\frac{d^2\zeta}{dx^2}\right)_{pT}$ is equal to 0, because it is a point of the spinodal curve, and at the same time $\left(\frac{d^3\zeta}{dx^3}\right)_{pT}$ is equal to 0.

The differential equation of the spinodal curve is

$$\left(\frac{d^3\zeta}{dx^3}\right)_{pT} dx + \left(\frac{d^2v}{dx^2}\right)_{pT} dp - \left(\frac{d^2\eta}{dx^2}\right)_{pT} dT = 0. \quad \dots (1)$$

The differential equation of the plaitpoint curve is

$$\left(\frac{d^4\zeta}{dx^4}\right)_{pT} dx + \left(\frac{d^3v}{dx^3}\right)_{pT} dp - \left(\frac{d^3\eta}{dx^3}\right)_{pT} dT = 0. \quad \dots (2)$$

From (1) follows:

$$\left(\frac{dp}{dT}\right)_{Spin} = \frac{\left(\frac{d^2\eta}{dx^2}\right)_{pT}}{\left(\frac{d^2v}{dx^2}\right)_{pT}}$$

If we substitute this value of $\frac{dp}{dT}$ in (2), we find:

$$\left(\frac{dT}{dx}\right)_{pl} = - \frac{\left(\frac{d^2v}{dx^2}\right)_{pT} \left(\frac{d^4\zeta}{dx^4}\right)_{pT}}{\left(\frac{d^3v}{dx^3}\right)_{pT} \left(\frac{d^2\eta}{dx^2}\right)_{pT} - \left(\frac{d^2v}{dx^2}\right)_{pT} \left(\frac{d^3\eta}{dx^3}\right)_{pT}} \dots (3)$$

and

$$\left(\frac{dp}{dx}\right)_{pl} = - \frac{\left(\frac{d^2\eta}{dx^2}\right)_{pT} \left(\frac{d^4\zeta}{dx^4}\right)_{pT}}{\left(\frac{d^3v}{dx^3}\right)_{pT} \left(\frac{d^2\eta}{dx^2}\right)_{pT} - \left(\frac{d^2v}{dx^2}\right)_{pT} \left(\frac{d^3\eta}{dx^3}\right)_{pT}} \dots (4)$$

From this equation (3) follows that $\left(\frac{dT}{dx}\right)_{pl}$ can become 0 when $\left(\frac{d^2v}{dx^2}\right)_{pT} = 0$. In this case $\left(\frac{dp}{dx}\right)_{pl}$ is not equal to 0. A similar case is found for substances, for which no three phase pressure occurs when there exists a minimum critical temperature. It is wellknown that in this case the binodal curve splits up, and that there is a point of inflection for the isopiestic in this point. There is a double plaitpoint also then, which originates or disappears at a certain temperature; but though we can speak of a double plaitpoint, the value of $\left(\frac{d^4\zeta}{dx^4}\right)_{pT}$ is not = 0 then.

In the case under consideration the value of $\left(\frac{d^4\zeta}{dx^4}\right)_{pT}$ is equal to 0 in the point at which a double plaitpoint appears or disap-

pears, as may be derived from the figs. 1, 2, 3, i. e. Between certain values of p and at suitable values of T there are isopiets, on which $\frac{d^2\xi}{dx^2}_{pT}$ is four times equal to 0. On such isopiets $\frac{d^3\xi}{dx^3}_{pT}$ is three times and $\frac{d^4\xi}{dx^4}_{pT}$ twice equal to 0. We now can choose the value of p and T such, that these two points in which $\frac{d^4\xi}{dx^4}_{pT}$ is 0, coincide. As then two values of x in which $\frac{d^2\xi}{dx^2}_{pT} = 0$ also coincide, such a point is a plaitpoint. For such points $\left(\frac{d^2\xi}{dx^2}\right)_{pT}$ and $\left(\frac{d^3\xi}{dx^3}\right)_{pT}$ and $\left(\frac{d^4\xi}{dx^4}\right)_{pT}$ is equal to 0. These three equations determine then the value of x , p and T , at which such a double plaitpoint appears or disappears.

If in (3) and (4) we put the quantity $\left(\frac{d^4\xi}{dx^4}\right)_{pT} = 0$, then both $\left(\frac{dT}{dx}\right)_{pl}$ and $\left(\frac{dp}{dx}\right)_{pl}$ will also be equal to 0, from which follows that not only the plaitpoint temperature, but also the plaitpoint pressure will present a maximum and a minimum. As we only assume the case that $\frac{dp}{dT}$ is positive, there will be found at the same time a maximum value or a minimum value for the two curves. In the points E and A there is therefore no maximum or minimum for the plaitpoint curves, and this is also to be expected for the curve of the three phase temperature, though this perhaps might call for further examination. For the properties which are to be derived by us this is, however, not of great importance.

Let us now proceed to describe the properties of the sections of the (p, T, x) -surface normal to the x -axis or in other words the course of the $(p, T)_x$ -curves.

We remark then in the first place that for values of x below x_D and above x_C the $(p, T)_x$ -curves will present their usual shape without any complication. For values of x between x_D and x_E and also for values of x between x_A and x_C there is a complication in these $(p, T)_x$ -lines. For values of x between x_D and x_E the three phase temperature lies higher than the plaitpoint temperature; the reverse is the case for x between x_A and x_C . On such $(p, T)_x$ -curves the usual plaitpoint occurs, but at a plaitpoint such curves, considered in themselves, do not present any particularity. But a point also occurs on them at which the three phase pressure is reached,

and at such a point the curve suffers an abrupt change of direction. As for every value of x the line $DEAC$ is met only once, this sudden change of direction occurs only once in a $(p, T)_x$ -curve. This determines the external course of such a section sufficiently. Beyond the point of change of direction the points for which W_{21} and V_{21} are equal to 0 will give rise to a maximum value and to a critical point of contact. But we confine ourselves here to the modifications which are the consequence of the three phase equilibria.

In the points, at which such an abrupt change of direction occurs, a part of the internal or hidden course of such a $(p, T)_x$ -curve begins and the series of figures (a, b, c, d etc.) indicates this hidden course for the values of x , for which the three phase curve is met. Seen on the $(p, T)_x$ -curve such a point presents itself as a node. The part of the curve coming from below continues through the node, also the part coming from above, while there is a third part which joins the points, where this onward course stops. The temperature of the node is, therefore, quite determined by the point at which $DEAC$ is cut by a line parallel to the T -axis with the given value of x as abscis. But the size of the hidden part is very different. As it has quite disappeared beyond x_D and x_C , it is but small for values of x only little greater than x_D or only little smaller than x_C . But chiefly the different hidden parts are distinguished by the occurrence or non-occurrence of a plaitpoint and when it occurs by the place where it occurs.

In what precedes it has already been remarked that the plaitpoint does not lie hidden for values of x beyond x_E and x_A . But for all values of x between x_E and x_A it lies on the hidden part, so on that which might be called the loop when the $(p, T)_x$ -curve is drawn. This appears at once when the $(p, x)_T$ -figures are consulted l.c. But depending upon the value of x the plaitpoint can have three different places. It may either lie on that part of the loop which may be considered as the continuation of the lower part of the $(p, T)_x$ -curve — or it may lie on the branch of the loop joining the points at which the onward course from below and above stops — or it may lie on the part which may be considered as the continuation of the part coming from above.

The first case occurs for x between x_E and x_M , the second when x lies between x_M and x_m and the third case when x lies between x_m and x_A . So if we have drawn a $(p, T)_x$ -curve, e.g. one of the figures of the series (a, b, c, d etc.), and when we proceed in the same direction in such a part, also following the loop, we follow the motion which the plaitpoint has when x changes continuously.

A plaitpoint always being a point where the stable and unstable region meet, it would be incorrect to speak of stable, metastable and unstable plaitpoints. But when we pay attention to the coexisting phases in the neighbourhood of the plaitpoint, the preceding names are appropriate for such phases according to the described situation of the plaitpoints. As long as the plaitpoint lies on the external part of the (p, T, x) -surface, the coexisting phases in its neighbourhood are stable; as long as it lies on those parts of the loop which may be considered as a continuation of the external branches, the coexisting phases in its neighbourhood are metastable, and when the plaitpoint lies on the remaining part of the loop, the coexisting phases in its neighbourhood are unstable.

In the series of the figures (a, b, c, d etc.) is, besides the loop of the $(p, T)_x$ -curve and the place of the plaitpoint, also the shape of the spinodal curve indicated. This spinodal curve is the section of the spinodal surface with the plane which has the chosen value of x . All the points of the loop which lie below the spinodal curve represent unstable phases and those which lie above it, metastable or stable ones. Thus e. g. in fig. 4, in which the plaitpoint lies on the retrograde branch of the loop, the spinodal curve is a curve which cuts the loop in two more points. In concordance with the figures 4, 5, 6 l. c. are the points of intersection indicated by the letters D and C . By raising the temperature in these figures, the point C is moved to the left, and when the temperature is lowered, D moves to the right, which makes it possible for them to come into the chosen x -plane.

If from a $(p, T)_x$ -curve for a chosen value of x the curve is derived which belongs to a value of $x + dx$, the value of $\left(\frac{dp}{dx}\right)_T$ must be known for every value of T .

If $\left(\frac{dp}{dx}\right)$ is = 0, the $(p, T)_x$ -curve for the values x and $x + dx$, must have the same value for p . If we draw both the $(p, T)_x$ -curve and the curve $(p, T)_{x+dx}$ as has been done in the figures 4, 5 and 6, there will be intersection of these two (p, T) -curves in all the points in which $\left(\frac{dp}{dx}\right)_T = 0$. In the figures mentioned the curve for $x + dx$ is represented by — . — ., and now the two (p, T) -curves will cut everywhere where the spinodal curve cuts the first (p, T) -curve, according to the property that for coexisting phases $\left(\frac{dp}{dx}\right)_T = 0$ when $\left(\frac{d^2\xi}{dx^2}\right)_{pT} = 0$. Also in the point where the spinodal curve touches the curve $(p, T)_x$, so in the plaitpoint, such an intersection of the two following $(p, T)_x$ -curves

J. D. VAN DER WAALS. The shape of the sections of the surface of saturation normal to the x -axis, in case of a three phase pressure between two temperatures.

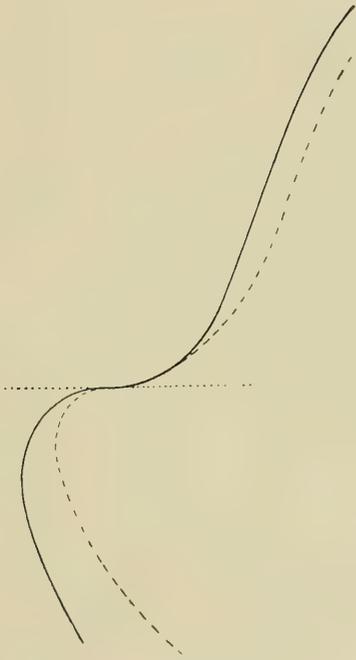


Fig. 1.

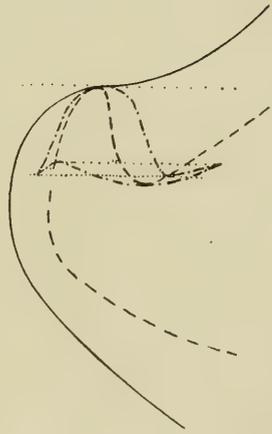
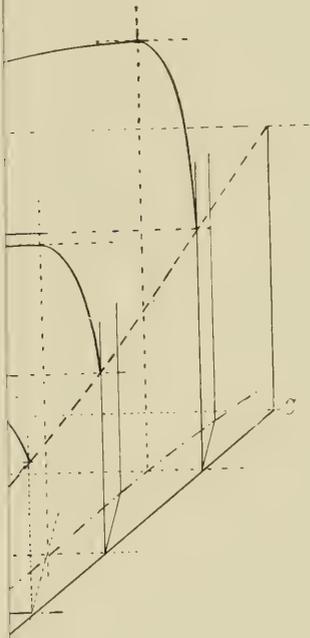


Fig. 2



the x-axis,



X

J. D. VAN DER WAALS. The shape of the sections of the surface of saturation normal to the x -axis, in case of a three phase pressure between two temperatures

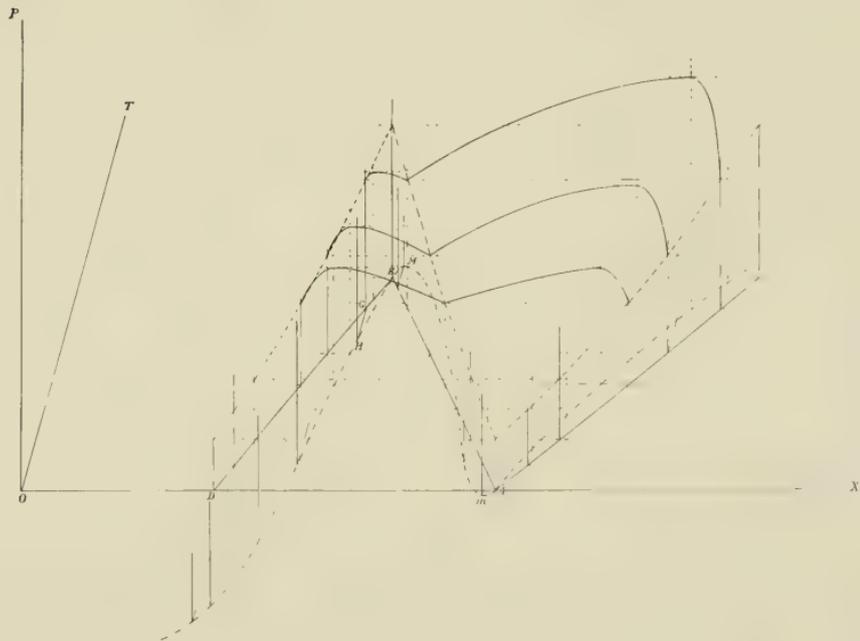


Fig. 3.

J. D. VAN DER WAALS. The shape of the sections of the surface of saturation normal to the x-axis, in case of a three phase pressure between two temperatures.

Fig. 4.

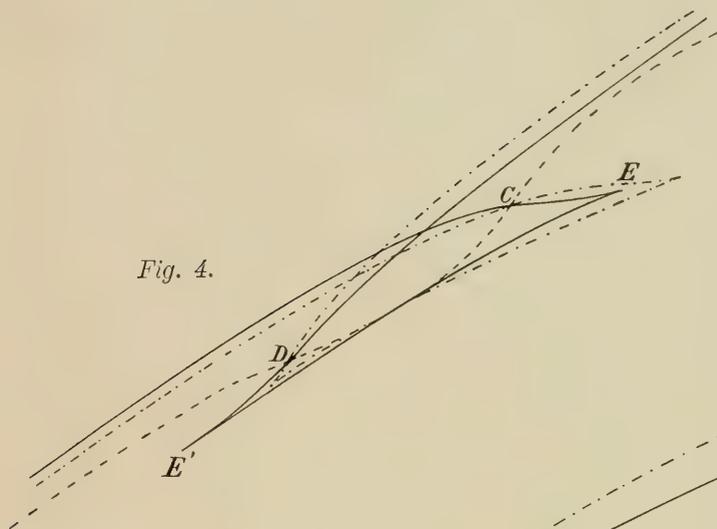


Fig. 5.

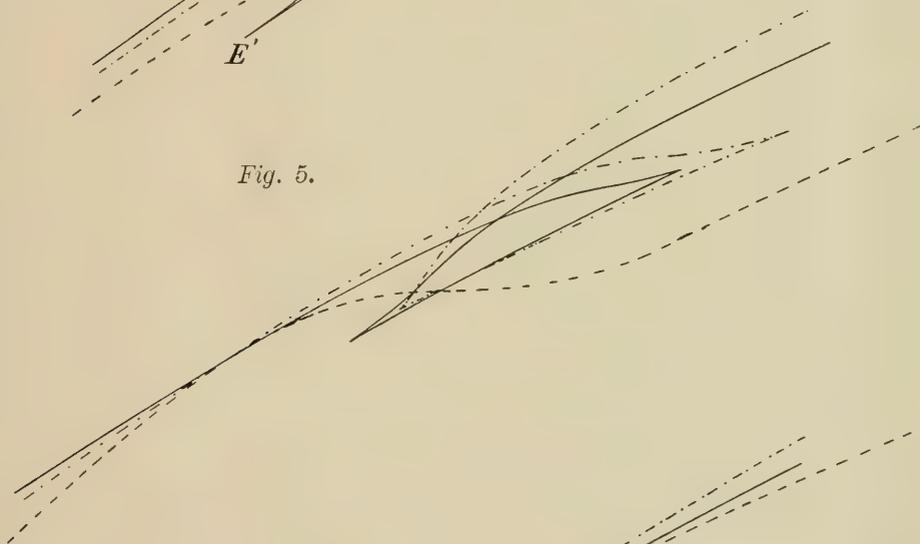
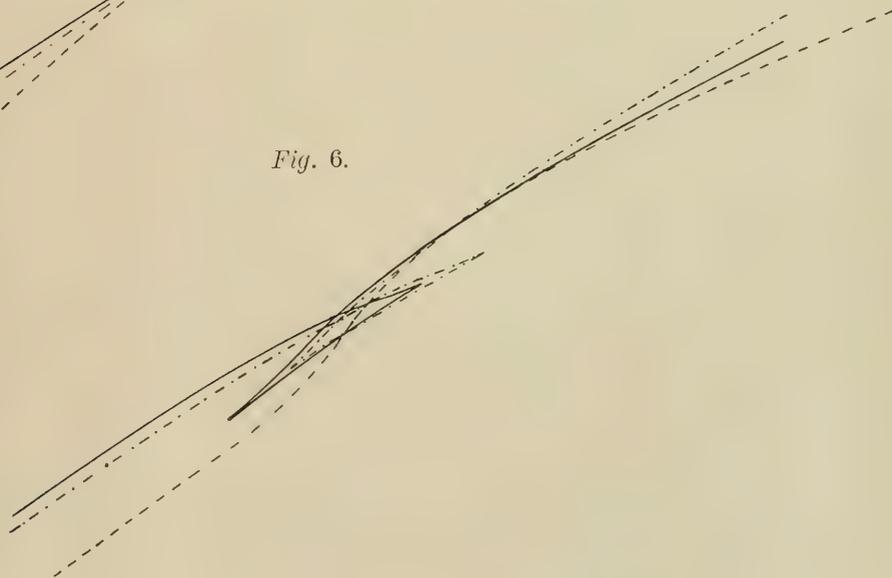


Fig. 6.





a



e



b



J. D. VAN DER WAALS. The shape of the sections of the surface of saturation normal to the x axis, in case of a three phase pressure between two temperatures.



Fig. 7

takes place. This may be assumed as already known from the properties of a $(p, T)_x$ -curve, when there are no complications by hidden equilibria. It might possibly be expected that in a plaitpoint, where besides $\left(\frac{d^2\xi}{dx^2}\right)_{pT}$, also $\left(\frac{d^3\xi}{dx^3}\right)_{pT}$ is equal to 0, double intersection and so contact would take place. If, however, we develop the equation which teaches us the value of $\left(\frac{dp}{dx}\right)_T$ viz.

$$v_{21} \left(\frac{dp}{dx_1}\right)_T = (x_2 - x_1) \left(\frac{d^2\xi}{dx_1^3}\right)_{pT}$$

for the case of a plaitpoint in the form :

$$\left(\frac{d^2v_1}{dx_1^2}\right)_{pT} \frac{(x_2 - x_1)^2}{2} \left(\frac{dp}{dx_1}\right)_T = (x_2 - x_1) \left\{ \frac{(x_2 - x_1)^2}{2} \left(\frac{d^4\xi}{dx_1^4}\right)_{pT} \right\}$$

or

$$\left(\frac{dp}{dx_1}\right)_T = (x_2 - x_1) \frac{\left(\frac{d^4\xi}{dx_1^4}\right)_{pT}}{\left(\frac{d^2v_1}{dx_1^2}\right)_{pT}}$$

it appears that in the case of a plaitpoint, the quantity $\left(\frac{dp}{dx}\right)_T$ is only once equal to 0 on account of the factor $x_2 - x_1$.

It may be remarked here for the better understanding of the series of figures (a, b, c etc.) that the first set of four viz. a to d holds for values of x lying between a point halfway x_E and x_A and the point E itself, x moving to continually smaller values. Fig. d holds for x_E . The second set of four values holds for x between x_E and x_D , and Fig. g is the representation for $T = T_r$.

The remaining figures (b', c' etc.) hold for values of x lying on the right side. Fig. g' is the representation for $T = T_r$ on the right side and fig. d' holds for $x = x_A$.

Physics. — “*The (T, x) -equilibria of solid and fluid phases for variable values of the pressure*”, by Prof. J. D. VAN DER WAALS.

In two communications (October and November 1903) I discussed and represented in diagrams for the case of equilibrium between a solid and a fluid phase 1st the (p, x) -figures for constant value of T and 2nd the (p, T) -figures for constant value of x . So only the

treatment and discussion of the (T, x) -figures for constant value of p was left. I have not given the third communication, in which these last figures were to be discussed, first because they could be derived directly from the other communications on the discussed equilibrium and secondly because I would not make it appear as if I attached too much importance to the hidden equilibria, showing the continuity between the equilibria which can be observed and which seem discontinuous without the hidden ones. However, some noteworthy particularities would have presented themselves, and so, induced by questions of Dr. SMITS on subjects in which suchlike particularities occur and at his request, I will briefly discuss at least the principal cases.

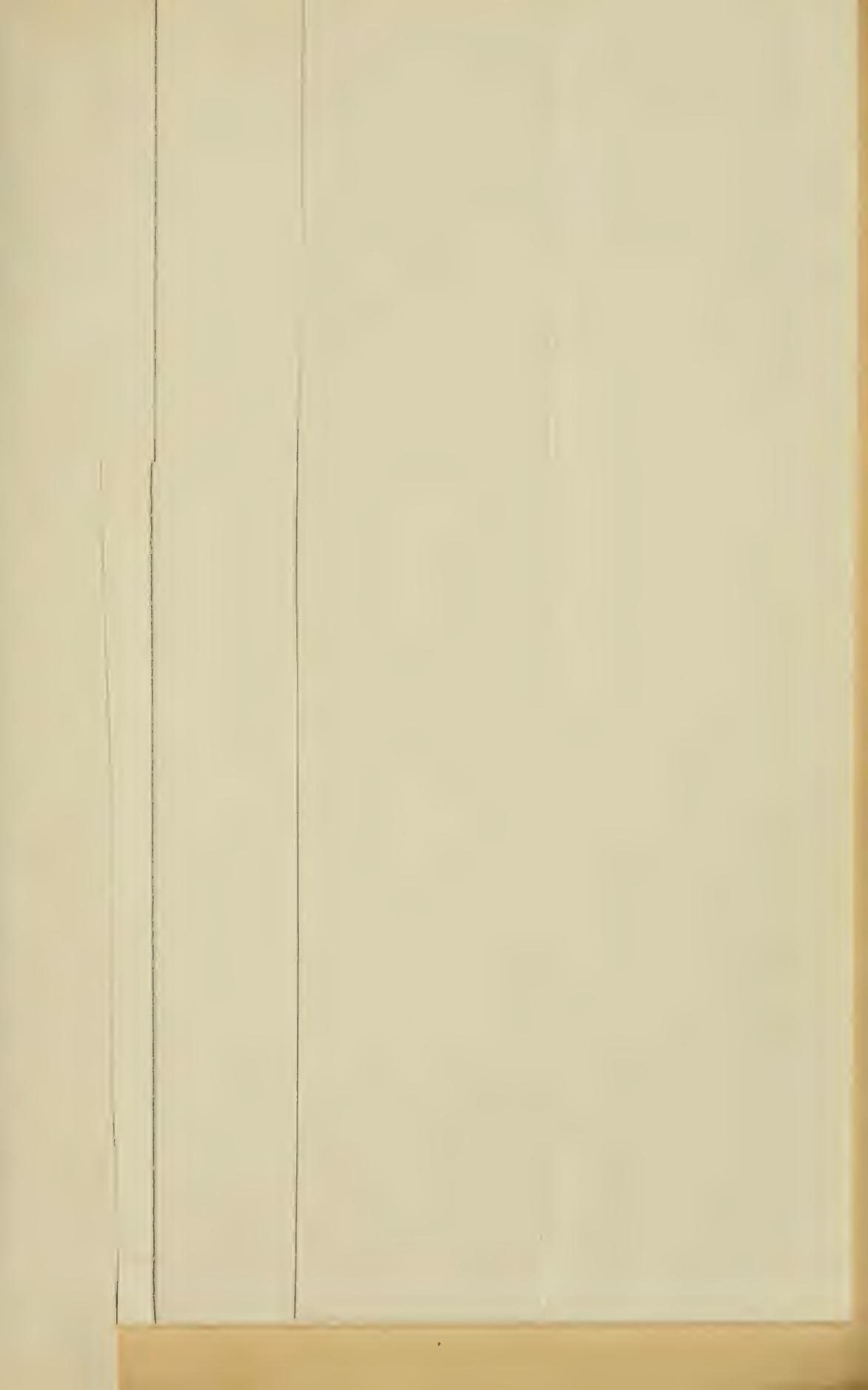
The differential equation (see the preceding communication) has the following form for constant value of p :

$$(x_s - x_f) \left(\frac{d^2 \xi}{dx_f^2} \right)_{pT} dx_f + \frac{w_{sf} dT}{T} = 0.$$

Let us think the $(T, x)_p$ -curve of the fluid equilibria inter se construed. If the second component is more volatile than the first, the two branches of this curve descend. In fig. 1 this (T, x) -curve is closed on the side of the second component, and it is therefore assumed that the pressure chosen lies above the critical pressure of this component. Further in fig. 1 the curve of the fluid phases has been drawn, which coexist with the solid body. For so far as these phases lie within the curve of the fluid equilibria, they are not to be realised or with difficulty. In fig. 1 it has been assumed that the circumstances are chosen in such a way that this curve passes the region of fluid equilibrium twice, as is the rule for lower pressures and so also for lower temperatures.

If the value of the pressure increases, and so also the value of T , the curve of the fluid equilibria inter se ascends, while its form is modified at the same time. The curve of the equilibria with the solid phase ascends also with p , but in a smaller degree, at least on the side of the liquid equilibria. Now in fig. 1 we have ascribed such a value to the pressure, that there are still two different three phase equilibria, while in fig. 2 a value is ascribed to p , at which the solid body coexists with a plaitpoint phase of the fluid equilibria — so that above that pressure the curve of the equilibria with the solid phase passes only once through the region of the equilibria inter se of the fluid phases. In fig. 3 p has ascended so far that there is again equilibrium between the solid body and a plaitpoint phase.

For still higher value of p there are no longer three phase equilibria and the curve for the equilibria of the solid body with a fluid



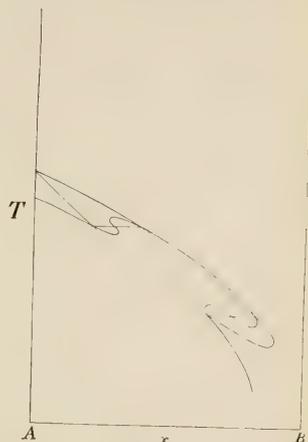


Fig. 1

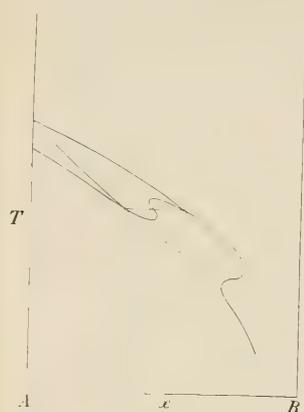


Fig. 2



Fig. 3

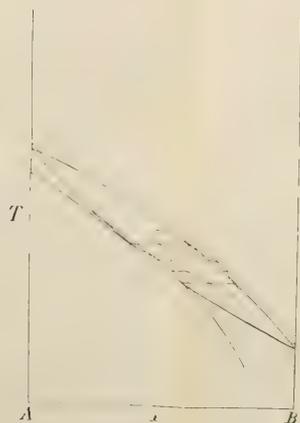


Fig. 5

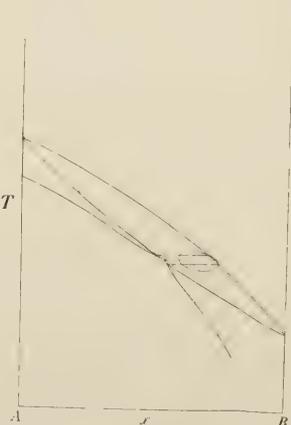


Fig. 6

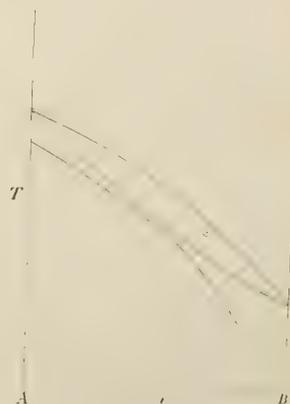


Fig. 7

phase has got quite detached from the curve for the equilibria inter se of the fluid phases.

In the two previous communications on this subject *l. c.* I discussed the values of $\frac{d^2\zeta}{dx^2_{pT}}$ and w_{sf} , and I refer to them for more particulars on the course of the $(T,x)_p$ -curves.

I will only discuss here one more particular point occurring in these curves for the case that the two surfaces of equilibrium, viz. that for a solid phase with a fluid phase and that for the fluid equilibria inter se, get detached at a value of T and p below that of the plaitpoints.

The figures 4, 5, 6 and 7 refer to this. In this case the two intersections of the curve of equilibrium between the solid and the fluid phase with the region of the fluid phases will meet at a certain pressure in a point of the spinodal curve on the liquid side, and then concur to one single curve. In this case the meeting point becomes a double point, and at still higher values of p a part is detached, as it is drawn in fig. 6, and at still higher value of p it has contracted to a single point lying on the spinodal curve on the vapour side.

It has further been assumed in these diagrams that the two branches of the spinodal curve, also if we have to do with a (p,x,T) -surface, lie inside the surface. At high temperatures and in the neighbourhood of a plaitpoint this is, of course, the case. At lower temperatures, however, the branch of the spinodal curve, which lies on the liquid side in a (v,x,T) -surface, moves to the vapour side in a (p,x,T) -surface, and gets even far outside the surface. In the same way the branch of the spinodal curve, which lies on the vapour side in a (v,x,T) -figure, moves to the liquid side in a (p,x,T) -surface, and at low temperatures it has even got outside.

This is the consequence of the fact, that the value of x and T determines a phase indubitably only when moreover the value of v is given. If the value of p is given, then three different phases may be indicated by this value. I shall, however, not enter more closely into the treatment of the complications which are the consequence of this, here. I shall only just mention that the point where the hidden equilibria disappear in fig. 7, can lie in quite another place than is the case in fig. 7.

Physics. — “On the hidden equilibria in the p - x -diagram of a binary system in consequence of the appearance of solid substances.” By Dr. A. SMITS. (Communicated by Prof. J. D. VAN DER WAALS).

1. Some time ago Prof. VAN DER WAALS¹⁾ showed that in a binary mixture (A, B) one of the two p - T -lines for the three phase pressure, viz. that which runs from the eutectic point to the higher-melting substance (B), can present some particularity.

It proved, namely, that at the triplepoint this p - t -line must have the direction of the melting line (of B).

As for most substances $v_l > v_s$, or in other words the substance expands when melting, increase of pressure causes as a rule a rise of the melting point.

If in the p - t -projection, (Fig. 1), the triplepoint of the substance B is denoted by d , then the melting line dg will in most cases run from the triplepoint to the right, and as the three phase line cd must have the direction of dg at d , this three phase pressure line will have to present the particularity, that it does not only possess a maximum of pressure, but also a maximum of temperature, as is represented in Fig. 1 in an exaggerated manner.

2. As has been shown before²⁾ and will be further discussed in the second paper, in a dissociating composition the same course may be found on a larger scale, and it is this part of the three phase line, that is the most important in compositions. Therefore it seemed desirable to me to examine the p - x -diagrams from the triplepoint to higher temperatures for the simple case discussed just now, and to treat the compositions afterwards.

3. The p - x -diagram at the triplepoint, and at a temperature slightly higher are presented in Fig. 2.

As appears from Fig. 1, we find a double section of the three phase line for the first time at the triplepoint, when coming from lower temperatures, and a consequence of this is, that besides at the triplepoint pressure, three phases may also occur at a much higher pressure. This case is more closely defined in Fig. 2 by the p - x -diagram corresponding to the temperature t_1 . The lowest three phase pressure or the triplepoint pressure is repre-

1) These Proc. Vol. VI, p. 230.

2) BAKHUIS ROOZEBOM, Zeitschr. f. phys. Chem. 4. 31.
STORTENBEKER, " " " " 3. 71.

sented by the point g , where the liquid curve acg , the vapour curve aeg and the solubility isotherm $f'ceg$ meet.

The second three-phase pressure is represented by the curve ecs and lies considerably higher. The coexisting phases have here different concentration, and are denoted by e, c and s . Here c is the saturated liquid phase and e the vapour phase which coexists with the solid phase s .

If we now start from these three phases, and lower the pressure at constant temperature, we reach the region for solid B + vapour, as Fig. 1 represents. So below the three phase pressure ecs and above the triplepoint pressure of B , only vapour can occur by the side of solid B in stable condition, and the curve representing the vapours which can coexist with solid B is the lowest branch of the continuous solubility isotherm, viz. eg .

The line ac denotes the unsaturated liquids coexisting with the vapours lying on the line ae . The lines cg and eg represent metastable conditions, viz. supersaturated solutions with their coexisting vapours. The curve $c f'$, the upper part of the solubility isotherm represents the liquids coexisting with solid B .

The second $p-x$ -diagram, represented in Fig. 2, corresponds with a somewhat higher temperature t_2 . We are now above the triplepoint temperature and the lowest three phase pressure is not a triplepoint pressure now, but perfectly comparable with the highest three phase pressure. A result of this is, that we get below the lowest three phase pressure a reflection of what takes place above the highest three phase pressure. The solubility isotherm $f'_1 c_1 e_1 e'_1 c'_1 f'_1$ cuts, as it were, a portion out of the region for liquid + vapour, on account of which between the two occurring three phase pressures indicated by the curves $e_1 c_1 s_1$ and $e'_1 c'_1 s'_1$, only solid B can coexist with vapour in stable condition. The line $c'_1 f'_1$, like $c_1 f_1$ represents now the liquids coexisting with solid B , and the portion $e_1 e'_1$ the vapours coexisting with solid B .

As to the whole course of the solubility isotherm it may be observed that this line has now two maxima, two minima and four vertical tangents. For the portion $f'_1 c_1 e_1$ the points of contact of the vertical tangents lie in the metastable or the stable region, whereas those for the second piece $e'_1 c'_1 f'_1$ are situated in the unstable region.

At higher temperatures the three phase pressures draw nearer and nearer to each other and coincide finally, as may be seen from fig. 1.

When we examine this change in the $p-x$ -diagram it appears that the points e_1 and c_1 move downward and at the same time to the right, whereas the points e'_1 and c'_1 move upward and to the left.

As to the points a_1 and g_1 , they move upward with increase of temperature.

The result of these shiftings must of course be, as has been just said, that at the maximum temperature of the three phase line (see Fig. 1) the two three phase pressures become equal, and the points e_1 and e'_1 , like e_1 and e'_1 , coincide; then the solubility isotherm does not cut the liquid line any longer, but just touches it in the point where e_1 and e'_1 have coincided, after which no three phase pressure is possible and the solubility isotherm has got detached from the liquid line.

Though all this seems very simple, the representation of the intermediate stages presented some difficulties, which Prof. v. D. WAALS was kind enough to remove by allowing me to examine some T - x -diagrams corresponding with pressures respectively smaller, equal and larger than the three phase pressure, in which exactly the same succession of states occurred¹⁾.

What has been drawn in accordance with this in the figs. 3, 4 and 5, may be brought into words in the following way:

When the two three phase pressures have drawn so near, that the two branches of the solubility isotherm *would touch*, intersection takes place, and we get a curve as is indicated by $f'_1 e_1 e'_1 e_1 e'_1 f'_1$ in Fig. 3. Immediately afterwards, i.e. at somewhat higher temperature a portion gets detached, as represented in Fig. 4 and we get two solubility isotherms; one is $f e c' f'$ and the other forms a closed curve $e e' d$, a part of which ($e e'$) runs through the stable region.

At the maximum temperature of the three phase line the two three phase pressures $e c s$ and $e' c' s'$ have coincided, as is represented in the diagram corresponding with the temperature t_6 , in Fig. 4, and the solubility isotherm $f_1 c_1 f'_1$ no longer *cuts* the liquid curve, but only *touches* it in the point e_1 .

With the exception of this one point it runs therefore wholly through the stable region. The other *closed* branch no longer *cuts* the vapour curve, but only touches it in e_1 ; further this branch as a whole has contracted through the shifting of d to d_1 . This second branch of the solubility isotherm lies therefore at the maximum three phase pressure partly in the unstable region, partly in the metastable region.

At a temperature slightly above the maximum temperature of the three phase curve t_7 , the solubility isotherm $f f'$ is quite detached from the liquid curve, as is represented in Fig. 5; in the same

¹⁾ See the foregoing paper by VAN DER WAALS.

way the closed branch has got detached from the vapour branch, and has further contracted. At the temperature t_s the distance between the solubility isotherm $f_1 f'_1$ and the liquid curve has increased, and the closed branch has vanished, after having contracted to a point.

4. In the figs. 6, 7 and 8 I have drawn the $v-x$ -sections of the $v-x-t$ -space diagram for the case discussed here; they follow immediately from the $v-x$ -sections, given by me last year¹⁾.

The section indicated by continuous lines in Fig. 6 holds for the triplepoint temperature t_1 . There $a e c b$ is the region for liquid + vapour, $e h c$ the three phase triangle, $h e d$ the region for solid B + vapour, $b c f m$ the liquid region and $c h n f$ the region for solid B + liquid.

The curve for solid-fluid or the solubility isotherm $d e c f$ meets the metastable vapour branch $e d$ exactly on the line for the substance B , because at the triplepoint temperature of B the vapour which is in equilibrium with solid B , is perfectly the same as that which is in equilibrium with liquid B .

At a somewhat higher temperature the curve for solid-fluid cuts the vapour and liquid curve twice each, just as was the case in the $p-x$ -diagram. The curve for solid-fluid has then a shape as is indicated by the dotted line $f'_1 c_1 e_1 e'_1 c'_1 f'_1$ in fig. 6²⁾. Just as in the $p-x$ -diagram, this line cuts a piece out of the liquid-vapour region; in consequence we get two separated regions for liquid and vapour viz. $a_1 e_1 c_1 b_1$ and $e'_1 d_1 h_1 c'_1$. From this particular situation ensues further the existence of two three phase triangles, viz. $c_1 e_1 g_1$ and $c'_1 e'_1 g_1$, between which is situated the region for solid B + gas $g_1 e_1 e'_1$, two liquid regions $b_1 c_1 f'_1 m$ and $h_1 c'_1 f'_1$ and two regions for solid B + liquid viz. $g_1 c_1 f_1$ and $g_1 c'_1 f'_1$.

With increase of temperature the line solid B + fluid assumes the shape of a loop, as is indicated by the line $f c e' e c' f'$ in fig. 7; on this follows immediately detaching of a part, splitting up into two branches, viz. into the line $f'_1 c'_1 e_1 f_1$ and the closed line $e_1 e'_1 o$. At the maximum three phase temperature (fig. 8) the line $f c f'$ touches the liquid line and the closed line $e o e$ touches the vapour line. Above this temperature the two lines get detached from the liquid, respectively the vapour line and the closed line $e_1 o_1 e_1$ disappears as a point in the metastable region.

¹⁾ These Proc. Vol. VI, p. 484.

²⁾ At a temperature, only very little higher than the triplepoint temperature, a part of the branch $e'_1 c'_1 f'_1$ will fall outside the line for B .

5. Fig. 9 represents the most interesting part of the projection of the p - t - x -space diagram on the p - T -plane for the case that the plait-point curve meets the solubility curve, as with *ether* and *anthraquinone*. In this fig. the possibility has moreover been assumed, that the second plaitpoint temperature t_2 of a saturated solution lies above the triplepoint temperature t_3 . Fig. 10 represents for this case the p - x -sections corresponding with the temperatures t_1 and t_2 (see fig. 9).

The section for t_1 differs from the second section in Fig. 2 only in this, that the liquid branch passes continuously into the vapour branch with the point K as plaitpoint. If we now pass on to lower temperatures, the downmost three phase pressure becomes smaller and the upmost greater, while the plaitpoint pressure diminishes. In consequence of these last two changes the points e , c and K get nearer and nearer to each other, and when we have descended to the temperature t_2 , the points e , c and K have coincided or in other words the upmost three phase pressure has become a plaitpoint pressure; this circumstance is accounted for in the p - x -section, corresponding with the temperature t_2 (Fig. 10).

At the temperature t_3 , the triplepoint temperature, for which no p - x -section is drawn here, because it immediately follows from that for t_2 , the remaining downmost three phase pressure has become triplepoint pressure, and the points e'_1 , c'_1 and g_1 have coincided.

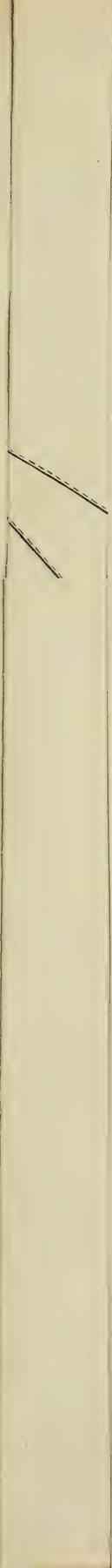
Below this temperature the p - x -sections over a certain temperature-range consist only of a solubility isotherm of the shape of $e'_1 q f_1$ in Fig. 10, as has been discussed before.

That the case assumed in Fig. 9 is not often to be realized, is obvious, but that it is a possible case, is, in my opinion, not doubtful

Amsterdam, June 1905. Chemical Laboratory of the University.

Physics. — “*Contribution to the knowledge of the p - x - and the p - T -lines for the case that two substances enter into a combination which is dissociated in the liquid and the gasphase.*” By Dr. A. SMITS. (Communicated by Prof. J. D. VAN DER WAALS).

The purpose of the following paper is to give a connected representation which is in logical connection with the p , x , t -diagram which has been recently drawn up by BAKHUIS ROOZEBOOM and in which it is assumed that only the components can occur as solid phases, for the most important particularities of the equilibria between a vapour,



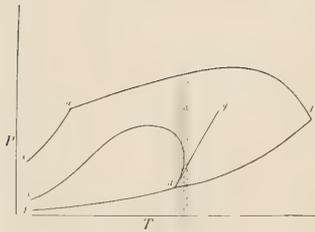


Fig. 1

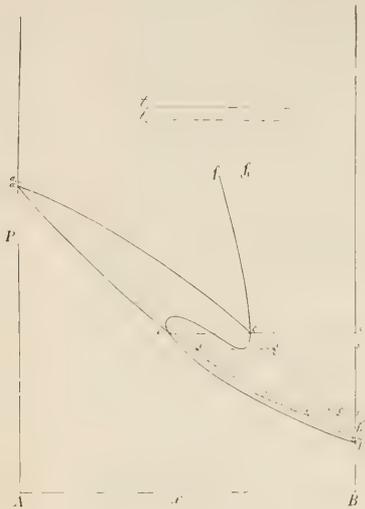


Fig. 2

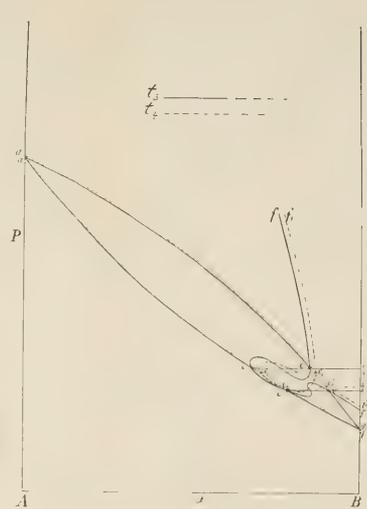


Fig. 3

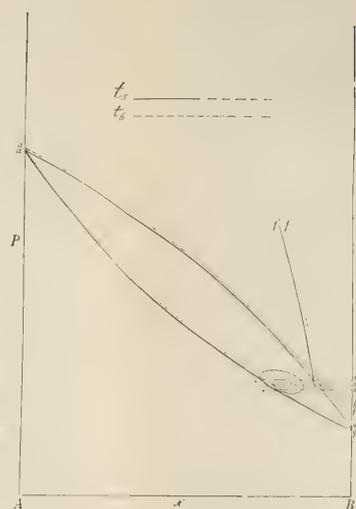


Fig. 4

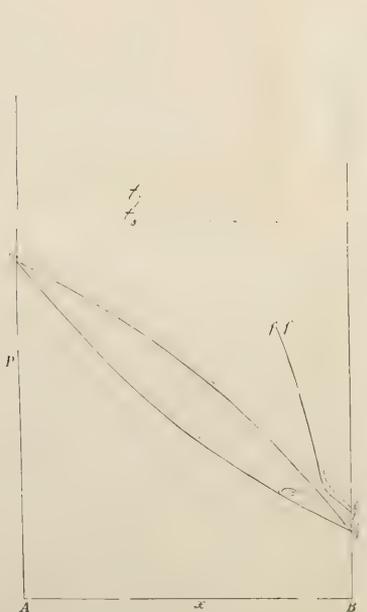


Fig. 5

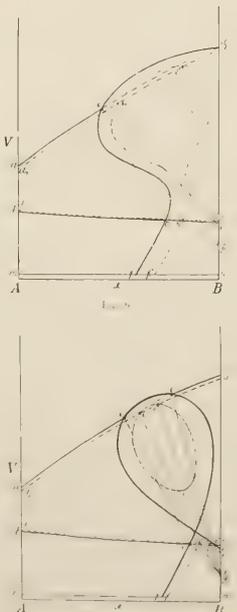


Fig. 7

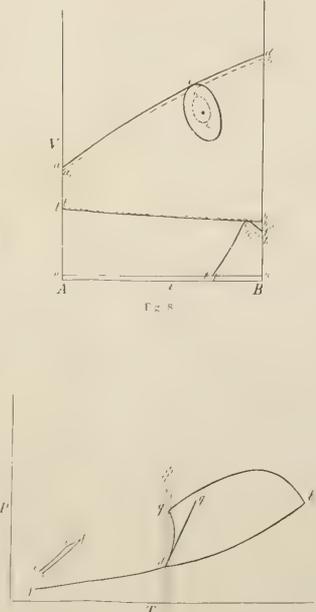


Fig. 8

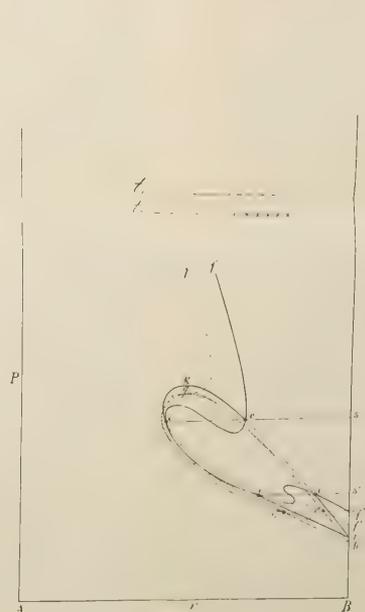


Fig. 10

liquid and solid phase for the case that the last is a dissociable combination.

Some of the points mentioned in what follows had already been given by him ¹⁾, but it was not till now that they could be combined into a connected whole through the knowledge obtained during the last time (see inter alia the preceding paper).

1. For the case that two substances A and B enter into a combination, I shall distinguish three cases.

1st that the vapour tension of the combination lies between that of the components. (fig. 1).

2nd that the vapour tension of the combination is smaller than that of the components. (fig. 2).

3rd that the vapour tension of the combination is greater than that of the components. (fig. 3).

2. If we bear in mind that for the case that the combination *does not* dissociate, a p - x -section for the system $A + AB + B$ is to be considered as a junction of the two systems $A + AB$ and $AB + B$, it is not difficult to combine the p - x -sections for the system $A + AB + B$ for different temperatures into one diagram.

If we first examine case 1, where the vapour tension of AB lies between that of the components, it may be observed, that in the system $A + AB$, A is the substance with the higher and AB that with the lower vapour tension, whereas in the system $AB + B$, AB has the higher and B the lower vapour tension. Bearing this in mind, we get, led by the diagrams given by me before ²⁾, to fig. 1, in which the hatched regions $amEE_1l$, $EE_1ee_1e_2de_2c_1c$, $dc'E'E_1e'$ and $E'E_1l'l_1l_2l_3a'm'_3m'_2m'_1m'$ indicate the vapours and liquids which coexist with solid phases (A , AB , AB and B) at different temperatures. We shall call these regions henceforth the *three phase regions*; they have as base the line which joins the points E with E_1 respectively E' with E'_1 and are bounded on one side by a vapour line and on the other side by a liquid line. The latter has already been called solubility curve before. At and below the eutectic temperature the p - x -section is simplest and it consists for each of the two systems of two lines representing the vapours which can coexist with solid A or solid AB respectively with solid AB or solid B . Such a p - x -section is found in the lines $ko g_o E'_1 k'$, where it must be expressly stated that $o g_o$ and $g_o E'_1$ do not form a continuous curve, but are two separate branches, which cut at g_o .

¹⁾ Rec. Trav. chim. 5, 335 (1886).

²⁾ These Proc. Vol. VI, p. 484.

In the point o coexists a vapour with the two solid phases A and AB and the point E'_1 denotes the composition and the pressure of the vapour phase which can coexist at the eutectic temperature with a liquid E' and two solid phases AB and B .

In the second p - x -section the curves $k_1 l$, $g_1 e$, $g_1 e'$ and $k'_1 l'$ represent vapours coexisting with solid phases; the lines mc and $m'e'$ denote the liquids coexisting with the vapours el and $e'l'$, while the lines ms , cf , $c_1 f'$ and $m's'$ represent liquids coexisting with solid phases.

What change this section is subjected to with rise of temperature is so easy to follow from the diagram, that it does not call for a discussion.

It may only be observed here that for the case that the combination reaches its critical point sooner than the components, we get somewhat above this temperature a p - x -section which consists of two loops $b_3 x$ and $b'_3 y$, in which the vapour branches have continuously passed into the liquid branches, and an opening has been formed between the two loops. This, however, does not complete the p - x -section, for, solid phases may still occur by the side of liquids at higher pressures, though above the critical temperature of AB and the melting point of A and B , when viz. A , B and AB melt with increase of volume, as generally happens. Thus the lines $k_3 s_4$, $g_3 f_4$, $g_3 f'_4$ and $k'_3 s'_4$ represent the liquids which can coexist with a solid phase at the same temperature.

After this discussion of fig. 1, it is not necessary to give a further explanation of figs. 2 and 3, which represent the second and third case, as these figures do not present any essential differences with fig. 1.

3. It is more interesting to see what happens, when the combination AB dissociates somewhat. In this case the total p - x -section is no longer to be considered as two separate p - x -figures joined, but as one whole and we arrive therefore at the conclusion, which sounds rather paradoxical, that the characteristic feature of a *combination* becomes apparent only when the combination is somewhat *decomposed* into its components. All the curves which meet at an angle in the figs. 1, 2 and 3 at the place of the line for the combination, now pass continuously into each other. This applies, therefore, not only to the gaslines, but also to the lines which bound the three phase regions.

With regard to the gradual transition of these three phase regions, it may be observed, that it does not take place at the point where the three phase region lines cut the line for AB , but always left

or right of this line, dependent on the mutual influence of the vapour tension of the components.

In order to elucidate this important point I have indicated in the figs. 4, 5 and 6 what shapes the three phase regions hatched in the figs. 1, 2 and 3 can assume in the neighbourhood of the line for the combination, in the case that a slight dissociation takes place in the liquid and gas phase. It is not improbable that there will also be dissociation in the solid phase in this case, but this is not taken into account here, in the first place because it is most likely exceedingly slight, and in the second place, because the diagram becomes much more intricate, when this dissociation is taken into account.

Fig. 4 corresponds to fig. 1, fig. 5 to fig. 2 and fig. 6 to fig. 3. For fig. 4 it may be remarked, that for the case that the vapour tension of the combination lies between the vapour tensions of the components, the liquid and the vapour line draw very near to each other somewhat past the line of the combination, on the side of the component with the smaller vapour tension, but that they do not reach each other, so that there remains a gap between them, from which follows, that in the series of liquids and vapours which can coexist with solid AB , not a single point can be pointed out where vapour, liquid, and solid phase have the same concentration, nor is there a point where a vapour and a liquid phase have the same concentration.

This latter is only the case when the vapour tension of the combination lies between those of the components, for when the vapour tension of the combination is smaller or greater than those of the components, we get according to a rule of GIBBS a three phase region with a minimum, fig. 5, or with a maximum, fig. 6, and at the place of this minimum or maximum the concentration of the vapour and the liquid phase must be identical.

If we now discuss figs. 4, 5 and 6 at the same time, we may remark, that there for a special temperature the situation is indicated of the two three phase pressures ecs and $c_1e_1s_1$ and the continuous line for solid-fluid or solubility-isotherm. This line must have an horizontal tangent at the point where it cuts the line for the combination. For this case is viz. $x_f = x_s$, or the concentration of the fluid phase is the same as the concentration of the solid phase and then it appears from the equation drawn up by VAN DER WAALS for the equilibrium solid fluid:

$$\frac{dp}{dx_f} = \frac{x_s - x_f}{V_{sf}} \left(\frac{\partial^2 \zeta}{\partial x_f^2} \right)_{PT}$$

that

$$\frac{dp}{dx_f} = 0.$$

If we now examine the changes with rise of temperature, it is noteworthy, as will presently become clear from the p - t -lines, that we have here to deal with changes quite analogous to those discussed in the preceding paper. The three phase pressure lines ecs and $c_1 e_1 s_1$ approach each other and coincide at ECS . This coincidence takes place at the maximum temperature of the p - t -line for the three phase pressure. One of the two three phase pressure lines sec and $s_1 e_1 c_1$ must therefore pass through the positions indicated by $e'_1 c'_1$ and $e'c'$, before it coincides with the other. Now it follows from the three phase pressure line $e'_1 c'_1$ that the gas phase e'_1 has the same concentration as the solid combination, while the liquid phase c'_1 has another concentration. The three phase pressure line $e'c'$ on the other hand indicates, that the liquid phase c' and the solid phase have the same concentration, while the gas phase e' has another concentration.

We see therefore, that the three phases solid-liquid-gas have not the same concentration at any pressure, but that they become two and two equal. We may express this also in this way: When a combination dissociates in the liquid and the gas state, then this combination has no longer a triplepoint, for this point has split up into two other points where vapour and solid respectively liquid and solid get the same concentration.

After I had written this paper, I found to my surprise, that already in 1897 VAN DER WAALS had arrived at the same result by a way which I intended to discuss later on and for which the diagrams had been already drawn¹⁾.

4. In order to make the difference between a non-dissociating and a dissociating combination more apparent, we consider the case, that we bring the dissociating combination AB in solid condition into a vacuum, and make the temperature rise continually.

The solid substance AB will, when the volume is not too large, coexist with its vapour, till the pressure has become equal to that indicated by the point e'_1 ; at this moment a third phase appears, viz. liquid. As the total concentration must always be that of AB , it is necessary that the concentration of the vapour phase lies on one side, and that of the liquid phase on the other side of the line for AB ; as follows from the figures 4, 5 and 6 this is really the case. With rise of temperature three phases continue to exist for some time side by side and the vapour and liquid phases coexisting with solid AB lie on the same horizontal line. The liquid phase lies on the liquid branch $c'c'_1$ and the vapour phase on the vapour

¹⁾ Verslag Koninkl. Akad. 21 April 1897, 482.

branch $e'e_1'$, while the solid phase lies naturally on the line GG' .

With a suitable volume the three phases may now continue to exist over the whole range of pressure and temperature indicated by $e_1'c'$, but then the vapour phase must have disappeared when we have reached the point c' , for in the point c' the liquid has the same concentration as the solid combination.

Beyond the maximum, respectively minimum in figs. 5 and 6 the concentration of liquid and vapour is, of course, always different, just as in fig. 4, and as the line for the combination never coincides with this maximum, respectively minimum, when there is a maximum or minimum, in the above mentioned case the two phases will necessarily only get the same concentration, when two phases coexist.

At c' , we leave the three phase region, which we had entered at e_1' and coexistence of solid AB + liquid at higher temperatures can now only take place under higher pressure.

VAN DER WAALS has called the temperature of the point e_1' the *maximum sublimation temperature* and that of the point c' , the *minimum melting point temperature* or the *melting point proper* of the combination.

Further it is worthy of note that as appears from the figs. 4, 5 and 6, the highest three phase temperature cannot be reached when we start from pure AB , as this temperature corresponds with a total concentration which contains more A than the combination.

It is obvious from the foregoing, that the distinguishing feature between a non-dissociating and a dissociating substance is this, that whereas for a non-dissociating substance the three phases can only exist at one temperature, they can coexist for a dissociating substance over a certain temperature range. We may express this also in this way: a non-dissociating substance has only a three phase *point*, but a dissociating substance a three phase *line*.

Before leaving figs. 4, 5 and 6 I will point out, that the solubility-isotherm at the maximum three phase temperature has a shape which is indicated by the line $f'Cf'_1$. This line touches the liquid branch at C and has an horizontal tangent at the point where it cuts the line for the combination. At higher temperature the solubility isotherm gets detached from the liquid line and moves as a whole upward.

5. It is obvious that the two three phase pressure lines ecs and $e_1c_1s_1$ must coincide at the maximum three phase temperature, but where the place of coincidence in the three phase regions must be drawn is a point which calls for further elucidation from the sub-joined p - t -projections.

In the figs. 8, 9 and 10, I have drawn projections for the cases 1, 2 and 3. Fig. 8 corresponds to case 1, fig. 9 to case 2 and fig. 10 to case 3. The meaning of the different lines is indicated by letters; thus A denotes the solid substance A , B the solid substance B and AB the solid substance AB , L denotes liquid and G gas. E and E' are the two eutectic points, a and a' the triplepoints of pure A and B .

The p - t -projections show further that we have here a three phase line for $AB + L + G$ consisting of two branches passing continuously into each other, and that we must find here the phenomena discussed in the preceding paper, on a larger scale. As already appeared from the p - x -sections, the triplepoint has split up into two points F and F' . In the point F there is contact with the line for $AB + L$ and in F' with the line for $AB + G$.

Though for the systems $AB + L$ and $AB + G$ we have to deal with systems of two components in two phases, they behave as monovariant systems, because the concentration of the two phases is identical. This is however not the case for the system liquid $AB +$ vapour, and this is the reason why the line for $L + G$, which begins in F , cannot be represented; at constant temperature, the pressure is here still depending on the volume.

The point F does *not* correspond to the maximum three phase temperature, and that is the cause of the analogy with the case discussed in the preceding paper.

For the cases 1 and 2 the three phase line must have the direction of the melting line at the melting point F , as VAN DER WAALS has proved. As in most cases $v_l > v_s$, the melting line runs from the melting point to the right. This involves the necessity that the point F , (see fig. 8a) lies below R , i. e. at a pressure smaller than that corresponding to the maximum three phase temperature. If we therefore proceed to higher pressure, the succession is: F' , F , R . It is also obvious from the relative situation of these three points, that in figs. 4 and 5 the pressure corresponding to the maximum three phase temperature ECS , must lie somewhat above the melting point pressure $e'c'$.

Let us now consider the rare case that $v_l < v_s$, so that the melting line runs to the left, as is represented in fig. 8b. Then the point F lies above the point R , and the succession towards higher pressure is F' , R , F . A consequence of this situation is, that in this case the two three phase pressure lines ecs and $c_1e_1s_1$ (figs. 4 and 5) must coincide between the pressures corresponding to F' and F . This, however, not being the only modification which occurs in figs. 4 and

5, I have represented in fig. 7 the figure into which fig. 4 is changed when $v_l < v_s$.

We see then, that something peculiar appears i. e. a continuous closed solubility isotherm $Gecfc_1e_1$, which contracts more and more with rise of temperature, and disappears from the stable region at the maximum three phase pressure.

When the lower three phase pressure line $c_1e_1s_1$ has ascended to $e_1'c_1'$, or in other words, when we consider the temperature of the point F' , the solubility isotherm has assumed the shape indicated by the line $e_2e_1'c_1'f_1c_2$. At this temperature the *minimum* of the solubility isotherm, which was still in the stable region before, gets into the metastable region. If we raise the temperature up to the melting point of AB or to the temperature of the point F , the former phenomenon is repeated with respect to the *maximum*, which just below this temperature was still to be found in the stable region. Accordingly at still higher temperature no maximum or minimum occurs in the portions of the solubility-isotherm passing through the stable region, and we only retain the lines c_3c_3' and e_3e_3' . These lines become smaller and smaller with rise of temperature, and the two three phase pressure lines e_3c_3 and $e_3'c_3'$ approach each other more and more, till they have coincided at the maximum three phase temperature in ESC . The branches of the solubility isotherm touch at this temperature exactly in the points E and C . With further rise of temperature they retreat altogether to the metastable and unstable region, after which they disappear¹⁾.

In the case that $v_l > v_s$ solid AB can still coexist with liquid above the maximum three phase temperature, viz. under higher pressure, but this is not the case when $v_l < v_s$, which also follows already from the figs. 8a and 8b.

We see further that in fig. 8 two three phase lines occur with a maximum temperature, in fig. 9 only one, and in fig. 10 three.

Fig. 9 shows, that the case 2, where the vapour tension of the combination is smaller than that of the components, is certainly the most interesting case, as it can yield a three phase line with a minimum and two maxima, which had been unknown up to now.

As to the situation of the two branches of this peculiar three phase line we may still remark that only one of the possible cases is drawn here. These branches may pass through each other or partially coincide, but this does not make any essential difference.

Remarkable complications present themselves, when it is assumed

¹⁾ Later on I hope to discuss the course of the solubility isotherm in the metastable and unstable regions between the temperatures of F' and F more in details.

that meetings take place between solubility lines and plaitpoint lines, but to this I hope to come back afterwards.

In the lower parts of figs. 8, 9 and 10 the projections of the solubility lines on the T - x -plane or the melting curves under the varying three phase pressure are represented. From this we see that these lines, commencing at the components or the combination, must not always be drawn descending from the beginning, but that they will often first ascend, and descend after having reached a maximum.

These particularities have disappeared when we trace the melting curves at *constant pressure* or a t - x -section at constant p .

Amsterdam, June 1905. Chemical Laboratory of the University.

(August 17, 1905).

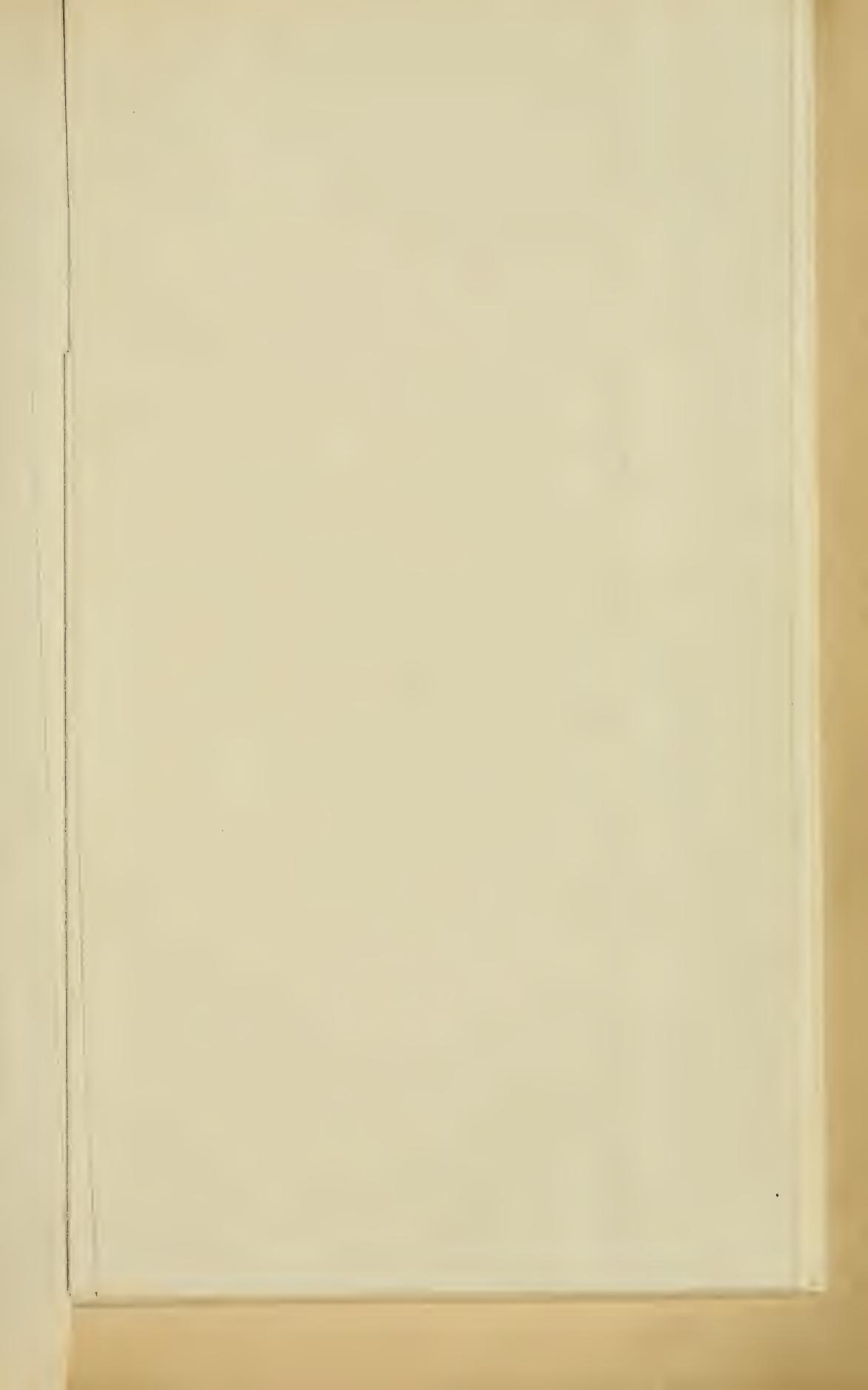




Fig. 1

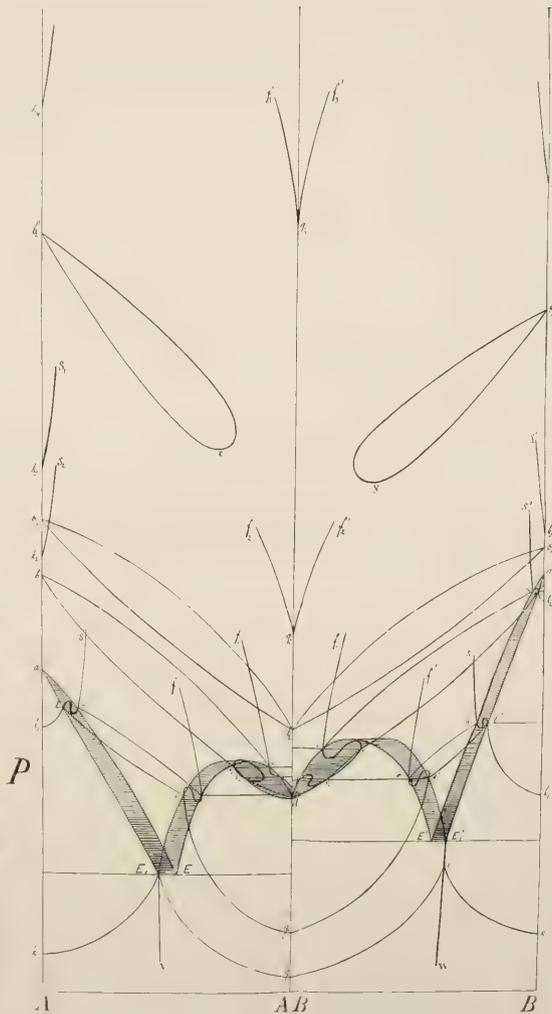


Fig. 2

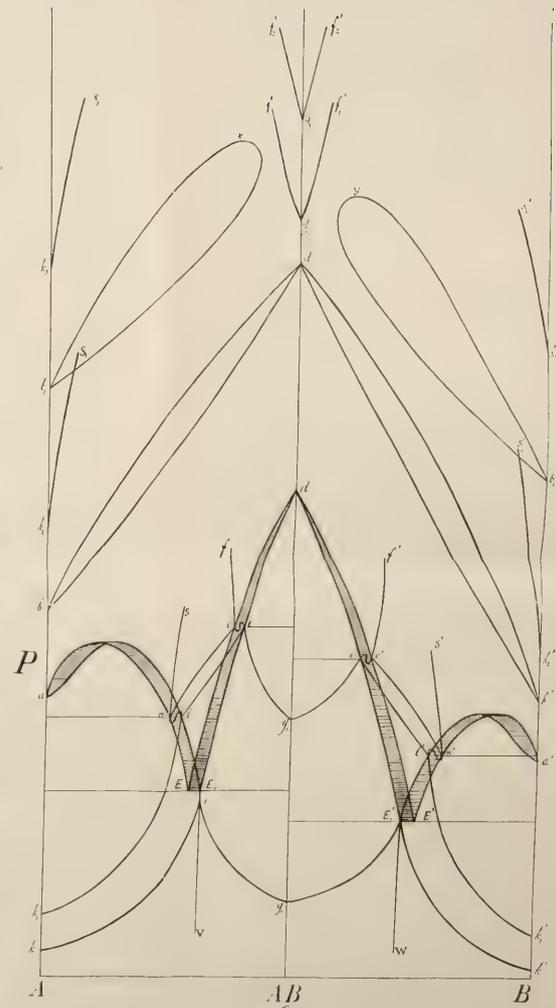


Fig. 3



A. SMITS. "Contribution to the knowledge of the P_x and the PT lines for the case that two substances enter into a combination which is dissociated in the liquid and the gasphase."

Three phase regions in the neighbourhood of the line for AB, so near the melting-point temperature of AB

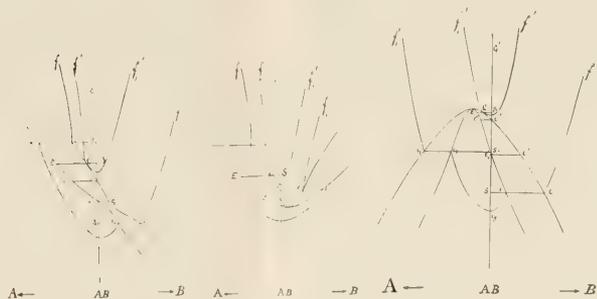


Fig. 4. Vapour tension comb. *between* that of the components. Fig. 5. Vapour tension comb. *smaller* than that of the components. Fig. 6. Vapour tension comb. *greater* than that of the components.

E C S corresponds to the highest three phase temperature.

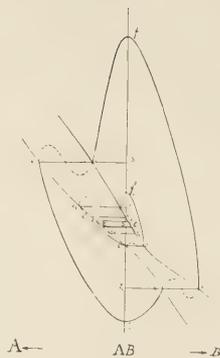


Fig. 7

Vapour tension combination *between* that of the components.

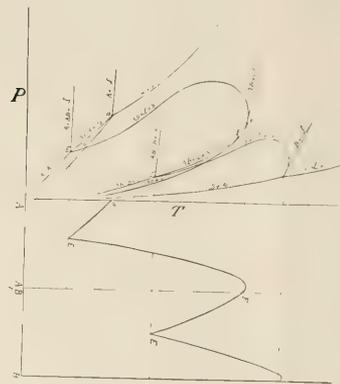


Fig. 8.

Vapour tension comb. *greater* than that of the components.

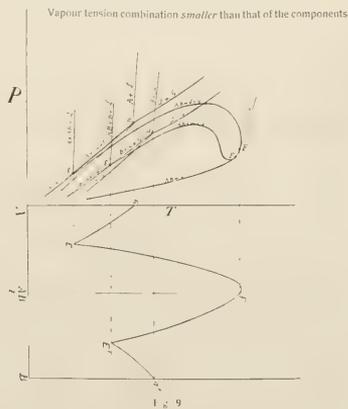


Fig. 9

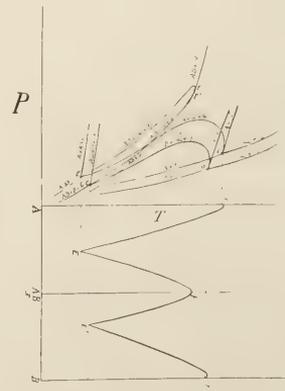


Fig. 10.



Fig. 8a



Fig. 8b.

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM.

PROCEEDINGS OF THE MEETING
of Saturday September 30, 1905.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige
Afdeling van Zaterdag 30 September 1905, Dl. XIV).

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The following papers were read:

Physiology. — “*Analysis of the curves obtained with the string galvanometer. Mass and tension of the quartz wire and resistance to the motion of the string.*” By Prof. W. EINTHOVEN.
(Sequel to former communications on the string galvanometer).

(Communicated in the meeting of April 22, 1905).

C O N T E N T S.

1. Introduction.
2. The principles of the method.
3. The mass of the string.
4. The resistance to the motion of the string.
5. The acceleration.
6. Analysis of some curves.
7. Absolute measurements of the mass of the string and of the resistance to its motion.
8. The tension of the quartz wire.
9. The practicability of the galvanometer for special purposes.

1. *Introduction.*

When recording the movements of the quartz wire in the string galvanometer with the object of becoming acquainted with various irregular oscillations of electric tension or current, we may in many cases see in the directly recorded curve an accurate or nearly accurate image of the oscillations sought. These cases are met with if the deviations of the quartz wire are aperiodic and quicker than the oscillations to be recorded. As an instance we mention here the galvanometric tracing of the human electrocardiogram, the various tops of which are reproduced in the exact proportions by the recorded curve, as was shown on a former occasion¹⁾.

When very rapid oscillations are to be recorded, it is necessary to make the deflections of the galvanometer also of very short duration, which can easily be done by giving a great tension to the string. In doing this, the movements of the string must in some way be damped, however, in order to avoid oscillations. The condenser method can render good service here²⁾, especially if it is applied in such a way that the motion of the string is nearly brought to the limit of aperiodicity.

¹⁾ Vide: these “Proceedings” 6, p. 107, 1903.

²⁾ Vide: these “Proceedings” 7, p. 315, 1904.

We must remark, however, that the galvanometer loses in sensitiveness when its deflections become quicker. If the time of a deflection which is always kept at the limit of aperiodicity is reduced a times, the sensitiveness diminishes a^2 times.

Now it sometimes happens that very rapid alternations of current must be measured, which are so small, that they require a sensitive position of the galvanometer in order to be perceptible and measurable and in these cases the condenser method can no longer be applied.

If under these circumstances the deflections of the galvanometer are less rapid than the oscillations of the current which must be studied, the curve, recorded by the quartz wire, will no longer render these oscillations accurately. We must then, as has also been done with many capillary-electrometric curves, calculate from the properties of the instrument used and the data of the directly recorded curve, the value of the real oscillations. This calculation may lead to the construction of a new curve, which now in all particulars is the correct expression of the oscillations.

The manner in which capillary-electrometric curves may be calculated, is known ¹⁾. Do the curves, recorded by the string galvanometer, fulfil the same conditions and is it possible to apply the *same* calculation to them?

The answer to this question must in general be negative. We shall try in this paper to analyse the curves of the string galvanometer and to show that they admit of equally accurate constructions as the capillary-electrometric curves, but that the manner in which they are calculated is different.

In this connection some properties of the galvanometer, more especially the tension and mass of the string and the resistance to the motion of the string must be discussed. We shall try to express the value of these three quantities in absolute measure, by which a clearer light will be shed on their significance for the practicability of the instrument generally and for the modifications which might advantageously be made in order to render the galvanometer serviceable for special purposes.

2. *The principles of the method.*

In the analysis of the curves, recorded by the string galvanometer we start from the assumption that the resistance offered by the air

¹⁾ For literature on this subject vide: PFLÜGER's Archiv f. d. ges. Physiol. Bd. 99, p. 472, 1903.

to the motion of the quartz wire, increases proportionally to the velocity of motion of the wire.

This assumption, which is justified on theoretical grounds, will later appear to be also practically proved by the results of analysis.

If we assume it to be true, we must also expect the motion of the string to be completely determined by the laws that govern the motion of an oscillating body with electromagnetic damping. For electromagnetic damping, as in our case the air-damping, develops a resistance, increasing proportionally to the velocity of the moving body. In the string galvanometer both electromagnetic and air-damping occur. They can be expressed in the same units and their combined effect is always equal to the effect of either of them, if only in the latter case the amount is made equal to the sum of the two, taken separately. In other words: if r_a represents the resistance through air-damping ¹⁾ and r_b the resistance through electromagnetic damping, we may reckon for the total damping resistance:

$$r = r_a + r_b (1)$$

The laws of motion of an oscillating body with electromagnetic damping are e. g. extensively dealt with in KOHLRAUSCH' textbook ²⁾. They agree with the laws determining the charge or discharge of a condenser through a conductor having resistance and self-induction, which are found in various textbooks on electricity ³⁾. The formulae given in the above-mentioned works form the foundation of our further calculations.

If we denote by:

m the virtual mass of the image of the string,

r the virtual resistance, damping the motion of the string,

c the sensitiveness of the galvanometer for constant currents,

two conditions may present themselves. In the first the motion is oscillatory and

$$r < \sqrt{\frac{4m}{c}} (2)$$

in the second condition the motion is aperiodic and

$$r > \sqrt{\frac{4m}{c}} (3)$$

¹⁾ Besides the air-damping and the ordinary electromagnetic damping still other, very feeble, damping influences are active, which may however be neglected here. They will be dealt with in chapter 7.

²⁾ Lehrbuch der praktischen Physik, S. 448. 1901.

³⁾ Vide e.g. J. A. FLEMING. The alternate current transformer. London. I, p. 370. 1890.

The units in which m , r and c are expressed and the meaning which must be attributed to the words "virtual mass of the image of the string" and "virtual resistance" are dealt with in the following considerations on

3. *The mass of the string.*

In practice it is impossible or scarcely possible to find the mass of the string by direct weighing. For this the weight is too small. Also a calculation of the mass from the dimensions and the specific gravity of quartz and silver does not lead to the desired result, since the measurement of the diameter of the fine thread and of the thickness of the still much thinner layer of silver cannot be carried out with the necessary accuracy, the more so because the layer of silver often shows inequalities and its thickness is irregular.

So we must proceed in another way and we reach our purpose in the simplest way if we start from the "virtual mass of the image of the string". The image of the middle of the quartz thread, which is projected with great magnification, moves along a straight line over a millimetre scale each time the string deflects. Instead of this image we imagine a material point, acted on by a force which is equal to the force that moves the whole string. The acceleration experienced by the fictitious material point from this force, determines what we call the "virtual mass of the image of the string".

The unit in which this virtual mass must be expressed depends of course on the units chosen for the force and the acceleration. As the cause of the motion of the string is the electric current passed through the galvanometer, the moving force can be expressed in units of intensity of current. We choose for this purpose the micrampere.

The unit of acceleration is determined by the units chosen for the distance and the time. In accordance with the millimetre scale along which the image moves, the distance is expressed in millimetres, while it is found practical to take the millimetre also as the unit of time. For the deflection of the quartz thread is recorded on a plane which is moved along with uniform velocity perpendicularly to the direction of the motion of the image, so that in the recorded curves, from which we must always derive the data for further calculation, time is represented by a length.

The above mentioned units of force, distance and time form a system which may be called the millimetre-micrampere or $[mm-\mu A]$ system. Expressed in this system the unit of virtual mass m is the mass which experiences from a force of 1 micrampere an acceleration of 1 mm. distance per mm. of time.

The unit of virtual resistance (or better of the virtual resistance coefficient) ¹⁾ r is the force of 1 micrampere resisting the motion of the string when the image of the string moves with a velocity of 1 mm. distance per 1 mm. of time. The unit of sensitiveness c is the sensitiveness with which a force of 1 micrampere causes a deflection of the image of 1 mm.

These units are constant as long as the field intensity H between the poles of the electromagnet, the length l of the quartz thread, the magnification b of the image of the string and the speed V of the recording plane remain unchanged.

If the string is strongly stretched and is suddenly passed by a constant current, it will perform damped oscillations. We have then the condition which we will in the first place consider more closely and which is expressed by formula (2):

$$r < \sqrt{\frac{4m}{c}} \dots \dots \dots (2)$$

To this case also the following formulae (4) and (5) apply:

$$\tau = 2\pi \sqrt{mc} \dots \dots \dots (4)$$

$$T = \tau \sqrt{1 + \frac{A^2}{\pi^2}} \dots \dots \dots (5)$$

Here τ means the period which we would obtain without damping, whereas T represents the real period with damping.

$$A = \lg n k, \dots \dots \dots (6)$$

k being the damping ratio, $k = \frac{\alpha_1}{\alpha_2} = \frac{\alpha_2}{\alpha_3} = \dots$ etc. in which $\alpha_1, \alpha_2, \alpha_3$ are the deflections with damping.

From the formulae (4), (5) and (6) follows:

$$m = \frac{T^2}{c \{39,5 + 4 (\lg n k)^2\}} \dots \dots \dots (7)$$

As the period T is expressed in millimetres, the value of m changes if the velocity V of the recording plane is changed. In our measurements V was nearly always 500 mm. per second. Only with a few photograms the sliding frame had a different velocity, so that with these a reduction will have to be applied in order to render the values of m comparable.

¹⁾ The word "resistance coefficient" expresses the meaning of r better than the word resistance. But the latter is simpler and is also used as a coefficient in the theory of electricity, where it denotes ohmic resistance. In this paper we shall repeatedly use "resistance" instead of "resistance coefficient".

In order to express m_x in the millimetre-micrampere units for a photogram of which the speed of the sliding frame is V_x mm. per second, m_β being the known value for a speed V_β , we use the relation:

$$m_x = m_\beta \times \left(\frac{V_x}{V_\beta} \right)^2 \dots \dots \dots (8)$$

From what precedes we see that the measurements required for a calculation of the value of m when the value of V is known, are limited to:

- the sensitiveness c ,
- the deflections $\alpha_1, \alpha_2 \dots$ etc. and
- the period T .

The measurement of the sensitiveness c presents no difficulties.

The intensity of the current is known from the electromotive force of the source and the resistances used. The source consisted of storage cells, the electromotive force of which remained very constant and might be put at 2 Volts, while the resistances were taken either from manganin resistance coils or from a graphite resistance of SIEMENS and HALSKE which had previously been checked.

The deflection of the quartz thread is measured on the photogram on which the network of square millimetres is found. With the magnifying glass it is easy to estimate 0.1 mm., so that a deflection of 30 mm., which is often used, is known with an accuracy of 0.3%.₀

If the permanent deflection is u mm., the intensity of the current = i micrampere, then the sensitiveness is $c = \frac{u}{i}$ millimetres per micrampere.

The values of the oscillations α_1, α_2 , etc. are, like the permanent deflection, read off directly from the network of square millimetres. But as these values are smaller than u and the absolute error in each measurement remains unchanged = 0.1 mm., the accuracy of the value found for $k = \frac{\alpha_1}{\alpha_2} = \frac{\alpha_2}{\alpha_3} \dots$ etc. is not great. Moreover a

distinct difference is often found between $\frac{\alpha_1}{\alpha_2}$ and $\frac{\alpha_2}{\alpha_3}$, so that we are

obliged to calculate a mean value, e. g. by putting $k = \sqrt{\frac{\alpha_1}{\alpha_3}}$.

Fortunately the value of k , as it occurs in our measurements, has only a small influence on the final result, relatively large variations in k scarcely causing any difference in the calculated value of m .

Of the greatest importance is the measurement of the period T which in formula (7) occurs squared. The total amount of T is always very small, in some cases even less than 1 mm. so that it is desirable to carry out this measurement with an accuracy of a very small fraction of a millimeter.

For this purpose I first used an excellent astronomical instrument, destined for the investigation of celestial photograms, and which was put at my disposal by the kindness of the director of the Leyden Observatory ¹⁾.

Later I used exclusively an ordinary microscope stand, pattern I^a of the firm CARL ZEISS. The stand is provided with the large movable cross table of the same firm. On this table a small wooden board is fastened, which follows the cross movements, being always supported by a smooth plane on which it can slide easily. On this board, which has in the middle a spacious opening, the photographic plate to be measured is placed.

As object-glass a_1 is used with a focal distance of 40 mm., while for the eye-piece that of RAMSDEN is used, also made by ZEISS, with micrometer screw and drum reading. The eye-piece is so adjusted that the direction of motion of the measuring wire coincides with the direction of the abscissae of the photogram. After the microscope has been sharply focussed on the photogram and at the same time care has been taken that the image to be measured and the image of the crosswire lie in the same optical plane, the microscope tubes are firmly screwed on to the stand by means of a clamp, which is expressly made for this purpose. The tubes must be quite immovably connected with the stand. Also the eye-piece is screwed on to the microscope tube so that it can be touched with the hand without observing the slightest displacement of the crosswire with respect to the image to be measured. For measurements requiring some accuracy these arrangements are indispensable.

With the microscope tubes pushed in, 1 scale division of the drum corresponds to a little less than 5μ on the photogram, and since 0.1 of a scale division can easily be estimated, the error in the reading is less than 0.5μ . It would be a mistake, however, to suppose that also the result of the whole measurement can now be known with the same accuracy. For there remain errors of a different origin.

So e.g. we start in our measurements from the shadow lines which in the photogram form the net of square millimeters, a base

¹⁾ I wish to express here my best thanks to Prof. VAN DE SANDE BAKHUYZEN for his kind assistance.

which in itself is not free from errors. The ordinates of the net are recorded by a quickly revolving disk with spokes, casting 500 shadows per second on the photographic plate. The variations in the rotational speed of the disk cause only small errors. Reserving a more extensive description of this time-marker for a later occasion, we may here mention that the rotational speed is very constant and, in all probability, always agrees to 0.1 % with the pre-determined value. But we have no guarantee that the mutual distances of the spokes, although carefully marked off on the lathe, come up to the same standard.

The greatest errors are probably made by the setting of the cross-wire. To be sure, surprisingly sharp settings can be made on the fine, sharp top, representing the turning point of a movement of the string, so that a greater error than 1μ need not be made, but often it is necessary to mark the exact middle of a broader top; in which case the error becomes larger, of course. With many of our measurements of the period T the error must be estimated at 1 to 2%.

We shall now give the results of some measurements.

With a speed of the sensitive plate of $V = 100$ mm. per second, some photograms were taken of string n^o. 10.

The sensitiveness was $c = 10.92$ mm. per micrampere,

the period $T = 0.43$ mm.

the damping ratio $k = 3.3$

With these data the value of m is calculated from formula (7) at $3.76 \times 10^{-4} [mm - \mu A]$.

For a comparison with following results this value is reduced by formula (8) for a speed of the sensitive plate of 500 mm. per second. We find then $m = 9.4 \times 10^{-3} [mm - \mu A]$.

Another series of measurements with the same string gave, at any rate as far as the second figure, exactly the same result. The speed of the sensitive plate was now 500 mm. per second.

Besides c was $= 3.5$ mm. per micrampere,

$T = 1.16$ mm. and

$k = 1.83,$

from which we calculate again $m = 9.4 \times 10^{-3} [mm - \mu A]$.

The agreement in the two final results is the more remarkable because of the great difference in the sensitiveness c and the period T .

String 13 is thinner than 10, having besides a smaller conductive resistance. The measurements with sudden passing of a constant current, show that with $V = 500$ and $c = 5.69$, the value of T is 1.32 and that of k 3.1. From this we calculate from formula (7) that the mass m is $6.9 \times 10^{-3} [mm - \mu A]$

Finally we mention still two series of measurements with a still thinner string, n° 14.

In the first photogram we find with $V = 500$, and $c = 5,75$ that T is 1, and $k = 3,8$ from which is calculated $m = 3,7 \times 10^{-3}$ [mm — μA].

In the second photogram V is unchanged but $c = 3,15$, $T = 0,705$ and $k = 3,16$.

From this we calculate $m = 3,5 \times 10^{-3}$ [mm — μA]. So we may take for the mass of string n° 14 the mean value which is $m = 3,6 \times 10^{-3}$ [mm — μA].

4. *The resistance to the motion of the string.*

The resistance to the motion of the string can be determined in various ways. We shall begin with a description of the method which may be considered to give the most accurate results.

Let the quartz thread be only moderately stretched, and let it suddenly be passed by a current of constant intensity. Let the deflection of the thread be recorded on a rapidly moved sensitive plate, so that a curve is obtained, which is schematically represented in the following figure 1.

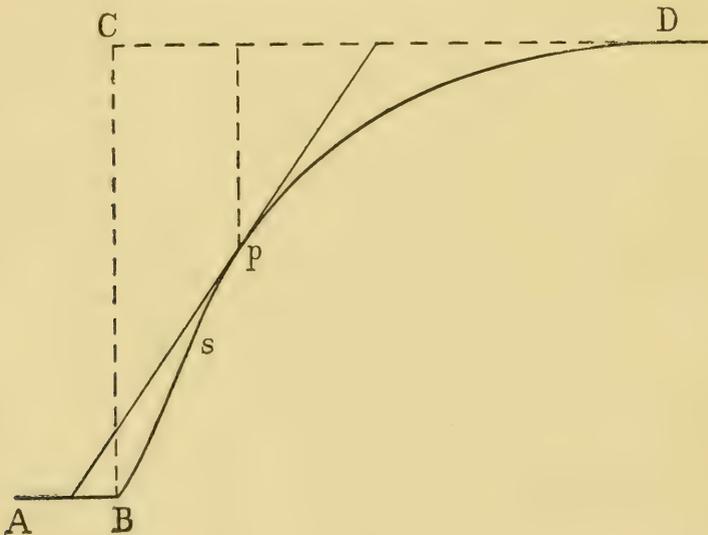


Fig. 1.

From A to B the quartz thread is in the 0-position. At B the constant current is made, by which the image of the string is moved upward until it reaches its second position of equilibrium about D .

The fundamental formula, found in the above-mentioned text-books¹⁾, which represents this curve, runs:

$$\frac{d^2q}{dt^2} + \frac{r}{m} \frac{dq}{dt} + \frac{1}{mc} q = 0 \quad (9)$$

Here m , r and c have the same meaning as before, namely m the virtual mass of the image of the string, r the virtual resistance, damping the motion of the string, and c the sensitiveness of the galvanometer for constant currents. t means the time and q the distance of the image of the string from its second position of equilibrium or in other words: the distance of any point p of the curve from the line CD .

All units are expressed in the millimetre-micrampere or $[mm-\mu A]$ system.

Calling ϱ the radius of curvature in any point of the curve, we have:

$$\varrho = \pm \frac{\left\{ 1 + \left(\frac{dq}{dt} \right)^2 \right\}^{\frac{3}{2}}}{\frac{d^2q}{dt^2}} \quad , \quad (10)$$

and further putting the tangent of the angle of inclination $\frac{dq}{dt} = v$, we may write:

$$q = crv + cm \frac{(1 + v^2)^{\frac{3}{2}}}{\varrho} \quad (11)$$

Here ϱ is positive when v increases, negative when v decreases with increase of t .

For the case that we may put $\varrho = \infty$ formula (11) simplifies into:

$$q = crv \quad (12)$$

This case must present itself somewhere in a point s of the curve. From B to s the curve is concave upward, from s to D concave downward, s itself being the point of inflection. For the point s $\varrho = \infty$, so that for this point formula (12) applies. We write it in the form

$$r = \frac{q}{cv} \quad (13)$$

In order to determine the value of the resistance r by means of this formula, the sensitiveness c of the galvanometer must be known,

¹⁾ Vide KOHLRAUSCH l. c. p. 450 and FLEMING l. c. p. 368.

while two quantities must be measured with respect to the points s of the curve, viz. its distance q from the second position of equilibrium and the tangent v of the angle of inclination.

These measurements are made with the same microscope stand I^a , already mentioned in the preceding chapter, on the table of which the photographic plate can be moved by screw motions in two mutually perpendicular directions.

For object-glass a_1 is again used or another more strongly refractive lens, while for an eye-piece an arrangement is used which must be explained now.

At the outside of a HUYGENS eye-piece n^o. 2 a pointer is fastened. When the eye-piece is turned round the optical axis, this pointer moves over a circular dial, screwed on to the microscope tube and divided into degrees. In this way we can read off how much the eye-piece is turned in the microscope tube. Moreover in the focal plane of the ocular lens of the eye-piece a fine crosswire is found, which is so set that the crossing point lies at the centre of the field of view. Hence, when the eye-piece is turned in the microscope tube, while the crosswire turns, the crossing point will remain immovable. The whole arrangement, of which the principal parts have been taken from the analyser of a ZEISS polarisation microscope, works very accurately and enables us to make a number of measurements in a short time. This is done in the following way:

A photographic negative or better still a diapositive is placed under the microscope, so that one of the directions of motion of the cross table coincides with the direction of the abscissae of the photogram. Next the whole microscope tube is again immovably screwed fast at such a height that the real image of the figure to be measured lies in the same plane with the wires of the eye-piece. In this way one can by means of the screws of the cross table easily and quickly cause the image of any point of the photogram to coincide with the crossing point of the eye-piece.

One begins with placing an absciss in the crossing point, and then turns the eye-piece so that one of the two crossed wires, e. g. wire A coincides with this absciss. Then an arbitrary point P of the curve is placed at the crossing point. The eye-piece is now turned again in such a way that the wire A forms a tangent line to the curve at P . The angle through which the eye-piece must be turned in order to get from the first into the second position, is the angle of inclination of the curve at P . It is read on the graduated circle in whole degrees, tenths being estimated. So a tangent can be drawn at any point of the curve after it has been brought to the crossing

point of the ocular wires, and the angle of inclination of the curve at this point can be measured. The method which also deserves recommendation for the measurement of other, especially capillary-electrometric curves, leaves little to be desired as to ease and quickness. Its accuracy can be judged from the following results.

In the reticular scales, which together with the movements of the quartz thread are photographed on the plates, the ordinates are not perfectly perpendicular to the abscissae, which must be ascribed to the circumstance that the image of the slit, formed by the cylindrical lens on the photographic plate, is not perfectly perpendicular to the direction of motion of the sliding frame. I did not carry out my original intention of correcting this error by a calculation, since the deviation only amounts to $0^{\circ}.3$.

Besides we can, when measuring angles of inclination less than 45° , take an absciss as base, when above 45° an ordinate, by which proceeding the deviation becomes of still less importance.

But from measurements of this deviation by means of the turning eye-piece, it appears that the measurements of angles can be made with errors not exceeding $0^{\circ}.1$. This will be seen from the following table.

T A B L E I.

Number of the plate.	Direction of the abscissae.	Direction of the ordinates.	Difference in direction between abscissae ordinates.	Deviation from the average value of $89^{\circ}.7$.
A 22	$110^{\circ}.8$	$21^{\circ}.05$	$89^{\circ}.75$	$+ 0^{\circ}.05$
A 37	$200^{\circ}.6$	$111^{\circ}.0$	$89^{\circ}.6$	$- 0^{\circ}.1$
A 123	$123^{\circ}.0$	$33^{\circ}.3$	$89^{\circ}.7$	0
A 124	$122^{\circ}.8$	$33^{\circ}.0$	$89^{\circ}.8$	$+ 0^{\circ}.1$
A 132	$122^{\circ}.9$	$33^{\circ}.2$	$89^{\circ}.7$	0

No nearer explanation is wanted. In the last column but one we find the results of the measurement of the angles under which in various photographic plates the abscissae are cut by the ordinates. Taking for the average value an angle of $89^{\circ}.7$, we see that the greatest deviation from this value is only $0^{\circ}.1$.

It must be remarked, however, that the direction of the tangent in a point of the curve cannot be determined so accurately as the

direction of an absciss or an ordinate. The stronger the curvature of a curve and the more rapid the changes of curvature take place, the more uncertain the determination of the direction of the tangent at any point becomes.

The point s at which the curve under examination has no curvature, is easily found under the microscope.

A number of points in which the curve is cut by the abscissae or ordinates, are successively brought to the crossing point of the wires in the eye-piece and in all these points the angles of inclination are measured in the above described manner. It is noticed that with increase of the abscissae the angles of inclination first increase and then decrease. At the point of transition must be situated the required point at which the curvature of the curve is 0 or $\rho = \infty$.

In this way the angle of inclination in the point sought, is directly known, while the distance of this point from the second position of equilibrium of the quartz thread can at once be read off on the reticular scale. Millimetres are directly indicated, tenths must be estimated.

A curve written by the quartz thread has in many cases a fairly considerable breadth. We can then consider it as a double curve, and carry out the measurement of the angles of inclination as well at the upper as at the lower side of the image of the quartz thread, in this way applying a control by which the accuracy of the final result is enhanced.

Before mentioning the amounts found by direct measurement, we must dwell a moment on the velocity of motion of the sliding frame. Most photograms were taken with a speed V of 500 mm. per second. In order to render values of v that are expressed in the millimetre-micrampere system, but were measured with different values of V , mutually comparable, they are all calculated for $V = 500$. For this purpose we use the formula:

$$r_{\beta} = r_{\alpha} \frac{V_{\beta}}{V_{\alpha}} \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \quad (14)$$

in which r_{α} means the virtual resistance of the quartz thread with a speed of the frame of V_{α} mm. per second, r_{β} being the corresponding value with a speed V_{β} .

We must further take into account the circumstance that the reticle on the photogram does not always consist of accurate squares. As was already mentioned in the preceding chapter, the rotational velocity

of the spoked disk, by which the ordinates are recorded, is very constant. The error in the absolute amount may be estimated at no more than 0,1 %. But the velocity of motion of the frame cannot be so accurately regulated. The speed of a frame, once moving, may be considered perfectly constant, but between photograms, taken at various times, the speed may differ fairly much. Hence the distances between the ordinates in one plate are somewhat greater than in another.

The distance between the abscissae is absolutely the same in all plates. We could not expect otherwise, since the abscissae are recorded by the shadow of a glass scale; mounted in a fixed position at a few millimetres, distance from the movable frame. The glass scale, containing very fine division lines, was expressly made for our purpose by the firm ZEISS.

The mutual distances of the abscissae and also of the ordinates are measured under the microscope by means of the millimetre divisions with nonius, which are found on the above described cross table. For 30 scale divisions along an ordinate we invariably find 30,1 mm. so that 1 scale division along an ordinate may always be put = 1,0033 mm.

The scale divisions along an absciss in the middle half or middle third part of the same plate are also equal, as may be seen e. g. from the following measurements of photogram A 34, see table II.

It must be remembered that the nonius did not enable us to read with a greater accuracy than 0,1 or 0,05 mm. so that for these comparatively rough measurements the mutual distances of the

T A B L E II.

Number of the ordinate.	Reading on the millimetre scale.	Length of 10 scale divisions along an absciss in millimetres.
0	61.2	—
10	51.5	9.7
20	41.9	9.6
30	32.2	9.7
40	22.5	9.7
50	12.8	9.7
60	3.15	9.65

ordinates must be considered as perfectly equal. More accurate measurements have already been mentioned in the preceding chapter and need not be discussed again.

From the table follows that in the examined photogram 1 scale division along an absciss = 0.9675 mm. Since the length of a scale division along an ordinate has already been given in millimetres we can directly express a scale division along an absciss in scale divisions along an ordinate. Calling this value d , we find in photogram A 34 $d = 0,964$. In other photograms we found values for d , varying between 1,033 and 0,901.

If d deviates somewhat considerably from unity, the value of the tangent of the angle of inclination will have to be corrected. If the tangent of the measured angle of inclination is v , we shall have to take the product vd instead of v in the computation of r .

Formula (13) is then replaced by

$$r = \frac{q}{c v d} \quad . \quad (15)$$

We now give some results of measurements, for convenience' sake assembled in the following table III.

T A B L E III.

Number of the quartz thread.	Number of the photogram.	q in millimetres.	c in millimetres per micrampere.	v	d	V in millimetres per sec.	r_a in [$mm-\mu A$] calculated for $V = 500$.
10	50	23.5	1093	6.02	1.032	100	0.0193
13	A 37	21.8	798	1.637	0.975	500	0.0174
14	A 123	23.6	1133	1.322	0.984	500	0.0160
14	A 124	21.6	563	3.006	0.901	500	0.0155

During the recording of the curves to which the numbers of this table refer, always a great resistance — more than 1 Megohm — was inserted in the galvanometer circuit, so that the electromagnetic damping might be neglected and the resistance r_a to the motion of the string was only caused by the air. We see that the value of r_a , which for all the curves has been calculated for $V = 500$, decreases in the order of the numbers 10, 13 and 14 of the quartz threads. In the same order also the thickness of the silvered strings diminishes. The diameter is:

for string 10	without silver	2,4 μ ,	silvered	3,0 μ
„ „	13	„ „	1,6 μ ,	„ 2,5 μ
„ „	14	„ „	1,7 μ ,	„ 1,9 μ

We leave unsettled what function the air-damping is of the diameter of the string, but wish to point out here particularly the influence which the damping may experience from the layer of silver on the quartz threads being more or less smooth. Especially string 14 has an almost perfectly smooth coat of silver, while the skin of string 10 shows distinctly visible inequalities.

We will now investigate whether the amount of r_a for a definite string may be regarded as constant, however much the tension of the quartz thread and thereby the velocity of its deflections may be modified.

For this it is necessary to measure r_a once more with a strongly stretched string and oscillating deflections, but the methods which are at our disposal for this purpose do not nearly furnish such accurate results as could be given above. We mention here two methods of measuring.

In the first place the same method as above may be used, but this time it is applied under unfavourable conditions. As the string makes rapid movements, the tangent of the angle of inclination becomes large, so that its amount cannot be determined with the desired accuracy. Besides the uncertainty in the value of q also increases very much.

Of the curves, by means of which in the preceding chapter the mass of the string was calculated, plate A 61 of string 13 shows the greatest value of T , viz. $T = 1,32$ mm. I therefore have chosen this curve for an attempt to determine the value of r by formula (15)

$$r = \frac{q}{cvd}.$$

A resistance of more than 1 Megohm was inserted in the galvanometer circuit so that the electromagnetic damping might be neglected and consequently r might be put $= r_a$. The following values were found:

$$\begin{aligned} q &= 9 \quad \text{mM.} \\ c &= 5,69 \text{ mM. per micrampere.} \\ v &= 88,1 \\ d &= 0,979. \end{aligned}$$

As the quartz thread with rapid motion writes a fine line on the sensitive plate, the angles of inclination can be measured with great

accuracy. An error of 0,1° is possible, however, in the measured value of the angle. And if the real angle is 0,1° greater than the value found, the tangent must be taken 104,2 instead of 88,1. So an error of 0,1° in the measurement would cause here an error of over 18 % in the final result. Putting the uncertainty in the value of q at 1,5 mm., also the probable error, caused by this alone, is found to be 17 %.

The measuring arrangement which we used, does not enable us to make the result more correct.

In the second method of determining the value of the resistance to the motion of the string with a strongly stretched, oscillating string, we make use of the following formula: ¹⁾

$$\lg n k = \frac{rT}{4m} \dots \dots \dots (16)$$

in which the letters have the same meaning as before, viz.

- k = the damping ratio,
- r = the resistance sought,
- T = the period of the oscillatory deflections,
- m = the mass of the string.

We write formula (16) in the form:

$$r = \frac{4m \lg n k}{T} \dots \dots \dots (17)$$

and substitute for m the value which we found, according to formula (7) of the preceding chapter, to be

$$m = \frac{T^2}{c \{39,5 + 4 (\lg n k)^2\}} \dots \dots \dots (7)$$

We then find:

$$r = \frac{4T \lg n k}{c \{39,5 + 4 (\lg n k)^2\}} \dots \dots \dots (18)$$

In order to obtain comparable results, we always calculate r for a speed of the sliding frame $V = 500$ mm. per second, using again formula (14) $r_{\bar{z}} = r_z \frac{V_{\bar{z}}}{V_z}$;

From the two last mentioned formulae the value of r is now calculated for four out of the five curves which in the preceding chapter served for the determination of m . During the recording of these curves a great resistance of more than 1 Megohm was each time inserted in the galvanometer circuit, so that the resistance to

¹⁾ Vide e.g. KOHLRAUSCH l. c. p. 448.

the motion of the string was again caused by friction of the air only. Hence we may identify r with r_a . The results of the calculation are found assembled in the following table IV.

T A B L E IV.

Number of the quartz thread.	Number of the photogram.	lg k .	T in millimetres.	c in millimetres per micramp.	V in millimetres per sec.	r_a in $[\frac{mm}{\mu A}]$, calculated for $V = 500$.
10	46	(1.19)	0.43	10.92	100	(0.0207)
„	A 48	(0.604)	1.16	3.5	500	(0.0196)
13	A 61	(1.13)	1.32	5.69	500	(0.02355)
14	A 129	(1.335)	1.—	5.75	500	(0.0199)

Also these results lack the accuracy which can be obtained when the motion of the string is slow. The difficulty lies in the value of k which, as was remarked before, presents a great uncertainty.

In the following table V the average values r_a are given as they

T A B L E V.

Number of the quartz thread.	r_a with feeble tension of the quartz thread.	r_a with strong tension of the quartz thread.	Ratio of r_a with strong tension to r_a with feeble tension.
10	0.0193	(0.0201)	1.04
13	0.0174	(0.0210)	1.21
14	0.0157	(0.0199)	1.27

were found by calculation according to the three methods mentioned.

We see that the value of r_a is a little greater with a greater tension of the quartz thread. From this we must infer that the resistance, caused by the friction of the air, does not increase quite proportionally to the velocity of motion of the string, but that with very rapid motions of the string the increase of the resistance of the air is a little greater.

Practically, however, this result has no influence on our further calculations. The increase in the value of r_a may be called very small. The greatest increase was in the ratio of 1 : 1.27, while

tensions of the quartz thread were used, varying from 1 to 324. That with smaller tensions of the string than were used above, the proportionality between the velocity of the string and the frictional resistance of the air, is maintained, has been sufficiently proved on a former occasion ¹⁾. A standardising curve with a sensitiveness of 1 mm. deflection for 10^{-10} Ampere, was recorded on a photographic plate, which moved with a velocity of 10 mm. per second. After the sensitiveness had been reduced ten times and the speed of the plate had been ten times increased another standardising curve was written. This latter shows the same shape as the former, both curves can be so superposed that they coincide over nearly their whole length.

So we may say that the tensions may vary from 1 to nearly 3000, the value of r_a being only slightly altered.

Let us now consider the amount of the electromagnetic damping, expressed by r_b . The value of r_b is nothing else than the ponderomotive force which the string experiences by its motion in the magnetic field when the velocity of the image of the string is unity.

If this ponderomotive force is rendered in the [mm— μA] system, it is expressed by a certain number of micramperes with the given length of the thread and the given intensity of the field.

The calculation can be made in the following way.

The electromotive force E , generated in a wire, which is perpendicular to the lines of force of a homogeneous magnetic field, and is displaced with a velocity of v_1 centimetres per second in a direction which at the same time is perpendicular to its length and to the lines of force, is

$$E = v_1 l H \times 10^{-8} \text{ Volt,}$$

in which l means the length of the wire in centimetres and H the intensity of the field in C. G. S. units.

When the middle part of the string moves with a velocity v_1 , the average velocity of all the parts of the string may be put $\frac{2}{\pi} v_1 = 0,637 v_1$, so that for the electromotive force e , generated by a deflection of the quartz thread, we may write

$$e = 0,637 v_1 l H \times 10^{-8} \text{ Volt. (19)}$$

Moreover we have

$$v_1 = v \times \frac{V}{10b}, \text{ (20)}$$

¹⁾ See these "Proceedings" 6, p. 107, 1903.

in which, as above, v_1 means the velocity of the middle of the string expressed in centimetres per second, v the velocity of the image of the string, expressed in millimetres distance per millimetre of time, V the velocity of the frame in millimetres per second and b the magnification used.

Substituting in formula (19) the value v as given in formula (20), we have

$$e = \frac{0,637 v V l H \times 10^{-9}}{b} \text{ Volts.}$$

Calling the resistance in the galvanometer circuit w Ohms, the intensity of the current I , caused in the circuit by the motion of the quartz thread and expressed in micramperes, is

$$I = \frac{e \times 10^6}{w} = \frac{0,637 v V l H \times 10^{-3}}{wb} \text{ micramperes. . . . (21)}$$

The ponderomotive force, experienced by the string, is expressed by $I[mm-\mu A]$.

Hence if we put in formula (21) $v = 1$, I becomes $= r_b$ so that we have

$$r_b = \frac{0,637 V l H \times 10^{-3}}{wb} [mm - \mu A] (22)$$

From the above formula (22) it appears that, in order to calculate r_b , we must know V , l , w , b and H . Of these quantities the four first mentioned can be measured with sufficient accuracy, while on the other hand the value H of the intensity of the field presents some difficulty. Opposite the middle of the string there is an opening in the pole shoes of the electromagnet, by which in that place the intensity of the field, although not zero, yet becomes much smaller than in any other place of the slit-shaped space, in which the quartz thread moves.

Measurements of the intensity of the field in different parts of this slit-shaped space showed that in those places where the intensity is greatest it may be put at about 22500 (C. G. S.), the current of the field magnet being regulated at 2.7 Amp. With this current of the field magnet nearly all our observations were made. The average intensity of the field, calculated over the whole length of the slit, appeared to be about 10% less, i.e. about 20250 (C.G. S.). But this value for H is inadmissible since the places of least intensity are found at the middle of the slit where the lines of force exert the greatest influence on the motion of the string. For H we shall have to reckon considerably less than the average value of 20250

(C. G. S.), and since sufficiently extensive measurements of the strength of the field in all parts of the slit are wanting, H would have to be estimated approximately. Rather than doing this we shall follow an entirely different way.

It is possible, namely, to get to know r_b in a different manner. For this the resistance to the motion of the string must be measured twice, first when a very great conductive resistance is inserted in the galvanometer circuit and then after the conductive resistance in this circuit has been made as small as possible. In the first case the resistance to the motion of the string consists of air-damping only, in the second case of air-damping and electromagnetic damping combined. The difference between the two values gives us the value of the electromagnetic damping. Remembering formula (1) we write:

$$r_b = r - r_a \dots \dots \dots (23)$$

When the value of r_b has become known by means of r and r_a H can be calculated. For this purpose we write formula (22) in the form:

$$H = \frac{r_b b w \times 1000}{0.637 \sqrt{l}} \dots \dots \dots (24)$$

We have $b = 660$, $V = 500$ and $l = 12.7$, so that we may write for H :

$$H = 163.2 \times r_b w \dots \dots \dots (25)$$

H was computed for string 13. Plate A 34 shows a curve, recorded, when suddenly a constant potential difference was established between the ends of the quartz-thread, the galvanometer circuit being closed by a small external resistance, the amount of which may be neglected. Analysis of the curve shows that $q = 24.8$, $c = 89.4$, $v = 0.98$ and $d = 0.964$, from which we derive by means of the formula $r = \frac{q}{cvd}$ (15) that $r = 0.0294$.

Formerly we found r_a to be 0.0174, from which follows that $r_b = 0.0120$.

The conductive resistance of the quartz-thread is $w = 9000$ Ohms, and from this we compute by means of formula (25) that $H = 17600$ [C. G. S.].

Two tables follow now. In table VI are found for three quartz-threads the data, enabling us to calculate the value of r by formula (15). The speed of the sliding frame is always 500 mM. per second, the galvanometer circuit being closed by a small external resistance, the amount of which may be neglected.

TABLE VI.

Number of the quartz-thread.	Conductive resistance w of the quartz-thread.	Number of the photo gram.	q in millimetres.	c in millimetres per micramp.	v .	d	r in [mm— νA].
10	10000	A 22	20.7	535	1.24	1.005	0.0312
13	9000	A 34	24.8	894	0.98	0.964	0.0294
14	17800	A 132	26.4	582	2.33	0.927	0.0210

In table VII we find the values of r_a from table III together with those of r from table VI. The difference between the two values is indicated in the last column but one by r_b ; the last column gives the value of r_b as calculated by formula (22), for H the value 17600 [C. G. S.] having been taken.

The accordance between the values of these two columns is very satisfactory and may be considered as a proof of the accuracy with which in general the resistance to the motion of the string may be determined by means of the formula $r = \frac{q}{cvd}$ (15).

The ratio of the directly measured values of r_a and r is

	for string 10	as	1 : 1,615
„	„ 13	„	1 : 1,69
„	„ 14	„	1 : 1,34

TABLE VII.

Number of the string.	w in Ohms.	r_a measured.	r measured.	r_b calculated from the measured values of r and r_a .	r_b calculated from the length of the string and the field-intensity.
10	10000	0.0193	0.0312	0.0149	0.0108
13	9000	0.0174	0.0294	0.0120	0.0120
14	17800	0.0157	0.0210	0.0053	0.0061

To conclude this chapter we give some remarks concerning the condition for which the motion of the quartz-thread just reaches the limit of aperiodicity. In this condition we have the relation :

$$c = \frac{4m}{\nu^2} \dots \dots \dots (26)$$

According to this formula one would be induced to determine the value of c from m and r , but it will appear in chapter 6 that for small tensions of the quartz-thread the virtual mass of the image of the string is not a constant value.

Hence it is not or hardly possible to derive from measurements that were performed with other tensions of the string, the value of m for the case that the limit of aperiodicity has been reached. And if m is unknown c cannot be calculated, of course.

So if one wants to know the sensitiveness for which the limit of aperiodicity is reached, one is obliged to determine this directly by experiment. The results of a number of such determinations which, as will be understood, were only made in a rough way, are found united in the following table VIII.

From the data of the preceding table and from the values of r it would be possible to calculate the values of m .

Similarly those of the time-constant¹⁾ \mathbf{T} by the formula $\mathbf{T} = \frac{rc}{2}$.

These calculations, however, must be omitted, since c has a far too small degree of accuracy here, to attach any importance to the results.

T A B L E VIII.

Number of the string.	Sensitiveness c for the limiting value of aperiodicity.	
	with air-damp- ing only.	with air-damping and electro- magnetic damp- ing combined.
10	(120)	(50)
13	(130)	(45)
14	(115)	(55)

5. The acceleration.

When analysing a curve, recorded by the capillary electrometer, if we wish to know the potential difference which at a certain moment exists between the mercury and the sulphuric acid, we have, besides the properties of the instrument and the speed of the recording

¹⁾ See FLEMING, l.c. pp. 377 ff.

plane only to take into account the velocity of the motion of the meniscus. When analysing a curve, however, recorded by the string galvanometer, the analogous data are not sufficient in general. It will often be necessary to take into account not only the velocity but also the acceleration presented by the image of the string.

This must be ascribed to the fact that in the capillary electrometer the resistance to the motion of the meniscus is very great¹⁾ compared with the mass of the mercury thread, so that this mass may be neglected, when it is desired to calculate the existing potential difference from the velocity of motion, whereas with the string galvanometer the resistance to the motion of the quartz-thread is very small, and hence the mass of the thread in many cases has a distinct influence on the velocity of its deflections.

These considerations may be succinctly rendered by formula (11), already developed in the preceding chapter:

$$q = crv + cm \frac{(1 + v^2)^{\frac{3}{2}}}{\rho} \dots \dots \dots (11)$$

If v is very great compared with m the second term behind the = sign may be dropped and the formula becomes

$$q = crv \dots \dots \dots (12)$$

This formula (12) can be applied as well for the analysis of capillary electrometric curves as for curves of the string galvanometer for which v is small and ρ large.

On the other hand, for moderate values of v and ρ the mass m may no longer be neglected, so that then analysis of the curve will only be possible if besides the velocity also the acceleration can be measured. This acceleration, expressed as virtual acceleration of the image of the string in millimetres distance per millimetre of time, is

nothing else but $\frac{(1 + v^2)^{\frac{3}{2}}}{\rho}$.

Assuming as known the general conditions under which a curve is written by the string galvanometer, and also the distance from any point of the curve to the zero line, one will have to measure the tangent v of the angle of inclination and also ρ the radius of curvature, in order to calculate the potential difference which existed between the ends of the quartz-thread at the moment, that the arbitrary point mentioned was recorded. Under unchanged general conditions each

¹⁾ On the influence of frictional resistance on the movement of the meniscus in LIPPMANN's capillary electrometer, see these "Proceedings" II, p. 108, 1899.

point may be said to be fully characterised by its distance from the zero line and the values of v and ϱ .

The distance from the zero line may very easily be determined by the presence of the square millimetre net, while in a preceding chapter it was pointed out how v is measured. So we have only to describe the best way of ascertaining the value of the radius of curvature ϱ .

Three different methods were tried for measuring ϱ of which one only proved practicable. The other two will only be briefly mentioned. First a reduced diapositive was made photographically of a large drawing on which a number of circles with different, accurately known radii were represented. On the diapositive the radii vary systematically from 0,5 mm. to ∞ . It must be so laid on the curve to be measured that one of the circles coincides with the curve in any point of this latter. By direct comparison the value of ϱ in that point will then be known.

In the second method three points of the curve are measured, situated at small but mutually equal distances. Calling k the distance of the two extreme points and p the distance of the middle point from the straight line that joins the two extreme points, the radius of curvature at the spot where the measurement is made, is

$$\varrho = \frac{k^2 + 4p^2}{8p}.$$

Here k represents the chord and p the height of the circular arc under measurement.

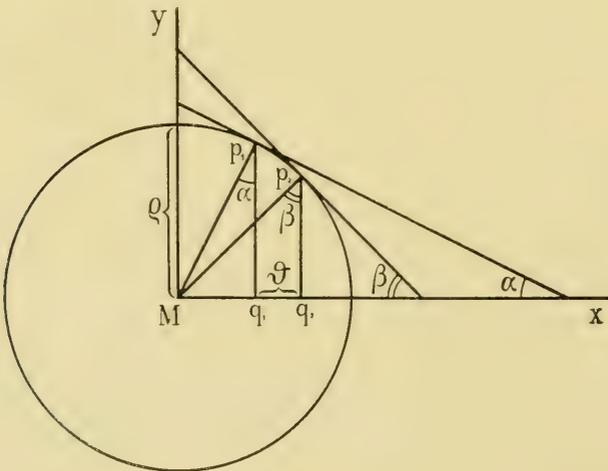


Fig. 2.

The third method, the only one that could be applied with good results, as was remarked above, consists in measuring the angles of inclination in two points of the curve, situated near each other.

Let p_1 and p_2 be two near points of a curve, the radius of curvature of which keeps the same value q in all points between p_1 and p_2 , the angle of inclination at p_1 being represented by α and that in p_2 by β .

MX is an absciss in the coordinate system which was recorded as a net of square millimetres together with the curve, but has been omitted in the figure, while MY , p_1q_1 and p_2q_2 are ordinates.

It is seen from the figure that

$$\sin \alpha = \frac{Mq_1}{q} \text{ and } \sin \beta = \frac{Mq_2}{q} .$$

Putting $Mq_2 - Mq_1 = \mathfrak{D}$ we have

$$q = \frac{\mathfrak{D}}{\sin \beta - \sin \alpha} (27)$$

The value of \mathfrak{D} can be read off in a simple manner on the net of square millimetres, while the angles α and β must be measured by means of the eye-piece with cross-wires. This arrangement and the accuracy that can be obtained by it, have already been dealt with in the preceding chapter; we now put the question in what cases the determination of q may or may not be practically useful.

Let us once more consider formula (11)

$$q = crv + cm \frac{(1+v^2)^{\frac{3}{2}}}{q} , (11)$$

this time as the expression of a curve, representing the damped oscillations of a strongly stretched quartz-thread. For each reversing point the value of v must be put = 0. Hence for a reversing point the formula becomes

$$q = \frac{cm}{q}$$
$$m = \frac{q}{c} q , (28)$$

in which the sensitiveness c is an accurately known quantity. So it would only be necessary to determine q and q in order to be able to calculate at once a value for m from every reversing point.

But here the practical difficulty lies in the quick variations which q shows already for moderate values of q . The time \mathfrak{D} has now to be taken so small that it can no longer be measured with sufficient

accuracy, at any rate with our measuring arrangement, when the microscope has been mounted with the cross-wire eye-piece. And hence ϱ itself becomes inaccurately known.

So we conclude that measuring ϱ has no practical value when we want to know the value of m for a strongly stretched oscillating string. Moreover this value has already been determined for this case in a satisfactory manner by the method described in chapter 3.

But the measurement of ϱ does obtain practical value when we want to know the virtual mass of the image of a string, which has written a curve with a feeble or moderate tension of the quartz-thread¹⁾. When analysing different curves it is not sufficient to use the calculated real mass of the quartz-thread, since, as has already been mentioned and will still more clearly appear in the following chapter, the virtual mass of the image of the string is very considerably modified by changes in the tension of the quartz-thread.

We finally remark that when the velocity v is great, also the angles α and β become large, by which the difference of the sines diminishes for the same difference of the angles. This causes a diminution of the accuracy with which ϱ can be known.

Also when ϱ becomes very great the determination loses in accuracy, since then for an equal value of v the difference between $\sin \alpha$ and $\sin \beta$ greatly diminishes. But this drawback is of no practical consequence, as in the analysis of a curve the value of ϱ , as soon as it gets beyond a certain limit, may be put ∞ without a large error.

6. *Analysis of some curves.*

We give in this chapter the results of the analysis of some curves, written, when a known, constant potential difference was suddenly established between the ends of the quartz-thread:

The first of the curves to be dealt with was recorded with a rather feeble tension of the quartz-thread, i.e. with a rather sensitive position of the galvanometer. 1 mm. ordinate = $1,87 \times 10^{-9}$ Amp. or the sensitiveness $c = 535$. The speed of the sensitive plate is $V = 500$ mm. per sec., so the value of 1 mm. absciss = 2σ .

We call $t = 0$ the moment when the electric current is started. Now the angles of inclination of the curve are measured at $t = 1 \sigma$, 2σ , 3σ , etc. In the following table IX, in the first column the values of t are expressed in thousandths of a second and in the

¹⁾ How a separate calculation of ρ can be avoided here, will appear in the following chapter.

TABLE IX. (String 10, Plate A 22).

1	2	3	4	5	6
t in thou- sandths of a second.	v	$r c v$	q in milli- metres. Measured.	q in milli- metres. Calculated.	Difference between the measured and calcu- lated value of q in mm.
0	—	—	24.6	—	—
1	0.762	12.7	24.2	17.8	— 6.4
2	0.863	14.5	23.8	21.7	— 2.1
3	1.000	16.7	23.3	23.4	0.1
4	1.083	18.1	22.7	23.8	1.1
6	1.238	20.7	21.4	20.7	— 0.7
—	(1.236)	(20.7)	(20.7)	(20.7)	(0)
8	1.235	20.7	21.1	20.7	0.6
10	1.139	19.1	18.9	18.4	— 0.5
12	1.103	18.5	17.7	17.9	0.2
14	1.028	17.2	16.6	16.4	— 0.2
16	0.945	16.0	15.5	15.5	0
18	0.926	15.5	14.5	15.0	0.5
20	0.856	14.2	13.6	13.6	0
22	0.798	13.4	12.7	13.0	0.3
24	0.770	12.9	11.9	—	1.0
26	0.705	11.8	11.1	—	0.7
28	0.680	11.4	10.4	—	1.0
30	0.615	10.3	9.7	—	0.6
32	0.572	9.6	9.1	—	0.5
34	0.541	9.1	8.5	—	0.6
36	0.501	8.4	8.0	—	0.4
38	0.481	8.1	7.5	—	0.6
40	0.451	7.6	7.1	—	0.5
42	0.423	7.1	6.5	—	0.6
44	0.398	6.7	6.2	—	0.5
46	0.368	6.2	5.8	—	0.4
48	0.361	6.0	5.4	—	0.6
50	0.350	5.9	5.1	—	0.8
52	0.314	5.2	4.7	—	0.5
54	0.303	5.1	4.4	—	0.7
56	0.279	4.7	4.1	—	0.6
66	0.181	3.0	2.8	—	0.2
76	0.135	2.3	2.0	—	0.3
86	0.0945	1.6	1.5	—	0.1
96	0.0682	1.1	1.0	—	0.1

second column the values of the tangent v of the angles of inclination existing at these moments.

In the third column the values of the product rcv are given, calculated in the following manner.

If of the first part of the curve the concave side is directed upward, the concave part of the second half is directed downward. At the point of inflection $\varrho = \infty$.

Here by formula (13)

$$r = \frac{q}{cv} \dots \dots \dots (13)$$

or

$$rc = \frac{q}{v},$$

so that from the values here given for q and v , the value of rc can be calculated. For any other point of the curve the constant value rc is then multiplied by the value of v for that point.

In the fourth column the values of q , i.e. the distances of the image of the string from the second position of equilibrium, are given as the results of direct measurements.

In the fifth column the values of q are given as calculated from the formula

$$q = crv + cm \frac{tg\beta - tg\alpha}{\varrho}, \dots \dots \dots (28a)$$

while in the sixth column the differences between the measured and calculated values of q are given.

The above formula (28a) requires some explanation.

It is obtained by replacing in formula (11) the value $\frac{(1 + v^2)^{\frac{3}{2}}}{\varrho}$ by $\frac{tg\beta - tg\alpha}{\varrho}$.

As was remarked above $\frac{(1 + v^2)^{\frac{3}{2}}}{\varrho}$ or $\frac{d^2 q}{dt^2}$ is nothing else but the expression for the acceleration. Since we used as the only method for measuring ϱ the measurement of two angles α and β , see fig. 2, we can also, these angles being known, find an approximate expression for the acceleration by means of their tangents.

The velocity at the point p_1 , fig. 2, is given by $tg\alpha$, at the point p_2 by $tg\beta$. The difference in velocity is $tg\beta - tg\alpha$. Assuming the acceleration to be constant during the time ϑ , it is expressed by

$$\frac{tg\beta - tg\alpha}{\vartheta}$$

By using formula (28a) instead of (11) we considerably simplify the calculations. In the first place it becomes unnecessary to look up the sines of α and β , while the tangents of these angles are already known, since they were wanted for the determination of crv . And then it is not necessary to calculate the values of $(1 + v^2)^{\frac{3}{2}}$.

The data, serving for the determination of the acceleration, have been collected in table. X. One also finds in the sixth column the

TABLE X (string 10, Plate A 22).

1	2	3	4	5	6	7	8
t in thousandths of a second.	s in milli- metres.	tgz	$tg\beta$	$\frac{tg\beta - tgz}{s}$	Difference between rcv and the measured values of q in millimetres.	$\frac{tg\beta - tgz}{s}$ in millimetres.	Algebraic sum of the values of the two preceding columns in millimetres.
1	1	(0.696) ¹⁾	0.836	0.167	— 11.5	5.1	— 6.4
2	1	0.762	1.000	0.238	— 9.3	7.2	— 2.1
3	1	0.863	1.083	0.220	— 6.6	6.7	0.1
4	2	0.863	1.238	0.187	— 4.6	5.7	1.1
6	—	—	—	(0)	— 0.7	(0)	— 0.7
8	—	—	—	(0)	0.6	(0)	0.6
10	2	1.235	1.103	— 0.066	0.2	— 0.7	— 0.5
12	2	1.139	1.028	— 0.055	0.8	— 0.6	0.2
14	2	1.103	0.945	— 0.079	0.6	— 0.8	— 0.2
16	2	1.028	0.926	— 0.051	0.5	— 0.5	0
18	2	0.945	0.856	— 0.045	1.0	— 0.5	0.5
20	2	0.926	0.798	— 0.064	0.6	— 0.6	0
22	2	0.856	0.770	— 0.043	0.7	— 0.4	0.3

1) z has been calculated here by the formula $z = 2\gamma - \beta$, in which γ represents the angle of inclination of the curve at the time $t = 1$.

difference between rcv and the measured value of q , in the seventh column the value of $c m \frac{tg\beta - tga}{\vartheta}$ and in the last column the algebraic sum of the values of the sixth and seventh columns.

If our measurements had an absolute precision the values of the last column would all be $= 0$.

In the calculation of the tables IX and X, the correction has been neglected which must be applied if a scale division along an absciss is not equal to a scale division along an ordinate. Thus we assumed that the net of square millimetres consists of real squares or in other words that $d = 1$. This has no influence on the calculated value of rcv , since the correction of r compensates that of v ; but it has an influence on the values of $\frac{tg\beta - tga}{\vartheta}$. But the differences are not of such an order of magnitude that the correction would be necessary; the general form of the curve remains unaltered.

The results of the measurements and calculations which are given in figures in the preceding table IX, can be illustrated by means of a diagram. In fig. 3 which corresponds to table IX, the net of square millimetres is represented at about twice its natural size. A scale division along an absciss $= 2 \sigma$; a scale division along an ordinate $= 1,87 \times 10^{-9}$ Ampère.

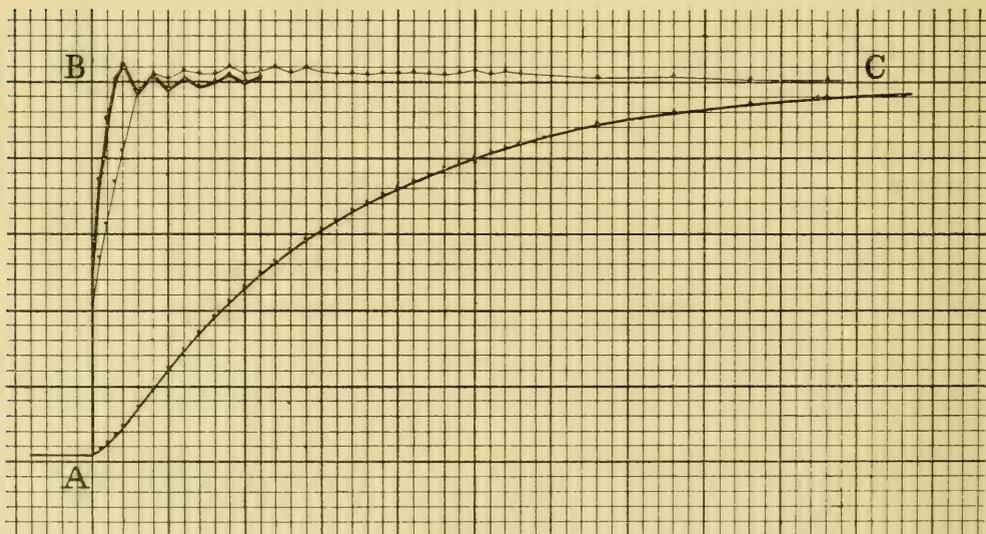


Fig. 3

String N^o. 10, Photograph A 22, Tables IX and X.

Absciss 1 scale division $= 2\sigma$; ordinate 1 scale division $= 1,87 \times 10^{-9}$ Amp.

The regularly bent line of medium thickness represents the recorded curve. At the moment $t=0$ the constant current is made. In the case of an ideal, absolutely accurate analysis we should find two straight lines, one of which would rise vertically from A to B , while the other from B to C would be horizontal. The results of the actual analysis according to column 5 of table IX are represented by the thick line, while the thin line represents the values of rv according to column 3 of this table.

For the virtual mass m two different values have been used; for the first 4 thousandths of a second m has been put 0.0567 which is 6 times the amount found in chapter 3. At $t=6\sigma$ and $t=8\sigma$, m has no influence, since at these times ϱ may be put $=\infty$. Beginning with $t=10\sigma$, m has again been reckoned but this time with a value 0.0187 which is twice the value of chapter 3.

If a single value is given to m the results become much less satisfactory and the question arises whether the whole analysis must not be considered worthless now that it appears to be impossible to assume a constant value for m .

In reply to this we remark in the first place that, as will presently appear, the variation in the value of m is only of account with a great sensitiveness of the galvanometer, i. e. with a feeble tension of the quartz thread. Besides, even with the most sensitive position of the galvanometer still an important part of the analysis can be usefully applied. For practically a curve, such as is obtained e. g. in many electrophysiological investigations, will consist of parts of various curvatures and will always show a number of points for which ϱ may be put $=\infty$ or the acceleration may be put $=0$. In all these points m need not be taken into account. Since r can be measured with great accuracy the analysis is in all respects satisfactory here.

Moreover the analysis can be applied wherever the curvature and at the same time the angle of inclination are not too great — in our case already in all points that are recorded later than 0.004 second after the starting of the current — as will appear from table IX and figure 3. For each definite tension of the quartz thread a definite value for m be taken.

The reason why in general m is represented by another value for different tensions of the quartz thread will be discussed in chapter 8. But here we must ask why m can also vary when the sensitiveness of the galvanometer and together with it the tension of the quartz thread remain unchanged. For an explanation of this unforeseen and somewhat disappointing phenomenon we have in the first

place sought for errors in the measurements, which might be occasioned by the not sharply defined edge of the quartz thread being

TABLE XI (string 14, Plate A 132).

1	2	3	4	5	6
<i>t</i> in thou- sandths of a second.	<i>v</i>	<i>r c v</i>	<i>q</i> in milli- metres. Measured.	<i>q</i> in milli- metres. Calculated	Difference between the measured and calcu- lated values of <i>q</i> in millim.
0	—	—	32.7	—	—
1	1.664	18.8	31.9	27.0	— 4.9
2	1.872	21.2	31.0	29.9	— 1.1
3	2.069	23.4	30.0	30.8	0.8
4	2.215	25.0	29.2	29.7	0.5
5	2.290	25.9	28.0	28.4	0.4
6	2.332	26.4	26.9	26.4	— 0.5
—	(2.332)	(26.4)	(26.4)	(26.4)	(0)
7	2.332	26.4	25.9	26.4	0.5
8	2.204	25.0	25.0	24.5	— 0.5
10	2.087	23.6	23.0	23.0	0
12	1.881	21.3	21.1	20.6	— 0.5
14	1.753	19.8	19.5	19.2	— 0.3
16	1.613	18.3	17.9	17.9	0
18	1.511	17.1	16.5	16.7	0.2
20	1.418	16.0	15.1	15.5	0.4
22	1.280	14.5	13.9	14.0	0.1
24	1.179	13.3	12.8	13.0	0.2
26	1.111	12.6	11.7	12.3	0.6
28	1.032	11.7	10.7	11.4	0.7
30	0.942	10.7	9.9	—	0.8
32	0.848	9.6	9.0	—	0.6
34	0.821	9.3	8.2	—	1.1
36	0.751	8.5	7.5	—	1.0
38	0.676	7.7	6.9	—	0.8
40	0.635	7.2	6.3	—	0.9
42	0.563	6.4	5.8	—	0.6
44	0.504	5.7	5.2	—	0.5
46	0.456	5.2	4.8	—	0.4
48	0.423	4.8	4.4	—	0.4
50	0.382	4.3	4.0	—	0.3
52	0.350	4.0	3.7	—	0.3
56	0.304	3.4	3.1	—	0.3
60	0.254	2.9	2.6	—	0.3
70	0.151	1.7	1.7	—	0

TABLE XII (string 14, plate A 132.)

1	2	3	4	5	6	7	8
t in thousandths of a second.	s in milli- metres.	$tg\alpha$	$tg\beta$	$\frac{tg\beta - tg\alpha}{s}$	Difference between $r c v$ and the measured values of q in millime- tres.	$cm \frac{tg\beta - tg\alpha}{s}$ in millimetres.	Algebraic sum of the values of the two preceding columns in millimetres.
1	1	(1.488) ¹⁾	1.872	0.384	— 13.1	8.2	— 4.9
2	1	1.664	2.069	0.405	— 9.8	8.7	— 1.1
3	1	1.872	2.215	0.343	— 6.6	7.4	0.8
4	1	2.069	2.290	0.221	— 4.2	4.7	0.5
5	1	2.215	2.332	0.117	— 2.1	2.5	0.4
6	—	—	—	(0)	— 0.5	(0)	— 0.5
7	—	—	—	(0)	0.5	(0)	0.5
8	2	2.332	2.087	— 0.122	0	— 0.5	— 0.5
10	2	2.204	1.881	— 0.161	0.6	— 0.6	0
12	2	2.087	1.753	— 0.167	0.2	— 0.7	— 0.5
14	2	1.881	1.613	— 0.134	0.3	— 0.6	— 0.3
16	2	1.753	1.511	— 0.121	0.4	— 0.4	0
18	2	1.613	1.418	— 0.097	0.6	— 0.4	0.2
20	2	1.511	1.280	— 0.115	0.9	— 0.5	0.4
22	2	1.418	1.179	— 0.119	0.6	— 0.5	0.1
24	2	1.280	1.111	— 0.084	0.5	— 0.3	0.2
26	2	1.179	1.032	— 0.073	0.9	— 0.3	0.6
28	2	1.111	0.942	— 0.084	1.0	— 0.3	0.7

photographically distorted where the curve bends. But the errors so caused are far too small to explain the matter; moreover they are

¹⁾ α has again been calculated here by the formula $\alpha = 2\gamma - \beta$, see the note at the foot of table X.

to a great extent eliminated if the measurements at the lower side of the string are controlled by measurements at the upper side.

The most likely explanation has to be sought, in my opinion, in the lack of homogeneity of the magnetic field. The middle part of the quartz thread is placed between the objectives of the microscopes, where the magnetic field is only very feeble compared with the field in which the other parts of the thread are placed. The ponderomotive force which causes the quartz thread to deflect, when it is passed by a current, is consequently smaller in the middle of the string than at the two ends. These latter, so to say, draw aside the middle part and so it can be understood that with feeble tension of the quartz thread the displacement of the middle part lags.

The stronger the tension of the quartz thread the more regularly it will move over its whole length. So we may expect that for a less sensitive position of the galvanometer the values which we must take for m will be more equal among each other.

In tables XI and XII and figure 4 belonging to them, we will first give the analysis of a curve written by string n^o. 14. The tables

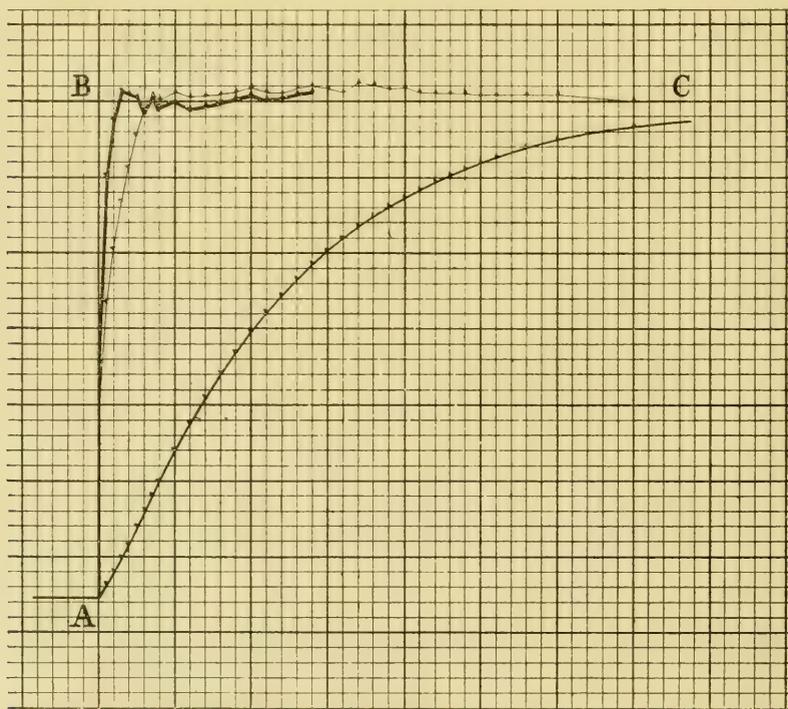


Fig. 4.

String N^o. 14, photogram A 132, Tables XI and XII.

Absciss 1 scale division = 2τ , ordinate 1 scale division = $1,72 \times 10^{-9}$ Amp.

or diagram require no nearer explanation since they are in every respect analogous to those of string n^o. 10 that were discussed above. We have here again $V = 500$ hence 1 mm. absciss = 2σ . Further $c = 582$, so 1 mm. ordinate = 1.72×10^{-9} Amp. The value of m has been put during the first 5 thousandths of a second at 0.037 which is rather more than 10 times the value found in chapter 3. At $t = 6\sigma$ and $t = 7\sigma$, m has no influence. Beginning with $t = 8\sigma$, m has been taken into account again, this time with a value of 0.00688 or rather more than 1.9 times the value of chapter 3.

Some other curves, also recorded with a sensitive position of the galvanometer show after analysis diagrams that agree completely with the two above described diagrams 3 and 4. So they require no nearer elucidation here.

We will not omit, however, to give the results of the analysis of a curve recorded with a less sensitive position of the galvanometer. The numbers are collected in tables XIII and XIV, which like the corresponding diagram 5 have been arranged in the same manner as the preceding tables and diagram. They represent a curve written by string 14, with 1 megohm in the galvanometer circuit. Here we have $c = 115.2$, hence ordinate 1 mm. = 8.67×10^{-9} Amp., while absciss 1 mm. is again = 2σ .

The value of m can be kept constant here at a value which is 1.45 times greater than the value which would hold for strong tension of the string.

We see that most of the examined points are calculated with an error, smaller than 1 mm. and that the correction is already pretty accurate after 1σ . After 1σ the error amounts to 1.4 on a total deflection of 30.6 mm., i. e. 4.6 %. This proves that by means of analysis of the curve with a sensitiveness of the galvanometer $c = 115.2$, for which 1 mm. deflection corresponds to a current of 8.67×10^{-9} Amp., the real intensities of the current can be known beginning at 1σ after starting the current, and then progressing 0.5σ each time.

In all probability these times can still be materially shortened when the speed of the photographic plate is increased. With the curves mentioned in this paper a speed of the sliding frame of 500 mm. per second has chiefly been used, but it is evident that with improved mechanical appliances it will be possible to attain greater speeds. We have lately succeeded in obtaining very regular speeds of 1 M. per second.

At the end of this chapter we remind the reader that an analysis of the curves is only necessary when it is desired to measure very

TABLE XIII (string 14 plate A 125).

1	2	3	4	5	6
t in thou- sandths of a second.	v	$r c v$	q in milli- metres. Measured.	q in milli- metres. Calculated.	Difference between the measured and calculated values of q in millim.
0	—	—	30.6	—	—
0.5	10.78	18.2	28.4	22.2	— 6.2
1	12.71	21.45	25.6	24.2	— 1.4
1.5	13.15	22.2	22.2	(22.2)	(0)
2	12.71	21.45	19.3	18.7	— 0.6
2.5	10.89	18.4	17.0	15.2	— 1.8
3	10.02	16.9	14.2	14.3	0.1
3.5	8.71	14.7	12.0	11.7	— 0.3
4	7.50	12.65	10.2	10.1	— 0.1
5	5.700	9.6	7.3	7.8	0.5
6	4.504	7.6	4.9	6.0	1.1
7	3.078	5.2	3.3	3.9	0.6
8	2.251	3.8	2.1	3.0	0.9
9	1.688	2.85	1.2	2.1	0.9
10	1.163	2.0	0.6	1.4	0.8
11	0.740	1.2	0.2	0.8	0.6

feeble currents in very short times. As soon as the galvanometer may be less sensitive, by applying a method of damping which was formerly described, curves may be obtained, directly recording the accurate intensity of the current in less than 1σ .

TABLE XIV (string 14, plate A 125).

1	2	3	4	5	6	7	8
t in thousandths of a second.	ϑ in milli- metres.	$tg\alpha$	$tg\beta$	$\frac{tg\beta - tg\alpha}{\vartheta}$	Difference between r_{cv} and the measured values of q in millime- tres.	$cm \frac{tg\beta - tg\alpha}{\vartheta}$ in millimetres.	Algebraic sum of the two preced- ing columns in millimetres.
0.5	0.5	(9.36) ¹⁾	12.71	6.70	— 10.2	4.0	— 6.2
1	0.5	10.78	13.15	4.74	— 4.2	4.8	— 1.4
1.5	—	—	—	(0)	(0)	(0)	(0)
2	0.5	13.15	10.89	— 4.52	2.1	— 2.7	— 0.6
2.5	0.5	12.71	10.02	— 5.38	1.4	— 3.2	— 1.8
3	0.5	10.89	8.71	— 4.36	2.7	— 2.6	0.1
3.5	0.5	10.02	7.50	— 5.04	2.7	— 3.0	— 0.3
4	1	10.02	5.700	— 4.32	2.5	— 2.6	— 0.1
5	1	7.50	4.504	— 3.00	2.3	— 1.8	0.5
6	1	5.700	3.078	— 2.622	2.7	— 1.6	1.1
7	1	4.504	2.251	— 2.253	1.9	— 1.3	0.6
8	1	3.078	1.688	— 1.390	1.7	— 0.8	0.9
9	1	2.251	1.163	— 1.088	1.6	— 0.7	0.9
10	1	1.688	0.740	— 0.948	1.4	— 0.6	0.8
11	1	1.163	(0.439) ²⁾	— 0.724	1.0	— 0.4	0.6

¹⁾ Calculated, see the note at the foot of table X.

²⁾ β has here been calculated in the same way as the first α of the table.

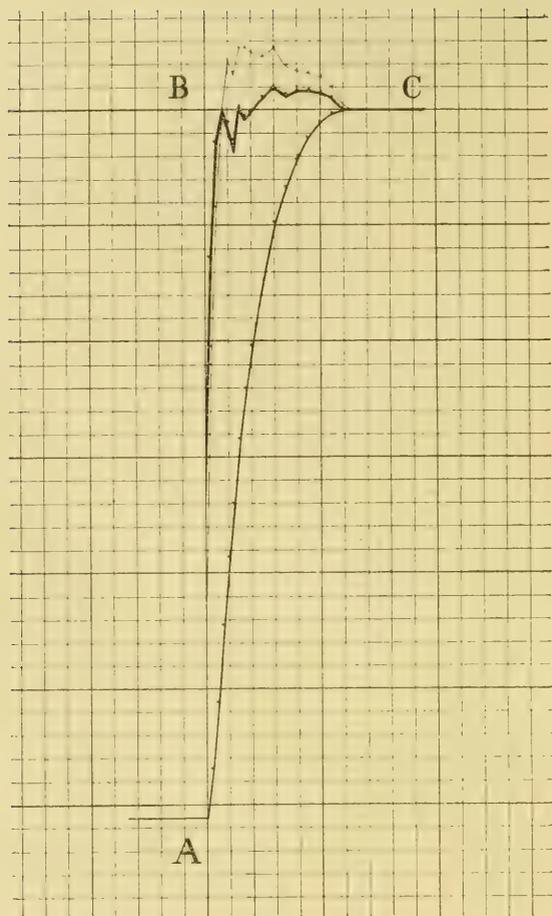


Fig. 5.

String N^o. 14, photogram A 125, Tables XIII and XIV.

Absciss 1 scale division = 2σ , ordinate 1 scale division = $8,67 \times 10^{-9}$ Amp.

7. *Absolute measures of the mass of the string and the resistance to the motion of the string.*

As soon as m , the virtual mass of the image of the string is known in millimetre-micrampere units, it is not difficult to calculate the real mass of the string in grammes. In order to do this we must first in formula (7) express the values of T and c in the ordinary units of the (C.G.S.)-system and then the circumstance has to be taken into account that although the middle of the string and consequently the image of the string performs rectilinear oscillations,

yet the motion of the quartz thread as a whole has a more complicated character.

Calling m_1 the real mass of the string in grammes, T_1 the period in seconds and c_1 the sensitiveness in centimetres deflection of the middle of the string per dyne, we have

$$m_1 = m \times \left(\frac{T_1}{T}\right)^2 \times \frac{c}{c_1} \times \frac{\pi^2}{8} \dots \dots (29)$$

The factor $\frac{\pi^2}{8}$ is introduced by the circumstance we mentioned already above. The method by which the amount of this factor is calculated will be given later, after the tension of the string will have been dealt with. We now proceed to a nearer discussion of the values of $\frac{T_1}{T}$ and $\frac{c}{c_1}$.

T represents the time in millimetres while the velocity of motion of the sliding frame is V mm per second. The time in seconds is consequently

$$T_1 = \frac{T}{V}$$

or

$$\frac{T_1}{T} = \frac{1}{V} \dots \dots \dots (30)$$

In order to determine the value of $\frac{c}{c_1}$, we must take into account the magnification used, b , the strength of the magnetic field H and the length of the string l .

H is expressed in (C.G.S.) units and l in centimetres.

c , as was mentioned before, is the sensitiveness, expressed in millimetres deflection of the image of the string per micrampere, c_1 being the sensitiveness, expressed in centimetres deflection of the middle of the string itself per dyne.

The force deflecting the quartz thread when a current of 1 micrampere is passed, is $\frac{Hl}{10^7}$ dynes. Hence

$$c = c_1 \times \frac{Hl}{10^7} \times 10b,$$

or

$$\frac{c}{c_1} = \frac{Hlb}{10^6} \dots \dots \dots (31)$$

By means of the formulae (29), (30) and (31) we can now express m_1 in m and find :

$$m_1 = \frac{\pi^2}{8} m \times \frac{Hlb}{10^6 V^2} \dots \dots \dots (32)$$

The accuracy with which m_1 can be calculated in grammes depends of course in the first place upon the accuracy with which m is known in $[mm-\mu A]$ units and further upon the accuracy of the values of H , l , b and V . The latter quantity occurs in formula (32) squared and so would have a preponderant importance. But the time-recording arrangement which we used, works, as we saw formerly, with so great an accuracy that we may neglect errors in the value of V .

Also l and b can be measured with sufficient accuracy, while for H the value has been taken which we found in chapter IV, namely 17600 [C. G. S.].

The error in the absolute value of m_1 I estimate at a few percent. In formula (32) we have.

$$\begin{aligned} H &= 17600, \\ l &= 12,7, \\ b &= 660, \\ V &= 500, \end{aligned}$$

from which follows that $m_1 = 7,28 \times 10^{-4} m \dots \dots \dots (33)$

In chapter III we found that:

for string N ^o .	10	$m = 9,4 \times 10^{-3}$	$[mm - \mu A]$
,,	,,	13	$m = 6,9 \times 10^{-3}$ „ „
,,	,,	14	$m = 3,6 \times 10^{-3}$ „ „

By formula (33) we calculate from this the mass of the strings in absolute measure :

for string N ^o .	10	$m_1 = 6,85 \times 10^{-6}$	gram.
,,	,,	13	$m_1 = 5,02 \times 10^{-6}$ „
,,	,,	14	$m_1 = 2,62 \times 10^{-6}$ „

We passingly remark that for recording sounds we use a very light short string : a 2,5 cM. long, 1 μ thick quartz thread, of which the weight may be estimated at about $1,5 \times 10^{-7}$ grammes.

From the length l , the diameter d of the naked quartz thread and the specific gravity of quartz s , the weight of the quartz may be calculated as

$$g = \frac{d^2}{4} \pi ls.$$

This weight is only inaccurately known on account of the uncertainty in d . But combined with the value of m_1 it may serve us to obtain a rough idea of the relative weights of quartz and silver in the string. Calculated in this manner we find this ratio

string 10	:	1	quartz to	3.5	silver
„ 13	„	1	„ „	6.4	„
„ 14	„	1	„ „	2.4	„

We now proceed to express the resistance to the motion of the string in absolute measure. According to the definition formerly given r is the virtual resistance to the motion of the string in micramperes, when the image of the string moves with a velocity of 1 mm distance per 1 mm time.

We call r' the resistance to the motion of the string in dynes when the middle of the string moves with a velocity of 1 cM. per second.

The above mentioned unit r refers to a strength of field H , a length of the quartz thread l , a magnification b and a speed of the writing plane V .

Since the force of $1 \mu A$ is equal to $\frac{Hl}{10^7}$ dynes, we may write :

$$r' = r \times \frac{Hl}{10^7} \times \frac{10 b}{V}$$

or

$$r' = r \times \frac{Hlb}{10^6 V} \dots \dots \dots (34)$$

Substituting in this the above values for H , l , b and V , we get

$$r' = 0,295 r \dots \dots \dots (35)$$

It is unnecessary to give here the absolute measures of the electromagnetic damping. These were discussed in chapter IV where they served us for accurately determining the value of H .

On the other hand the absolute measures of the air-damping r'_a may find a place here.

In chapter IV the air-damping was found

for string N ^o . 10	$r_a = 0,0193$	[mm — μA]
„ „ „ 13	$r_a = 0,0174$	„ „
„ „ „ 14	$r_a = 0,0157$	„ „ .

By formula (35) we calculate from this

for string N ^o . 10	$r'_a = 0,00569$	dynes.
„ „ „ 13	$r'_a = 0,00513$	„
„ „ „ 14	$r'_a = 0,00463$	„

It would be desirable to compare these values with those that might be calculated by means of the kinetic theory of gases. But then we ought to bear in mind that we have combined in r'_a other causes of damping besides the air-damping.

These causes are threefold :

1 If the magnetic field is non-homogeneous, there may arise vortex currents in the layer of silver during a deflection of the quartz thread.

2. If the string is para- or diamagnetic, it may by its motion induce currents in the iron of the pole shoes.

3. Also a non-magnetic string will induce a movement of electricity in the pole shoes when it is passed by a current and moves.

But all three causes are so small that they may probably be neglected compared with the air-damping.

8. *The tension of the quartz thread.*

S.

In order to calculate the tension of the quartz thread under various circumstances, we begin with assuming a special case, namely that the thread is strongly stretched and is placed over its entire length in a homogeneous magnetic field. A constant current passed through the galvanometer causes a permanent deflection of the thread which assumes the shape of a catenary.

Calling u_1 the deflection of the middle of the thread and i_1 the ponderomotive force experienced by the thread, the tension is:

$$S = \frac{i_1 l}{8u_1} \dots \dots \dots (36)$$

Here S and i_1 are expressed in dynes, while the deflection u_1 and the length l are given in centimetres.

Now

$$\frac{u_1}{i_1} = c_1 \dots \dots \dots (37)$$

in which c_1 , denotes the sensitiveness of the galvanometer, as was already mentioned with formula (29), expressed in centimetres deflection of the middle of the thread per dyne.

From formulae (36) and (37) follows that

$$S = \frac{l}{8c_1} \dots \dots \dots (38)$$

And from (31) and (38) we derive that the tension is

$$S = \frac{Hl^2 b}{8 \times 10^6 c} \dots \dots \dots (39)$$

Substituting again for H , l and b their values, viz. $H = 17600$, $l = 12.7$ and $b = 660$, we find $S = 234 \times \frac{1}{c}$ dynes, which result, calculated in grammes, gives for the value of the tension

$$S = 0.239 \times \frac{1}{c} \text{ grammes} \quad (40)$$

We see from these formulae that the tension is inversely proportional to the sensitiveness.

For a sensitiveness $c = 1$ the tension would be 239 milligrammes. Assuming with THRELFALL¹⁾ that a thin quartz thread has a tensile strength of 100 kilogrammes per mM^2 section, when using a string of $2.39 \mu^2$ section or 1.75μ diameter, the sensitiveness of the galvanometer may be diminished to $c = 1$, i.e. to 1 mm. deflection for 1 micrampere without the thread breaking. The strongest tension we applied with string n^o. 14 corresponds to a sensitiveness of 1 mm. deflection for 3×10^{-7} Amp., hence $c = 3.3$, while the diameter of the string amounts to 1.7μ .

From these data it appears that the maximum tension used by us is still 3 times smaller than the tensile strength of the string. We remark here that this limit has only been calculated for the quartz, while the silver which might also contribute something to the strength has been left out of account.

String n^o. 10, when uncoated, has a diameter of 2.4μ . From this we calculate that it will bear such a tension that the sensitiveness of the galvanometer is reduced to a minimum of $c_{\min} = 0.529$. The maximum of the practically applicable sensitiveness is $c_{\max} = 10^5$.

The ratio $\frac{c_{\max}}{c_{\min}} = 1.89 \times 10^5$ indicates the possible variation in sensitiveness, which may undoubtedly be called enormous.

The value found for c_{\max} gives rise to some remarks about the corresponding tension S_{\min} . According to formula (40) we should find for $c = 10^5$ a tension of 2.39×10^{-6} grammes, an absurd value, since the weight of string n^o. 10, here used as an example, amounts to 6.85×10^{-6} grammes, i.e. nearly three times more, and since of course the tension in a vertically stretched string cannot possibly be less than its weight. But this absurd result is easily explained by remembering that formula (40) only holds if the quartz thread is strongly stretched and so behaves as a string, which was premised in the calculation of the tension.

From the results obtained we must conclude that with feeble tension the quartz thread no longer moves like a string. There are sufficient data to prove that the motion of the quartz thread does not even completely agree with the vibration of a string when the

¹⁾ Philosoph. Magaz. Vol. 30 (5), p. 99. 1890.

sensitiveness has been diminished to $c = 100$ and hence the tension is over 300 times the proper weight of the thread.

We must not lose sight of the fact that besides the stretching arrangement there are various forces which act on the quartz thread. If the thread is so thin that its elasticity may be neglected while only gravity has to be reckoned with, it will assume, when entirely relaxed, the shape of a catenary. If it is paramagnetic it will be bent towards one of the poles in the strong magnetic field which is never perfectly homogeneous. And if its elasticity may not be neglected, it will assume shapes, determined by the position and the direction of the extremities at the places of attachment, while also a slight torsion about the longitudinal axis may make itself felt.

When the tension of the thread is gradually increased by screwing the upper end of the thread upwards, it is easy to observe with the microscope the moment at which the thread is pulled straight.

Before the thread is straight its middle will be displaced nearly in a horizontal plane when the stretching arrangement is screwed up. After the thread has been pulled straight the middle is displaced upwards on account of the elongation of the thread, this displacement being half that of the extremity of the thread. The thread once having been pulled straight, already a small increase in tension will force it to move like a stretched string.

The results of the calculation about the tension of the quartz thread are in agreement with the relation existing between this latter and the distance of the two extremities of the thread. Of most of the quartz threads it might be assumed that they were just on the verge of being stretched when their sensitiveness corresponded to about 1 mm. deflection for 10^{-8} Amp., or $c = 100$. In this position very small changes in the mutual distance of the extremities cause already great differences in the sensitiveness. But when the mutual distance of the extremities has once been so far shortened or lengthened that the sensitiveness has thereby become either considerably increased, e. g. to 1 mm. deflection for 10^{-10} Amp., or considerably reduced, e. g. to 1 mm. deflection for 10^{-7} Amp., conditions are altered. Then great displacements can be given to the upper end of the quartz thread by means of the stretching arrangement, causing only relatively small changes in sensitiveness.

Further the sensitiveness of the thread, once stretched, shows an increase which is inversely proportional to the increase in length. So e. g. with string n^o. 13 the sensitiveness will be diminished for an extension of 100μ from $c = 100$ to $c = 10$, and for another 100μ from $c = 10$ to $c = 5$. The sensitiveness is inversely proportional

to the tension so that we may say that the increments of the tension are proportional to the increments of the length, which must be expected for a stretched elastic thread. For increments in length of ratios 0 : 1 : 2 the increments in tension are as $\left(\frac{1}{100}\right) : \frac{1}{10} : \frac{1}{5}$ or as $\left(\frac{1}{10}\right) : 1 : 2$.

We now proceed to derive the factor $\frac{\pi^2}{8}$ in formula (29) and suppose again that the string is strongly stretched and is placed over its whole length in a homogeneous magnetic field.

According to the laws, obeyed by the vibrations of a string, we have :

$$S = \frac{4lm_1}{\tau_1^2},$$

in which τ_1 denotes the period in seconds if no damping were present, while, as was mentioned before, S represents the tension in dynes, l the length in centimetres and m_1 the real mass of the string in grammes.

Now by formula (38) we also have $S = \frac{l}{8e_1}$ so that we may write

$$\frac{4lm_1}{\tau_1^2} = \frac{l}{8e_1}$$

or

$$m_1 = \frac{\tau_1^2}{32e_1} \dots \dots \dots (41)$$

From formula (4) we know that $\tau = 2\pi\sqrt{mc}$ or $m = \frac{\tau^2}{4\pi^2c}$, from which follows, having regard to formula (41), that

$$\frac{m_1}{m} = \left(\frac{\tau_1}{\tau}\right)^2 \times \frac{c}{e_1} \times \frac{\pi^2}{8},$$

and since $\frac{\tau_1}{\tau} = \frac{T_1}{T}$ we may also write

$$m_1 = m \times \left(\frac{T_1}{T}\right)^2 \times \frac{c}{e_1} \times \frac{\pi^2}{8}.$$

This formula is identical with formula (29) which proves that the factor sought by us is indeed $\frac{\pi^2}{8}$.

We make a short digression here about the calculation of the sought factor for the case that the motion of the quartz thread deviates from the vibration of a string. We shall still assume, however, that the thread is over its whole length in a homogeneous magnetic field.

In the first place it is easy to tell when the sought factor must be equal to unity. The stretched thread ought then always to move perpendicularly to its length, and ought to execute in its entirety exactly the same movements which in reality are only executed by the middle of the string.

In the second place we shall make the calculation for the case that the two halves of the thread after deflection, form the two sides of an isosceles triangle, while we assume that the movements of the middle of the thread are the same as those of the middle of a real string. The sought factor then gets the value $\frac{3}{2}$ and is found in the following manner.

The kinetic energy of the thread is calculated while it is in the phase of its quickest motion. Let the velocity of the middle of the thread then be v_1 and let the mass xm_1 be distributed evenly over the whole length of the thread. Under these circumstances and with the assumption that the two halves of the thread always remain straight lines, the kinetic energy is

$$E = \frac{xm_1v_1^2}{6} (42)$$

Let the first mentioned imaginary thread for which we found the factor 1 have a mass m_1 and let it execute the same movements as the middle of the last mentioned thread. Then its energy in the same phase of motion will be

$$E_1 = \frac{m_1v_1^2}{2} (43)$$

Call the permanent deflection u_1 and the total ponderomotive force k , then the work done by the ponderomotive force when a deflection has been made, is

in the first case $E_1 = k \times u_1,$

in the second case $E = k \times \frac{1}{2} u_1,$

so that $E_1 = 2 E (44)$

From formulae (42), (43) and (44) now follows that

$$\frac{xm_1v_1^2}{3} = \frac{m_1v_1^2}{2}$$

and consequently that $x = \frac{3}{2} .$

9. *The practicability of the string galvanometer for special purposes.*

For some purposes it may be desirable in order to judge of the

internal resistance would be 5180 ohms and the normal sensitiveness 35×10^6 .

We will now discuss some other conditions by which the practicability of the galvanometer for various purposes is determined.

Galvanometric methods may be divided into:

- I. Those in which an oscillating deflection is required.
- II. Those in which the deflection must preferably be aperiodic.

The first methods are subdivided into *IA*, those with a slow period as in an ordinary ballistic galvanometer, and *IB*, those with a quick period, as in the optical telephone of MAX WIEN and the vibration galvanometer of RUBENS.

The methods mentioned under *IA* are applied for the measurement of capacities and of small times by POUILLET'S method, in general always when small quantities of electricity have to be measured.

Now the properties of the string galvanometer enable us to measure these small quantities of electricity also with an aperiodic deflection. If the electric current is only of short enough duration the deflection of the string is in fact proportional to the quantity of electricity passed.

For the smallest quantity of electricity which can still be demonstrated we found on a former occasion ¹⁾ as the result of a rough calculation 5×10^{-12} ampere-seconds, corresponding to the charge of a sphere of 4.5 cm. radius at a potential of 1 volt. This calculation was for a deflection of 0.1 mm. of string n^o. 10. For string n^o. 18 the actual measurement was made. The sensitiveness appeared to be a little greater still: 1 mm. deflection for 4×10^{-11} coulombs, so that with this thread a quantity of 4×10^{-12} coulombs can be demonstrated.

But the sensitiveness for small quantities of electricity would still be considerably increased if the damping of the motion of the string could be removed or diminished, e.g. by enclosing the string in a vacuum. We should then obtain a slowly oscillating quartz thread which would be thousands of times more sensitive than the most sensitive ballistic galvanometers now existing.

IB. The string galvanometer can very well serve as an optical telephone or as a vibration galvanometer and so advantageously replace the telephone as well for measurements of self-induction as of electrolytic resistances.

¹⁾ See these "Proceedings" 6, p. 707, 1904.

For the first purpose I used it with good results¹⁾ when instead of the silvered quartz thread a thin metal wire was stretched between the poles of the electromagnet. It appeared to be very easy to make the period of the vibrations of the string agree with that of the alternating currents used. In a few seconds one has increased or diminished the tension of the string accurately to the desired amount and for my purpose neither the sensitiveness nor the certainty of the reading left anything to be desired.

If it should be necessary to increase the sensitiveness, a vacuum could be applied, by which one would be enabled to obtain less damped vibrations even of the lightest quartz thread. It must be remarked that a vacuum is not always necessary for obtaining little damped vibrations, especially when alternating currents of very short period, e. g. of 0.001 second and less are used. For the greater the tension of the quartz thread, the smaller the damping ratio becomes.

II. The methods in which the deflection of the galvanometer must preferably be aperiodic are distinguished as II A, those with slow, and II B, those with quick deflection.

II. A. Of those with slow deflection we choose two examples: the measurement of currents with great external resistance, such as is applied for examining insulation resistances and the measurement of currents with small external resistance such as thermo-currents.

In both these measurements deflections of long duration, e. g. of 10 to 20 seconds can be used with good result. Here the normal sensitiveness of the quartz thread in the galvanometer, as it is now mounted with strong air-damping in the Leyden laboratory, no longer plays a part. Under these circumstances the mass has only a small influence on the movement of the thread and the velocity of the deflection is chiefly determined by the amount of the damping. This latter only depends on the friction of the air when insulation resistances are measured.

If by applying a vacuum the movement of the quartz thread could be brought near the limit of aperiodicity and at the same time the deflection could be made slow by sufficiently relaxing the tension of the thread, an instrument would be obtained by which insulation resistances could be measured, many thousands of times greater than is now possible with the most sensitive galvanometers.

In the measurement of thermo-currents some of the good points of

¹⁾ Ueber Nervenreizung durch frequente Wechselströme. PFLÜGER'S Archiv f. d. ges. Physiol. 82, S. 101, 1900. See also "Onderzoekingen" Physiol. Laborat. Leyden. 2nd series IV and V.

the string galvanometer come out least. Besides the difficulty of the air-damping one meets here that of the electromagnetic damping, which soon becomes very considerable.

With unchanged strength of the field the electromagnetic damping is inversely proportional to the ohmic resistance of the circuit. With thread n° 10 the air-damping and electromagnetic damping are as 1 : 0.6, the ohmic resistance in the closed circuit being 10.000 ohms. When measuring an insulation resistance the electromagnetic damping vanishes and the thread will want about 15 seconds for a deflection, when the sensitiveness is regulated at 1 mm for 10^{-11} amp. When measuring a thermo-current, for which the external resistance in the circuit may be neglected and only the galvanometric resistance of 10.000 ohms has to be reckoned, for the same sensitiveness the duration of a deflection will be 1.6 times greater i.e. 24 seconds. Putting the condition that the duration of a deflection shall not exceed 15 seconds, one has to be contented with a 1.6 times less sensitiveness and obtains 1 mm deflection for 1.6×10^{-11} amp. or for 1.6×10^{-7} volt.

Since a deflection of 0.1 mm can still be observed in practice, the now existing galvanometer will be able to show a P. D. of 1.6×10^{-8} volt when thermo-currents are measured.

The application of a vacuum would only little increase the sensitiveness for small potential differences, and would not reduce the minimum to more than 0.6×10^{-8} volt. Also using a quartz thread with smaller resistance will only cause little change in this sensitiveness. If the ohmic resistance becomes n times less the smallest observable difference of potential will become $\left(\frac{1}{n} + 0.6\right) \times 10^{-8}$ volt.

But there are two means for increasing the sensitiveness for a potential difference, which must be mentioned. They consist in making the strength of the field smaller and in shortening the quartz thread.

We suppose the string to be placed in a vacuum so that the damping of its motion is only caused by electromagnetic influences. It is further assumed that the deflections are aperiodic and so slow that the influence of the mass of the string on its velocity of motion may be neglected. If under these conditions the strength of the field is reduced a times, and at the same time the tension of the string a^2 times, for an equal duration of a deflection the sensitiveness will be a times increased.

But it is easy to show that a useful diminution of the intensity of the field cannot be driven very far. For it must be remembered

that the influence of the mass of the string on its velocity of motion can only then be neglected, if a strong damping is present.

If by diminishing the intensity of the field one goes on reducing the damping, and yet wishes to retain the aperiodicity of the deflection, one will be at last obliged to make the quartz thread, the ohmic resistance remaining the same, still lighter than it is already.

We can generalise these considerations, and at the same time calculate the obtainable maximum of sensitiveness for thermo-currents in absolute measure, if we proceed as follows.

We put the condition that the deflection of the thread shall be aperiodic and that the duration of a deflection shall not exceed a pre-determined amount, e.g. 10 seconds. The most favourable conditions are then obtained if the movement of the thread is just brought at the limit of aperiodicity.

We further assume that of damping influences only the electromagnetic damping has to be reckoned, either because the thread is in a vacuum, or because the electromagnetic damping has so increased that relatively to it the air-damping may be neglected.

At the limit of aperiodicity the formula, mentioned at the close of chapter IV, holds :

$$c = \frac{4m}{r^2} \dots \dots \dots (26)$$

and besides

$$\mathbf{T} = \frac{2m}{r},$$

in which \mathbf{T} represents the time constant¹⁾.

Both formulae refer to the [mm— μA] system. Expressing r_1 in dynes, m_1 in grammes and \mathbf{T}_1 in seconds, we get

$$r_1 = \frac{l^2 H^2}{v} \times \frac{2}{\pi} \times 10^{-9} \text{ dynes} \dots \dots \dots (46)$$

$$c = \frac{m_1 l H}{r_1^2} \times \frac{32}{\pi^2} \times 10^{-6} \text{ b millimetres per micrampere.} \dots (47)$$

and

$$\mathbf{T}_1 = \frac{m_1}{r_1} \times \frac{16}{\pi^2} \text{ seconds} \dots \dots \dots (48)$$

From formulae (46), (47) and (48) we derive that

$$c = \frac{v}{Hl} \times 10^3 \pi \times b \mathbf{T}_1 \dots \dots \dots (49)$$

1) See FLEMING, l. c. p. p. 377 seq.

Calling c_s the sensitiveness for a potential difference, expressed in millimetres deflection per microvolt, we have

$$c = c_s w$$

from which follows, together with formula (49) that

$$c_s = \frac{1}{Hl} \times 10^3 \pi \times b \mathbf{T}_1 \dots \dots \dots (50)$$

We further derive from formulae (46) and (48) that

$$\mathbf{T}_1 = \frac{m_1 w}{l^2 H^2} \times \frac{8 \times 10^9}{\pi} \dots \dots \dots (51)$$

These last two formulae (50) and (51) furnish us with all the data for easily examining the influence of various changes in the galvanometer on its sensitiveness for thermo-currents.

In the first place we point out that making a thread thinner or thicker has no influence on the sensitiveness c_s , if only the product $m_1 w$ in formula (51) remains unaltered.

Using a metal wire, the value of $m_1 w$ remains naturally the same however the thickness of the wire may vary, if always wires of the same metal and of the same length are used. It may be advantageous to use a heavy, thick wire, since then the air-damping may be neglected, without the wire requiring to be placed in a vacuum. Also the practical difficulties of applying a very feeble tension may perhaps in this case be more easily solved by means of an elastic stretching arrangement than when a thin wire is used.

In the second place we point out that by formula (50) the sensitiveness c_s is inversely proportional to the intensity of the field and to the length of the wire.

We first give our attention to the intensity of the field and imagine a thread of constant length $l = 12.7$ cm. The question how far the intensity of the field may under these conditions be diminished, can be answered by means of formula (51).

In order to raise the sensitiveness to a maximum, the field strength must be reduced to a minimum. If \mathbf{T}_1 and l are constant, then according to (51) $m_1 w$ must be made a minimum. Using a thread of homogeneous material, $m_1 w$ is only determined by the nature of the material, so that the question about the minimum of H is reduced to the question for what material $m_1 w$ is a minimum. As far as I can judge this is the case for aluminium, which has for $l = 12.7$ cm. a value of $m_1 w_{Al} = 1.394 \times 10^{-3}$.

Assuming for \mathbf{T}_1 the value 2.5 seconds, the deflection has been nearly completed after 10 seconds. A distance of 1.85 % of the total deflection remains to be travelled through then. After 12.5 sec. this

distance has been reduced to 0.68 %, after 15 seconds to 0.25 % of the total deflection.

Now putting in formula (51) $\mathbf{T}_1 = 2.5$, $l = 12.7$ and $m_1 w$ as minimum $= 1.394 \times 10^{-3}$, the minimum of H works out at 940 (C.G.S.) By formula (50) we calculate from this the maximum of sensitiveness $c_s = 434$ mm per microvolt.

Let us now consider the shortening of l . If a limit was soon found where diminution of H ceased to be useful, this is not the case with the shortening of l , which may be pushed as far as we like as long as no practical difficulties are met with. By making l shorter e.g. a times, as well the mass as the ohmic resistance are each reduced a times. The value of $m_1 w$ thus becomes a^2 times less, so that \mathbf{T}_1 remains unaltered (formula 51) and the sensitiveness c_s (formula 50) becomes a times greater.

A last remark may follow about the two formulae (50) and (51). We first assume that they are both valid, and that the values of $m_1 w$, l and H have been so chosen that $\mathbf{T}_1 = 2.5$. We next assume that the mass m_1 is changed, while all the rest of the instrument, including w , remains constant, and ask how the movement of the wire is altered by this. When m_1 is increased, the motion of the wire becomes oscillatory. When m_1 is diminished the motion remains aperiodic but transgresses the limit of aperiodicity. The duration of the deflection is lengthened while the sensitiveness remains the same.

This latter case agrees with the actual conditions in the string galvanometer used by myself. The mass of the quartz thread is in reality very small. If it were $= 0$ the duration of the deflection would be exactly twice as great as when m_1 possessed the desired value. Hence there is under these circumstances an advantage in increasing the mass of the wire to a certain value.¹⁾

String n^o. 18 has a mass and an air-damping which were not accurately measured, but which will not differ much from the corresponding values of string n^o. 10. Its ohmic resistance is about 2 times smaller, however, and amounts to 5100 ohms. With a time of deflection of about $\frac{1}{2}$ minute the sensitiveness is $c_s = 20$ mm. per microvolt. If I could increase the mass of this string in a practicable manner, I should with unaltered sensitiveness bring the

¹⁾ The time constant is doubled when $m = 0$. See FLEEMING l. c.

It may be superfluous to remark that for the measurement of insulating resistances increase of m_1 will offer the same advantages as were mentioned above for the measurement of thermo-currents.

motion at the limit of aperiodicity, and obtain a time of deflection of about 15 seconds.

We remark here that thread n^o. 18 may easily be so feebly stretched that its time of deflection becomes about one minute, by which the sensitiveness is increased to $c_s = 40$ mm. per microvolt. Since, as is proved by the photograms, 0.1 mm. can still be read off, with thread 18 a P.D. of 2.5×10^{-9} volt can actually be demonstrated. Also with this feeble tension of the thread the zero point remains constant, while the image of the quartz thread remains sharp over a pretty long part of the scale. It may be considered remarkable that one should be able to displace so slowly with the greatest regularity a suspended little thread of only a few thousandths of a milligramme weight.

II *B*. We now come to the methods in which the deflection of the galvanometer must be aperiodic and at the same time quick.

These methods in the first place find an application in electro-technics, e. g. for investigating the shape of the oscillations of potential and current obtained by means of dynamos, interrupters, induction apparatus, etc. For these purposes the oscillograph is already used with good results, which instrument possesses a considerably smaller sensitiveness than the string galvanometer, but yet can be of excellent service in the measurement of stronger currents.

In the second and for our purpose most important place the methods mentioned under II *B* find their application in electrophysiology. Here in many cases the string galvanometer cannot be replaced by any other instrument.

A number of electrophysiological investigations of the most various kind can be made with the same string. So in the laboratory the same string n^o. 18 is now used for investigating the electrocardiogram, cardiac sounds and sounds generally, retinal currents and nerve currents. Yet we will briefly discuss here the conditions which must be fulfilled by a string, chosen from a number of available strings, in order to yield the best results in a certain electrophysiological investigation.

Let us begin with the tracing of the human electrocardiogram. The current may here be derived from both hands. The hands and lower arms are immersed in large porous pots, filled with a solution of NaCl, placed in glass vessels, containing a solution of ZnSO₄. In the zinc sulphate solution are amalgamated zinc cylinders, connected by connecting wires with the galvanometer. Under these circumstances the ohmic resistance of the human body varies with different persons from 1000 to 2000 ohms, an amount considerably smaller than the

resistance of a thin, silvered quartz thread. Of the formerly mentioned quartz threads 10, 13 and 14, thread 13 will give the best results in tracing the electrocardiogram, since of this thread the ohmic resistance is smallest. To be sure, the normal sensitiveness of thread 14 is about 1.4 times greater, but the currents, received by this thread from the pulsating heart, will be about twice weaker on account of the greater resistance.

Besides having a smaller ohmic resistance thread 13 has over thread 10 the additional advantage of possessing a smaller air-resistance to its motion. This latter property here plays an important part. For in order to obtain deflections of practicable magnitude, e.g. of 10 to 15 mm., the sensitiveness of the galvanometer must be so adjusted that a potential difference of 10^{-4} volt in the circuit corresponds to 1 mm. ordinate. For obtaining this the quartz thread must be rather feebly stretched, so that the deflections are aperiodic and under these circumstances a diminution of the resistance to the motion of the string will cause a quicker deflection.

Sticking to the condition that a potential difference of 10^{-4} volt shall correspond to 1 mm. ordinate, we trace with string 13 a human electrocardiogram which is almost absolutely accurate.

With string 10 and especially with string 14, however, curves are then recorded which require corrections. Although the amounts of these corrections are small, and do not go beyond a whole millimetre, so that in many cases they may be neglected, it is not superfluous briefly to remember here the cause of these deviations. It is found in the relation between the velocity of the deflection of the galvanometer and the velocity of the oscillations in potential caused by the action of the heart.

The quicker the galvanometer deflects, the more accurate the photogram of the oscillation of potential will be.

The sensitiveness of string 14 must be so adjusted for tracing the human electrocardiogram that about 1 mm. ordinate corresponds to 0.5×10^{-8} amp. Now with this quartz thread the limit of aperiodicity is in a circuit with small external resistance only reached with an about four times greater tension of the string. If by applying a vacuum the resistance to the motion of the string could be diminished so that the limit of aperiodicity were already reached at the first mentioned sensitiveness, when tracing the electrocardiogram the velocity of motion of the string would be considerably increased, so that then also string 14 might reproduce the oscillations of potential with almost absolute accuracy.

We now pass to the discussion of a second example from electro-

physiology, the investigation of the action-currents of a nerve. Here the galvanometer has to fulfill conditions which in many respects differ from those described above. Choosing as our object the nerve of a frog, from which the current must be led to the galvanometer, we shall have to count with a great external resistance, e.g. of 10^5 ohms.

Compared with this the resistance of the galvanometer, even that of thread n°. 14 may be called small. The potential difference caused by the action of the nerve, and available for the current to be measured, is considerably greater than that which is met with in the investigation of the human electrocardiogram, but the duration of a nerve action current is shorter and is measured by only a few thousandths of a second.

These data show us the way in choosing a quartz thread.

In the first place we easily perceive that the differences in the ohmic resistance of the quartz threads can only have an insignificant influence on the intensity of the action current, since the resistance of the nerve itself in the circuit is preponderant. Further, the deflection of the quartz thread must be very quick, hence the tension great; and since an oscillating deflection must be avoided, it will be desirable to adjust the tension so that the motion of the string is brought to the limit of aperiodicity. But even under these circumstances the deflection is not quick enough for accurately reproducing the action current of the nerve. We must therefore apply means that enable us to increase the velocity of deflection without the motion becoming oscillatory. We shall have to try to increase the damping, and can for this purpose apply with good result the "condenser method" formerly described by us.¹⁾

So we come to requirements here which are opposed to those which we had repeatedly to put in the above described methods. Whereas applying a vacuum had then to be considered an important advantage, now increasing the damping becomes an urgent necessity.

Under these conditions the conception of a normal sensitiveness comes out to its full advantage and it may be briefly stated that of a number of threads of equal ohmic resistance that with the greatest normal sensitiveness is to be preferred. If the external resistance in the circuit is great compared with the resistance of the galvanometer, then of a number of threads with equal normal sensitiveness that with the greatest ohmic resistance will have to be preferred.

For the investigation of the action current of the nerve of a frog,

¹⁾ See these "Proceedings" 7, p. 315. 1904.

among the three threads mentioned, n^o. 14 will have to be preferred, since the amount of the normal sensitiveness as well as the resistance of this thread exceed those of the two other threads.

Finally we make some remarks as to the manner in which the velocity of deflection may be raised to a maximum. A great velocity is in general obtained at the expense of the sensitiveness. But there are a number of investigations, notably the recording of sounds,¹⁾ in which the sensitiveness of the string galvanometer may be very considerably diminished. Even when the string, at the risk of breaking, is stretched to its maximum and hence its sensitiveness reduced to a minimum, relatively feeble sounds can still drive the image of the string out of the field of vision.

By strongly stretching string 14 we could impart to it an oscillatory motion of which the period was $T = 1,41 \sigma$. If the oscillations were damped by means of the condenser method, a deflection could be obtained, requiring a time of $0,8 \sigma$ and proportional to the current to be measured with an error of 3%²⁾. If an accuracy of 0,3% was desired, one had to be contented with a time of deflection of $2,2 \sigma$. The sensitiveness was here 1 mm deflection for 3×10^{-7} amp.

From the data of the preceding chapter follows that under these conditions the tension of string 14 can be still 3 times increased before its breaking point is reached. Hence if the string is so strongly stretched that it is at the point of breaking, its deflections will become $\sqrt{3}$ times quicker, so that its oscillations will show a period $T = 0,815 \sigma$. In practice we have not raised the tension of string 14 so high, however.

The question how to obtain quicker oscillations was simply solved by using a shorter wire. String 20, which was already discussed above, has a diameter of 1μ and is 25 mm long. With a practicable tension that could be applied without risk of breaking, it performed with a sensitiveness of 1 mm deflection for 10^{-5} amp. oscillations of a period of $0,31 \sigma$.

This period corresponds to a tone of 3230 vibrations per second, about g^4 sharp or almost the highest tone of an ordinary piano. We remark that the string can still be shortened and be more strongly stretched, so that a much higher number of vibrations can easily be reached, while it must also be borne in mind that a string with slow deflection can yet very accurately record sound vibrations

1) On the method of recording sounds see these "Proceedings" 6 p. 707, 1904.

2) See these "Proceedings" 7, p. 315, 1904.

of high frequency. So strings 10, 13 and 14 reproduced with feeble tension and slow deflection the sound waves of a tuning fork of 2380 whole vibrations per second. The recorded period was about 24 times shorter than the proper period of the quartz thread. If the same ratio of periods holds for string 20, this latter must be able to reproduce with ease tones of 77000 whole vibrations per second. On a following occasion I hope to return to the recording of sounds. Also a discussion of the practical execution of some of the experiments described above and a description of different designs of the string galvanometer will have to be postponed to a following paper.

Zoology. — “*On a new species of Corallium from Timor.*” By SYDNEY J. HICKSON, Professor of Zoology in the Victoria University of Manchester. (Communicated by Prof. MAX WEBER).

The species of corals included in the family Coralliidae have been arranged by systematists in the four genera, *Corallium*, *Pleurocorallium*, *Hemicorallium* and *Pleurocoralloides*.

The genus *Hemicorallium* of Gray was merged with *Pleurocorallium* by Ridley in 1882, and quite recently KISHINOUE has called attention to the difficulty there is in maintaining the distinction between *Pleurocorallium* and *Corallium*.

One of the principal characters of *Pleurocorallium* is the presence in the coenenchym of peculiar twinned spicules which Ridley calls “opera-glass” shaped spicules. These “opera-glass” shaped spicules are not supposed to occur in the genus *Corallium*. Whether future investigations will support the view of KISHINOUE or not is a question which need not be considered here, but the absence of “opera-glass” shaped spicules in the specimen about to be described justifies its position in the genus *Corallium*, that is, to the genus that includes *Corallium nobile* the precious coral of the Mediterranean sea and the seas of the Cape Verde islands and *Corallium japonicum* one of the precious corals of the Japanese seas.

Before proceeding to a description of the new species a few words may be written concerning the geographical distribution of the family. *Corallium nobile* occurs in the Mediterranean sea and off the Cape Verde islands. Some species attributed to the genus *Pleurocorallium* occur off the island Madeira, and quite recently a specimen of *Pseudocorallium johnsoni* has been dredged off the coast of Ireland.

Off the coast of Japan occurs *Corallium japonicum* and several species which would be included on the old system in the genus *Pleurocorallium* but are referred to the genus *Corallium* by KISHINOUE.

Isolated specimens of Coralliidae were also obtained off Banda in 200 fathoms, the Ki islands 140 fathoms and Prince Edward Island 310 fathoms by the Challenger and there is a doubtful record of a specimen of *Pleurocorallium secundum* from the Sandwich islands. Fisheries of more or less importance have been carried on in the Mediterranean Sea, off the Cape Verde Islands and off the coast of Japan, but there is not, I believe, any historical record of a systematic fishery for precious coral in any other part of the world.

In 1901 the value of the coral obtained off the coast of Japan was over £ 50,000 and it is a fact of considerable interest that a large part of this was exported by the Japanese to Italy.

The coral Fishery of Japan is of very recent growth for in the time of the Daimyos the collection and sale of coral was prohibited, and it was not until the time of the Meji reform 1868 that it began to assume important dimensions.

That the Japanese of old times valued the precious coral is shown in the numerous "Netsukes" and other ornaments which are decorated with it; but the origin of this coral is not definitely known.

On many of the Netsukes the coral is represented in the hands of darkskinned fishermen, "Kurombo"; never in the hands or nets of the Japanese.

Now the art of Japan is quite sufficiently accurate to prove that the Kurombo were not Ainos nor Japanese, nor Malays nor Europeans; but the curly-hair, the broad noses and other features that are consistently shown render it almost certain that the Kurombo were Melanesians or Papuans.

The only regions where such folk live that have hitherto yielded specimens of precious coral are the Banda seas. As already mentioned the Challenger discovered precious coral in deep water off the Banda and Ki islands, but the specimens were "dead" and it was consequently impossible to determine definitely to what species they belong, but they were referred by Ridley to the species *Pleurocorallium secundum*.

In the material that was kindly sent to me by Prof. MAX WEBER from the rich collections of H. M. SIBOGA there were a few small pieces of a beautiful coral which I recognised at once to be a Coralliid. There can be no doubt that it was alive when captured by the dredge and it reached me, not fully expanded, but in a good state of preservation.

The locality of this find was station 280 i. e. at a depth of 1224

metres in the middle of the strait that separates the E. end of the island of Timor from the small island Lette or in other words on the Southern boundary of the Banda Sea.

The axis of this coral is covered with very little or hardly any crust, is apparently as hard as the best Italian coral and is of a good colour, although a little darker than that which is regarded by the jewellers as the best quality.

The discovery of this specimen suggests that the dark skinned "Kurombo" fisherman that supplied the ancient Japanese jewellers with their precious coral, lived some where within the region of Timor. It is of course improbable that they were able to fish in such a great depth as 1224 metres, but as the species of *Corallium* range in depth from 10 fathoms to several hundred fathoms, it is quite possible that they had knowledge of shallow waters off their coast where the coral grew abundantly.

It is not for me to suggest that there is a prospect of a valuable coral fishery in the Banda seas; but now that it is known that living precious coral does occur in deep water in this region of the world it would not be a matter of surprise to scientific men if it were subsequently found at depths sufficiently shallow to be obtained by ordinary fishing boats.

The specimen obtained by the Siboga does not agree exactly with any known Coralliidae in those characters which are used by systematists for the separation of species and it is necessary to find a new name for it, and I should like with Her royal permission to name it *Corallium reginae* in honour of Her Majesty the Queen of Holland whose interest in Zoological Science in general and in the researches of H. M. Siboga in particular has been manifested on more than one occasion.

The specimen agrees with other species of the genus *Corallium* in the absence of the curious "opera glass" shaped spicules and the presence of spicules of the octoradiate type only in the general coenenchym.

It differs from *Corallium* and agrees with many species referred to the genus *Pleurocorallium* in having the branches arranged principally in one plane and the zooids scattered irregularly on one face or surface of this plane.

The autozooids are indicated by well-defined verrucae projecting about 1—5 m.m. from the general surface of the coenenchym. These verrucae are large as compared with other species being about 1—4 m.m. in diameter. The coenenchym is thin, and the axis hard and

either not marked or very faintly marked in some places by longitudinal striations.

The base of the main stem of the specimen is 6 m.m. in diameter and the primary branches are 4—5 m.m. in diameter.

Some further particulars concerning the anatomy of the species will be described with illustrations in a future publication. For the present the diagnosis of the species given above is sufficient. Before concluding this preliminary note I have, with very great regret, to record that on Sept. 22nd a fire broke out in my laboratory and some portions of the specimen were seriously burned and scorched. Fortunately there is still a considerable fragment that appears to be uninjured.

Physics. — “*Properties of the critical line (plaitpoint line) on the side of the components.*” By Prof. VAN DER WAALS.

By CENTNERSZWER and SMITS' observations, by a remark of VAN 'T HOFF and by VAN LAAR's calculations ¹⁾ a discussion has been carried on on the rise of the critical temperature of a substance in consequence of an admixture. In this it has been perfectly overlooked that already more than ten years ago the principal properties of the critical line, and also the properties at the beginning and at the end of this line were discussed and determined by me ²⁾.

For normal substances, I found by a thermodynamic method, which is a perfectly sure way, for the quantity mentioned the formula (9) (l. c. p. 89)

$$T \left(\frac{dx}{dT} \right)_0 = \frac{\frac{\partial^2 \varepsilon}{\partial v^2}}{\frac{\partial^3 \psi}{\partial x \partial v^2} - \frac{1}{MRT} \left(\frac{\partial^2 \psi}{\partial x \partial v} \right)^2}$$

I shall explain further on why I make some reservation for abnormal substances.

And with the aid of the equation of state I derived from (9) formula (11)

$$\frac{d \log T}{dx_0} = \frac{d \log \frac{a}{b}}{dx_0} + \frac{9}{16} \left(\frac{d \log \frac{a}{b^{2/3}}}{dx_0} \right)^2$$

¹⁾ These Proc. p. 144.

²⁾ Verslag Kon. Akad. v. Wet. 25 Mei 1895, p. 20 and 29 Juni 1895, p. 82.

As in this derivation of (11) from (9) the quantity b of the equation of state was supposed constant, (11) must only be considered as an approximation.

If for the present we keep to this form, (11) may also be written :

$$\frac{dT}{T dx_0} = \frac{dT_z}{T_z dx_0} + \frac{9}{16} \left(\frac{dT_z}{T_z dx_0} + \frac{1}{3} \frac{db}{b dx_0} \right)^2 \dots \dots (1)$$

And taking into consideration that $b = \frac{T_z}{8 \times 273 p_z}$ we find finally :

$$\frac{dT}{T dx_0} = \frac{dT_z}{T_z dx_0} + \left(\frac{dT_z}{T_z dx_0} - \frac{1}{4} \frac{dp_z}{p_z dx_0} \right)^2 \dots \dots (2)$$

The quantity T_z occurring in this equation, represents the critical temperature of the unsplit mixture. For this quantity I have already demonstrated in my *Théorie Moléculaire* that it may get a minimum value for some sorts of mixtures — and the observations of KUENEN, QUINT and others have furnished instances of the existence of such a minimum value. If the admixture should be of such a nature that such a minimum value existed, it would, of course, be perfectly absurd to substitute $T_{z_2} - T_{z_1}$ for $\frac{dT_z}{dx}$. But the existence of such a minimum critical temperature is only to be expected, at any rate only observed, when T_{z_2} and T_{z_1} differ little. When they differ much, $\frac{dT_z}{dx_0}$ can be represented by $T_{z_2} - T_{z_1}$ at least with approximation. As b depends on x linearly at least with some approximation, we may write

$$\frac{1}{b} \frac{db}{dx_0} = \frac{\frac{T_{z_2}}{p_{z_2}} - \frac{T_{z_1}}{p_{z_1}}}{\frac{T_{z_1}}{p_{z_1}}}$$

Let us with these approximate values compare equation (1) with KEESOM's observations on the mixtures of carbonic acid and oxygen ¹⁾. The critical temperatures of these substances differ sufficiently to enable us to use the approximate values. T_{z_2} (for oxygen) is namely about half of T_{z_1} (that of carbonic acid) — and so we put for $\frac{dT_z}{T_z dx_0}$ the value $\frac{154,2 - 304,02}{304,02} = -0,493$, and for

$$\frac{1}{b} \frac{db}{dx_0} \text{ the value } \frac{\frac{154,2}{50,7} - \frac{304,02}{72,93}}{\frac{304,02}{72,98}} \text{ or } -0,271. \text{ With these values}$$

¹⁾ These Proc. VI, p. 616.

we find:

$$\frac{dT}{Tdx_0} = -0,493 + \frac{9}{16} (-0,493 - 0,0903)^2 = -0,493 + 0,1914 = -0,302.$$

The value found by KEESOM for $x = 0,1047$ is $\Delta T = -8,99$. Supposing this value of x small enough to be substituted for dx_0 , we

$$\text{find } \frac{dT}{Tdx_0} = -0,284.$$

For $x = 0,1994$ this value of ΔT found by KEESOM is equal to $-18,47$; with these data we should find $\frac{dT}{Tdx_0} = -0,304$, so perfectly equal to the value calculated by means of (1). We have here not a molecular increase of the critical temperature, but a decrease, as indeed, was to be expected, because we had to do with the addition of a more volatile component.

Though I derived formula (9), on which formula (11) of 1895 and formula (1) of this communication are founded, in more than one way in my two communications of 1895, I will derive them once more here in order to have an opportunity to discuss somewhat more fully some questions which present themselves in the derivation.

For the plaitpoint line the simple relation:

$$\frac{dp}{dT} = \frac{\left(\frac{\partial^2 \eta}{\partial x^2}\right)_{pT}}{\left(\frac{\partial^2 v}{\partial x^2}\right)_{pT}},$$

holds, which, $\left(\frac{\partial^2 \eta}{\partial x^2}\right)_{pT}$ not being directly known, may be brought under the following form:

$$T \frac{dp}{dT} = T \left(\frac{dp}{dT}\right)_{vx} + \frac{\left(\frac{\partial^2 \epsilon}{\partial v^2}\right)_{xT} \left(\frac{dv}{dx}\right)_{pT}^2 + 2 \left(\frac{\partial^2 \epsilon}{\partial x \partial v}\right)_T \left(\frac{dv}{dx}\right)_{pT} + \left(\frac{\partial^2 \epsilon}{\partial x^2}\right)_{vT}}{\left(\frac{d^2 v}{dx^2}\right)_{pT}}.$$

The factors of $\left(\frac{dv}{dx}\right)_{pT}^2$ and $\left(\frac{dv}{dx}\right)_{pT}$ and also $\left(\frac{\partial^2 \epsilon}{\partial x^2}\right)_{vT}$ being finite quantities, and on the other hand $\left(\frac{dv}{dx}\right)_{pT}$ being infinitely great, when the plaitpoint lies at $x = 0$, we may write for this case:

$$T \frac{dp}{dT} = T \left(\frac{dp}{dT}\right)_{vx} + \left(\frac{\partial^2 \epsilon}{\partial v^2}\right)_{xT} \frac{\left(\frac{dv}{dx}\right)_{pT}^2}{\left(\frac{d^2 v}{dx^2}\right)_{pT}} \dots \dots \dots (3)$$

If we put $\frac{\partial^2 \psi}{\partial x^2} \frac{\partial^2 \psi}{\partial v^2} - \left(\frac{\partial^2 \psi}{\partial x \partial v} \right)^2 = f$, then $f = 0$, because the plaitpoint is a point of the spinodal line. In the same way:

$$\frac{\partial f}{\partial v} \left(\frac{dv}{dx} \right)_{pT} + \frac{\partial f}{\partial x} = 0$$

because it concerns a plaitpoint.

If we multiply the numerator and the denominator of the fraction occurring in (3) by $\left(\frac{\partial^2 \psi}{\partial v^2} \right)^2$, we get:

$$T \frac{dv}{dT} = T \left(\frac{dp}{dT} \right)_{vx} + \left(\frac{\partial^2 \epsilon}{\partial v^2} \right)_{xT} \frac{\left(\frac{\partial^2 \psi}{\partial x \partial v} \right)^2}{\left(\frac{\partial^2 \psi}{\partial v^2} \right)^2 \left(\frac{d^2 v}{dx^2} \right)_{pT}}$$

The value of $\left(\frac{d^2 v}{dx^2} \right)_{pT} \left(\frac{\partial^2 \psi}{\partial v^2} \right)^2$ we derive from:

$$\left(\frac{dv}{dx} \right)_{pT} = - \frac{\left(\frac{\partial^2 \psi}{\partial x \partial v} \right)}{\frac{\partial^2 \psi}{\partial v^2}}$$

and find then:

$$- \left(\frac{\partial^2 \psi}{\partial v^2} \right)^2 \left(\frac{d^2 v}{dx^2} \right)_{pT} = \frac{\partial^2 \psi}{\partial v^2} \frac{\partial^3 \psi}{\partial x^2 \partial v} - 2 \frac{\partial^2 \psi}{\partial x \partial v} \frac{\partial^3 \psi}{\partial x \partial v^2} + \frac{\frac{\partial^3 \psi}{\partial v^3}}{\frac{\partial^2 \psi}{\partial v^2}} \left(\frac{\partial^2 \psi}{\partial x \partial v} \right)^2$$

As for the critical point of a component both $\frac{\partial^2 \psi}{\partial v^2}$ and $\frac{\partial^3 \psi}{\partial v^3}$ is equal to 0, the last equation becomes:

$$- \left(\frac{\partial^2 \psi}{\partial v^2} \right)^2 \left(\frac{d^2 v}{dx^2} \right)_{pT} = \left(\frac{\partial^2 \psi}{\partial x \partial v} \right)^2 \lim \frac{\frac{\partial^3 \psi}{\partial v^3}}{\frac{\partial^2 \psi}{\partial v^2}} - 2 \frac{\partial^2 \psi}{\partial x \partial v} \frac{\partial^3 \psi}{\partial x \partial v^2}$$

The limiting value of $\frac{\partial^3 \psi}{\partial v^3}$ can be found from the equation which expresses that the critical point of the component is a plaitpoint, viz.:

$$\frac{\partial f}{\partial v} \frac{\partial^2 \psi}{\partial x \partial v} = \frac{\partial f}{\partial x} \frac{\partial^2 \psi}{\partial v^2} \quad ^1)$$

¹⁾ In a derivation of the discussed formula in my communications of 1895 I put $\frac{\partial f}{\partial v} = 0$. It would have been more accurate, if I had put this quantity infinitely small compared to $\frac{\partial f}{\partial x}$.

Now

$$\frac{\partial f}{\partial v} = \frac{\partial^3 \psi}{\partial x^2 \partial v} \frac{\partial^2 \psi}{\partial v^2} + \frac{\partial^2 \psi}{\partial x^2} \frac{\partial^3 \psi}{\partial v^3} - 2 \frac{\partial^2 \psi}{\partial x \partial v} \frac{\partial^3 \psi}{\partial x \partial v^2}$$

and

$$\frac{\partial f}{\partial x} = \frac{\partial^3 \psi}{\partial x^3} \frac{\partial^2 \psi}{\partial v^2} + \frac{\partial^2 \psi}{\partial x^2} \frac{\partial^3 \psi}{\partial x \partial v^2} - 2 \frac{\partial^2 \psi}{\partial x \partial v} \frac{\partial^3 \psi}{\partial x^2 \partial v}$$

or taking into consideration $\frac{\partial^2 \psi}{\partial x^2} \frac{\partial^2 \psi}{\partial v^2} = \left(\frac{\partial^2 \psi}{\partial x \partial v} \right)^2$ and $\frac{\partial^2 \psi}{\partial v^2} = 0$

$$\frac{\partial f}{\partial v} = \left(\frac{\partial^2 \psi}{\partial x \partial v} \right)^2 \lim \frac{\frac{\partial^3 \psi}{\partial v^3}}{\frac{\partial^2 \psi}{\partial v^2}} - 2 \frac{\partial^2 \psi}{\partial x \partial v} \frac{\partial^3 \psi}{\partial x \partial v^2}$$

and

$$\frac{\partial^2 \psi}{\partial v^2} \frac{\partial f}{\partial x} = \left(\frac{\partial^2 \psi}{\partial x \partial v} \right)^4 \lim \frac{\frac{\partial^3 \psi}{\partial x^3}}{\left(\frac{\partial^2 \psi}{\partial x^2} \right)^2} + \left(\frac{\partial^2 \psi}{\partial x \partial v} \right)^2 \frac{\partial^3 \psi}{\partial x \partial v^2}.$$

By equating $\frac{\partial f}{\partial v} \frac{\partial^2 \psi}{\partial x \partial v}$ and $\frac{\partial f}{\partial x} \frac{\partial^2 \psi}{\partial v^2}$ we find:

$$\frac{\partial^2 \psi}{\partial x \partial v} \lim. \frac{\frac{\partial^3 \psi}{\partial v^3}}{\frac{\partial^2 \psi}{\partial v^2}} - 2 \frac{\partial^3 \psi}{\partial x \partial v^2} = \left(\frac{\partial^2 \psi}{\partial x \partial v} \right)^2 \lim. \frac{\frac{\partial^3 \psi}{\partial x^3}}{\left(\frac{\partial^2 \psi}{\partial x^2} \right)^2} + \frac{\partial^3 \psi}{\partial x \partial v^2}.$$

For normal substances the limiting value of $\frac{\frac{\partial^3 \psi}{\partial x^3}}{\left(\frac{\partial^2 \psi}{\partial x^2} \right)^2}$ is known.

From $\psi = MRT \{ (1-x) l(1-x) + x l x \} - \int p dv$ follows:

$$\left(\frac{\partial \psi}{\partial x} \right)_v = MRT l \frac{x}{1-x} - \int \frac{\partial p}{\partial x} dv$$

$$\left(\frac{\partial^2 \psi}{\partial x^2} \right) = MRT \frac{1}{x(1-x)} - \int \frac{\partial^2 p}{\partial x^2} dv$$

$$\left(\frac{\partial^3 \psi}{\partial x^3} \right) = - \frac{MRT(1-2x)}{x^2(1-x)^2} - \int \frac{\partial^3 p}{\partial x^3} dv$$

for $x = 0$ we get $\frac{\frac{\partial^3 \psi}{\partial x^3}}{\left(\frac{\partial^2 \psi}{\partial x^2} \right)^2} = - \frac{1}{MRT}$.

For abnormal substances this quantity would probably be found of the same value, but this would require a closer investigation, into which I shall not enter here. For this reason I have made a reservation for abnormal substances above.

For the value of $\left(\frac{dp}{dT}\right)_{x_0}$ of the plaitpoint curve we get now the equation:

$$T \left(\frac{dp}{dT}\right)_{x_0} = T \left(\frac{\partial p}{\partial T}\right)_{vx} + \frac{\partial^2 \epsilon}{\partial v^2} \frac{\left(\frac{\partial^2 \psi}{\partial x \partial v}\right)}{\left(\frac{\partial^2 \psi}{\partial x \partial v}\right)^2 \frac{1}{MRT} - \frac{\partial^3 \psi}{\partial x \partial v^2}} \quad \dots \quad (4)$$

The critical point of the component is an homogeneous phase, in the same way the plaitpoint is a new homogeneous phase. But the quantities T_x, v_x and $x = 0$ increase by dT_x, dv_x and dx_0 . Hence:

$$dp = \left(\frac{\partial p}{\partial T}\right)_{cx} dT_x + \left(\frac{\partial p}{\partial x}\right)_{vT} dx_0 + \left(\frac{\partial p}{\partial v}\right)_{xT} dv_x$$

and $\left(\frac{\partial p}{\partial v}\right)_{xT}$ being 0, also

$$T \left(\frac{dp}{dT}\right)_{x_0} = T \left(\frac{\partial p}{\partial T}\right)_{cx} + \left(\frac{\partial p}{\partial x}\right)_{vT} \frac{T dx_0}{dT}$$

comparing with (4) we find the value sought of

$$\frac{dT}{T dx_0} = \frac{\frac{\partial^2 p}{\partial x \partial v} + \frac{1}{MRT} \left(\frac{\partial p}{\partial x}\right)_{vT}}{-\frac{\partial^2 \epsilon}{\partial v^2}}$$

According to the equation of state, supposing b constant, we get:

$$\epsilon = -\frac{a}{v}, \left(\frac{\partial \epsilon}{\partial v}\right) = \frac{a}{v^2} \text{ and } \frac{\partial^2 \epsilon}{\partial v^2} = -\frac{2a}{v^3}. \text{ The value of } \left(\frac{\partial p}{\partial x}\right)_{vT} \text{ is equal}$$

to $\left\{ \frac{MRT}{(v-b)^2} \frac{db}{dx} - \frac{da}{dx} \frac{1}{v^2} \right\}$ and of $\left(\frac{\partial^2 p}{\partial x \partial v}\right)$ equal to

$-2 \left\{ \frac{MRT}{(v-b)^2} \frac{db}{dx} - \frac{da}{dx} \frac{1}{v^3} \right\}$, and so

$$\frac{dT}{T dx_0} = \frac{2 \left\{ \frac{da}{dx} \frac{1}{v^3} - \frac{MRT}{(v-b)^3} \frac{db}{dx} \right\} + \frac{1}{MRT} \left\{ \frac{da}{dx} \frac{1}{v^2} - \frac{MRT}{(v-b)^2} \frac{db}{dx} \right\}^2}{\frac{2a}{v^3}}$$

or

$$\frac{dT}{T dx_0} = \left\{ \frac{da}{adx} - \frac{MRT}{a} \frac{v^3}{(v-b)^3} \frac{db}{dx} \right\} + \frac{a}{2vMRT} \left\{ \frac{1}{a} \frac{da}{dx} - \frac{MRT}{a} \frac{v^2}{(v-b)^2} \frac{db}{dx} \right\}^2.$$

If we put, as is found with constant value of b , $v = 3b$ and $MRT = \frac{8}{27} \frac{a}{b}$, we find the value given above:

$$\frac{d \log T}{dx_0} = \frac{d \log \frac{a}{b}}{dx} + \frac{9}{16} \left(\frac{d \log \frac{a}{b^{2/3}}}{dx_0} \right)^2$$

In what precedes the relation between the variation of T , and that of x has been discussed for the beginning of the plaitpoint line. Let us now proceed to the discussion of the relation between the variation of p and that of T .

From the equation of $\frac{dp}{dT}$ given above, we derive:

$$\left(\frac{T dp}{p dT} \right)_{x_0} = \frac{T}{p} \left(\frac{\partial p}{\partial T} \right)_{vx} + \frac{1}{p} \left(\frac{\partial p}{\partial x} \right)_{vT} \frac{T dx_0}{dT}$$

Now in the critical point of a component $\left(\frac{\partial p}{\partial T} \right)_v$ is equal to $\frac{dp}{dT}$ for the saturated vapour tension. And for numerous substances $\frac{T dp}{p dT}$ for the saturated vapour tension is about 7 in the critical point. $\frac{T dx_0}{dT}$ now being known, we want still the knowledge of $\frac{1}{p} \left(\frac{\partial p}{\partial x} \right)_{vT}$ for the calculation of $\left(\frac{T dp}{p dT} \right)_{x_0}$ for the plaitpoint line.

We can calculate $\frac{1}{p} \left(\frac{\partial p}{\partial x} \right)_{vT}$ by means of the equation of state.

If we put again b constant, we find the value indicated above:

$$\frac{1}{p} \left(\frac{\partial p}{\partial x} \right)_{vT} = \frac{1}{p} \left\{ \frac{MRT}{(v-b)^2} \frac{db}{dx} - \frac{da}{dx} \frac{1}{v^2} \right\}$$

or

$$\frac{1}{p} \left(\frac{\partial p}{\partial x} \right)_{vT} = \frac{a}{v^2} \left\{ \frac{8}{27} \frac{1}{b} \frac{db}{dx} \frac{v^2}{(v-b)^2} - \frac{1}{a} \frac{da}{dx} \right\}$$

With $v = 3b$ and $p = \frac{1}{27} \frac{a}{b^2}$ we should find for carbonic acid and oxygen

$$\frac{1}{p} \left(\frac{\partial p}{\partial x} \right)_{vT} = 3 \times (0,493 + 0,0903^1)$$

or

¹⁾ See page 273.

$$\frac{1}{p} \left(\frac{\partial p}{\partial x} \right)_{cT} = 1,75.$$

According to KEESOM's observations the value of $\left(\frac{T dp}{p dT} \right)$ for the beginning of the plaitpoint line is equal to $-6,3$ for $x = 0,1047$, and equal to $-6,08$ for $x = 0,1995$. From this we calculate, with $\frac{T}{p} \left(\frac{\partial p}{\partial T} \right)_{vx} = 6,7$ (the value found for carbonic acid) $\frac{1}{p} \left(\frac{\partial p}{\partial x} \right) = 3,921$ and $3,824$ — so more than double the value which follows from the equation of state, when we put there b independent of the volume.

The values given by KEESOM for pressure and temperature of the critical tangent point, and of the critical point of the unsplit mixture, furnish a means to test the reliability of the value of $\frac{1}{p} \left(\frac{\partial p}{\partial x} \right)_{vT}$, as it has been calculated from his observations.

For the mixture $x = 0,1047$, Δp amounted to $9,9$ for the critical tangent pressure and ΔT to $-7,69$ for the critical tangent temperature.

If we again write for this homogeneous phase:

$$dp = \left(\frac{\partial p}{\partial T} \right)_{vx} dT + \left(\frac{\partial p}{\partial x} \right)_{vT} dx$$

or

$$\frac{1}{p} \frac{dp}{dx} = \left(\frac{T}{p} \frac{\partial p}{\partial T} \right)_{vx} \frac{dT}{T dx} + \frac{1}{p} \left(\frac{\partial p}{\partial x} \right)_{vT},$$

we find:

$$\frac{9,9}{72,93 \times 0,1047} = 6,7 \frac{-7,69}{304,02 \times 0,1047} + \frac{1}{p} \left(\frac{\partial p}{\partial x} \right)_{vT}$$

or

$$1,297 + 1,62 = \frac{1}{p} \left(\frac{\partial p}{\partial x} \right)_{vT} = 2,917.$$

And from the observations for $x = 0,1994$

$$\frac{16,72}{72,93 \times 0,1944} = 6,7 \frac{-14,71}{304,02 \times 0,1994} + \frac{1}{p} \left(\frac{\partial p}{\partial x} \right)_{vT}$$

or

$$1,15 + 1,635 = \frac{1}{p} \left(\frac{\partial p}{\partial x} \right)_{vT} = 2,785.$$

For the homogeneous phase of the critical circumstances of the unsplit mixture which cannot be realized, KEESOM found $\Delta p = -5,23$ and $\Delta T = -18,34$ by the application of the law of the corresponding states. From these data we find:

$$\frac{-5,23}{72,93 \times 0,1047} = 6,7 \frac{-18,34}{304,02 \times 0,1047} + \frac{1}{p} \left(\frac{\partial p}{\partial x} \right)_{cT}$$

or

$$= 0,685 + 3,86 = \frac{1}{p} \left(\frac{\partial p}{\partial x} \right)_{vT} = 3,18.$$

The fact that Δx , ΔT and Δp cannot be considered as differentials will undoubtedly contribute to the circumstance that this quantity shows such different values if calculated from KEESOM's observations.

But though the calculated values for $\frac{1}{p} \left(\frac{\partial p}{\partial x} \right)_{vT}$ are not the same, it appears sufficiently that the value of this quantity lies in the neighbourhood of 3, and probably above it. That the equation of state gives a so much lower value if we put b constant, must be attributed to the fact that the influence of this erroneously introduced simplification is great here, whereas this simplification caused hardly any error in the calculation of $\frac{T dx_0}{dT}$. The value of $\frac{1}{p} \left(\frac{\partial p}{\partial x} \right)_{vT}$ we found equal to:

$$= \frac{a}{v^2 p_x} \left\{ \frac{1}{a} \frac{da}{dx} - \frac{8}{27} \frac{v^2}{(v-b)^2} \frac{1}{b} \frac{db}{dx} \right\}.$$

With $v_x = 3b$ we find the value 3 for $\frac{a}{v^2 p_x}$, while the second

factor becomes equal to $\frac{dl}{dx} \frac{a}{b} + \frac{1}{3} \frac{dlb}{dx}$. But it is sufficiently known that the critical volume is much smaller than $3b$, and that the variability of b accounts for it. The same cause to which it is due that at the critical volume $\frac{T}{p} \left(\frac{\partial p}{\partial T} \right)_v$ is found equal to $1 + 6$, instead of $1 + 3$, causes us to find $\frac{a}{v^2 p_x}$ equal to 6 instead of to 3. Let us briefly prove this.

$$T \left(\frac{\partial p}{\partial T} \right)_v = \frac{MRT}{v-b} = p + \frac{a}{v^2}$$

$$\frac{T}{p} \left(\frac{\partial p}{\partial T} \right)_v = 1 + \frac{a}{pv^2}$$

In the critical circumstances the value of the first member is about 7 or $\frac{a}{p_x v_x^2} = 6$. If we use this value, we find for $\frac{1}{p} \left(\frac{\partial p}{\partial x} \right)_{vT}$ double the previous value, i. e. 3,5. The second factor of $\frac{1}{p} \left(\frac{\partial p}{\partial x} \right)_{vT}$

will now have to suffer some modification too, and as I shall show in

another communication, be equal to $\frac{1}{a} \frac{da}{dx} - \frac{5}{6} \frac{1}{b} \frac{db}{dx} = \frac{dl}{dx} \frac{a}{b} + \frac{1}{6} \frac{1}{b} \frac{db}{dx}$,

but the difference is slight — and this factor and others of a similar form occurring in the value of $\frac{dT}{Tdx}$, the value of $\frac{dT}{Tdx}$, calculated on the supposition of b variable, may be considered as sufficiently accurate.

We must therefore not expect to find a perfectly complete discussion of the problem in what precedes. If this was wanted, a closer investigation would be required for the determination of $\left(\frac{\partial p}{\partial x}\right)_v$ and $\frac{\partial^2 p}{\partial x \partial v}$, if we take b dependent, not only on x , but also on v —, and hence put :

$$b = b_{\infty} \left\{ 1 + \alpha \left(\frac{b_{\infty}}{v} \right) + \beta \left(\frac{b_{\infty}}{v} \right)^2 \text{ etc.} \right\},$$

while $b_{\infty} = (b_1)_{\infty} (1 - x) + (b_2)_{\infty} x$ is put. But in the following communication I shall show that in this particular case, the component being in critical circumstances, we can determine the value of these quantities without entering into a closer investigation.

Physics. “*The properties of the sections of the surface of saturation of a binary mixture on the side of the components.*” By Prof. VAN DER WAAALS.

I have brought the differential equation of the p, x, T -surface of a binary mixture into the following form :

$$v_{21} dp = (x_2 - x_1) \left(\frac{\partial^2 \xi}{\partial x_1^2} \right)_{pT} dx_1 + \frac{w_{21}}{T} dT.$$

In this equation $\left(\frac{\partial^2 \xi}{\partial x_1^2} \right)_{pT}$ is equal to $\left(\frac{\partial^2 \psi}{\partial x_1^2} \right)_{vT} - \frac{\left(\frac{\partial^2 \psi}{\partial x_1 \partial v} \right)^2}{\frac{\partial^2 \psi}{\partial v^2}}$.

For x_1 infinitely small $v_{21} = v_2 - v_1$, $\left(\frac{\partial^2 \xi}{\partial x_1^2} \right)_{pT} = \left(\frac{\partial^2 \psi}{\partial x_1^2} \right)_{vT} = \frac{MRT}{x_1(1-x_1)}$

and for w_{21} we may substitute the molecular heat of evaporation of the component, which we shall denote by Mv . The above equation is then simplified to

$$(v_2 - v_1) dp = \frac{MRT}{x_1} (x_2 - x_1) dx_1 + \frac{Mr}{T} dT.$$

The properties of the initial direction of the sections normal to the T -axis, normal to the p -axis and normal to the x -axis are given by this equation and they are known when the value of $\frac{x_2 - x_1}{x_1}$ is known.

If x_1 and v_1 represent the value of x and of the molecular volume of the liquid phase, and in the same way x_2 and v_2 these quantities for the vapour phase, then the equation :

$$(v_2 - v_1) dp = MRT \frac{x_2 - x_1}{x_2} dx_2 + \frac{Mr}{T} dT$$

holds for the vapour phase.

As the difference of the specific volumes of liquid and vapour of a component is generally represented by u , $v_2 - v_1 = Mu$, and this equation might also be written

$$udp = RT \frac{x_2 - x_1}{x_1} dx_1 + \frac{r}{T} dT.$$

For the section normal to the x -axis, so for the component itself, we find the well-known equation of CLAPEYRON :

$$\frac{r}{u} = T \frac{dp}{dT}.$$

For this section it is not required to know $\frac{x_2}{x_1}$, but for the other sections it is indispensable.

This relation is found by means of the property which says, that $\left(\frac{\partial \psi}{\partial x}\right)_{vT}$ must have the same value for liquid and vapour phase.

From :

$$\psi = MRT \{(1-x) l(1-x) + xlx\} - \int^v p dv + F(T)$$

we find :

$$\left(\frac{\partial \psi}{\partial x}\right)_{vT} = MRT l \frac{x}{1-x} - \int \frac{\partial p}{\partial x} dv,$$

and equating this value for the two phases we get :

$$MRT l \frac{x_1}{1-x_1} - \int^{v_1} \left(\frac{\partial p}{\partial x}\right)_{vT} dv = MRT l \frac{x_2}{1-x_2} - \int^{v_2} \left(\frac{\partial p}{\partial x}\right)_{vT} dv$$

or

$$MRT l \frac{x_1}{x_2} \frac{1-x_2}{1-x_1} = \int_{v_2}^{v_1} \left(\frac{\partial p}{\partial x}\right)_{vT} dv,$$

and so for x_1 and x_2 infinitely small :

$$MRT l \frac{x_2}{x_1} = \int_{v_1}^{v_2} \left(\frac{\partial p}{\partial x} \right)_{vT} dv.$$

If we represent the mean value of $\left(\frac{\partial p}{\partial x} \right)_{vT}$ between the values v_1 and v_2 by $\overline{\left(\frac{\partial p}{\partial x} \right)_{vT}}$, we may also write :

$$MRT l \frac{x_2}{x_1} = (v_2 - v_1) \overline{\left(\frac{\partial p}{\partial x} \right)_{vT}}$$

This mean value can also be represented under another form by the following consideration. According to Maxwell's rule

$$p_c (v_2 - v_1) = \int_{v_1}^{v_2} p dv,$$

when p_c denotes the tension of the saturated vapour of the component, from which follows :

$$\frac{\partial p_c}{\partial x} (v_2 - v_1) + p_c \frac{d(v_2 - v_1)}{dx} = \int_{v_1}^{v_2} \left(\frac{\partial p}{\partial x} \right)_{vT} dv + p_c \frac{d(v_2 - v_1)}{dx}$$

or

$$\frac{\partial p_c}{\partial x} (v_2 - v_1) = \int_{v_1}^{v_2} \left(\frac{\partial p}{\partial x} \right)_{vT} dv = (v_2 - v_1) \overline{\left(\frac{\partial p}{\partial x} \right)_{vT}}.$$

The quantity $\frac{\partial p_c}{\partial x}$ represents the molecular increase of the tension of the saturated vapour for the unsplit mixture, assuming for p_c the approximate value

$$lp_c = lp_s - f \frac{T_x - T}{T}$$

$\frac{\partial p_c}{\partial x}$ is found from :

$$\frac{1}{p_c} \frac{\partial p_c}{\partial x} = \frac{1}{p_s} \frac{\partial p_s}{\partial x} - \frac{f}{T} \frac{\partial T_x}{\partial x}$$

For the present let us continue to write :

$$MRT l \frac{x_2}{x_1} = (v_2 - v_1) \frac{\partial p_c}{\partial x}$$

or

$$\frac{x_2}{x_1} = e \frac{(v_2 - v_1) \frac{\partial p_c}{\partial x}}{MRT}$$

Let us now first consider the initial direction of the sections normal to the T -axis. It can now be found from:

$$\log \left\{ 1 + \frac{(v_2 - v_1)}{MRT} \frac{dp}{dx_1} \right\} = \frac{v_2 - v_1}{MRT} \frac{\partial p_c}{\partial x} \text{ for the liquid branch and}$$

$$\log \left\{ 1 - \frac{v_2 - v_1}{MRT} \frac{dp}{dx_2} \right\} = - \frac{v_2 - v_1}{MRT} \frac{\partial p_c}{\partial x} \text{ for the vapour branch.}$$

For very low temperatures we may put $\frac{p(v_2 - v_1)}{MRT}$ about equal to unity, and so:

$$\log \left\{ 1 + \frac{dp}{dx_1} \right\} = \frac{\partial p_c}{\partial x} = \left[\frac{\partial l p_x}{\partial x} - \frac{f}{T} \frac{\partial T_x}{\partial x} \right]$$

and

$$\log \left\{ 1 - \frac{dp}{dx_2} \right\} = - \frac{\partial p_c}{\partial x} = - \left[\frac{\partial l p_x}{\partial x} - \frac{f}{T} \frac{\partial T_x}{\partial x} \right]$$

For the case that $\frac{\partial p_c}{\partial x} = 0$, $\frac{dp}{dx_1}$ and $\frac{dp}{dx_2}$ is also equal to 0, and it may therefore happen, that the two branches of the p, x -line touch in the beginning, and that both have an horizontal tangent.

As condition for this circumstance we have:

$$\frac{f}{T} \frac{dT_x}{dx} = \frac{dl p_x}{dx}$$

which may also be written:

$$f \frac{T_x}{T} \left(\frac{1}{a} \frac{da}{dx} - \frac{1}{b} \frac{db}{dx} \right) = \left(\frac{1}{a} \frac{da}{dx} - \frac{2}{b} \frac{db}{dx} \right)$$

or

$$f \frac{T_x}{T} \frac{dT_x}{dx} = \frac{dT_x}{dx} - \frac{db}{dx}$$

or

$$\left(f \frac{T_x}{T} - 1 \right) \frac{dT_x}{dx} = - \frac{db}{dx}$$

E.g. for $T = \frac{1}{2} T_x$

$$\frac{dT_x}{dx} + \frac{1}{13} \frac{db}{dx} = 0.$$

For higher temperatures $\frac{p(v_2 - v_1)}{MRT}$ is smaller than unity and for the critical temperature of the component this quantity is even equal to 0. In this case we may write $\frac{v_2 - v_1}{MRT} \frac{dp}{dx_1}$ for $\log \left(1 + \frac{v_2 - v_1}{MRT} \frac{dp}{dx_1} \right)$ and we find

$$\frac{dp}{dx_1} = \frac{\partial p_c}{\partial x},$$

and in the same way

$$\frac{dp}{dx_2} = \frac{\partial p_c}{\partial x}.$$

The first conclusion we draw from this is, that at the critical temperature the liquid branch and the vapour branch have always the same tangent, and therefore touch. The initial direction is given by the quantity $\frac{\partial p_c}{\partial x}$ or by $\overline{\left(\frac{\partial p}{\partial x}\right)_{vT}}$. But as at the critical temperature $v_2 = v_1$, the mean value of $\left(\frac{\partial p}{\partial x}\right)_{vT}$ is equal to the value which $\left(\frac{\partial p}{\partial x}\right)_{vT}$ has at that volume equal for vapour and liquid. We have therefore at the critical temperature:

$$\left(\frac{dp}{dx_1}\right)_T = \left(\frac{dp}{dx_2}\right)_T = \left(\frac{\partial p}{\partial x}\right)_{vT}$$

or

$$\frac{1}{p} \left(\frac{dp}{dx_1}\right)_T = \frac{1}{p} \left(\frac{dp}{dx_2}\right)_T = \frac{1}{p} \left(\frac{\partial p}{\partial x}\right)_{vT} = \frac{\partial \ln p_c}{\partial x} = -(f-1) \frac{dT_x}{dx} + \frac{dlb}{dx}$$

The second conclusion we draw is that at the critical temperature

$$\frac{1}{p} \left(\frac{\partial p}{\partial x}\right)_{vT} = -6 \left\{ \frac{dT_x}{dx} + \frac{1}{6} \frac{dlb}{dx} \right\}$$

which has been put in the preceding communication, but has not been proved there.

That at the critical point $\left(\frac{dp}{dx_1}\right)_T$ and $\left(\frac{dp}{dx_2}\right)_T$ is equal to $\left(\frac{\partial p}{\partial x}\right)_{vT}$ we might have immediately concluded, without following the elaborate way by which we have now arrived at this conclusion. In the same way that at the critical point $\left(\frac{dp}{dT}\right)_x = \left(\frac{\partial p}{\partial T}\right)_{vx}$.

Let us first consider a simple substance. If we pass from one homogeneous phase to another, at which v is increased by dv , and T by dT , then

$$dp = \left(\frac{\partial p}{\partial v}\right)_T dv + \left(\frac{\partial p}{\partial T}\right)_v dT.$$

If $\left(\frac{\partial p}{\partial v}\right)_T = 0$, as is the case at the critical point, then:

$$dp = \left(\frac{\partial p}{\partial T}\right)_v dT,$$

and so every $\frac{dp}{dT} = \left(\frac{\partial p}{\partial T}\right)_v$, also with such a change at which the

volume changes, as is the case with saturated vapour. From this follows the well known property that at the critical point $\frac{T}{p} \left(\frac{dp}{dT} \right)$ for saturated vapour is equal to $\frac{T}{p} \left(\frac{\partial p}{\partial T} \right)_r$.

If with a binary mixture we pass from one homogeneous phase to another, at which v is increased by dv , T by dT and x by dx , then :

$$dp = \left(\frac{\partial p}{\partial v} \right)_{xT} dv + \left(\frac{\partial p}{\partial T} \right)_{vx} dT + \left(\frac{\partial p}{\partial x} \right)_{vT} dx.$$

If $\left(\frac{\partial p}{\partial v} \right)_{xT} = 0$, as is the case at the critical point of the component, then :

$$dp = \left(\frac{\partial p}{\partial T} \right)_{vx} dT + \left(\frac{\partial p}{\partial x} \right)_{vT} dx$$

also for such variations in which the volume changes.

The differential equation of the surface of saturation :

$$v_{21} dp = \frac{w_{21} dT}{T} + (x_2 - x_1) \left(\frac{\partial^2 \xi}{\partial x_1^2} \right)_{\rho T} dx_1$$

holds for the transition of an homogeneous liquid phase to a subsequent one and in the same way :

$$v_{12} dp = \frac{w_{12} dT}{T} + (x_1 - x_2) \left(\frac{\partial^2 \xi}{\partial x_2^2} \right)_{\rho T} dx_2$$

for the transition of an homogeneous vapour phase to a subsequent one.

If the first liquid phase and the first vapour phase is the critical phase of the component, the three last equations must be identical, and so $\frac{w_{21}}{T v_{21}} = \frac{w_{12}}{T v_{12}} = \left(\frac{\partial p}{\partial T} \right)_{rx}$, or $\frac{r}{T u} = \frac{-r}{-T u} = \left(\frac{\partial p}{\partial T} \right)_{vx}$.

In the same way $\frac{x_2 - x_1}{v_{21}} \left(\frac{\partial^2 \xi}{\partial x_1^2} \right)_{\rho T} = \frac{x_1 - x_2}{v_{12}} \left(\frac{\partial^2 \xi}{\partial x_2^2} \right)_{\rho T} = \left(\frac{\partial p}{\partial x} \right)_{vT}$, as has been proved above as holding for the critical point of the component.

From the general equation :

$$\frac{x_2}{v_1} = e \frac{v_2 - v_1}{MRT} \overline{\left(\frac{\partial p}{\partial x} \right)_{vT}}$$

follows, when $v_2 - v_1$ is infinitely small,

$$\frac{x_2 - x_1}{x_1} = \frac{v_2 - v_1}{MRT} \overline{\left(\frac{\partial p}{\partial x} \right)_{vT}},$$

and

$$\left(\frac{x_2 - x_1}{x_1} \frac{MRT}{v_2 - v_1} \right)_z = \left(\frac{\partial p}{\partial x} \right)_{vT} \cdot 1)$$

If at lower temperatures the initial direction of the p, v -line is traced for the liquid phase, and also that for the vapour phase, then these directions are usually different. Between these two directions lies the direction for the line which denotes the course of the quantity p_c . If this last line is an ascending one, this is also the case for the two others, and reversely. If the admixture is called more volatile

1) Though it falls outside the scope of our subject, which only treats of properties on the side of the surface of saturation, I will make a single remark on the mixtures for which liquid and vapour have the same concentration, because these mixtures have many properties which the components also

possess. Also for these mixtures the equation: $MRT l \frac{x_2}{x_1} = \int_{v_1}^{v_2} \left(\frac{\partial p}{\partial x} \right)_{vT} dv$, or

$MRT l \frac{x_2}{x_1} \overline{\left(\frac{\partial p}{\partial x} \right)_{vT}}$ holds. For these cases $\frac{x_2}{x_1} = 1$ and so $\overline{\left(\frac{\partial p}{\partial x} \right)_{vT}} = 0$. So for

a mixture for which this equation would hold at the critical circumstances, $\left(\frac{\partial p}{\partial x} \right)_{vT}$ itself would be equal to 0. As also $\frac{\partial^2 \psi}{\partial x^2} \frac{\partial^2 \psi}{\partial v^2} = \left(\frac{\partial p}{\partial x} \right)_{vT}^2$ must be equal to 0,

also $\left(\frac{\partial p}{\partial v} \right)_{vT} = 0$, and from:

$$dp = \frac{\partial p}{\partial v_x T} dv + \left(\frac{\partial p}{\partial x} \right)_{vT} dx + \left(\frac{\partial p}{\partial T} \right)_{vx} dT$$

follows:

$$\frac{dp}{dT} = \left(\frac{\partial p}{\partial T} \right)_{vx}$$

Already in 1895 I made the remark, which follows from this, viz. that for the point of the plaitpoint curve, at which the line which is sometimes called the line of KONOWALOW, meets the plaitpoint line, contact must take place and that just

as for a simple substance $\frac{T}{p} \frac{dp}{dT}$ = is about 7.

Now I will add that from $\left(\frac{\partial p}{\partial v} \right)_{vT} = 0$ follows in the same way, as has been derived above, that:

$$\frac{d \log T_x}{dx} + \frac{1}{6} \frac{d \log b}{dx} = 0 \text{ is,}$$

and not

$$\frac{d \log T_x}{dx} + \frac{1}{3} \frac{d \log b}{dx} = 0,$$

as would follow when b is put constant. Already QUIR pointed out that the last equation was not satisfied in his observations. According to an oral communication the equation given here would be in much better harmony with his observations.

than the component, when it causes the quantity p_c to decrease, then the general rule holds, that both $\frac{dp}{dx_1}$ and $\frac{dp}{dx_2}$ are positive when the admixture is more volatile than the pure substance and reversely.

In general these three directions approach each other at higher temperature and at the critical temperature they coincide. An exception to the rule that with rising temperature the lines approach, must be allowed for the case that for certain value of T the quantity $\frac{\partial p_c}{\partial x} = 0$. In this case the three directions mentioned coincide at that value of T ; as they must again coincide at $T = T_c$, and as the quantity $\frac{\partial p_c}{\partial x}$ varies with T , they will first diverge up to a certain maximum amount, and finally approach each other again.

The rule about the approaching of the lines might also be represented in the following manner, which would render my meaning more precisely. If we write $\frac{\partial p}{\partial x_1}$ under the following form, which follows directly from the above:

$$\frac{\frac{dp}{dx_1}}{\frac{dp_c}{dx}} = \frac{e^{\frac{p_c(v_2-v_1)}{MRT}} \frac{dp_c}{dx} - 1}{\frac{p_c(v_2-v_1)}{MRT} \frac{dp_c}{dx}}$$

or putting $\frac{p_c(v_2-v_1)}{MRT} \frac{dp_c}{dx} = k$ and $\frac{\frac{dp}{dx_1}}{\frac{dp_c}{dx}} = U$

$$U = \frac{e^k - 1}{k}$$

from which follows:

$$\frac{dU}{dT} = \frac{1}{k} \frac{dk}{dT} \left\{ e^k - \frac{e^k - 1}{k} \right\}.$$

The factor $\left(e^k - \frac{e^k - 1}{k} \right)$ is always positive for k positive, and always negative for k negative, and is only equal to 0 for $k = 0$; and k equal to 0 occurs only at the critical temperature and when $\frac{\partial p_c}{\partial x} = 0$. For all other values of k can $\frac{dU}{dT}$ only be equal to 0, when $\frac{dk}{dT}$ is equal to 0. When this quantity is equal to 0, there is a maximum

or a minimum value for $\frac{dp}{dx_1}$ and the variation of this quantity can

reverse its sign with rising temperature. Reversely when $\frac{dk}{dT}$ cannot be equal to 0, reversal of sign cannot take place in the variation of this quantity.

From $k = \frac{p_c(v_2 - v_1)}{MRT} \frac{dp_c}{dx}$ follows as condition of $\frac{dk}{dT} = 0$.

$$\frac{dp_c}{dx} \frac{d \left[\frac{p_c(v_2 - v_1)}{MRT} \right]}{dT} + \frac{p_c(v_2 - v_1)}{MRT} \frac{d^2 p_c}{dT dx} = 0.$$

$$\text{Now } lp_c = lp_x - f \frac{T_x - T}{T}, \quad \frac{dp_c}{dx} = \frac{dp_x}{dx} - \frac{f}{T} \frac{dT_x}{dx}, \quad \frac{d^2 lp_c}{dx dT} = \frac{f}{T^2} \frac{dT_x}{dx}.$$

If we put $\frac{dp_x}{dx} = \frac{f}{T_1} \frac{dT_x}{dx}$, in which T_1 can have all possible values

from $-\infty$ to $+\infty$, then $\frac{dk}{dT} = 0$ may also be written :

$$- \frac{Td \left[\frac{p_c(v_2 - v_1)}{MRT} \right]}{\left[\frac{p_c(v_2 - v_1)}{MRT} \right] dT} = \frac{1}{\frac{1}{T_1} - \frac{1}{T}} = \frac{1}{\frac{T}{T_1} - 1}$$

The first member of this equation is always positive, at lower temperatures nearly equal to 0, and at the critical temperature infinitely great. So the second member must also be positive. Or, if this equation is to be satisfied $T_1 < T$, but positive. In all the cases, therefore, in which T_1 is negative, $\frac{dk}{dT}$ cannot become equal to 0, and no reversal of sign takes therefore place in the course of $\frac{dp}{dx_1}$ with the temperature.

So the reversal of sign only occurs, when in the equation

$$\frac{dp_x}{dx} = \frac{f}{T_1} \frac{dT_x}{dx}$$

T_1 lies between 0 and T_x . The two extreme values give for $T_1 = 0$

the value of $\frac{dT_z}{dx} = 0$, and for $T_1 = T_z$ the value of $\frac{dT_z}{T_z dx} = -\frac{1}{6} \frac{db}{bdx}$

so the well-known limits for mixtures for which $\frac{dp_c}{p_c dx}$ can be equal to 0.

For the initial direction of the section normal to the p -axis, the following equation holds :

$$-\frac{1}{T} \left(\frac{dT}{dx_1} \right)_p = \frac{RT}{r} \left\{ \frac{x_2 - x_1}{x_1} \right\} = \frac{RT}{r} \left\{ e^{\frac{u}{RT} \frac{dp_c}{dx}} - 1 \right\}$$

and

$$-\frac{1}{T} \left(\frac{dT}{dx_2} \right)_p = \frac{RT}{r} \left\{ \frac{x_2 - x_1}{x_2} \right\} = \frac{RT}{r} \left\{ 1 - e^{-\frac{u}{RT} \frac{dp_c}{dx}} \right\}$$

Both yield at the critical temperature of the components :

$$-\left(\frac{dT}{T dx} \right)_p = \frac{RT}{r} \frac{u}{RT} \frac{dp_c}{dx} = \frac{u}{r} \frac{dp_c}{dx} = \frac{\frac{1}{p_c} \frac{dp_c}{dx}}{\frac{T}{p} \frac{dp}{dT}} = \frac{1}{7} \frac{1}{p_c} \left(\frac{dp_c}{dx} \right)_z$$

According to results obtained before, we may also write :

$$-\frac{1}{T} \left(\frac{dT}{dx_z} \right)_p = -\frac{6}{7} \left\{ \frac{dT_k}{T_z dx_z} + \frac{1}{6} \frac{1}{b} \frac{db}{dx_z} \right\}.$$

Physics. — “*The exact numerical values for the properties of the plaitpoint line on the side of the components.*” By Prof. VAN DER WAALS.

In my two previous communications, inserted in the proceedings of this meeting, viz. I on the properties of the plaitpoint line on the side of the components and II on the properties of the sections of the surface of saturation on the side of the components, it has again appeared, that the thermodynamic treatment of such problems enables us to find a complete general solution — but also that if we want to compute numerical values in special cases, the knowledge of the equation of state is indispensable. In some cases it will be sufficient, if we make use of an approximate equation of state; but as soon as the density of the substance is comparable to that in the critical state, the numerical values calculated by means of the approximate equation of state can deviate strongly from reality. This is specially the case with quantities which either refer to the volume, or are in close connection with it. Thus it is known, that already the critical volume of a simple substance is not

equal to $3b$, the value furnished by the equation of state, in which b is put constant, but that this equation is found rather nearer to $2b$. This may be accounted for by taking into account that b is variable and decreases with the volume. In a mixture b also depends on the composition. Accordingly the quantity $\frac{db}{dx}$ is an intricate expression for mixtures, and must in general be distinguished from $\left(\frac{db}{dx}\right)_v$. If the way in which b depends on volume and composition, was accurately known, then there would not be left any difficulties but those of toilsome and intricate calculations. But it is sufficiently known, that the way in which b , even for a simple substance, depends on v , has not yet been fixed with perfect certainty, and that in any case the knowledge of the numerical values, which occur in given forms of b , is wanting. These considerations led me to believe that this would be an objection to deriving theoretically the properties of the beginning of the plaitpoint line with perfect certainty — and also to determining the numerical values exactly. It has however, appeared to me that the knowledge of how b depends on x and v is not required for this exact determination; but that for this purpose it suffices to know two quantities which have been experimentally determined for the critical state of a simple substance.

Let us call f the value which $\frac{T}{p} \left(\frac{\partial p}{\partial T}\right)_v = \frac{T}{p} \frac{dp}{dT}$ has in the critical conditions of the component, and α , the critical coefficient, so that $MRT_\alpha = \alpha(pv)_\alpha$.

From $p = \frac{MRT}{v-b} - \frac{a}{v^2}$ follows $\frac{MRT}{p(v-b)} = f$ and $\frac{a}{pv^2} = f - 1$.

The equality of $MRT = \alpha pv = f(v-b)p$, gives the value

$$v = \frac{f}{f-\alpha} b$$

for the critical volume, in which we have to keep in view, that now that b is put variable with the volume, b represents the value which this quantity has in the critical state. With $f=7$ and $\alpha = \frac{15}{4}$ we find $\frac{v}{b} = \frac{28}{13}$, whereas with $f=4$ and $\alpha = \frac{8}{3}$ we should find the value $\frac{v}{b} = 3$. For carbonic acid KEESOM has found $f=6,7$ and $\alpha = 3,56$, from which would follow $\frac{v}{b} = \frac{6,7}{3,14} = 2,134$.

If in $MRT = \kappa pv$ we put the value of v , we find:

$$MRT = pb \frac{\kappa f}{f - \kappa}.$$

With $f = 4$ and $\kappa = \frac{8}{3}$ the factor of $pb = 8$, and with $f = 7$ and $\kappa = \frac{15}{4}$ this factor is found to be only slightly different viz. $8 \frac{1}{13}$. For the calculation of the value of b in the critical condition we get therefore:

$$b = \frac{MRT f - \kappa}{p \kappa f} \quad \text{or} \quad \frac{T \kappa}{p \kappa} \frac{1}{273} \frac{f - \kappa}{\kappa f}.$$

If we put the value of v in the equation $\frac{a}{pv^2} = f - 1$, we find:

$$p = \frac{a}{b^2 \frac{f^2 (f - 1)}{(f - \kappa)^2}}$$

The factor of b^2 , which with $f = 4$ and $\kappa = \frac{8}{3}$ has the well known value of 27, is found slightly above 27,8 with $f = 7$ and $\kappa = \frac{15}{4}$.

If in $MRT = \kappa pv$ we substitute the values found for p and v , we find:

$$MRT = \frac{a \kappa (f - \kappa)}{b f (f - 1)}.$$

If we again put $f = 4$ and $\kappa = \frac{8}{3}$, we find $MRT = \frac{8}{27} \frac{a}{b}$; with $f = 7$ and $\kappa = \frac{15}{4}$ the factor $\frac{a}{b}$ is equal to $\frac{1}{3.446}$; also this value differs but little from $\frac{8}{27} = \frac{1}{3.375}$.

For the calculation of a with the critical values of T and p , the formula:

$$a = \frac{(MRT)^2 f - 1}{p \kappa^2}$$

holds.

The factor $\frac{f - 1}{\kappa^2}$ is equal to $\frac{27}{64} = \frac{1}{2,37}$ with $f = 4$ and $\kappa = \frac{8}{3}$. With $f = 7$ and $\kappa = \frac{15}{4}$ it is again only slightly different, viz. $\frac{96}{225} = \frac{1}{2,34}$.

For the critical condition $\left(\frac{\partial p}{\partial v}\right)_T$ must be 0. From this follows:

$$\frac{MRT}{(v-b)^2} \left(1 - \frac{\partial b}{\partial v}\right) = 2 \frac{a}{v^3},$$

and after substitution of the values found for MRT and v

$$1 - \frac{\partial b}{\partial v} = 2 \frac{z(j-1)}{j^2}.$$

With $f = 4$ and $z = \frac{8}{3}$ it follows naturally that $\frac{\partial b}{\partial v} = 0$, whereas with $f = 7$ and $z = \frac{15}{4}$ it follows that:

$$1 - \frac{\partial b}{\partial v} = \frac{45}{49}.$$

In the same way $\left(\frac{\partial^2 p}{\partial v^2}\right)_T$ must be 0 in the critical state. From this follows:

$$-b \frac{\partial^2 b}{\partial v^2} = 2 \frac{z(j-1)(j-z)(j-4)}{f^4}.$$

With $f = 4$ and $z = \frac{8}{3}$ this value is of course equal to 0. With $f = 7$ and $z = \frac{15}{4}$ we find:

$$-b \frac{\partial^2 b}{\partial v^2} = 0,1827 \text{ } ^1).$$

Let us now proceed to calculate the value of $\frac{dT}{Tdx}$ at the beginning of the plaitpoint line. We have the formula:

$$\frac{dT}{Tdx_0} = \frac{\left(\frac{\partial^2 p}{\partial v \partial x}\right)_T + \frac{1}{MRT} \left(\frac{\partial p}{\partial x}\right)_{vT}^2}{-\frac{\partial^2 \epsilon}{\partial v^2}},$$

and have therefore to determine $\left(\frac{\partial p}{\partial x}\right)_{vT}$ and $\left(\frac{\partial^2 p}{\partial x \partial v}\right)_T$ for the critical condition, but on the supposition that b varies with the volume and that

¹⁾ This high value of $-b \frac{\partial^2 b}{\partial v^2}$ supports the hypothesis that b , in its dependence on the volume, has a more intricate form than is represented by a series of ascending powers of $\left(\frac{b_\infty}{v}\right)$.

$\frac{db}{dx}$ has different values depending on the variations of the volume.

Now

$$\left(\frac{\partial p}{\partial x}\right)_{cT} = \frac{MRT \left(\frac{\partial b}{\partial x}\right)_v}{(v-b)^2} - \frac{da}{dx} \frac{1}{v^2} = -\frac{a}{v^2} \left\{ \frac{1}{a} \frac{da}{dx} - \frac{MRT}{a} \left(\frac{\partial b}{\partial x}\right)_v \frac{v^2}{(v-b)^2} \right\}$$

If we call $\frac{db}{dx}$ the value denoting the change of b with change of x , when we make also the volume vary in such a way that the mixture is again in the state which may be called the critical state of the unsplit mixture, then:

$$\frac{db}{dx} = \left(\frac{\partial b}{\partial x}\right)_v + \frac{\partial b}{\partial v} \left(\frac{dv}{dx}\right)_{kr}$$

and v_z being $= b \frac{f}{f-z}$, $\left(\frac{dv}{dx}\right)_z = \frac{db}{dx} \frac{f}{f-z}$, when f and z are constant, which is the case when the law of corresponding states is fulfilled. We find then:

$$\left(\frac{\partial b}{\partial x}\right)_v = \left(1 - \frac{\partial b}{\partial v} \frac{f}{f-z}\right) \frac{db}{dx}.$$

We have to know:

$$\frac{MRT}{a} \left(\frac{\partial b}{\partial x}\right)_v \frac{v^2}{(v-b)^2} = \frac{MRT}{\frac{a}{b}} \frac{v^2}{(v-b)^2} \left\{ \frac{f \left(1 - \frac{\partial b}{\partial v}\right) - z}{f-z} \right\} \frac{1}{b} \frac{d}{dx}.$$

When we substitute the values found above for MRT , v and $1 - \frac{\partial b}{\partial v}$

we find $\frac{f-2}{f-1} \frac{1}{b} \frac{db}{dx}$ — and so:

$$\frac{1}{p} \left(\frac{\partial p}{\partial x}\right)_{vT} = -\frac{a}{pv^2} \left\{ \frac{1}{a} \frac{da}{dx} - \frac{f-2}{f-1} \frac{1}{b} \frac{db}{dx} \right\}$$

or

$$\frac{1}{p} \left(\frac{\partial p}{\partial x}\right)_{vT} = -(f-1) \left\{ \frac{d \frac{a}{b}}{dx} + \frac{1}{f-1} \frac{db}{dx} \right\}$$

This value is in a high degree dependent on f .

With $f=4$ we find $\frac{1}{p} \left(\frac{\partial p}{\partial x}\right)_{vT} = -3 \left\{ \frac{dT_z}{T_z dx} + \frac{1}{3} \frac{db}{bdx} \right\}$.

With $f=7$ on the other hand $\frac{1}{p} \left(\frac{\partial p}{\partial x}\right)_{vT} = -6 \left\{ \frac{dT_z}{T_z dx} + \frac{1}{6} \frac{db}{bdx} \right\}$.

In the preceding communication I have concluded to the same value from the equality of $\left(\frac{\partial p}{\partial x}\right)_v$ and $\frac{dp_c}{dx}$ in the critical circumstances, and by means of the empirical formula — $l \frac{p_c}{p_z} = f \frac{T_z - T}{T}$. For from this formula follows

$$\frac{dp_c}{p_c dx} = \frac{dp_z}{p_z dx} - f \frac{dT_z}{T dx}$$

or

$$\frac{1}{p_z} \frac{dp_c}{dx} = \frac{dT_z}{T_z dx} - \frac{1}{b} \frac{db}{dx} - f \frac{dT_z}{T_z dx}$$

or

$$\frac{1}{p} \left(\frac{\partial p}{\partial x}\right)_{vT} = - (f-1) \left\{ \frac{dT_z}{T_z dx} + \frac{1}{f-1} \frac{db}{dx} \right\}.$$

But we could arrive at this equation in a much simpler way still. From:

$$dp = \left(\frac{\partial p}{\partial x}\right)_{vT} dx + \left(\frac{\partial p}{\partial T}\right)_v dT \quad \left(\frac{\partial p}{\partial v}_{xT} = 0\right)$$

follows, when dT is put equal to dT_z (taking for dT_z the variation of the critical temperature of the unsplit mixture)

$$\frac{1}{p_z} \frac{dp}{dx} = \frac{1}{p} \left(\frac{\partial p}{\partial x}\right)_{vT} + \left(\frac{T}{p} \frac{dp}{dT}\right) \frac{dT_z}{T_z dx}$$

and so

$$\frac{1}{p} \left(\frac{\partial p}{\partial x}\right)_{vT} = \frac{1}{p_z} \frac{dp_z}{dx} - f \frac{dT_z}{T_z dx}.$$

And this equation is not only preferable because it is shorter, but also because it is independent of the circumstance whether the law of corresponding states is applicable or not. The value of f in this derivation is that of the component.

Besides $\left(\frac{\partial p}{\partial x}\right)_{vT}$ we have to determine the value of $\left(\frac{\partial^2 p}{\partial x \partial v}\right)_T$.

For this quantity we find:

$$\left(\frac{\partial^2 p}{\partial x \partial v}\right)_T = -2 \frac{MRT}{(v-b)^3} \left(1 - \frac{\partial b}{\partial v}\right) \left(\frac{\partial b}{\partial x}\right)_v + MRT \frac{\frac{\partial^2 b}{\partial x \partial v}}{(v-b)^3} + 2 \frac{da}{v^3}$$

or

$$\left(\frac{\partial^2 p}{\partial x \partial v}\right)_T = \frac{2a}{v^3} \left\{ \frac{1}{a} \frac{da}{dx} - \frac{MRT}{a} \frac{v^3}{(v-b)^3} \left(1 - \frac{\partial b}{\partial v}\right) \left(\frac{\partial b}{\partial x}\right)_v + \frac{MRT}{2a} \frac{v^3}{(v-b)^3} \frac{\partial^2 b}{\partial x \partial v} \right\}.$$

In this expression only the quantity $\frac{\partial^2 b}{\partial x \partial v}$ is unknown. We determine it from:

$$\left(\frac{\partial b}{\partial x}\right)_v = \left\{1 - \frac{\partial b}{\partial v} \frac{f}{f-\alpha}\right\} \frac{db}{dx}.$$

From this follows:

$$\frac{\partial^2 b}{\partial x \partial v} = -b \frac{\partial^2 b}{\partial v^2} \frac{f}{f-\alpha} \left(\frac{1}{b} \frac{db}{dx}\right).$$

If we substitute the values given above for $MRT, v, \left(1 - \frac{\partial b}{\partial v}\right)$ and $-b \frac{\partial^2 b}{\partial v^2}$ in the expression for $\left(\frac{\partial^2 p}{\partial x \partial v}\right)_T$, we find for the value of the second term $-\frac{1}{b} \frac{db}{dx} 2 \frac{(f-2)}{f}$ and for the value of the third term $+\frac{1}{b} \frac{db}{dx} \frac{f-4}{f}$.

The value of $\left(\frac{\partial^2 p}{\partial x \partial v}\right)_T$ is then found equal to:

$$\left(\frac{\partial^2 p}{\partial x \partial v}\right)_T = \frac{2a}{v^3} \left\{ \frac{1}{a} \frac{da}{dx} - \frac{1}{b} \frac{db}{dx} \right\}$$

or

$$\left(\frac{\partial^2 p}{\partial x \partial v}\right)_T = \frac{2a}{v^3} \frac{dT_x}{T_x dx},$$

and for $\frac{\left(\frac{\partial^2 p}{\partial x \partial v}\right)_T}{\frac{\partial^2 p}{\partial v^2}}$ we find the simple value $\frac{dT_x}{T_x dx}$; so exactly the same

value as follows from the equation of state, in which b is put constant. This gives rise to the conjecture that this relation might be found merely from thermo-dynamic relations independent of the knowledge of the equation of state, and this is indeed the case.

Let us consider the quantity $\left(\frac{\partial p}{\partial v}\right)_T$. It is equal to 0 in the critical state of the component. Let us pass from this homogeneous critical phase to another in which the volume has changed with dv , the composition with dx , and the temperature with dT .

Let us put dT again equal to dT_x , so let us assume that the mixture with dx molecules of the second kind is again in an homogeneous critical phase, then $\left(\frac{\partial p}{\partial v}\right)_T$ is again equal to 0.

From:

$$d\left(\frac{\partial p}{\partial v}\right)_T = \left(\frac{\partial^2 p}{\partial v^2}\right)_{T_x} dv + \left(\frac{\partial^2 p}{\partial x \partial v}\right)_T dx + \left(\frac{\partial^2 p}{\partial v \partial T}\right)_x dT_x$$

follows, because $d\left(\frac{\partial p}{\partial v}\right)_T$ and $\left(\frac{\partial^2 p}{\partial v^2}\right)_{T_x}$ are equal to 0:

$$\left(\frac{\partial^2 p}{\partial x \partial v}\right)_T = -\left(\frac{\partial^2 p}{\partial v \partial T}\right)_x \frac{dT_x}{dx},$$

and from the relation:

$$T\left(\frac{\partial p}{\partial T}\right)_v - p = \frac{\partial \epsilon}{\partial v}$$

follows:

$$T\left(\frac{\partial^2 p}{\partial v \partial T}\right) = \frac{\partial^2 \epsilon}{\partial v^2}.$$

And from this we find again now only from thermodynamic relations what we have derived already above.

As we found, also by means of mere thermodynamics:

$$\left(\frac{\partial p}{\partial x}\right)_{xT} = -fp \left\{ \frac{dT_x}{T_x dx} - \frac{1}{f} \frac{dp_x}{p_x dx} \right\}$$

we may put without making use of the equation of state:

$$\frac{dT}{T dx_0} = \frac{dT_x}{T_x dx} - \frac{f^2 p^2}{MRT} \frac{\partial^2 \epsilon}{\partial v^2} \left\{ \frac{dT_x}{T_x dx} - \frac{1}{f} \frac{dp_x}{p_x dx} \right\}^2.$$

The factor $-\frac{f^2 p^2}{MRT} \frac{\partial^2 \epsilon}{\partial v^2}$ may be reduced to a simple form, but for

the determination of the value of this factor it is required to know the equation of state. If we write $fp = \frac{MRT}{v-b}$, and $\frac{\partial^2 \epsilon}{\partial v^2} = -2 \frac{a}{v^3}$, this factor becomes equal to $\frac{MRT}{(v-b)^2} \cdot \frac{2a}{v^3}$ and as $\frac{MRT}{(v-b)^2} \left(1 - \frac{\partial b}{\partial v}\right) = \frac{2a}{v^3}$

follows from $\left(\frac{\partial p}{\partial v}\right) = 0$, we get:

$$-\frac{f^2 p^2}{MRT} \frac{\partial^2 \epsilon}{\partial v^2} = \frac{1}{1 - \frac{\partial b}{\partial v}} = \frac{f^2}{2z(f-1)},$$

so with $f=7$ and $z = \frac{15}{4}$ the value of this factor becomes equal to $\frac{49}{45}$. Hence we have:

$$\frac{dT}{T dx_0} = \frac{dT_x}{T_x dx} + \frac{49}{45} \left\{ \frac{dT_x}{T_x dx} - \frac{1}{7} \frac{dp_x}{p_x dx} \right\}^2.$$

If we introduce the quantity b instead of $\frac{dp_x}{p_x dx}$, we find:

$$\frac{dT}{Tdx_0} = \frac{dT_z}{T_z dx} + \frac{f-1}{2z} \left\{ \frac{dT_z}{T_z dx} + \frac{1}{f-1} \frac{db}{b dx} \right\}^2$$

With $f=4$ and $z = \frac{8}{3}$ we find again $\frac{f-1}{2z} = \frac{9}{16}$, but with $f=7$ and $z = \frac{15}{4}$, $\frac{f-1}{2z}$ rises to 0,8. With $f=6,7$ and $z = 3,56$ (Keesom's values for carbonic acid) the value is not appreciably different from 0,8. If we calculate with $\frac{dT_z}{T_z dx} = -0,493$ and $\frac{1}{b} \frac{db}{dx} = -0,271$, $f=6,7$ and $z = 3,56$ the value of $\frac{dT}{Tdx_0}$, we find for this value $-0,259$. Though 0,259 is smaller than the values calculated from Keesom's observations, 0,284 for $x=0,1047$ and 0,304 for $x=0,1994$, we must not forget that the calculated value would hold for the limiting case, viz $x=0$; and the fact that for $\Delta x=0$ a smaller value than 0,284 would have to be expected is at least in harmony with the circumstance that the amount is found higher for a higher value of x .

It is evident from all this that though we cannot do quite without the equation of state for the calculation of $\frac{dT}{Tdx}$ for the plaitpoint line, yet it is not necessary to know the form of the quantity b .

For the calculation of the quantity $\frac{T}{p} \frac{dp}{dT}$ for the beginning of the plaitpoint line we have from the formula:

$$dp = \left(\frac{\partial p}{\partial x} \right)_{vT} dx + \left(\frac{\partial p}{\partial T} \right)_{vx} dT$$

the relation:

$$\left(\frac{T}{p} \frac{dp}{dT} \right)_{\rho l} = \frac{T}{p} \left(\frac{\partial p}{\partial T} \right)_v + \frac{1}{p} \left(\frac{\partial p}{\partial x} \right)_{Tv} \frac{Tdx_0}{dT}$$

or

$$\left(\frac{T}{p} \frac{dp}{dT} \right)_{\rho l} = f + \frac{-(f-1) \left\{ \frac{dT_z}{T_z dx} + \frac{1}{(f-1)} \frac{1}{b} \frac{db}{dx} \right\}}{\frac{dT_z}{T_z dx} + \frac{f-1}{2z} \left\{ \frac{dT_z}{T_z dx} + \frac{1}{(f-1)} \frac{1}{b} \frac{db}{dx} \right\}^2}$$

or in numerical value for the mixture of oxygen and carbonic acid:

$$\left(\frac{T}{p} \frac{dp}{dT} \right)_{\rho l} = 6,7 + \frac{-5,7 \{-0,493 - 0,047\}}{-0,259} = 6,7 - 11,28 = -4,58$$

With the mixture $x=0,1047$ KEESOM has found $-6,3$ and with $x=0,1995$ the amount found was $-6,08$.

If we take the product of $\frac{T dp}{p dT}$ and $\frac{dT}{T dx}$ we find the value of $\frac{1}{p} \frac{dp}{dx}$ for the beginning of the plaitpoint line. As both $\frac{T dp}{p dT}$ and $\frac{dT}{T dx}$ are negative for the mixture of carbonic acid and oxygen, the value of $\left(\frac{1}{p} \frac{dp}{dx}\right)_{pl}$ is positive.

Anatomy. — “BOLK’s *centra in the cerebellum of the mammalia*”.

By D. J. HULSHOFF POL (from the laboratory for Psychiatry and Neurology at Amsterdam). (Communicated by Prof. C. WINKLER).

In his well-known researches about the cerebella of mammalia¹⁾, BOLK concludes: that “the Lobus anterior cerebelli does contain the centre of coordination for the muscle-groups of the head, the Lobus simplex the centrum of coordination for those of the neck; the non-symmetrical centre of coordination for both left and right extremity is situated in the Lobus medianus posterior, whilst each of the Lobuli ansiformes is the seat of one of the symmetrical centra, respectively for both right, and for both left extremities.”²⁾

Within the same line of research, VAN RIJNBEEK³⁾ at LUCIANI’s laboratory in Roma, experimenting on two dogs, extirpated a portion of the cerebellum, with the aim of taking away the right part of the Lobus simplex.

The secondary symptoms, which were observed during the first days after the operation, having passed away, the animal experimented upon continued shaking its head, as if it meant to say “no”.

This symptom resembled very much a trouble in the coordination, and such being indeed the case, it would have confirmed the hypothesis of BOLK. Therefore it was important to determine with as much exactness as possible, which portion of the cerebellum had been removed.

To this purpose the preparation, fixed in formol, was offered

1) Prof. Dr. L. BOLK. *Das Cerebellum der Säugetiere*. PETRUS CAMPER, Vol III, part. I. Amsterdam.

2) Prof. Dr. L. BOLK. *Over de physiologische beteekenis van het cerebellum*. De Erven BOHN, Haarlem. 1903.

3) G. A. VAN RIJNBEEK. *Tentative di localizzazione funzionali nel cervelletto*. Archivio di fisiologia. Vol. I. Fasc. V.

for examination to Professor WINKLER, who had the kindness to leave its further elaboration to me.

Since the sections, that should be made subsequently, were to be stained after the WEIGERT—PAL method, the cerebellum was immediately after its arrival in Amsterdam refixed in MULLER'S liquid. It was only when this had been performed that the photographs were taken (fig. I and II).

The white spots that are seen on the figures, were caused by celloidine, by means of which the pieces were pasted together. It was necessary to do this, because the cerebellum, was received here being cut into three pieces.

In the middle of the surface of the cerebellum we observe a cavity. If this cavity is divided into four parts along the longitudinal axis of the cerebellum, nearly one quarter is lying to the left of the median line, two other quarters are lying in the right median part, and another quarter (probably the smallest one) is lying in the right lateral part.

The form of this cavity on the surface of the cerebellum, as far as it is lying in the median portion, is nearly that of a truncated isosceles triangle having for its basis the paramedian line.

The greater part of this triangle (nearly three quarters) is lying in the right half, and only one fourth in the left half of the cerebellum.

What imports most now is to find out to which subdivision of the cerebellum belong the convolutions from which van RIJNBERK has extirpated this small piece.

In fig. I and II, next to the defect (fig. II sub 1), our attention is drawn immediately by a deep furrow (fig. II sub 2*a*), that has become to all probability more clearly visible by the process of fixation, than may have been the case during life.

The sulcus primarius is the furrow penetrating deepest to the medullary nucleus and continuing forward till near the sinus Rhomboidalis, causing in this way the lobus anterior and the lobus posterior to be connected, for by far the greater part, only by a ridge of medullated nerve-substance. We may therefore safely assume that, the cerebellum having been eventually shrivelled, this sulcus, lying between two portions so deeply divided, will become more distinctly visible.

At first view therefore we might hold the furrow indicated sub 2*a* fig. II, to be probably the sulcus primarius. Such being the case, all that is lying before this furrow would be lobus anterior, all that is lying behind it lobus posterior.

On examining the anterior portion, this is found to consist of two

parts, that may be discriminated with sufficient distinctness (fig. II, 3 and 4). What we find indicated sub 3 is a coniform swelling, consisting of a succession of folia, separated by sulci running in the direction of the margo mesencephalicus.

Accordingly it does not offer any difficulty to recognise in this portion the lobus anterior.

The case is different however for the folium behind this part (fig. II sub 4) lying before the sulcus mentioned sub 2*a*.

It would belong to the anterior lobe if this furrow were indeed the sulcus primarius; but as it is lying behind the sulcus sub 2*b*, the direction of which is totally different from that of the other sulci of the lobus anterior, the question arises whether this convolution sub 4 does indeed belong to the anterior lobe.

The direction of this gyrus is totally different from that of all the other convolutions lying before it, because it does encompass the basis of the coniform swelling. Whilst the convolutions in the anterior part are ranged regularly behind one another, the convolution sub 4 does diverge from that arrangement, because the former convolutions are implanted in this latter. Relying only on the difference in direction between these convolutions, one would be inclined to consider as the sulcus primarius rather the sulcus sub 2*b* than that sub 2*a*.

We see however, that the convolution sub 4, like that of the coniform swelling, is running from the right to the left. It is uninterrupted and the initial direction of this curved convolution is likewise towards the margo mesencephalicus. This — in addition to the fact, that Bolk in his description of the cerebella of different mammalia, likewise reckons the lower and more deviating convolutions to the lobus anterior — supports the opinion that the sulcus sub 2*b* is not the sulcus primarius, as we might suppose, if relying only on the difference in direction between the convolutions sub 3 and 4.

The macroscopical description will therefore have to leave undecided the question, whether the convolution sub 4 must be reckoned to the lobus anterior or to the lobus posterior.

Nevertheless it is of the greatest importance to delimitate exactly to which portion of the cerebellum this convolution belongs, because it has become evident from the figures I and II, that on the surface it is precisely in this convolution that the greater part of the defect is situated. The examination of sagittal sections of the cerebellum will have to decide this question.

All that is lying behind the anterior lobe belongs to the posterior

lobe. This posterior part, with the exception of its first convolutions, is divided into one median and two lateral portions by the sulci paramediani, which run parallel to the median line.

Consequently all that is lying between the two paramedian sulci forms the median part of the lobus posterior, all that is lying to the right and to the left of them forms the lateral part of this lobe.

In figure II sub 11 we find the sulcus intercruralis. This furrow is lying in the middle of the lobus ansiformis, (fig. I). The convolutions that start originally from the median line as crus primum (fig. II sub 9) and bend gradually, when arrived in the ultimate lateral part, to return thence as crus secundum (fig. II sub 10) to the median part, take before reaching it another bent, this time straight backward; to continue further as lobus paramedianus (fig. II sub 12) parallel to the sulcus paramedianus.

In describing further the lobus posterior we will confine ourselves, for the sake of convenience, to the left half.

Of course in fig. I and II all that is lying to the left of the sulcus paramedianus belongs to the lateral part, and consequently may not be reckoned to the lobus simplex, the convolutions of this latter, according to BOLK, continuing without any interruption from the right to the left.

Applying this test to fig. I, we find that the extreme end of the left sulcus paramedianus is stopped by a convolution indicated sub 5 fig. II.

Thence it might be concluded, that the convolutions indicated sub 5 and 6 in fig. II, accordingly lying above the sulci paramediani and below the lobus anterior, form the lobus simplex.

On a closer examination of the lowest of these two gyri, i. e. the gyrus sub 5, we find however, that to the left of the white spot (the end of the dotted line), in the lateral part of the gyrus therefore, a narrow furrow may still be observed, that does not continue to the median line. According to BOLK therefore, this convolution does not belong to the lobus simplex, as the incomplete furrows in this lobe, like those in the lobus anterior, ought to start from the median line.

The cause, why the interruption of this gyrus sub 5 is not, as usually, visible on the surface, must be sought in the fact that the sulcus paramedianus disappears in the depth, and does not therefore penetrate into this convolution on the surface.

The last convolution, sub 6, fulfills in every respect the conditions claimed by BOLK for the convolutions of the lobus simplex; as it

lies directly behind the lobus anterior, and continues without interruption from the right to the left, whilst incomplete furrows, not starting from the median line, do not occur in it. Moreover the convolutions forming the crus primum, lie adjacent to it and originate in it.

This convolution sub 6 thus forming the lobus simplex on the surface, does not continue very far on the more lateral part, as may be seen in the figure. It is therefore little developed.

Now if we follow to the right the course of the convolution sub 4 fig. II, about which it is not yet decided whether it belongs to the anterior or to the posterior lobe, we find that this convolution loses itself in the cavity sub 1. It may be said therefore that the operation has extirpated at least on the surface, a part of the left median portion and the whole of the right median portion of this gyrus.

I have stated already that the cavity broadened to the right, and attained its largest breadth in the prolongation of the sulcus paramedianus. By the photograph sub I it becomes evident, that in this place the lesion extends over the convolutions lying before and behind.

A convolution of the lobus anterior lying before the convolution sub 4, and a convolution of the lobus simplex behind it, we may therefore assume, in as much as it is allowed to draw conclusions from the macroscopical aspect, that in the right median part at least one convolution of the lobus anterior and one of the lobus simplex have been injured. It must remain undecided whether the principal defect, situated in the convolution sub 4 fig. II, ought to be reckoned to the lobus anterior or to the lobus simplex.

It was on purpose I did not hitherto say anything about the macroscopical deviations in the right lateral portion, because, as was stated before, the whole of it was divided from the left portion of the cerebellum and having been thrivelled in the course of the elaboration, it no longer fitted exactly unto the median part, as may distinctly be seen in fig. I and II.

In order therefore to avoid eventual errors I neglect the macroscopical description of the lateral portion of the posterior lobe. This omission does not involve unsurmountable difficulties, because the description of the sagittal sections remains still to be given, and by means of these latter we shall have to find out which portions have been destroyed and which have been left intact.

The cerebellum having been fixed for some time at the laboratory in MULLER'S liquid it was inclosed in celloidine and cut in serial sections.

Photograph III has been taken of a section on the left border of the defect, i.e. on the spot where the lesion begins on the left.

Photograph IV has been taken of a section from the right median part, directly adjacent to the median line.

Photograph V represents a section from the middle of the median portion.

Photograph VI represents a section very close to the prolongation of the sulcus paramedianus dexter, but still within the median portion.

Photograph VIII represents a section from the left lateral, being the un-injured portion. It corresponds with the place in the right lateral part, represented by photograph VII.

If, by the aid of photograph III, we try to delimitate the exact situation, especially of the different convolutions around the sulcus primarius, it does not present any great difficulty to know which is the lobus anterior and which the lobus posterior.

The furrow, lying opposite the sinus Rhomboidales (R.), is the sulcus primarius (s. p.). All that is lying before this sulcus, to the left of it in fig. III, belongs to the lobus anterior, all that is lying behind it, to the right in the figure, belongs to the lobus posterior.

The strongly developed anterior lobe is divided into four lower lobules, which I have indicated sub 1, 2, 3 and 4, conform to BOLK's description.

Accordingly these numbers correspond with the lobes, designated in the human cerebellum as Lingula, Lobus centralis and Culmen.

For the posterior lobe I likewise followed BOLK's division, and accordingly designated the folia by *a*, *b*, *c* and *d*; *a* corresponding with Nodus, *b* with Uvula, *c* with Pyramis and *d* with Tuber vermis, Folium cacuminis and Declive. This latter would be the Lobus simplex.

The rationality of BOLK's division is demonstrated clearly by this preparation, as the medullary rays of the folia are all of them separately implanted in the medullary nucleus.

The sinus Rhomboidales, the roof of the fourth ventricle, is designated sub R. Opposite to it, accordingly in the figure straight above it, and separated from it only by the medullary nucleus, we find the sulcus primarius (s. p.).

As we stated before, it could not be decided with any certainty from the macroscopical description whether the sulcus primarius was to be sought for sub 2*a* or sub 2*b* (fig. II), and consequently the situation of the defect could not be precisely defined; it is therefore necessary to determine with the utmost exactness in their mutual

relation the respective situations of the sulcus primarius, the adjacent gyri and the lesion.

To this purpose I have designated in fig. III sub α and sub β the two convolutions lying next to the sulcus primarius on the surface.

Looking at α , which represents the first convolution of the lobus posterior on the surface, we find that it consists of a secondary radius medullaris ending in a bifurcation on the surface. Such not being the case with the adjacent secondary medullary rays of c_2 , this convolution may be likewise easily recognized in the next figures.

The same thing may be said for β , which represents the most posterior convolution of the lobus anterior on the surface. For we observe that the medullary ray of the lobule N^o. 4 divides itself into two portions: the posterior one β being the prolongation of the thick primary radius medullaris and therefore easily recognised.

In photograph III, representing, as may be remembered, a section taken from the place where to the left the lesion begins, we see clearly that not the entire convolution β has been destroyed, but mainly that portion of it that is lying next to the sulcus primarius. The convolution of the lobus posterior, lying behind it, has not been injured at all, its surface, on the spot where this convolution bends inward towards the sulcus primarius being distinctly visible.

This spot (α) being of importance in order to determine whether the lobus posterior, in case the lobus simplex, has been injured, I have designated it likewise on the other photographs (IV, V and VI). Anticipating for a moment on the subsequent description of these photographs, I may state that they show clearly that this spot on the surface, where the convolution bends inward, presents nowhere any trace of lesion.

The direct conclusion to be derived from this fact is that the lobus simplex has not been injured AT ITS SURFACE.

As to the convolution β however matters stand differently.

In fig. III already we may see that from 4, representing the posterior folium of the lobus anterior, the posterior secondary convolution β in the upper part has been almost entirely destroyed. Only a small piece of its most anterior portion remains.

In the direction of the medullary nucleus the lesion extends only over the upper third part of the sulcus primarius.

The secondary radius medullaris is still distinctly visible at the spot where it is united to the anterior convolution.

Surveying the successive aspects of the lesion in the figures IV, V and VI, we find that in IV a very small remnant of the convolution sub β still subsists, whilst the secondary radius medul-

laris has been cut off almost up to the place of bifurcation of the primary radius.

The lesion itself penetrates inward, a little into the medullary nucleus, moreover the secondary and tertiary lobules, lying adjacent to the sulcus primarius, are for the greater part, if not wholly, destroyed.

This becomes still more evident from the fig. V and VI, where all that belongs to the convolution β , has been destroyed. The lesion itself penetrates still deeper, in fig. V it has nearly cleft the radius medullaris, in fig. VI it has done so entirely.

We may therefore conclude: *that in the median portion, more especially in its right half, the posterior lobule of the lobus anterior has been seriously injured, that even nearly the whole of it has been removed.*

I stated already, that from the anterior portion of the lobus posterior, i. e. the lobus simplex, nothing has been destroyed on the surface, as the place where it bends inward sub a , remains visible on all sections in fig. III, IV, V and VI. Deeper however, the case becomes different.

In fig. IV we observe that all secondary lobules, lying adjacent to the sulcus primarius in the depth, have been completely destroyed. In fig. V there has been removed still more, nearly the whole of the secondary radius medullaris having been extirpated. In fig. VI it is entirely destroyed, whilst moreover the primary radius medullaris of the small lobe c_2 , has been completely divided from the medullary nucleus.

We may thence conclude that, *though the lobus simplex in its median portion is not injured at its surface, on the contrary in the depth, in the portion adjacent to the sulcus primarius, it has been entirely destroyed, even those convolutions that remained intact on the surface in the paramedian area (figure III sub a) having been divided from the primary radius medullaris.*

Considering next the lateral portion, fig. VIII enables us to survey the situation and the division of the folia under ordinary circumstances. The sulcus primarius (s. p.) still subsists, as the convolution sub 4 fig. II, the last convolution of the lobus anterior, is removed considerably sideways. All that lies before this sulcus, accordingly to the left in fig. VIII, belongs to the lobus anterior. Consequently the small lobe sub 1 is the last folium of this lobe. All that lies behind the sulcus primarius, thus belongs again to the lobus simplex sub 2.

Considering next fig. VII, it is shown thereby that on both sides

of the sulcus primarius the secondary lobules have been all destroyed, and moreover from the lobus anterior even nearly the whole of the radius medullaris.

Accordingly we find for the *lateral portion* the same result as for the median right half, i. e. *that besides the greater part of the lobus simplex, also a part of the lobus anterior has been destroyed.*

Originally we intended not only to find out by means of the sections, which portion of the cerebellum had been taken away by VAN RIJNBEEK, but likewise to demonstrate the microscopical changes subsequent to the lesion. To this purpose we used the WEIGERT-PAL method of staining.

Unfortunately however, on microscopical examination, it was shown that nearly the whole mass of medulla had taken a granular aspect. It was therefore impossible to study the nerve-fibres, and any secondary degeneration they might have suffered with the method of WEIGERT-PAL, and for MARCHI-preparation the cerebellum proved unfit.

Nevertheless one fact remains worthy of attention: in the part of fig. VI, designated sub *a*, accordingly in that portion, separated by the operation from the central medullaris originating in it, the radius medullaris not only is stained black as distinctly as the other secondary medullary rays, but moreover the PURKINJE corpuscles and their ramifications in this portion (stained by means of osmium acid), do not present any changes worth mentioning, if compared to those of the other, un-injured lobules.

S U M M A R Y.

A. According to BOLK's theory, the Lobus simplex is the seat of an unsymmetrical centrum of coördination for the muscle-groups of the neck.

B. Operating on a dog, VAN RIJNBEEK extirpated a part of the cerebellum, about the Lobus simplex. In consequence of this operation, its secondary symptoms having passed away, the animal retained a continual movement of the head as if it meant to say "no".

C. Investigations at the laboratory in Amsterdam taught us that the operation had destroyed:

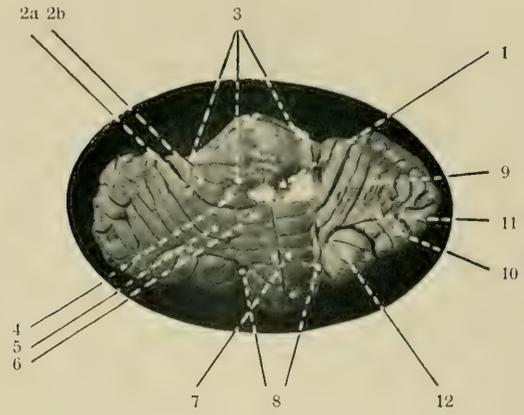
- a.* in the left median part, next to the median line, a small superficial portion of the last gyrus of the Lobus anterior;
- b.* between the median line and the paramedian line to the right;
 - 1st. nearly the whole of the last gyrus of the Lobus anterior;
 - 2nd. nothing from the Lobus simplex at its surface;

D. J. HULSHOFF POL. BOLK's centra in the cerebellum of the mammalia."

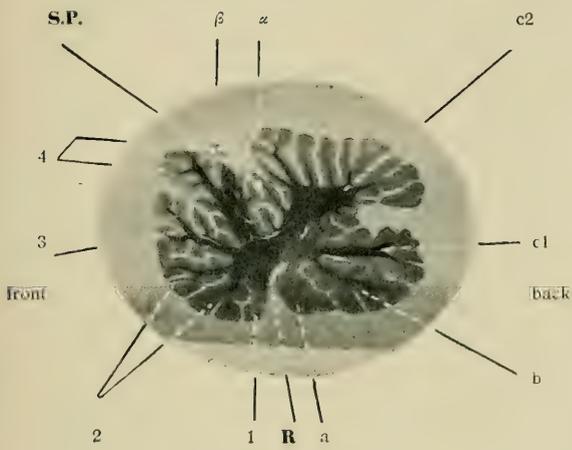
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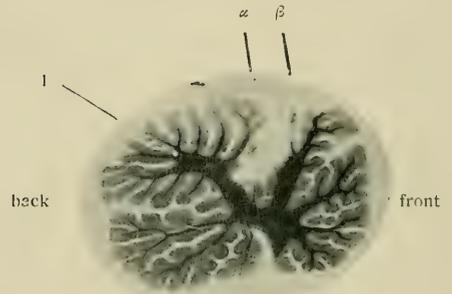
II



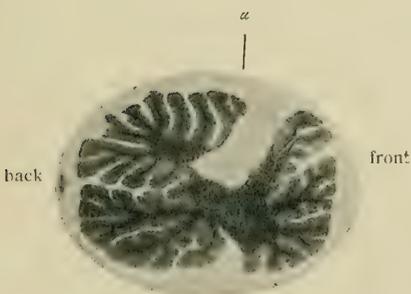
III



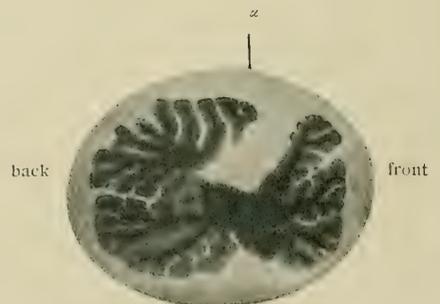
IV



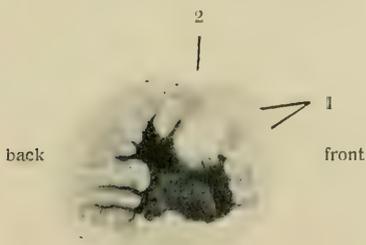
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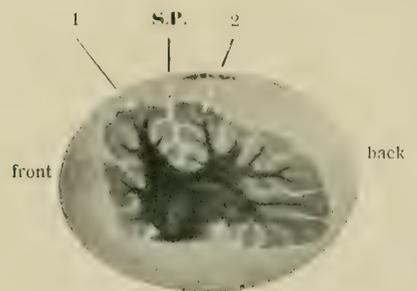
VI



VII



VIII



3rd, nearly the whole of the Lobus simplex in the depth, whilst, towards the paramedian line, likewise those portions of gyri, which remained intact on the surface, have been divided from the primary radius medullaris.

c. In the part, situated to the right of the paramedian line, as far as the lesion extends ;

1st. nearly the whole of the posterior folium of the Lobus anterior ;

2nd. the greater part of the Lobus simplex.

Physiology. — “*The designs on the skin of the vertebrates, considered in their connection with the theory of segmentation.*” By Dr. G. VAN RIJNBERK. (Communicated by Prof. C. WINKLER).

That there exists some connection between the distribution of pigments in the skin and its segmental innervation will be evident to any one who has made some investigations into the questions concerning the theory of segmentation. Different authors have made numerous unconnected researches about this subject. SHERRINGTON ¹⁾ has pointed out that the stripes of the zebra are ranged in segments on neck and trunk ; whilst he identifies the cross-stripe over the shoulders of the ass with its dorsal axis-line for the anterior extremity. WINKLER ²⁾ has drawn attention to the fact that deep-coloured rabbits often show white spots, presenting a marked conformity in distribution and extension with the analgetic areas that are produced when one or two of the posterior roots of the spinal nerves have been cut through. It may therefore readily be assumed that these white spots find their origin in the fact that either one or several segments lack the faculty of producing pigment. ALLEN ³⁾ has demonstrated that certain series of spots on the skin of the squirrel correspond with the points of entrance into the hypodermis of series of skinbranches of the intercostal and other homologous nerves. Two

¹⁾ C. S. SHERRINGTON, Experiments in examination of the peripheral distribution of the fibres of the posterior roots of some spinal nerves. *Philosoph. Transactions of the Royal Society.* London, vol. 184 B. p. 757.

²⁾ C. WINKLER, Ueber die Rumpfermatome. *Monatschrift für Psychiatrie und Neurologie.* Bd. XIII, 1903, h. 3, S. 173.

³⁾ H. ALLEN, The distribution of the colour-marks of the mammalia. *Proceedings of the Academy of Nat. Sciences of Philadelphia*, 1888, p. 84 et seq. — See also, *Science.* 1887.

years ago I myself¹⁾ collected some data, by means of which I endeavoured to justify the hypothesis, that in two species of sharks (*Scyllium Catulus* and *Sc. Canicula*) the deep-coloured transversal stripes correspond alternately with groups of five and of three segments, producing more pigment than the other segments.

My present endeavour will be to demonstrate some systematical views concerning the colourmarks on the skin of the vertebrates (birds excepted), on the basis of the rather extensive and detailed knowledge we possess about the segmental innervation of the skin.

To that purpose the first thing to be done is to define as clearly as possible the object of my investigations. In every animal the so-called "design" in its widest acceptation, originates in the contrasting effect of at least two colours or tints. Generally the next proceeding is to select one of these colours, that is then regarded as the "design" in a narrower sense, whilst the other colour is called the prime-colour. This choice is principally determined by esthetic motives: its criterion being either the difference in extension, — the less extensive colour being then taken for the design —, or else the difference in tint, the lightest tint being then regarded as the prime-colour. The irrationality of this method is evident, as has already been pointed out partially by J. ZENNECK²⁾ a disciple of EIMER. For when comparing together a few cartoons of equal size, on which are designed respectively: a small black figure with a large white margin, a small white figure with a large black margin, a large black figure with a narrow white margin and a large white figure with a narrow black margin, — nobody will think in either of these cases of taking the margin for the design: the figure remains the figure, whether it be large or small, black or white. Consequently it is neither by its tint, nor by its extension that the "design" ought to be distinguished, but only and exclusively by its significance. Applying this test to the distribution of colourmarks on the skin of animals (the design in its widest acceptation) we will accordingly have to determine at the outset in each case, which biological, morphological and physiological significance must be ascribed to the different portions of the design.

Their biological significance may be neglected here; necessarily the

1) G. VAN RIJNBERK, Beobachtungen über die Pigmentation der Haut von *Scyllium Catulus* und *Canicula* und ihre Zuordnung zu der segmentalen Hautinnervation dieser Thiere. — PETRUS CAMPER, Vol. III, 1904, part. 1, p. 137—173.

2) J. ZENNECK, Die Zeichnung der Boiden. Zeitschrift f. Wissenschaftliche Zoologie, Bd. 64, 1896, h. 1, u. 2, S. 234.

foremost condition to obtain correct notions concerning the pigmentation of the skin is to understand properly the morphological framework whereon the design is founded, and the manner in which it is physiologically determined. In endeavouring to elucidate these questions, it becomes evident that the simple distinction between "design" in a narrower sense and "prime-colour", is not sufficient for a rational description of the manifold pigmentations of the skin.

According to my opinion, we ought at least to distinguish three elements, constituting in their complete or partial combination the "design" in its widest acceptance. In order to obtain a proper distinction between these three elements, it is necessary to introduce a quantitative criterion into the problem. Besides the respective plus and minus in the pigmentation, we shall therefore have to make still another distinction, by opposing to the prime-colour respectively an excedent and a defect contrast in the production of pigment.

A few instances may suffice to elucidate this. In a white dog with black ears black represents the contrasting colour just as white does in a black horse with a white mark on its forehead. But in the first case it may be called an excedent contrast, in the second case a defect contrast. In an animal where the prevailing colour is brown showing both black and white marks, we find combined the three elements that ought to be distinguished: the brown prime-colour, the excedent and the defect-contrasts. Starting from these simple instances, we shall be able to compose a complete terminology, by means of which the most important elements of the pigmentation of the skin may be defined with tolerable exactness as to their shape, extension and distribution. For instance the white mark on the forehead of the black horse we will call an isolated defect contrast. Thus the dark stripes on neck and trunk of the *zebra* may be called regular serial diagonal excedent contrasts, whilst the stripes on *Galidictis* are regular serial longitudinal excedent contrasts. The morphological and physiological basis for distinguishing between excedent and defect-contrast, consists in the following points:

1. In a large series of cases excedent-contrasts are found in such places where the innervation of the skin is likewise strongest, whilst on the contrary defect-contrasts are found in such places where this innervation is feeblest. 2. We may observe that the excedent-contrasts often correspond as to their shape and distribution with the caricatures of the dermatoma¹⁾, whilst the defect contrasts often correspond

¹⁾ C. WINKLER and G. VAN RIJNBEEK, Structure and function of the trunk-dermatoma III. These Proc. IV, p. 509. Verslagen der Kon. Akademie v. Wetenschappen, 22 Febr. 1902.

with the analgetic areas called into existence by the destruction of sensibility in one or more segments.

A few instances may serve to illustrate this. The sensibility of the skin under normal circumstances is strongest within a system of lines and zones, corresponding with the average limits of the dermatoma (of more precise *limits* we cannot speak because of the overlaps). This has been proved clinically for man by LANGELAAN ¹⁾, experimentally for the dog by WINKLER ²⁾ and myself. Now if we observe the dark stripes of the zebra, we find that beyond any doubt these stripes, at least on neck and trunk, show a marked accordance in their distribution and direction with the average limits of the dermatoma, as these latter may be imagined to be, relying on the data procured by PEYER ³⁾, SHERRINGTON ⁴⁾, TÜRK ⁵⁾, WINKLER ⁶⁾ and myself respectively for the rabbit, the monkey and the dog.

Their number corresponds nearly with that of the segments of neck and trunk; on the neck and on the trunk they are somewhat wider apart than at the points of insertion of the extremities, this being in perfect accordance with the fact demonstrated by WINKLER and myself that at those points the ranks of the dermatoma are more thickly set. The distribution of the stripes on the extremities is not so easily explained. On superficial view they resemble rings, running around the extremity. In reality however each of these rings consists of two symmetrical semicircles, passing by pairs into one another by a definite angle on the outside and on the inside of the extremity. Connecting together the different points at which the semicircles meet, we obtain two lines corresponding with the dorsal and the ventral axis-lines of the extremity. The direction in which the stripes run (in a caudal direction from the axis-lines), corresponds with

1) J. W. LANGELAAN, On the determination of sensory spinal skinfields in healthy individuals. These Proc. III, p. 251.

2) See note 1 on the preceding page.

3) J. PEYER, Ueber die peripheren Endigungen der motorischen und sensibelen Fasern des Plexus brachialis. Zeitschrift f. rat. Medizin. N. 7, Bd. IV, 1854, S. 52.

4) C. S. SHERRINGTON, loco citato, and: Idem II Ibidem vol. 190, B. 1898, p. 45—186.

5) L. TÜRK, Vorläufige Ergebnisse von Experimental Untersuchungen zur Ermittlung der Hautsensibilitätsbezirke der einzelnen Rückenmarksnervenpaare. Sitzungsber. der K. K. Akad. der Wissensch. zu Wien 1856, and: Die Hautsensibilitätsbezirke der einzelne Rückenmarksnervenpaare. Aus dem literarischen Nachlasse von weil. Prof. Dr. L. TÜRK zusammengestellt von Prof. Dr. C. WEDL. Denkschriften der Math. Naturw. Classe der K. Akad. der Wissensch. zu Wien. Bd XXIX, 1869.

6) C. WINKLER and G. VAN RIJNBERK, On function and structure of the trunk-dermatoma I. These Proc. Vol. IV, p. 266; II. l. c. p. 308; III. l. c. p. 509; IV. l. c. Vol. VI, p. 347.

that followed by the limitlines of the segments of the skin. The number of the stripes, however, is greater than that of the segments can possibly be. But for this difficulty too a solution can be found. On considering the curve of sensibility of a normal trunk-skin, as it has been constructed by WINKLER and myself on the basis of our experiments, we find that at the dorsal median line, where the central areas overlap one another on an average for one third and the dermatomata for one half, a top of the curve i. e. a zone of summation corresponds with every average limit-line between two dermatomata. If now the overlaps amount to more than one half, as they do on the extremities, the curve of sensibility will be much more complicated and the zones of summation therefore more numerous. Accordingly the dark stripes on the extremities correspond likewise with the average lines of demarcation of the dermatomata. In the zebra the excedent of pigment apparently is distributed in accordance with the scheme of the intersegmental zones of summation, and the design resulting from this distribution may therefore be defined as consisting of intersegmental excedent-contrasts. Although this instance may not be entirely isolated, still it is a rather rare one. In many other cases we find that the excedent of pigment is not distributed in accordance with the uniform scheme of intersegmental demarcation, but arbitrarily accumulated in certain points or portions of the segments themselves. A large number of white domestic animals for instance present black spots, showing a marked similitude in their shape, distribution and extension with the figures, denominated by WINKLER caricatures of the dermatomata. The way in which the pigment is distributed, offers even an indication of that peculiar significance which the point of entrance of the skin-nerve apparently possesses for the innervation (maximum and ultimum moriens of the central areas, of the dermatomata and of the sensible skin-areas in general¹⁾). Thus the series of black dots in many species of sharks, amphibians, serpents and saurias, apparently correspond nearly with the serial ranging of the points of entrance of the dorsal and lateral nerve branches.

We will now turn to the defect contrasts. In deepcoloured specimens of our domestic animals white-tipped ears or tail, a white belly, or a white mark in the frontal median line of the head, or else white toes, are frequently to be met with. It needs not being demon-

¹⁾ On function and etc. These Proc. Vol. VI, p. 347. G. VAN RIJNBEEK: On the fact of sensible skin areas dying away in a centripetal direction. These Proc., Vol. VI, p. 346.

strated that such marks represent either absolute or relative eccentrical areas. Consequently I consider these marks to be eccentrical defect-contrasts. The white marks in rabbits, to which attention has been drawn by WINKLER, are of a very different nature, being expressions of segmental variability; in the series of equivalent segments, producing pigment, one or two have lost this faculty; thence results the defect, corresponding in shape, distribution and extension with the segmental analgetic areas. A further instance may be forwarded by the so-called Lakenveld cows, whose white "cloth-covering" around the trunk corresponds evidently with a series of pigment-less segments, which have become hereditary by artificial selection in breeding. The above-mentioned white feet may be reckoned likewise to these instances. In black dogs, horses or rabbits, white forefeet and a white mark on the breast are frequently to be met with. Evidently these mean something more than a simple eccentrical defect. It cannot be doubted that such cases represent phenomena of segmental omission.

It is known by the experiments of WINKLER ¹⁾ and myself that the most eccentric skin-segments of the fore-feet (7th and 8th cervical roots), consist only of the lateral portions of the dermatoma, the dorsal parts having entirely vanished whilst the ventral parts are lying exceedingly reduced at the ventral median line near the *manubrium sterni*. Accordingly this relation corresponds perfectly with that of the above described defect areas. For this reason I consider these latter ones to be segmental defect contrasts; they are the expression of a segmental defect-variability in the 7th and 8th cervical segment. Analogous cases are not rarely found. Frequently the white areas are so extensive that eventually a defect of the 5th and 6th cervical segment may be assumed besides that of the 7th and 8th. Analogous relations exist in the posterior extremity, though we know less about its segmental innervation.

I cannot possibly in these pages enter into more minute details concerning the question of the segmental distribution of the colour marks in the skin. An extensive essay on this subject is shortly to be published. The preceding explanations will however be of sufficient aid to form a judgment concerning my fundamental views and to understand the conclusions, stated in the following summary. Doubtless these conclusions may have some importance for clinical work, because they prove beyond any doubt the great significance of the segmental innervation for the trophic condition of the skin, and add

¹⁾ C. WINKLER and G. VAN RIJNBEEK, Something concerning the growth of the areas of the trunk-dermatoma on the caudal portion of the upper extremity. These Proc. VI, p. 392.

a new support to the probability of the hypothesis that a segmental basis lies at the root of many pathological states, as *naevus pigmentosus* etc.

CONCLUSIONS.

1. The distribution of the pigmentation on the skin of vertebrated animals is in a large series of cases the expression of peculiar relations in the segmental innervation of the skin.

2. In the "skin-design" taken in its widest acceptance, three elements ought to be distinguished: the prime-colour, the excedent-contrast and the defect-contrast.

3. In animals, whose skin is nearly wholly of one colour, the excedent-contrast may be *zonal* (dorsal) or isolated.

An isolated contrast frequently corresponds:

for the head

a. with a definite central nerve-area: (the excedent-contrast in the *N. trigeminus*), or else with definite portions of these areas (Point of entrance of the nerve in the hypodermis; the excedent-contrast *ex introitu*; the supraorbital mark).

for the remainder of the body:

b. with definite isolated skin-segments, more pigmented than the other segments, or with definite sub-divisions of these segments (caricatures of the dermatoma; segmental excedent variability; segmental excedent contrast).

c. with zones of intersegmental summation (intersegmental excedent contrast; the cross on the back of the ass).

4. The defect contrast in animals that are nearly wholly of one colour may appear as a lack of this colour either *zonal* (ventral) or *isolated*. The isolated defect contrast frequently corresponds with:

a. definite nerve-areas, being situated very eccentrical, either in absolute or in relative sense. (Tip of the tail, tips of the ears, ventral median line, frontal median line of the head, toes; they are all specimina of eccentrical defect-contrasts).

b. with definite non-pigmented skin-segments (phenomena of segmental-omission, segmental defect variability, segmental defect-contrasts).

5. EIMER'S type of the transversally striped animals ought to be divided into two sub-divisions:

a. animals with broad, dark transversal stripes, which are less numerous than the segments of the body (fishes, sauria's, serpents). These broad transversal stripes correspond probably with groups of strongly pigmented segments, alternating with other groups that are

less pigmented. (A transversal serially ranged segmental excedent contrast).

b. animals with narrow dark transversal stripes, more numerous than the segments of the body (mammalia, e.g. zebra's). These stripes correspond with zones of intersegmental summation. (A transversal serially ranged intersegmental excedent contrast).

6. ELMER's type of the animals with longitudinal stripes includes:

a. fishes, in which the dark longitudinal stripes, or else the dark dots and spots ranged in long rows, correspond apparently with the points of entrance into the hypodermis of the skin-branches of the peripheral nerves. (An excedent contrast *ex introitu*).

b. amphibians and reptiles. Probably the precedent hypothesis holds likewise for these.

c. mammalia. In the viverridae the longitudinal stripes apparently have been produced by the confluence of rows of spots, which were originally distributed intersegmentally. (Pseudo-longitudinal stripes).

7. ELMER's spotted type in the mammalia includes:

a. Irregular spotting. This is caused by segmental excedent and defect-variability.

b. Uniform dotting. We may imagine this to have been produced by the fragmenting of stripes, that occur un-interrupted in kindred species of animals (leopards).

Meteorology. — "*On frequency curves of meteorological elements.*"

Bij Dr. J. P. VAN DER STOK.

1. The application of the theory of probability to the results of meteorological investigations has hitherto been more limited than the nature of the data would lead us to expect.

It is not difficult to indicate the reason for this fact. Nearly all applications of the theory of errors to physical and astronomical problems are induced by the desire to determine a quantity with the greatest attainable precision; the remaining uncertainty affords a criterion for the value of the different methods employed and leads to experimental improvements, by means of which the errors, or departures from the average value, may be minimized.

These reasons for the application of the theory of errors fail in meteorology: for the greater part of meteorological quantities and climatological regions it is impossible to calculate average values within a reasonable time and with a moderate degree of precision and, if this were at all possible (e.g. for tropical stations), an increase

of precision would scarcely afford any advantage as we are unable to reduce the deviations by improving the observations. Moreover the knowledge of the most probable value is of minor importance as the frequency curves in general are very flat and we cannot attach the common idea of errors to the deviations which, after all, are more characteristic of meteorological conditions than absolute values.

Meteorological constants in the true sense of the word and to which the methods and terminology of the theory of errors are applicable, are nearly exclusively FOURIER constants, obtained by the analysis of periodical phenomena such as daily and annual variations, and to these it is certainly desirable to apply the criterion of the theory of errors more extensively than has hitherto been the case: the theory of errors in a plane can be immediately and advantageously used to get a clear understanding of the value of the results obtained.

If however we abandon this basis of the theory of errors and proceed upon the lines which have of late been followed by the sociological and biological sciences, the matter appears in a different light; in these sciences the principal object to be obtained is not so much the mean value as the occurrence of deviations, or rather the nature of the frequency curves.

Monthly means e.g. of barometric heights may be identical for January and July as far as the absolute values are concerned, but we may confidently expect the frequency curves for these months to bear a totally different character. It is also extremely probable that the frequency curves will show a considerable difference for places in different latitudes or differently situated in relation to the main tracks of depressions.

The constants which occur in the analytical expressions for these curves may then be considered as characteristics of the climate and, as in meteorology we possess more data than in most other branches of science, a more thorough study of details is possible.

The principal questions are:

a. In how far are monthly means in accordance with the common law of probability.

b. What is the form of the frequency curves constructed from daily means or from observations made at fixed hours in as far as these curves may be considered symmetrical.

c. An investigation of the skewness of these curves.

In this communication only the first of these problems will be considered.

2. The material chosen for this inquiry consists of:

1st. monthly means of barometric pressure at Helder, calculated for the 60 years period Aug. 1843 to July 1902, the total number being 720.

2nd. monthly means of barometric pressure at Batavia for 37 years, 1866–1902, altogether 444 data.

3rd. monthly means of atmospheric temperature for the whole of France during the 50 years period 1851–1900, altogether 600 data.

Up to 1873 the data for Helder have been taken from a meteorological journal kept by Mr. VAN DER STERR and, after his death, from the annals issued by the K. Met. Instituut.

A NEWMAN standard-barometer at Helder, which is known to have been in use as early as 1851, has recently been tested and does not show any appreciable errors, so that it may safely be assumed that also the records of the station-barometer are sufficiently accurate for our purpose.

The monthly means for Batavia have been taken from the returns published by the K. Magn. en Met. Observ., and those for France from ANGOT'S "*Études sur le climat de la France, Température,*" published in the Ann. du Bureau Central Météor. de France, Année, 1900, I. Mémoires, Paris, 1902, p. 34–118.

Table I gives the results of the calculations for Helder.

Let ε be the deviations of the individual data from the corresponding general average value and n the number of data available, then:

$$M = \sqrt{\frac{|\varepsilon^2|}{n-1}}, \text{ mean deviation,}$$

$$\mathfrak{D} = \frac{|\varepsilon|}{n}, \text{ average deviation,}$$

$$h = \frac{1}{M\sqrt{2}}, \text{ factor of steadiness,}$$

$$h' = \frac{1}{\mathfrak{D}\sqrt{\pi}}, \text{ idem.}$$

A = number of years required to obtain a general mean value with a probable error of ± 0.1 mm. for the barometric height and of $\pm 0^\circ.1$ C. for the atmospheric temperature.

This number, calculated from the formula:

$$\sqrt{A} = \frac{0.6745 M}{0.1},$$

is given instead of the probable error of the result with a view of showing how difficult, if not how impossible, it is to fix normal

values of meteorological elements, at least in high latitudes. The application of this formula is justified by the consideration that monthly means for a given month may, as far as our actual knowledge goes, be regarded as independent of each other, whereas e.g. daily means are certainly not so.

If the deviations are distributed according to the normal, exponential law :

$$\frac{h}{\sqrt{\pi}} e^{-h^2 x^2} dx \dots \dots \dots (1)$$

the quantity h' must be equal to h . Another criterion to ascertain whether the distribution of deviations is regulated by the normal law, as advocated by CORNU ¹⁾, is obtained by calculating π by means of the formula :

$$\pi = \frac{2 M^2}{\vartheta^2} \dots \dots \dots (2)$$

it is equivalent to the criterion previously mentioned as it holds only when $h = h'$.

The quantities M and h may be regarded as a measure of the

TABLE I. Monthly means of barometric height, Helder.

	M	ϑ	h	h'	A	π
January.....	5.01 mm.	4.04 mm.	0.141	0.140	1149	3.083
February....	4.85	3.82	0.146	0.148	1071	3.222
March.....	4.21	3.45	0.168	0.164	805	2.971
April.....	3.36	2.74	0.211	0.206	514	3.007
May.....	2.34	1.91	0.302	0.296	250	3.022
June.....	2.22	1.76	0.318	0.321	225	3.190
July.....	2.09	1.65	0.339	0.343	198	3.212
August	2.12	1.69	0.334	0.334	206	3.158
September....	3.01	2.45	0.235	0.230	411	3.079
October	3.35	2.62	0.211	0.215	510	3.262
November....	3.74	3.02	0.189	0.187	637	3.063
December.....	4.99	4.00	0.142	0.141	1132	3.106
Mean.....						3.198

¹⁾ Ann. de l'Observ. de Paris. XIII, 1876.

variability and steadiness of the climate from year to year in so far as this is determined by the oscillation of the atmospheric pressure. By analogy to the secular variation of the elements of terrestrial magnetism this instability might also be called secular variability.

Assuming this criterion to be correct, it appears from Table I that there is every reason to suppose that at Helder the deviations follow the normal law, the average value of π not differing more than 1.8 % from the real value.

On comparing the climate at Helder, which is highly variable from year to year, with the climate at Batavia (in so far as in this case also the variability of atmospheric pressure may be taken as a measure), we find totally different conditions.

A period of about ten years for the Eastmonsoon, and of twenty years for the Westmonsoon months is already sufficient to obtain total monthly means of the barometric height with a probable error of ± 0.1 mm. and for the dry months the available series of 37 years is quite sufficient to obtain a degree of certitude twice as great.

TABLE II. Monthly means of barometric height, Batavia.

	M	ϱ	h	h'	A	π
January.....	0.84 mm.	0.71 mm.	0 845	0.792	32	2.759
February.....	0.75	0.62	0.938	0.917	26	3.004
March.....	0.63	0.52	1.115	1.085	18	2.974
April.....	0.42	0.36	1.701	1.581	8	2.715
May.....	0.44	0.32	1.603	1.751	9	3.752
June.....	0.40	0.28	1.779	1.990	7	3.931
July.....	0.44	0.34	1.604	1.610	9	3.282
August.....	0.47	0.33	1.492	1.689	10	4.028
September.....	0.44	0.35	1.598	1.606	9	3.173
October.....	0.51	0.41	1 375	1.370	12	3.118
November.....	0.65	0.53	1.088	1.063	19	2.999
December.....	0.61	0.49	1.166	1.155	17	3.086
Mean.....						3.235

The application of the criterion as to whether the deviations follow

the normal law leads to a far less satisfactory result for this place than for Helder. The two values h and h' of the factor of steadiness show considerable and systematic discrepancies, the calculated values of π for May to August being collectively too great, and those for the other months too small. Although the total mean, 3.235, does not differ more than 3 % from the real value, these differences amount to + 15.7 % in the five dry months and to - 6.5 % in the seven months of the wet season.

Here, therefore, the secular variability cannot be regarded as a purely accidental quantity unless another law, more complicated than the normal one, applies and which is in some degree dependent upon the monsoons. This might be the case if the atmospheric pressure were dependent (and in a different manner in different seasons) upon another factor, for instance the temperature, the variability of which might still be according to the law of accidental quantities.

Similar systematic differences, varying with the season, between the calculated and the real value of π are not apparent in the results of the calculations for the atmospheric temperature in France, and the general average value of π does not differ from the real value more than 0.13 %.

TABLE III. Monthly means of atmospheric temperature, France.

	M	s	h	h'	A	π
	°	°				
January.....	2.07 C.	4.73 C.	0.344	0.326	195	2.869
February.....	2.03	4.70	0.356	0.332	188	2.855
March.....	1.59	4.25	0.446	0.452	115	3.230
April.....	1.20	0.92	0.588	0.616	66	3.444
May.....	1.32	4.07	0.536	0.529	79	3.067
June.....	1.14	0.91	0.629	0.623	59	3.150
July.....	1.29	4.00	0.548	0.565	76	3.347
August.....	1.08	0.88	0.653	0.641	53	3.029
September.....	1.19	0.94	0.594	0.600	64	3.205
October.....	1.25	4.02	0.565	0.551	71	2.991
November.....	1.50	4.22	0.472	0.464	102	3.043
December.....	2.41	4.84	0.294	0.306	264	3.418
Mean.....						3.137

In the paper already quoted, Mr. ANGOT assumed that the deviations do not show systematic differences in different months, and he subjects the deviations taken conjointly to the criterion of the law of errors.

This assumption is not justified by the results given in Table III, from which it is evident that the values of h are subject to considerable and systematic variations and, if a satisfactory agreement is still found between theory and observation, this can only be accounted for by the fact that the probability of the occurrence of deviations between fixed limits is expressed in a number of decimals too restricted to indicate the differences which, as for Helder and Batavia, must here exist between theory and practice.

No more can it be affirmed that, if a satisfactory accordance exists between the calculated and the observed number of deviations between given limits, the average value will also be the most probable one. In applying this criterion, as well as in calculating h' and π , a possible (and probable) skewness of the frequency curve is not taken into account because, by treating the deviations without regard to their sign, symmetry with respect to the ordinate of the centre of gravity of the figure is tacitly assumed.

As the number of years over which the observations extend is still far too small to allow frequency curves to be drawn for each month separately, it is still worth while to consider the deviations collectively, provided that at the same time the question be put, what form the law of deviations will assume when they are composed of groups which individually follow the normal law, the factor of steadiness being different for different groups. Even then the available data are insufficient to indicate with certainty a small degree of skewness in the frequency curve, so that only the symmetrical form can be sought for.

3. If, as in our case, the different groups occur with equal (sub) frequency, it is not difficult to indicate in what respects such a curve, the resultant of many elements, must differ from the normal curve. The groups characterised by large factors of steadiness will raise the number of small deviations above the number corresponding with an average factor and contribute only in a small degree to the number of large deviations, whereas, on the contrary, flat curves with small factors will give rise to a greater number of large deviations than is consistent with the normal law. Deviations of average magnitude will then occur to a less degree than is required by the common law; consequently in drawing the two curves, they will be seen to intersect at four points, as a minimum.

In a paper ¹⁾ published some years ago, SCHOLS has drawn the attention to the fact that differences of this description are almost always found when sufficiently extensive series of errors are put to the test of the normal law ; in this paper he shows that these differences cannot be explained by the omission of terms in BESSEL's development of the exponential law and suggests that their origin must be sought for in the superposition of observations of different degrees of precision.

In the observations alluded to by SCHOLS, it will in general not be possible to estimate these degrees of precision any more than the relative subfrequencies with which the different groups are represented in the result ; in the case of monthly means such as are being discussed here, the factors of steadiness are approximately known and the subfrequencies of the different groups are all identical.

If we arrange the 12 groups according to increasing values of h , it appears that we may take its change to be uniform ; consequently it is possible to find an approximate solution of the problem in finite form.

We have then to consider h as a variable quantity z and to ask what form the expression will assume for a sum of elementary surfaces:

$$C \int_{-\infty}^{\infty} e^{-z^2x^2} dx \dots \dots \dots (3)$$

if z varies in a continuous manner from h to H . If the subfrequency of these elementary groups be also regarded as a function of z (which occurs e.g. in the case of wind-frequencies), (3) must be equated to $\varphi(z) dz$, $\varphi(z)$ being subject to the condition :

$$\int_h^H \varphi(z) dz = 1 \dots \dots \dots (4)$$

The constant C is determined by the expression

$$C = \frac{z\varphi(z)dz}{\sqrt{\pi}} \dots \dots \dots (5)$$

and if, as in our case,

$$\varphi(z) = c$$

$$c = \frac{1}{H-h} \quad , \quad C = \frac{zdz}{(H-h)\sqrt{\pi}}$$

¹⁾ Versl. Wis. Nat. Afd. K. Akad. Wet. I. 1893 (p. 194—202).

the resulting probability of a deviation being situated between x and $x + dx$ is then:

$$\frac{dx}{(H-h)\sqrt{\pi}} \int_h^H z e^{-z^2x^2} dz$$

and the equation of the frequency curve:

$$y = \frac{1}{2(H-h)\sqrt{\pi}} \left[\frac{e^{-h^2x^2} - e^{-H^2x^2}}{x^2} \right] \dots \dots \dots (6)$$

Developing this expression we may put:

$$y = \frac{H+h}{2\sqrt{\pi}} e^{-\frac{H^2+h^2}{2}x^2} \left[1 + \frac{(H^2-h^2)^2}{2^2 \cdot 3!} x^4 + \frac{(H^2-h^2)^4}{2^4 \cdot 5!} x^8 \dots \right] \dots (7)$$

If we put:

$$\mu_n = 2 \int_0^\infty x^n y dx$$

we find with the help of:

$$2 \int_0^\infty \tau^n e^{-\tau^2} d\tau = \Gamma\left(\frac{n+1}{2}\right)$$

and

$$\int_0^\infty \frac{e^{-pz} - e^{-qz}}{z} dz = \log \frac{q}{p},$$

for the moments of different order with respect to the maximum ordinate:

$$\begin{aligned} \mu_0 &= 1 \quad , \quad \mu_2 = M^2 = \frac{1}{2Hh} \\ \mu_1 = \mathfrak{D} &= \frac{1}{(H-h)\sqrt{\pi}} \log \frac{H}{h} \quad , \quad \mu_3 = \frac{1}{2\sqrt{\pi}} \frac{H+h}{H^2h^2} \dots \dots (8) \end{aligned}$$

From a series of deviations following the law (6) the two characteristic constants H and h can be derived by computing the moments of the second and third order. They are found to be equal to the roots of the quadratic:

$$\begin{aligned} X^2 - pX + q &= 0 \\ p &= \frac{\mu_3\sqrt{\pi}}{2\mu_2} \quad , \quad q = \frac{1}{2\mu_2} \dots \dots \dots (9) \end{aligned}$$

If we had put a similar series to the test of the normal law (1) we should have found for the equation of the frequency curve;

$$y = \sqrt{\frac{Hh}{\pi}} e^{-Hhx^2}$$

or

$$y = \sqrt{\frac{Hh}{\pi}} e^{-\frac{H^2+h^2}{2}x^2} \left[1 + \frac{(H-h)^2}{2 \cdot 1!} x^2 + \frac{(H-h)^4}{2^2 2!} x^4 \dots \right]. \quad (10)$$

On comparing this expression with (7) it is at once seen that in this manner too great a number of small deviations must be found, as the module of the deviation zero, computed by (10)

$$\sqrt{\frac{Hh}{\pi}}$$

is always smaller than that derived from (7):

$$\frac{H+h}{2\sqrt{\pi}}$$

The position of the four points where the two curves intersect are found by equating the expressions (7) and (10); if the development can be stopped at the third term they are given by the roots of the biquadratic:

$$p X^4 - q X^2 + s = 0 \dots \dots \dots (11)$$
$$p = \frac{(H+h)^3}{6} - \sqrt{Hh}(H-h)^2, \quad q = 4\sqrt{Hh}$$
$$s = \frac{4(\sqrt{H}-\sqrt{h})^2}{(H-h)^2}$$

With the help of the form. (8) for \mathfrak{D} , it can be shown that, if a series of figures follows the law (6) the computation of π according to (2) must necessarily lead to values which are somewhat too high:

$$\frac{2\mu_2}{\mathfrak{D}^2} = \pi \frac{(H-h)^2}{Hh} \left(\log \frac{H}{h} \right)^{-2}$$

Putting:

$$H + h = p, \quad H - h = q,$$

we find:

$$\log \frac{H}{h} = 2 \frac{q}{p} \left(1 + \frac{1}{3} \frac{q^2}{p^2} + \frac{1}{5} \frac{q^4}{p^4} + \dots \right)$$
$$\frac{2\mu_2}{\mathfrak{D}^2} = \pi \frac{1 + \frac{q^2}{p^2} + \frac{q^4}{p^4} + \dots}{\left(1 + \frac{1}{3} \frac{q^2}{p^2} + \frac{1}{5} \frac{q^4}{p^4} + \dots \right)^2} > \pi \dots \dots (12)$$

4. In the following applications of these reasonings to deviations taken collectively for all months, the frequencies are reduced to a total number of 1000: by exponential law is understood the simple, normal law of errors (1),

TABLE IV. Barometer, Helder.

Dev. mm.	Observ.	Exp. L.	Diff.	Dev. mm.	Observ.	Exp. L.	Diff.
0.0—0.45	104	100	+ 4	5.95—6.45	21	25	— 4
0.45—0.95	129	108	+21	6.45—6.95	17	19	— 2
0.95—1.45	121	106	+15	6.95—7.45	14	15	— 1
1.45—1.95	101	100	+ 1	7.45—7.95	7	11	— 4
1.95—2.45	97	92	+ 5	7.95—8.45	18	8	+10
2.45—2.95	86	84	+ 2	8.45—8.95	8	6	+ 2
2.95—3.45	68	75	— 7	8.95—9.45	10	4	+ 6
3.45—3.95	50	65	—15	9.45—9.95	7	3	+ 4
3.95—4.45	43	56	—13	9.95—10.45	2	2	0
4.45—4.95	38	47	— 9	10.45—10.95	1	1	0
4.95—5.45	31	39	— 8	10.95—11.45	0	0	0
5.45—5.95	25	32	— 7	11.45—11.95	2	2	0

$$\mu_1 = 2.769, \mu_2 = 12.867, \mu_3 = 77.427,$$

$$h(\text{Exp. L}) = \frac{1}{\sqrt{2\mu_2}} = \sqrt{Hh} = 0.1971,$$

$$\pi(\text{form. 2}) = 1.069 \times 3.142.$$

Points of intersection observ. near dev. 2.95 and 7.95,

$$H = 0.2712, h = 0.1433(\text{form. 9}).$$

$$\pi(\text{form 12}) = 1.044 \times 3.142.$$

Points of intersection (form. 11) at dev. 2.60 and 9.19.

The sums of the differences between the limits of the observed points of intersection are, as given in Table IV, +48, —70, +22.

If we also wish to compare these quantities with the result of the theory, we have to integrate (6) between the limits deduced from (11). For the limits a and zero we find the frequency:

$$\frac{1}{\alpha(H-h)\sqrt{\pi}} [e^{-\alpha^2 H^2} - e^{-\alpha^2 h^2}] + \frac{2}{(H-h)\sqrt{\pi}} \left[H \int_0^{\alpha H} e^{-\tau^2} d\tau - h \int_0^{\alpha h} e^{-\tau^2} d\tau \right] \quad (13)$$

By means of this formula we find between the limits calculated by means of (11):

a	Form. (6)	Form. (10)	Diff.	Obs.
0—2.60	553	509	+44	+48
2.60—9.19	440	476	—36	—70
9.19—etc.	7	15	— 8	+22

As the situation of the second point of intersection according to the observations (7.95) shows a rather large discrepancy with that given by theory (9.19), it is natural that only the sums of the positive differences between the limits zero and the first point of intersection agree closely.

Taken as a whole it may be stated that the secular variability of barometric pressure at Helder is regulated by the law of accidental events as completely as might have been expected considering the scantiness of the material available.

A possible skewness of the curve is left out of consideration as has been already remarked; it can, however, be but unimportant as in 720 deviations 364 are positive and 356 negative.

The same cannot be ascertained of the secular variability of barometric pressure at Batavia; the differences between the observed frequencies and those calculated according to the exponential law are not of such a well marked description as for Helder, so that a determination of the points of intersection is out of the question; their situation can only be calculated as a result of theory.

TABLE V. Barometer, Batavia.

Dev. mm.	Observ.	Exp. L.	Diff.	Dev. mm.	Observ.	Exp. L.	Diff.
0.000—0.095	146	135	+11	0.995—1.095	34	25	+ 9
0.095—0.195	149	136	+13	1.095—1.195	7	18	—11
0.195—0.295	126	129	— 3	1.195—1.295	7	12	— 5
0.295—0.395	117	118	— 1	1.295—1.395	10	8	+ 2
0.395—0.495	101	104	— 3	1.395—1.495	5	5	0
0.495—0.595	95	89	+ 6	1.495—1.595	7	3	+ 4
0.595—0.695	50	74	—24	1.595—1.695	2	2	0
0.695—0.795	52	59	— 7	1.695—1.795	2	1	+ 1
0.795—0.895	59	46	+13	1.795—1.895	0	1	— 1
0.895—0.995	29	35	— 6	1.895—etc.	2	0	— 2

$$\mu_1 = 0.4395, \mu_2 = 0.3156, \mu_3 = 0.2915.$$

$$h (\text{Exp. L.}) = 1.2586, \pi (\text{form. (2)}) = 1.040 \times 3.142,$$

$$H = 1.989, h = 0.796.$$

$$\pi (\text{form. (12)}) = 1.0115 \times 3.142.$$

Points of intersection (form 11) at dev. 0.399 and 1.620. For the sums of deviations between these limits we find (form 13):

α	Form. (6)	Form. (10)	Diff.	Obs.
0 — 0.399	559	522	+ 37	+ 17
0.399 — 1.620	431	474	— 43	— 19
1.620 — etc.	10	4	+ 6	+ 2

It appears from these results that the calculation of π cannot always be regarded as a good criterion of the variability being regulated by the law of accidental events. From a series of numbers, composed, as the barometric departures for Batavia are, of groups which follow neither the simple normal law nor the more complicated law (6), still the calculation of π leads to a value which is correct within 1%.

TABLE VI. Temperature, France.

Dev. C°.	Observ.	Exp L.	Diff.	Dev. C°.	Oserv.	Exp. L.	Diff.
0.00—0.15	73	78	— 5	2.15—2.35	27	36	— 9
0.15—0.35	113	101	+12	2.35—2.55	18	29	—11
0.35—0.55	108	98	+10	2.55—2.75	8	24	—16
0.55—0.75	87	95	— 8	2.75—2.95	25	19	+ 6
0.75—0.95	100	88	+12	2.95—3.15	15	15	0
0.95—1.15	83	82	+ 1	3.15—3.35	12	11	+ 1
1.15—1.35	77	74	+ 3	3.35—3.55	8	9	— 1
1.35—1.55	60	66	— 6	3.55—3.75	12	6	+ 6
1.55—1.75	70	59	+11	3.75—3.95	5	5	0
1.75—1.95	58	50	+ 8	3.95—4.15	2	3	— 1
1.95—2.15	30	43	—13	4.15—etc.	9	9	0

$$\mu_1 = 1.207, \mu_2 = 2.394, \mu_3 = 6.703.$$

$$h (\text{Exp. L.}) = 0.4570, \pi (\text{form. (2)}) = 1.046 \times 3.142,$$

$$H = 0.7627, h = 0.2739,$$

$$\pi (\text{form. (12)}) = 0.140 \times 3.142.$$

Position of points of intersection (form. (11) at dev. 1.09 and 4.87. Sums of deviations between these limits (form. 13):

α	Form. (6)	Form. (10)	Diff.	Obs.
0 — 1.09	565	519	+ 46	+ 22
1.09 — 4.87	429	480	— 51	— 22

As a general result of this investigation it can be stated that, according to theory, in all three series the number of small deviations is greater than the simple exponential law would require, but to a somewhat less degree than would follow from the law formulated in (6).

The deviations of barometric pressure at Helder are in almost perfect accordance with this frequency law and, therefore, for each month separately with the normal law; the curve of deviations of atmospheric temperature in France still shows many irregularities, but, in general, it accords well with the law of form. (6); the secular variability of atmospheric pressure at Batavia is not regulated by the law of accidental events and its frequency curve shows characteristic peculiarities in different seasons.

Microbiology. — “*Methan as carbon-food and source of energy for bacteria*”. By N. L. SÖHNGEN. (Communicated by Prof. M. W. BEIJERINCK).

Methan, which is incessantly produced from cellulose in the waters and the soil, through the agency of microbes, and which, since vegetable life became possible on our planet must have been formed in prodigious quantities, yet occurs only in traces in our atmosphere.

As this gas is very resistant against chemical influences its disappearance in this way is highly improbable. But the conversion of methan into carbon dioxid and water produces a considerable quantity of heat, and so it seemed worth investigating whether there should exist any organic beings capable of feeding and living on it.

In the first place green plants were examined as to their power of decomposing methan in the light. To this end some waterplants were chosen, which seemed to offer most chance of success, considering that the formation of methan, as an anaerobic process, takes especially place in stagnant waters.

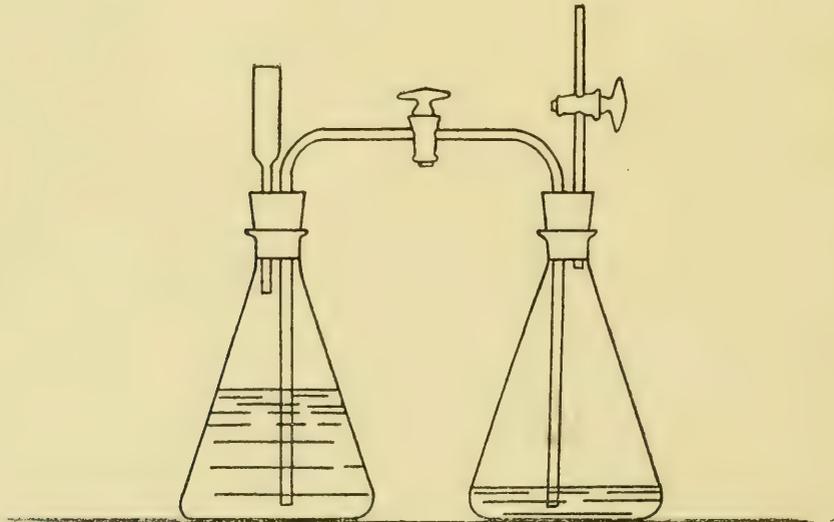
In this way positive results were obtained with several species of plants as *Callitriche stagnalis*, *Potamogeton*, *Eloдея canadensis*, *Batrachium*, *Hottonia palustris*, *Spirogyra*. So, for example, in one of the experiments in the light of a window to the North, with *Hottonio palustris*, put in a flask containing 500 cc. of methan and 500 cc. of oxygen, and inversely placed in a vessel filled with water, all the methan disappeared from 7—21 May, so within a fortnight.

In the dark, also, absorption of methane was with certainty observed.

However, the lapse of time preceding the first perceptibility of the process in different experiments with the same species of plant, varied very much, but when once set in it went on rapidly. When it was moreover observed, that by carefully washing the plants the setting in of the absorption was much slackened, whilst it seemed probable that just then an acceleration would follow in case the plant itself absorbed the methane, and especially when furthermore the absorption was observed to take place only after a slimy film had covered the water in the flask, it became evident that the oxidation was not caused by the green plant itself, but by microbes living on its surface.

In order to study the process more exactly an apparatus was constructed allowing us to pursue the absorption as well qualitatively as quantitatively.

It consists, as shown in the figure, of two Erlenmeyer-flasks of ± 300 cc., each closed by an indiarubber stopper with two perforations and joined by a twice curved glass tube reaching to the bottom of the flasks, which bears in the middle a glass cock. The flask, destined for the cultivation of the bacteria, bears, in the second perforation of the stopper, a tube with a glass cock to admit the gasmixture; the other flask is fitted with a glass tube filled with cotton wool.



The use of this apparatus is as follows: For the crude culture the first mentioned flask is quite filled with the culture liquid:

Distilled water	100
K ² HPO ⁴	0,05
NH ⁴ Cl	0,1
Mg NH ⁴ PO ⁴	0,05
Ca SO ⁴	0,01

and inoculated with garden soil, sewage or canalwater, of which the two last cause the quickest growth.

By the cock on the first flask a measured quantity of oxygen and methan is admitted by means of a gas burette. The liquid is thereby pressed into the other flask, and when it has lowered until a layer of about 1 cM. remains in the first flask, then the middle-cock is shut and at last the admission-cock.

The cultivation is effected at about 30° C. After a period, varying from 2—4 days, a film is observed on the liquid, which rapidly increases in thickness and then shows a distinct pink colour. Beneath the film the liquid, clear at first, begins to display a considerable turbidity caused by foreign microbes, which feed on the dead bacterial bodies of the floating film. Later on a great number of amoebes and monads develop in the film and in the liquid, evidently at the expense of the methan bacteria, no other material for food being present. In the other flask no film appears on the liquid.

Transports to a same liquid in an apparatus like the former, easily produce a new film, and, when garden soil is used for the infection, it grows even faster than in the crude culture.

An analysis of the gas after about a week, shows that the methan has quite or partly disappeared whilst a considerable quantity of carbonic acid is formed. The film is found chiefly to consist of bacteria belonging to one single species, which has proved to be the microbe which makes the methan disappear. It is a short, rather thick rodlet, immobile in the film, mobile or immobile in the plate cultures. Always the individuals are united by a layer of slime.

The length of this bacterium, which will provisorily be called *Bacillus methanicus*, is 4—5 μ , its thickness 2—3 μ .

It is not yet ascertained whether this species has already been found under other conditions of life and described elsewhere without the knowledge of its relation to methan. The question whether there exists only one or more than one species possessing the faculty to live on methan is also subjected to further investigation.

The methan bacterium is easily obtained in pure culture by cultivation on washed agar, containing the necessary salts, at a temperature of circa 30° C., in an atmosphere of $\frac{1}{2}$ methan and $\frac{2}{3}$ air,

with which an exsiccator is filled and into which the plates are introduced.

By streaking a young film from a liquid culture on the said solid medium already on the second day nearly pure slightly turbid colonies are obtained, quite distinguishable by their size and their slimy and lightly pink-coloured appearance. Such a colony, when early inoculated into the above apparatus forms, after some days, another bacterial film.

The methan, being in all the experiments the only source of carbon, necessarily at the same time must serve as food and as source of energy.

The quantity of carbonic acid in the culture flask indicates the amount of methan which has served as source of energy. The quantity of methan used for the formation of the bacterial bodies may be measured by subtracting the quantity of produced carbonic acid, expressed in cc., from the volume of disappeared methan.

So for example it was found that in an experiment in which were added successively 225 cc. CH^4 and 320.7 cc. O^2 to 102 cc. of liquid, the flasks contained after a fortnight

78 cc. CO^2
no CH^4
172 cc. O^2 .

In the culture liquid 21 cc. of carbonic acid were solved, so that 126 cc. of methan had been assimilated for building up the bacterial bodies, and $78 + 21$ cc. CH^4 for the respiration, 148.7 cc. of oxygen being assimilated.

Another experiment gave the following result.

Successively added 200 cc. CH^4
and 331 cc. O^2 .
to 108.5 cc. liquid.

After two weeks the gas contained

72.8 cc. CO
39 cc. CH^4
138 cc. O^2 .

In the culture liquid 18 cc. of carbonic acid were solved. Hence, 73.2 cc. CH^4 had been assimilated for the formation of the bacterial bodies, whilst 90.8 cc. CH^4 were converted into CO^2 .

Some oxidation experiments were performed with permanganate and sulphuric acid, in order to prove that a large quantity of organic material had accumulated. Thus, 100 cc. of the culture liquid, described in the first experiment, consumed: .

N. L. SÖHNGEN. "Methan as carbon-food and source of energy for bacteria."



Bacillus methanicus (800).

Crude film on culture liquid in methan-oxygen atmosphere. Between the bacteria mucus occurs.



Bacillus methanicus (1000).

Pure culture on agar with salts in methan-oxygen atmosphere.

Before the cultivation 0 cc. $\frac{1}{10}$ normal KMnO_4 .

After the cultivation 48.3 „ „ „

At a second experiment 100 cc. consumed:

Before the cultivation 0 cc. $\frac{1}{10}$ normal KMnO_4 .

After the cultivation 26.5 „ „ „

Even this rough estimation gives the convincing result that much organic matter is formed from the methan. Hence it follows that methan is the starting point for the production of a relatively rich flora of microbes, which as said above, may even at an early period contain amoebes and monads living from the methan bacteria.

There can thus be no doubt but methan is, though indirectly, of importance as a fish-food in the waters, as the said flora certainly serves as such.

Further investigations concerning the natural history of the methan bacteria and the relation between the assimilated methan and the amount of organic matter produced are in execution.

H. KASERER (Zeitschrift für das Versuchswesen in Oesterreich, Bd. 8 p. 789, 1905) seems also to have observed bacteria living on methan, but he gives no particulars.

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Physics. — “*Determination of the THOMSON-effect in mercury.*” By C. SCHOUTE. (Communicated by Prof. H. HAGA.)

This determination has been executed as a sequel to that, undertaken by Prof. H. HAGA, and published in the “*Annales de l'École Polytechnique de Delft*, I, 1885, p. 145; III, 1887, p. 43.”

A detailed account of the way, in which the experiments were carried out, has been given in my “*Dissertation*”. The results mentioned here were partly obtained afterwards.

The value of the THOMSON-constant was expressed by a relation, got by integration of the differential equation, which VERDET has given for the points of an unequally heated homogeneous conductor, when an electric current passes through it.

If the distribution of temperature is considered, after it has grown constant, and in some portion of the conductor, confined by two parts of a constant temperature, this equation is integrable, and the integral is quite simple for the points halfway between these limits of constant

temperature, when all over the part between them the external exchange of heat, by conduction, convection and radiation is small enough to be disregarded with respect to the other thermal effects.

The THOMSON-constant σ may then be expressed:

$$\sigma = \frac{i w}{2 J q \frac{U}{l}} \cdot \frac{\Delta_{Th} u}{\Delta_J u},$$

wherein i represents the strength of the current; w the resistance; J the mechanical equivalent of heat; q the section of the conductor; U the difference of temperature between the two parts of constant temperature; l the distance between those two parts; $2 \Delta_{Th} u$ the change of temperature which manifests itself in the middle-section when the current is reversed; and $\Delta_J u$ the rise of temperature in the same section according to Joule's law.

In order to be able to measure $4 \Delta_{Th} u$ instead of $2 \Delta_{Th} u$ the mercury was investigated in a U -shaped glass tube, put in a vertical position, the curved part up. The upper part of this U -tube was enclosed in a glass bulb, in which different fluids (acetone, water, aniline, glycerin) could be kept boiling by an electric current. In this way the upper part was kept at a constant temperature. For the same purpose the bottom parts of the legs of the U -tube, which were closed by small rods of platinum, were placed in running tapwater.

In the parts of non-uniform temperature this temperature was measured in sections halfway between the constant limits. If, after the current has been sent through in one direction, there should exist a certain difference of temperature between the two middle-sections, this difference will suffer a change of $4 \Delta_{Th} u$ by reversing the current, if the condition about the external exchange of heat is fulfilled:

Therefore the parts of non-uniform temperature were enclosed in a large vacuum-tube, for the greater part of glass, with a brass bottom and, for the sake of practical advantages, the glass boiling bulb and part of the condenser upon it were also enclosed in this tube.

In order to measure $\Delta_J u$, separate experiments were made, with as nearly as possible the same current. By making the current go first through one leg and then through the other the difference in temperature of the middle-sections was varied by $2 \Delta_J u$.

For measuring the temperature in the mercury the thermo-electric difference between this metal and platinum was used. Different kinds

of platinum acted quite differently in this regard. The strongest thermo-currents were obtained with *Pt Ir* of 10 to 20 %_o. A wire of this platinum was fused into each of the legs of the *U*-tube, as accurately as possible in the middle-section. These wires being connected and a sensitive galvanometer being introduced into the circuit, the temperature-differences Δ_{Thu} and $\Delta_{J'u}$ could be measured in proportion. Should we have wished to measure each of those quantities separately, it would have been necessary to determine the thermo-electric constants of this platinum with regard to mercury.

The inequality in temperature in the middle wires caused by an inevitable lack of symmetry in the *U*-tube was compensated by means of another thermo-couple. After each series of observations the galvanometer deflection, given by this couple with a known resistance and a known difference in temperature between the points of contact, was measured, in order to eliminate changes in the sensibility of the galvanometer or in the distance of the scale.

The quotient $\frac{U}{l}$ was determined indirectly. If the external exchange of heat could be neglected, the temperature-gradient must be the same all over the parts of non-uniform temperature, so long as the current did not pass through the mercury, apart from the distribution of temperature near the limits. And in the middle-section the gradient of temperature would remain very approximately the same, when the current did pass through it. Therefore the quantity $\frac{U}{l}$ could be said to be equal to the temperature-gradient in the middle-sections.

To measure this gradient in each of the legs of the *U*-tube on both sides of the middle-section at a given short distance both above and below it, another wire of platinum was fused in. The temperature-difference between these sets of wires divided by their distances was put for $\frac{U}{l}$.

The wires last mentioned were of a kind of platinum of which the thermo-electrical constants with regard to mercury had been accurately determined beforehand. As the same thing cannot be said about the wires in the middle-sections it is impossible to say anything definite about the uniformity of the gradient resulting from the experiments as they have been made. Preparatory experiments however have shown, that when *l* does not exceed certain limits, the gradient is sufficiently uniform.

Much trouble has been caused by wild thermo-electric currents.

Especially in a commutator for the galvanometer-current these difficulties arose. Contacts made by solid homogeneous copper have given the greatest satisfaction. With this arrangement for measuring the temperature the current through the U -tube, the chief current, had to be cut off for a moment during the reading of the galvanometer. Therefore the galvanometer commutator was combined with an interrupter for the chief current.

Changes in the meridian during the experiments were eliminated by noting, before the deflection, the position of the galvanometer-mirror when at rest. This position was more or less affected by the magnetic field of the chief current, but this obstacle was overcome by systematically combining readings with reversed chief current and galvanometer-current.

The galvanometer, made by CARPENTIER, was of the THOMSON-type. Provided with a sensitive set of magnets after PASCHEN, suspended by a quartz-fibre of $\pm 7 \mu$, with electromagnetical damping and with coils of small resistance (2,76 Ω), this instrument answered to all the special requirements of the problem.

The strength of the current was determined by measuring the drop of the potential at the ends of a known resistance, and comparing this with that at the poles of a WESTON-element. The potential differences were measured with a five-cell quadrant-electrometer (H. HAGA, These Proc. I p. 56).

The course of the experiments was the following :

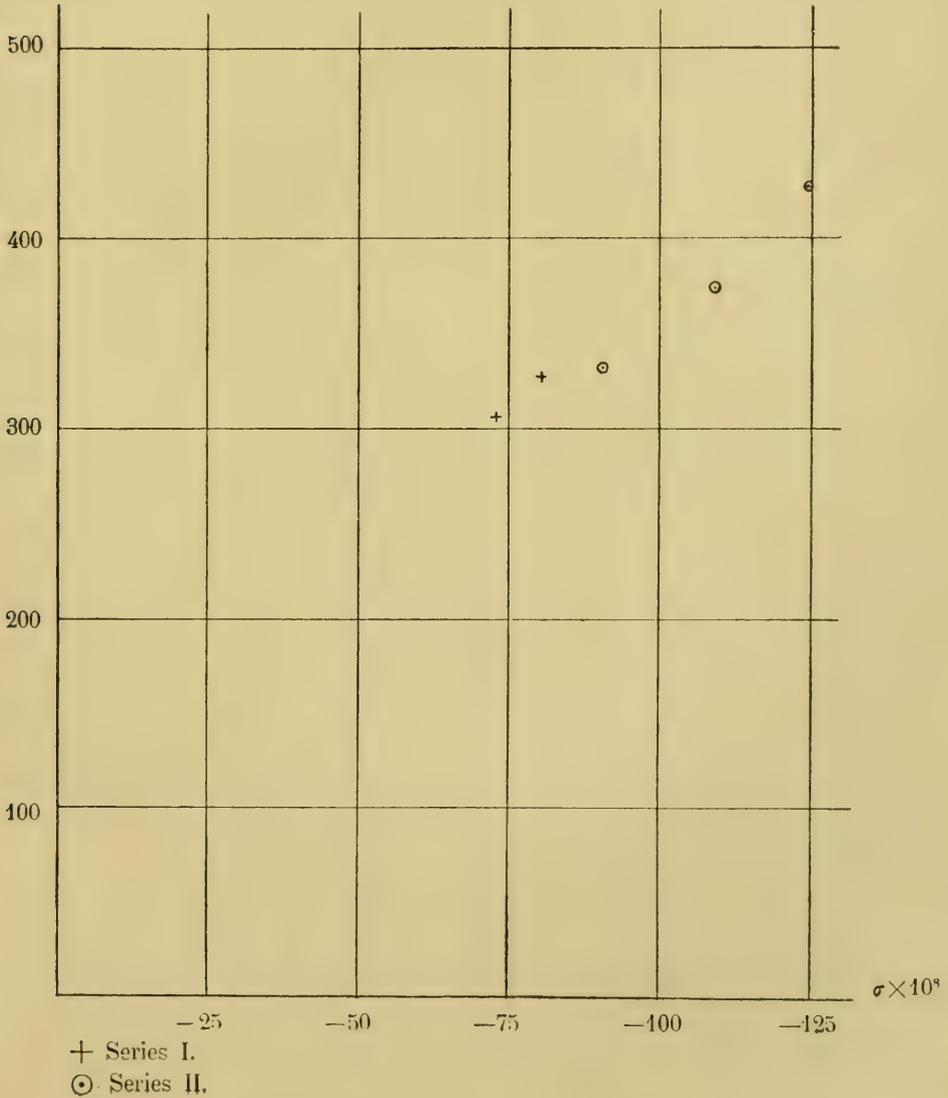
A sufficiently long time beforehand the fluid in the boiling-recipient was set boiling and the tapwater was allowed to run. Then the current in the U -tube was closed. When the distribution of the temperature had grown constant, the positions of the galvanometer resp. when at rest and deflected were read. After five minutes these readings were repeated, but now the commutator for the galvanometer was closed in the opposite direction. Then the current in the U -tube was reversed and after 10 or 15 minutes the galvanometer-readings were resumed. In a corresponding way the measuring of the Joule-heat was carried out.

In each series 8 deflections were read, as well for the determination of Δ_{Tku} as of $\Delta_{J'u}$; first four of one quantity, then eight of the other, and again four of the first. In the meanwhile during the time necessary for the temperature to become constant, the current strength was measured from time to time, and the temperature of the running water was read. In this way the following results have been obtained :

	t	$\sigma \times 10^8$
I	32°	— 73
	53°	— 80
II	58°	— 90
	100°	— 108
	154°	— 124

The values I are averages of the results of four series each, which have been given in my "Dissertation".

The values II have been obtained with another similar instrument T



under about the same conditions. They represent the averages of resp. 2, 2 and 1 series.

The meaning of those values for σ is: When a current of one ampère passes through a column of mercury, the THOMSON-effect will cause a quantity of heat, equal to σ (expressed in gram-calories) to be developed in one second between two consecutive sections of the temperatures $t - \frac{1}{2}^\circ$ and $t + \frac{1}{2}^\circ$, if the current goes in the direction of the increasing temperatures.

As the diagram added shows, the values I and II for σ lie all but in straight lines, passing through the origin, which means, that the THOMSON-effect is proportional to the absolute temperature (T).

The values II give $\frac{\sigma}{T} = -284 \times 10^{-11}$, and the combination of I and II give $\frac{\sigma}{T} = 267 \times 10^{-11}$.

It is not clear what has caused the difference between I and II. May be it is the effect of some difference in purity of the mercury which is known by experiments on other substances to strongly affect the THOMSON-constant.

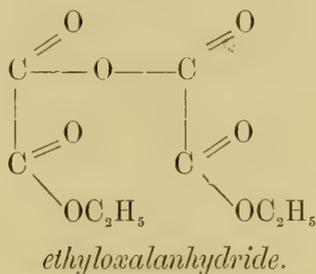
Chemistry. — Prof. FRANCHIMONT presents a communication from Dr. D. MOL on an investigation commenced in 1903 as to the "*ester anhydrides of dibasic acids.*"

Of the anhydrides of organic dibasic acids but very little is known; only the internal anhydrides, which cannot be formed except in those cases where the position of the two carboxyl groups in the molecule is stated to be favourable, have been investigated. But in some cases at least we may expect others formed in the same manner as those of the monobasic acids, namely by the co-operation of two molecules instead of the exercise of the two functions of the same molecule.

We may equally expect that when the dibasic acid has passed into a monobasic one, for instance by changing one of the acid functions into an ester or a salt, this will anyway yield an anhydride in the same manner as other monobasic acids.

Of some mixed anhydrides which are also esters we know, for instance, the ethyloxalylechloride but not the simple anhydrides. One of the chief methods of preparing the simple anhydrides is the one applied by GERHARDT in 1853, namely, the action of acid chlorides (mixed anhydrides) on salts. It is this method which, at any rate with oxalic acid, has at once yielded the desired product.

Dr. MOL allowed ethyloxalylchloride to act with the usual precautions on the potassium salt of acid ethyloxalate covered with ether and obtained a colourless liquid which distilled at 85°—90° under a pressure of less than 1 millimetre, solidified on cooling and then melted at 4°. The results of the elementary analysis and of the determination of the molecular weight agree with what is required by the desired anhydride



as does the decomposition by water. On being heated at the ordinary pressure it is decomposed with evolution of gas.

Dr. MOL obtained this substance in a still simpler manner by acting with oxychloride of phosphorus on an excess of potassium ethyl oxalate. The investigation is being continued with other dibasic acids.

Chemistry. — “*Thalictrum aquilegifolium*, a hydrogen cyanide-yielding plant.” By Dr. L. VAN ITALLIE. (Communicated by Prof. P. VAN ROMBURGH).

The communications from GUIGNARD (Compt. rend. de l'Acad. des Sciences du 24 Juillet 1905) as to the presence of a hydrogen cyanide-yielding glucoside in the leaves of *Sambucus nigra* L. and other varieties of elder have induced me to continue the experiments previously made in the same direction. I have been able to confirm the observations of GUIGNARD in every particular notwithstanding the figures which I found for the HCN-content are lower than those stated by him. This may, probably, be explained by the fact that I did not test the elder leaves until the beginning of September whilst GUIGNARD made his experiments in June.

From 100 grams of fresh leaves of *Sambucus nigra* I obtained 8,3 milligrs. and from 100 grams of *Sambucus nigra* var. *laciniata* 7,7 milligrs. of HCN. No HCN was obtained from 100 grams of *Sambucus Ebulus*.

The ornamental plant *Thalictrum aquilegifolium* (which appears to

grow wild in the environs of Nijmegen) appears, however, to be comparatively rich in HCN-yielding material.

If the leaves of this Ranunculaceus are crushed and digested with water for 12 hours at 30°—36° a hydrogen cyanide-containing distillate will be obtained on distillation.

The distillate from 100 grams of fresh leaves collected on Sept. 11 in the botanical garden of the Veterinary School yielded 248,8 milligrs. of AgCN = 50,2 milligrs. of HCN = 0,05 per cent. A volumetric experiment which showed 53 milligrs. of HCN confirmed this result.

A third experiment made with leaves, kindly forwarded to me from the Botanical Gardens at Groningen, gave 0,06 per cent of HCN in the distillate obtained from the same quantity of leaves.

I failed to obtain any HCN from the root of the plant and 142 grams of the fresh stem only yielded 4,4 milligrs. of HCN.

The leaves of *Thalictrum aquilegifolium* are therefore, comparatively rich in HCN-yielding material.

No HCN-containing distillate could be obtained from *Thalictrum flavum*, *Thalictrum minus* and *Thalictrum glaucum*.

Hydrogen cyanide could not be detected in the leaves in the free state. When fresh leaves were immersed in hot alcohol no HCN could be detected in the alcoholic distillate.

The hydrogen cyanide is formed during the digestion and is, therefore, most probably liberated from a glucoside by the action of an enzyme.

This enzyme is probably closely related to emulsin. I have obtained it, in an impure condition, by extracting the fresh, crushed leaves with water, and adding to the filtrate a large amount of alcohol. The precipitate so obtained was carefully dried; it very readily resolved amygdalin.

The glucoside present in *Thalictrum aquilegifolium* is not identical with amygdalin but is probably so with phaseolunatin isolated from *Phaseolus lunatus* by DUNSTAN and HENRY (Proc. Royal Soc. LXXII, 482, 1903), because in the hydrogen cyanide-containing distillate acetone can be detected, but no benzaldehyde. The presence of the former was shown from the iodoform-reaction with ammonia and tincture of iodine and the solubility of freshly precipitated mercuric oxide in the distillate.

Owing to the small quantity of leaves at my disposal it was useless to attempt the isolation of the glucoside in the pure state. I intend doing so next year, and also to watch the development of the glucoside in the plant.

I may, however, state provisionally that this glucoside is either insoluble or at most very slightly soluble in cold alcohol. When the leaves, after being dried in an airbath at 80°, and then powdered, were extracted with cold alcohol, no HCN and acetone could be obtained by enzyme-action from the alcoholic residue.

When the extracted powder after being dried was mixed with water, and then brought in contact with the enzyme, the aqueous distillate showed abundant evidence of the presence of HCN and acetone.

Utrecht, September 25, 1905.

Chemistry. — Prof. P. VAN ROMBURGH presents a communication: *“On the action of ammonia and amines on formic esters of glycols and glycerol”* (II).

As the action of ammonia and amines on allyl formate (Proc. June 24 '05) had yielded such good results to me, I have also included in my research other formic esters, and I now communicate, briefly, the results obtained with the formates of some polyhydric alcohols.

If gaseous ammonia is allowed to act on the diformate of glycol it is first absorbed slowly with evolution of heat. If, when the action is over, the liquid is distilled, nothing passes over at the boiling point of the diformate (174°), but the temperature rises at once to the boiling point of glycol, and then gradually to that of formamide. A complete separation of the two substances, whose boiling point only differs about 20°, does not succeed with small quantities, and although it has been proved that the reaction takes place readily and almost quantitatively, formamide cannot be obtained pure in this way.

One gram of the diformate when mixed with 2 grams of dipropylamine gave a slow rise from 18° to 42°. The liquid being distilled the formate again seemed to have disappeared, and a fraction could be obtained at the boiling point of the glycol, and another at that of dipropylformamide.

With 1.8 gram of benzylamine, 1 gram of glycol diformate gave a slow rise from 18° to 80°. On distillation, the formate seemed to have disappeared and the glycol being distilled off, nearly the theoretical amount of benzylformamide was left in a pure condition.

If gaseous ammonia is allowed to act on the diformate of propanediol (1. 2), which I prepared by heating this glycol with formic acid, phenomena are noticed analogous to those in the case of glycol

diformate. After the action is over the ester has again disappeared, and a mixture of propanediol (1. 2) and formamide has formed.

7 grams of this diformate being mixed with 10 grams of piperidine the temperature rose from 20° to 120° and on fractionation it again appeared that the ester had been completely converted into propanediol, whilst the formylpiperidine, after a few distillations, could be separated in a fairly pure condition. The boiling point was a little too low, probably owing to traces of the glycol.

With 7 grams of benzylamine, the diformate of propanediol (1. 2.) gave a rise from 20° to 110°. On distillation the formed glycol passed over at about 190°. The residue which had been heated to about 250° (thermometer immersed in the liquid) solidified on cooling, and consisted of nearly pure benzylformamide. It may be distilled at about 295° with only slight decomposition. The distilled product had a faint odour of carbylamine, and melted at 59°. By recrystallisation the melting point rose to 61°.

If gaseous ammonia is passed into a mixture of formines of glycerol, such as is obtained for instance by boiling glycerol with formic acid, or heating with oxalic acid, and then removing the free formic acid by distillation in vacuo, it is absorbed with great evolution of heat. After expelling the excess of ammonia and distilling in vacuo a rich yield of almost pure formamide is obtained.

In one of my experiments 66 grams of formine (yielding 65 % of formic acid on saponification) was saturated with ammonia. In the first distillation 22 grams of formamide m.p. 0° and 17 grams dito m.p. — 2° were separated whilst 40 grams of glycerol remained in the distilling flask. The yield was therefore practically the theoretical one so that this method may be recommended for the rapid preparation of formamide in large quantities.

With pure triformine¹⁾ the action of ammonia is slower than with the above mentioned mixture. Triformine of glycerol eagerly absorbs gaseous dimethylamine with strong evolution of heat, and on distillation in vacuo a good yield of the dimethylformamide b. p. 153° is obtained. Piperidine gives with triformine a considerable rise in temperature (from 20° to 70°).

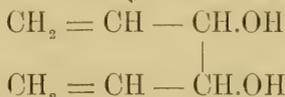
Dipropylamine forms with triformine, at first, two layers. After a little shaking (the temperature rose from 18° to 77°) the liquid becomes homogeneous, and by distillation in vacuo a good yield of the dipropylformamide formed could be readily obtained.

With diisobutylamine, triformine also gives two layers which do

¹⁾ I hope to communicate about this substance, shortly.

not disappear on shaking for a while, but if the liquid was allowed to stand over night it became homogeneous, and on distillation in vacuo yielded diisobutylformamide.

Formic esters of unsaturated glycols also seem to react readily with amines, at least Mr. W. VAN DORSEN, who is engaged in the Utrecht laboratory upon the study of the 3.4-dihydroxy-1.5-hexadiene



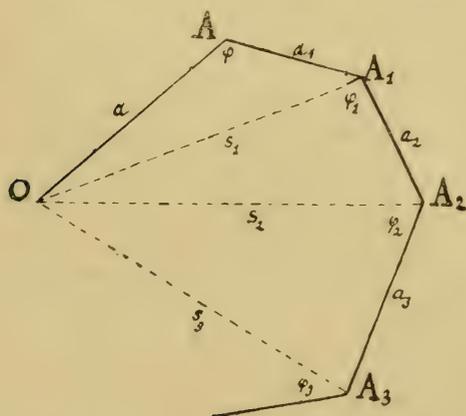
obtained, on mixing 1 gram of the diformate of this glycol with 1.3 gram of benzylamine, a rise in temperature from 18° to 65° , and after distilling off the glycol could readily isolate benzyiformamide m. p. 61° .

Mathematics. — “A local probability problem”. By Prof. J. C. KLUYVER.

The following problem was lately (Nature, July 27) proposed by Prof. PEARSON:

“A man starts from a point O , and walks l yards in a straight line; he then turns through any angle whatever, and walks another l yards in a second straight line. He repeats this process n times. I require the probability that after these n stretches he is at a distance between r and $r + dr$ from his starting point O .”¹⁾

I find that the general solution of this problem depends upon the theory of BESSEL'S functions, especially that in some particular cases it leads to the evaluation of certain definite integrals, involving these functions.



Let $OAA_1A_2A_3 \dots A_{n-1}$ be the broken line, the n stretches of which need not be all of the same length. Then the shape of the figure, not its orientation in the plane, is wholly determined by the lengths $a, a_1, a_2, \dots, a_{n-1}$ of the stretches, and by the magnitudes of the angles $\varphi, \varphi_1, \dots, \varphi_{n-2}$, formed at the origin of each stretch a_k by the stretch itself and by the radius vector s_{k-1} .

¹⁾ Recently (Nature, August 10) Prof. PEARSON stated, that the solution for n very large was already virtually contained in a memoir on sound by Lord RAYLEIGH.

In a turning point the rambler takes his new direction at random; hence for any angle φ_k , all values between 0 and 2π have an equal chance, and the probability that those angles are respectively included within the intervals, $\varphi_k, \varphi_k + d\varphi_k$, is equal to the product

$$\frac{1}{(2\pi)^{n-1}} d\varphi d\varphi_1 \dots d\varphi_{n-2}.$$

If we integrate this product over a region, determined by the condition that the n^{th} radius vector s_{n-1} remains less than a given distance c , the result will be the required probability $W_n(c; aa_1 a_2 \dots a_{n-1})$, that the ending point of the path lies within the distance c from the starting point O .¹⁾

The integration becomes less complicated, if we introduce in the usual way a discontinuous factor. Choosing a function $T(\varphi, \varphi_1, \dots, \varphi_{n-2})$ such, that it vanishes when $s_{n-1} > c$, and that it is equal to unity for $s_{n-1} < c$, to each of the variables φ_k we may give the whole range from 0 to 2π , and we have

$$W_n(c; aa_1 \dots a_{n-1}) = \frac{1}{(2\pi)^{n-1}} \int_0^{2\pi} \int_0^{2\pi} \dots \int_0^{2\pi} d\varphi d\varphi_1 \dots d\varphi_{n-2} T(\varphi, \varphi_1, \dots, \varphi_{n-2}).$$

For the function T we may take WEBER'S discontinuous integral, that is, we may put

$$T(\varphi, \varphi_1, \dots, \varphi_{n-2}) = c \int_0^{\infty} J_1(uc) J_0(us_{n-1}) du,$$

the integral being equal to zero or to unity according to s_{n-1} being larger or smaller than c .

This choice of the factor T makes a good deal of reduction possible.

If we consider the side c of a triangle as a function of the sides a and b and of the inclosed angle C , the relation holds

$$J_0(ua) J_0(ub) = \frac{1}{2\pi} \int_0^{2\pi} J_0(uc) dC,$$

and this formula can be repeatedly used in reducing the integral $W_n(c; aa_1 \dots a_{n-1})$.

So we get successively

¹⁾ In the case $n=2$, we have, supposing $a + a_1 > c > a - a_1$, $W_2(c; aa_1) = \frac{1}{\pi} \arccos \frac{a^2 + a_1^2 - c^2}{2aa_1}$. Of course for $c > a + a_1$ W_2 becomes equal to unity and it is zero for $a - a_1 > c$.

$$J_0(us_{n-2}) J_0(ua_{n-1}) = \frac{1}{2\pi} \int_0^{2\pi} J_0(us_{n-1}) d\varphi_{n-2},$$

$$J_0(us_{n-3}) J_0(ua_{n-2}) = \frac{1}{2\pi} \int_0^{2\pi} J_0(us_{n-2}) d\varphi_{n-1},$$

.....

$$J_0(ua) J_0(ua_1) = \frac{1}{2\pi} \int_0^{2\pi} J_0(us_1) d\varphi,$$

and consequently

$$W_n(c; aa_1 \dots a_{n-1}) = c \int_0^\infty J_1(uc) J_0(ua) J_0(ua_1) \dots J_0(ua_{n-1}) du.$$

From this result we infer, that the probability sought for is of a rather intricate character. The $n + 1$ functions J are oscillating functions, and have their signs altering in an irregular manner as the variable u increases. Hence even an approximation of the integral is not easily found, and as a solution of PEARSON'S problem it is little apt to meet the requirements of the proposer.

From a mathematical point of view the integral presents some interest. In fact, if we consider it as a function of c , it is readily seen to be continuous and finite for all real values of c , and the same holds for a certain number of derivatives with respect to c , but a closer inspection shows, that this analytic expression, regularly built up as it is, represents in different intervals different analytic functions. To make good this assertion, we have only to remember that the integral stands for the probability required in PEARSON'S problem. Hence we know beforehand, that it always must be positive and increasing with c , but that it never surpasses 1, this upper limit being actually reached as soon as c becomes greater than $a + a_1 + \dots + a_{n-1}$. Moreover, if we suppose $a > a_1 + a_2 + \dots + a_{n-1}$, the inequality $a > c + a_1 + a_2 \dots + a_{n-1}$ is possible for small values of c . And if the latter inequality holds, the rambler of PEARSON'S problem necessarily arrives outside the circle with radius c , and the probability is zero.

Thus, by solving the problem, we have found

$$c > a + a_1 \dots + a_{n-1}, \dots 1 \left. \vphantom{c} \right\} = c \int_0^\infty J_1(uc) J_0(ua) J_0(ua_1) \dots J_0(ua_{n-1}) du,$$

$$a > c + a_1 \dots + a_{n-1}, \dots 0 \left. \vphantom{a} \right\}$$

quite independently of the number of the J_0 -functions, showing

Putting $na = L$, $c = \frac{L}{a}$, we have

$$W_n(c; a^n) = W_n(c/L) = \int_0^\infty J_1(u) J_0\left(\frac{au}{n}\right)^n du.$$

Now by raising to the n^{th} power the ordinary power series for $J_0\left(\frac{au}{n}\right)$ we get

$$J_0\left(\frac{au}{n}\right)^n = 1 + \sum_{k=1}^{k=\infty} \frac{(-1)^k}{k!} \cdot \left(\frac{au}{n}\right)^{2k} \cdot \frac{S_k(n)}{k! n^{2k}},$$

where $S_k(n)$ stands for the sum of squares of the coefficients of the expansion $(u_1 + u_2 + \dots + u_n)^k$, so that

$$\frac{S_1(n)}{1! n^2} = \frac{1}{n}, \quad \frac{S_2(n)}{2! n^4} = \frac{1}{n^2} - \frac{1}{2n^3}, \quad \frac{S_3(n)}{3! n^6} = \frac{1}{n^3} - \frac{3}{2n^4} + \frac{2}{3n^5}.$$

Generally supposing n very large we may put approximately

$$\frac{S_k(n)}{k! n^{2k}} = \frac{1}{n^k},$$

and, substituting, we find that this approximation leads to the supposition

$$J_0\left(\frac{au}{n}\right)^n = e^{-\frac{\alpha^2 u^2}{4n}}.$$

For small values of u the approximation is good enough. It is true both functions behave quite differently when u becomes very large, but as they are rather rapidly converging to zero, the actual amount of their difference can be neglected. In particular I find that the integral

$$\int_n^\infty J_1(u) J_0\left(\frac{au}{n}\right)^n du$$

is of an order of smallness certainly higher than that of the expression

$$\frac{2n}{n-2} \cdot \left(\frac{2}{\pi}\right)^{\frac{n+1}{2}} \cdot \left(\frac{1}{a}\right)^{\frac{n}{2}},$$

while the order of smallness of the integral

$$\int_n^\infty J_1(u) e^{-\frac{\alpha^2 u^2}{4n}} du$$

is that of the expression

$$e^{-\frac{1}{4}\alpha^2 n} (J_0(n) - J_0(q)), \quad q > n.$$

Hence if only α be rather greater than unity, both integrals cannot have an appreciable difference and we may put

$$W_n(c/L) = \int_0^\infty J_1(u) e^{-\frac{u^2 \alpha^2}{4n}} du = 1 - e^{-\frac{n}{\alpha^2}} = 1 - e^{-n \frac{c^2}{L^2}}.$$

From this result it is evident, that $W_n(c/L)$ for n very large is always nearly unity. The rambler, walking along a very great number of very short stretches will almost certainly arrive in the neighbourhood of his starting point.

Putting $c = \frac{1}{n} L$, we find $W_n(c/L) = 1 - e^{-\frac{1}{n}} = \frac{1}{n} - \frac{1}{2n^2} \dots$, a result nearly equal to the true value $\frac{1}{n+1}$.

Returning to the general expression for $W_n(c; a a_1 \dots a_{n-1})$ we observe the possibility of differentiating the integral with respect to c in the usual way a number of $2m$ times, provided $2m < \frac{n+1}{2}$.

Supposing $c > a + a_1 + \dots + a_{n-1}$ and putting

$$J_0(ua) J_0(ua_1) \dots J_0(ua_{n-1}) = f(u),$$

we deduce by differentiation

$$1 = c \int_0^\infty J_1(cu) f(u) du,$$

$$0 = \int_0^\infty u J_0(cu) f(u) du \quad , \quad 0 = \int_0^\infty u^2 J_1(cu) f(u) du,$$

$$0 = \int_0^\infty u^3 J_0(cu) f(u) du \quad , \quad 0 = \int_0^\infty u^4 J_1(cu) f(u) du,$$

.

$$0 = \int_0^\infty u^{2m-1} J_0(cu) f(u) du \quad , \quad 0 = \int_0^\infty u^{2m} J_1(cu) f(u) du.$$

These equations allow us to introduce into the integral a new BESSEL function, the function $J_{2m+1}(u)$. For $J_{2m+1}(u)$ is connected with $J_0(u)$ and $J_1(u)$ by the relation

$$J_{2m+1}(u) = P_{0,2m}(u) J_1(u) - P_{1,2m-1}(u) J_0(u),$$

where

$$P_{0,2m}(u) = \frac{1}{u^{2m}} (b_0 + b_2 u^2 + \dots + b_{2m} u^{2m})$$

and

$$P_{1,2m-1}(u) = \frac{1}{u^{2m}} (b_1 u + b_3 u^3 + \dots + b_{2m-1} u^{2m-1})$$

are a pair of SCHLÄFLI'S polynomials.

Using this relation we obtain

$$b_0 = c^{2m+1} \int_0^\infty u^{2m} J_{2m+1}(uc) f(u) du,$$

and as

$$b_0 = \lim_{u=0} u^{2m} P_{0,2m}(u) = 2^{2m} m!$$

we have

$$2^{2m} m! = c^{2m+1} \int_0^\infty u^{2m} J_{2m+1}(uc) J_0(ua) J_0(ua_1) \dots J_0(ua_{n-1}) du$$

with the conditions

$$c > a + a_1 + \dots + a_{n-1} \quad , \quad m < \frac{n+1}{4}.$$

Evidently the value of the integral would be zero, if instead of the first of these conditions the condition

$$a > c + a_1 + \dots + a_{n-1}$$

was satisfied.

In the same manner we might differentiate and also integrate with respect to one or to several of the parameters a . This leads for instance to the following results

$$n \text{ even:} \quad 0 = \int_0^\infty J_1(uc) J_1(ua) J_1(ua_1) \dots J_1(ua_{n-1}) du$$

$$n \text{ odd:} \quad 0 = \int_0^\infty u J_1(uc) J_1(ua) J_1(ua_1) \dots J_1(ua_{n-1}) du.$$

$$c > a + a_1 + a_2 + \dots + a_{n-1}.$$

Still other results present themselves when PEARSON'S problem is slightly modified. Again putting

$$J_0(ua) J_0(ua_1) \dots J_0(ua_{n-1}) = f(u)$$

and writing q for c , we get by differentiation with respect to q

$$W_n(d\Omega) = \frac{1}{2\pi} \varrho d\varrho d\theta \int_0^\infty u J_0(u\varrho) f(u) du,$$

and here $W_n(d\Omega)$ means the probability that the ending point of the broken line falls on a given element $d\Omega$ of the plane, the polar coordinates of which are ϱ, θ .

By integrating over a given finite region we may deduce the probability that the rambler reaches that region ¹⁾.

First let the region be a rectangle R , and let the rectangular coordinates of its vertices be $\pm p, \pm q$, then we find for the corresponding probability

$$W_n(R) = \frac{1}{2\pi} \int_0^\infty u f(u) du \int_{-p}^{+p} d\xi \int_{-q}^{+q} d\eta J_0(u\sqrt{\xi^2 + \eta^2}).$$

Now we have

$$J_0(u\sqrt{\xi^2 + \eta^2}) = \frac{1}{2\pi} \int_0^{2\pi} \cos(u\xi \cos \alpha) \cos(u\eta \sin \alpha) d\alpha,$$

and therefore, effectuating the integrations with respect to ξ and to η ,

$$W_n(R) = \frac{4}{\pi^2} \int_0^\infty u f(u) du \int_0^{\frac{\pi}{2}} \frac{\sin(pu \cos \alpha) \sin(qu \sin \alpha)}{u^2 \sin \alpha \cos \alpha} d\alpha.$$

A somewhat simpler expression is found, if changing the variables we pass from u and α to

$$\begin{aligned} v &= u \cos \alpha, \\ w &= u \sin \alpha. \end{aligned}$$

Then the probability $W_n(R)$ is expressed as follows:

$$W_n(R) = \frac{4}{\pi^2} \int_0^\infty \int_0^\infty dv dw \frac{\sin pv}{v} \cdot \frac{\sin qw}{w} \cdot f(\sqrt{v^2 + w^2}).$$

Again an evaluation of this double integral is generally not practicable, but the problem itself gives the value of the integral, if both

¹⁾ If this region is a circle with radius c , the centre of which lies at a distance b from the starting point O , we have at once

$$W_{n+1}(c; baa_1 \dots a_{n-1}) = c \int_0^\infty J_1(uc) J_0(ub) J_0(ua) J_0(ua_1) \dots J_0(ua_{n-1}) du$$

for the probability, that the path ends inside the circle.

the coordinates p, q are surpassing the total length of the path. Then the probability becomes a certainty and it follows that

$$\frac{\pi^2}{4} = \int_0^\infty \int_0^\infty dv dw \frac{\sin pv}{v} \cdot \frac{\sin qw}{w} \cdot f(\sqrt{v^2 + w^2})$$

with the condition

$$p \text{ and } q > a + a_1 + \dots + a_{n-1}.$$

In the general case of the rectangle the probability $W_n(R)$ is independent of q , as soon as its length is superior to that of the path.

Assuming this to be the case, we remark that the value of the slightly transformed integral

$$W_n(R) = \frac{4}{\pi^2} \int_0^\infty \int_0^\infty dv dw \frac{\sin pv}{v} \cdot \frac{\sin w}{w} \cdot f\left(\sqrt{v^2 + \frac{w^2}{q^2}}\right)$$

remains unaltered, when q increases indefinitely, and we conclude that

$$\lim_{q=\infty} W_n(R) = \frac{4}{\pi^2} \int_0^\infty \frac{\sin pv}{v} f(v) dv \cdot \int_0^\infty \frac{\sin w}{w} dw = \frac{2}{\pi} \int_0^\infty \frac{\sin pv}{v} f(v) dv.$$

Thus we have solved another modification of PEARSON'S problem, for half the result, added to $\frac{1}{2}$, expresses the probability

$$W_n(F) = \frac{1}{2} + \frac{1}{\pi} \int_0^\infty \frac{\sin pv}{v} f(v) dv,$$

that the rambler, starting on his walk at a distance p of a straight frontier F , after walking along n stretches, will arrive at that side of the frontier he came from ¹⁾.

As before we are enabled in a particular case by the problem itself to assign the value of the integral. If we suppose that the rambler cannot reach the frontier, that is, if we take

$$p > a + a_1 + \dots + a_{n-1},$$

the probability becomes a certainty and we find

¹⁾ Obviously the probability $W_n(F)$ might have been derived from the probability $W_{n+1}(\omega + p; \omega a_1 \dots a_{n-1})$ by making ω indefinitely large. Therefore we may conclude that

$$\lim_{\omega=\infty} (\omega + p) \int_0^\infty J_1(u\overline{\omega + p}) J_0(u\omega) f(u) du = \frac{1}{2} + \frac{1}{\pi} \int_0^\infty \frac{\sin pv}{v} f(v) dv.$$

$$\frac{\pi}{2} = \int_0^{\infty} \frac{\sin vp}{v} J_0(va) J_0(va_1) \dots J_0(va_{n-1}) dv.$$

In the case $n = 1$, this is a known result to which another may be added, if we take $a > p$. When the single stretch a is inclined to the frontier under an angle less than

$$\text{arc sin } \frac{p}{a},$$

the Rambler remains at the same side and, all directions of the stretch being equally possible, we have

$$W_1(F) = \frac{1}{\pi} \left(\frac{\pi}{2} + \text{arc sin } \frac{p}{a} \right),$$

hence

$$\text{arc sin } \frac{p}{a} = \int_0^{\infty} \frac{\sin vp}{v} J_0(va) dv.$$

Mathematics. — “*A definite integral of KUMMER*”. By Prof. W. KAPTEYN.

In CRELLE'S Journal, Vol. 17, KUMMER has determined the value of the integral

$$U_p = \int_0^{\infty} e^{-x - \frac{b^2}{x}} x^p dx,$$

supposing b^2 to represent a positive quantity and p not an integer. He finds:

$$U_p = \Gamma(p+1) f(-p, b^2) + \Gamma(-p-1) b^{2p+2} f(p+2, b^2),$$

where

$$\begin{aligned} f(p, x) &= 1 + \frac{x}{1!p} + \frac{x^2}{2!p(p+1)} + \frac{x^3}{3!p(p+1)(p+2)} + \dots \\ &+ \dots = \sum_{s=0}^{\infty} \frac{x^s}{s!p(p+1)\dots(p+s-1)}. \end{aligned}$$

In the following pages we propose to study this integral for the case that p represents a positive integer, and at the same time to show that there is a simple connection between this integral and the integral

$$V_p = \int_b^{\infty} e^{-x - \frac{b^2}{x}} x^p dx,$$

where b is supposed to be positive.

It is rational to put in the integral of KUMMER

$$p = n - \varepsilon,$$

assuming n to be an integer and ε an arbitrary infinitesimal, and then to determine the limit for $\varepsilon = 0$.

Let us therefore examine the limit of

$$U_{n-\varepsilon} = \Gamma(n+1-\varepsilon) f(-n+\varepsilon, b^2) + \Gamma(-n-1+\varepsilon) b^{2n+2-2\varepsilon} f(n+2-\varepsilon, b^2)$$

for $\varepsilon = 0$.

Suppose

$$\Gamma(n+1-\varepsilon) = A_0 + A_1 \varepsilon + A_2 \varepsilon^2 \dots$$

$$f(-n+\varepsilon, b^2) = \frac{B_0}{\varepsilon} + B_1 + B_2 \varepsilon + \dots$$

$$\Gamma(-n-1+\varepsilon) = \frac{C_0}{\varepsilon} + C_1 + C_2 \varepsilon + \dots$$

$$b^{2n+2-2\varepsilon} = D_0 + D_1 \varepsilon + D_2 \varepsilon^2 + \dots$$

$$f(n+2-\varepsilon, b^2) = E_0 + E_1 \varepsilon + E_2 \varepsilon^2 + \dots$$

then

$$U_{n-\varepsilon} = \frac{A_0 B_0 + C_0 D_0 E_0}{\varepsilon} + [A_1 B_0 + A_0 B_1 + C_1 D_0 E_0 + C_0 D_1 E_0 + C_0 D_0 E_1] + \dots$$

and the limit

$$U_n = A_1 B_0 + A_0 B_1 + C_1 D_0 E_0 + C_0 D_1 E_0 + C_0 D_0 E_1,$$

for we shall see that

$$A_0 B_0 + C_0 D_0 E_0 = 0.$$

Let us now determine the various coefficients.

First we have

$$\Gamma(n+1-\varepsilon) = \Gamma(n+1) - \varepsilon \Gamma(n+1) \frac{\Gamma'(n+1)}{\Gamma(n+1)} + \dots$$

or if we put

$$\frac{\Gamma'(x)}{\Gamma(x)} = \psi(x),$$

$$\Gamma(n+1-\varepsilon) = n! [1 - \varepsilon \psi(n+1) + \dots],$$

thus

$$A_0 = n!,$$

$$A_1 = -n! \psi(n+1).$$

To find B_0 and B_1 we write

$$f(-n+\varepsilon, b^2) = \sum_{s=0}^{\infty} \frac{b^{2s}}{s!(-n+\varepsilon)(-n+1+\varepsilon)\dots(-n+s-1+\varepsilon)} +$$

$$+ \frac{1}{\varepsilon} \sum_{s=0}^{\infty} \frac{b^{2n+2+2s}}{(n+s+1)!(-n+\varepsilon)(-n+1+\varepsilon)\dots(-1+\varepsilon)(1+\varepsilon)\dots(s+\varepsilon)}$$

If

$$\frac{1}{(-n + \epsilon)(-n + 1 + \epsilon)\dots(-1 + \epsilon)(1 + \epsilon)\dots(s + \epsilon)} = \lambda(\epsilon) = \lambda(0) \left[1 + \epsilon \frac{\lambda'(0)}{\lambda(0)} + \dots \right],$$

then we easily find

$$\lambda(0) = \frac{(-1)^n}{n!s!}$$

and

$$\frac{\lambda'(0)}{\lambda(0)} = \frac{1}{n} + \frac{1}{n-1} + \dots + \frac{1}{1} - \left(\frac{1}{1} + \frac{1}{2} + \dots + \frac{1}{s} \right) = \psi(1+n) - \psi(1+s),$$

therefore

$$B_0 = \frac{(-1)^n b^{2n+2}}{n!} \sum_{s=0}^{\infty} \frac{b^{2s}}{s!(n+s+1)!} = \frac{(-1)^n b^{2n+2}}{n!(n+1)!} f(n+2, b^2)$$

$$B_1 = \frac{1}{n!} \sum_{s=0}^n \frac{(-1)^s (n-s)!}{s!} b^{2s} + \frac{(-1)^n b^{2n+2}}{n!(n+1)!} \psi(1+n) f(n+2, b^2) -$$

$$- (-1)^n \frac{b^{2n+2}}{n!} \sum_{s=0}^{\infty} \frac{\psi(1+s) b^{2s}}{s!(n+s+1)!}.$$

For the evaluation of C_0 and C_1 we have

$$\Gamma(-n-1+\epsilon) = \frac{1}{-n-1+\epsilon} \Gamma(-n+\epsilon),$$

$$\Gamma(-n+\epsilon) = \frac{1}{-n+\epsilon} \Gamma(-n+1+\epsilon),$$

.

$$\Gamma(-2+\epsilon) = \frac{1}{-2+\epsilon} \Gamma(-1+\epsilon),$$

$$\Gamma(-1+\epsilon) = \frac{1}{-1+\epsilon} \Gamma(\epsilon),$$

so

$$\Gamma(-n-1+\epsilon) = \frac{(-1)^{n+1}}{(n+1-\epsilon)(n-\epsilon)\dots(2-\epsilon)(1-\epsilon)} \Gamma(\epsilon).$$

Assuming

$$\frac{1}{(n+1-\epsilon)(n-\epsilon)\dots(2-\epsilon)(1-\epsilon)} = \mu(\epsilon) = \mu(0) \left[1 + \epsilon \frac{\mu'(0)}{\mu(0)} + \dots \right],$$

then

$$\mu(0) = \frac{1}{(n+1)!},$$

$$\frac{\mu'(0)}{\mu(0)} = \frac{1}{n+1} + \frac{1}{n} + \dots + \frac{1}{2} + 1 = \psi(n+2) - \psi(1),$$

whilst

$$\Gamma(\epsilon) = P(\epsilon) + Q(\epsilon)$$

$$\begin{aligned}
&= \frac{1}{\varepsilon} - \frac{1}{1+\varepsilon} + \frac{1}{2!} \frac{1}{2+\varepsilon} - \frac{1}{3!} \frac{1}{3+\varepsilon} + \dots + Q(\varepsilon) \\
&= \frac{1}{\varepsilon} + Q(0) - 1 + \frac{1}{2!2} - \frac{1}{4!3} + \frac{1}{4!4} - \dots
\end{aligned}$$

If we no notice that

$$Q(0) = \int_1^{\infty} \frac{e^{-x}}{x} dx = - \int_0^{e^{-1}} \frac{dy}{lgy} = - li(e^{-1})$$

and that out of the well known formula

$$li(e^{-x}) = -\psi(1) + lgx - x + \frac{x^2}{2!2} - \frac{x^3}{3!3} + \frac{x^4}{4!4} - \dots$$

follows

$$li(e^{-1}) = -\psi(1) - 1 + \frac{1}{2!2} - \frac{1}{3!3} + \frac{1}{4!4} - \dots,$$

then it is evident that

$$\Gamma(\varepsilon) = \frac{1}{\varepsilon} + \psi(1) + \dots,$$

from which ensues

$$\begin{aligned}
C_0 &= \frac{(-1)^{n+1}}{(n+1)!}, \\
C_1 &= \frac{(-1)^{n+1}}{(n+1)!} \psi(n+2).
\end{aligned}$$

Moreover we find

$$b^{2n+2-2\varepsilon} = b^{2n+2}(elgb)^{-2\varepsilon} = b^{2n+2}[1 - 2\varepsilon lgb + \dots],$$

so

$$\begin{aligned}
D_0 &= b^{2n+2} \\
D_1 &= -2b^{2n+2}lgb
\end{aligned}$$

and finally

$$f(n+2-\varepsilon, b^2) = \sum_{s=0}^{\infty} \frac{b^{2s}}{s!(n+2-\varepsilon)(n+3-\varepsilon)\dots(n+s+1-\varepsilon)}.$$

If again we put

$$\frac{1}{(n+2-\varepsilon)(n+3-\varepsilon)\dots(n+s+1-\varepsilon)} = r(\varepsilon) = r(0) \left[1 + \varepsilon \frac{r'(0)}{r(0)} + \dots \right],$$

we find

$$\begin{aligned}
r(0) &= \frac{1}{(n+2)(n+3)\dots(n+s+1)} \\
\frac{r'(0)}{r(0)} &= \frac{1}{n+2} + \frac{1}{n+3} + \dots + \frac{1}{n+s+1} = \psi(n+s+2) - \psi(n+2),
\end{aligned}$$

so that

$$E_0 = f(n+2, b^2),$$

$$E_1 = -\psi(n+2) f'(n+2, b^2) + \sum_{s=0}^{\infty} \frac{\psi(n+s+2)b^{2s}}{s!(n+2)\dots(n+s+1)}.$$

With the aid of these values we find

$$A_0 B_0 + C_0 D_0 E_0 = 0,$$

$$\begin{aligned} A_1 B_0 + A_0 B_1 &= \sum_{s=0}^n (-1)^s \frac{(n-s)!}{s!} b^{2s} - (-1)^n b^{2n+2} \sum_{s=0}^{\infty} \frac{\psi(1+s) b^{2s}}{s!(n+s+1)!}, \\ C_1 D_0 E_0 + C_0 D_1 E_0 + C_0 D_0 E_1 &= \\ &= \frac{(-1)^n}{(n+1)!} b^{2n+2} \left[2 \lg b f'(n+2, b^2) - \sum_{s=0}^{\infty} \frac{\psi(n+s+2) b^{2s}}{s!(n+2)(n+3)\dots(n+s+1)} \right], \end{aligned}$$

hence

$$\begin{aligned} U_n &= \sum_{s=0}^n (-1)^s \frac{(n-s)!}{s!} b^{2s} + \\ &+ (-1)^n b^{2n+2} \sum_{s=0}^{\infty} \frac{b^{2s}}{s!(s+n+1)!} [2 \lg b - \psi(1+s) - \psi(n+s+2)] \dots (1) \end{aligned}$$

Let us now determine U_n in another way to give this result another form. To this end we differentiate the equation

$$U_n = \int_0^{\infty} e^{-x-\frac{b^2}{x}} x^n dx,$$

we then get

$$-\frac{1}{2b} \frac{dU_n}{db} = \int_0^{\infty} e^{-x-\frac{b^2}{x}} x^{n-1} dx. \dots (a)$$

$$-\frac{1}{2b} \frac{d^2 U_n}{db^2} + \frac{1}{2b^2} \frac{dU_n}{db} = -2b \int_0^{\infty} e^{-x-\frac{b^2}{x}} x^{n-2} dx.$$

Out of the identity

$$x^n d \left(e^{-x-\frac{b^2}{x}} \right) = -e^{-x-\frac{b^2}{x}} x^n dx + b^2 e^{-x-\frac{b^2}{x}} x^{n-2} dx,$$

we moreover deduce by integrating between the limits 0 and ∞

$$-n \int_0^{\infty} e^{-x-\frac{b^2}{x}} x^{n-1} dx = - \int_0^{\infty} e^{-x-\frac{b^2}{x}} x^n dx + b^2 \int_0^{\infty} e^{-x-\frac{b^2}{x}} x^{n-2} dx,$$

hence we find for U_n the differential equation

$$\frac{d^2 U_n}{db^2} - \frac{2n+1}{b} \frac{dU_n}{db} - 4 U_n = 0. \dots (2)$$

This differential equation we also find if we put $x = 2i b$ and $v = \frac{U_n}{b^{n+1}}$ in BESSEL's equation :

$$\frac{d^2 v}{dx^2} + \frac{1}{x} \frac{dv}{dx} + \left(1 - \frac{(n+1)^2}{x^2}\right) v = 0,$$

therefore

$$U_n = b^{n+1} [A I^{n+1}(2i b) + B Y^{n+1}(2i b)].$$

In order to determine the constants properly I notice that the integral U_n for $b = 0$ is equal to $n!$ and vanishes for $b = \infty$; moreover we find

for $b = 0$ $b^{n+1} I^{n+1}(2i b) = 0,$

„ „ $b^{n+1} Y^{n+1}(2i b) = -(-i)^{n+1} \frac{n!}{\pi},$

for $b = \infty$ $b^{n+1} I^{n+1}(2i b) = \frac{b^{n+1}}{2\sqrt{\pi b}} e^{2b + \frac{(n+1)i\pi}{2}},$

„ „ $b^{n+1} Y^{n+1}(2i b) = \frac{b^{n+1}}{2\sqrt{\pi b}} e^{2b + \frac{(n+2)i\pi}{2}},$

thus

$$\begin{aligned} \pi &= -(-i)^{n+1} B, \\ 0 &= A + B e^{\frac{i\pi}{2}}, \end{aligned}$$

and finally

$$U_n = \pi i^{n+2} b^{n+1} [I^{n+1}(2i b) + i Y^{n+1}(2i b)] = \pi i^{n+2} b^{n+1} H_1^{n+1}(2i b)^1) ..(3)$$

That this value and the value (1) agree is easy to prove. For according to definition ¹⁾ we find:

$$\begin{aligned} \pi Y^{n+1}(2i b) &= 2 I^{n+1}(2i b) \left(\lg b + \frac{i\pi}{2} \right) - \left(\frac{1}{ib} \right)^{n+1} \sum_{s=0}^n \frac{(-1)^s (n-s)!}{s!} b^{2s} - \\ &- (i b)^{n+1} \sum_{s=0}^{\infty} \frac{b^{2s}}{s! (s+n+1)!} [\psi(s+1) + \psi(s+n+2)], \end{aligned}$$

from which ensues when we multiply by $i^{n+3} b^{n+1}$

$$\begin{aligned} n i^{n+2} b^{n+1} [I^{n+1}(2i b) + i Y^{n+1}(2i b)] &= 2 i^{n+3} b^{n+1} \lg b I^{n+1}(2i b) + \\ + \sum_{s=0}^n \frac{(-1)^s (n-s)!}{s!} b^{2s} - (-1)^n b^{2n+2} \sum_{s=0}^{\infty} \frac{b^{2s}}{s! (s+n+1)!} [\psi(s+1) + \psi(s+n+2)]. \end{aligned}$$

By

$$I^{n+1}(2i b) = (i b)^{n+1} \sum_{s=0}^{\infty} \frac{b^{2s}}{s! (s+n+1)!},$$

¹⁾ NIELSEN, Handbuch der Cylinderf. page 16.

the second member of the former equation becomes the second member of the equation (1).

Let us now examine

$$V_n = \int_b^\infty e^{-x-\frac{b^2}{x}} x^n dx \quad \dots \dots \dots (4)$$

Here too we can find a differential equation satisfied by this integral. By differentiating we find

$$-\frac{1}{2b} \frac{dV_n}{db} = \int_b^\infty e^{-x-\frac{b^2}{x}} x^{n-1} dx + \frac{1}{2} b^{n-1} e^{-2b} \quad \dots \dots (b)$$

$$-\frac{1}{2b} \frac{d^2 V_n}{db^2} + \frac{1}{2b^2} \frac{dV_n}{db} = -2b \int_b^\infty e^{-x-\frac{b^2}{x}} x^{n-2} dx - 2b^{n-1} e^{-2b} + \frac{n-1}{2} b^{n-2} e^{-2b} \quad \dots (c)$$

whilst the integration of the identity

$$x^n d \left(e^{-x-\frac{b^2}{x}} \right) = -e^{-x-\frac{b^2}{x}} x^n dx + b^2 e^{-x-\frac{b^2}{x}} x^{n-2} dx$$

between the limits b and ∞ furnishes

$$-b^n e^{-2b} - n \int_b^\infty e^{-x-\frac{b^2}{x}} x^{n-1} dx = - \int_b^\infty e^{-x-\frac{b^2}{x}} x^n dx + b^2 \int_b^\infty e^{-x-\frac{b^2}{x}} x^{n-2} dx .$$

So we find for V_n the differential equation

$$\frac{d^2 V_n}{db^2} - \frac{2n+1}{b} \frac{dV_n}{db} - 4V_n = (n+1)b^{n-1} e^{-2b} . \quad \dots (5)$$

If we now write the equations (a) and (b)

$$\frac{dU_n}{db} = -2b U_{n-1} . \quad \dots \dots \dots (6)$$

and

$$\frac{dV_n}{db} = -2b V_{n-1} - b^n e^{-2b} . \quad \dots \dots \dots (7)$$

it is easy to find out of (6) and (2)

$$U_n = -\frac{b}{2} \frac{dU_{n-1}}{db} + n U_{n-1}$$

and likewise out of (7) and (5)

$$V_n = -\frac{b}{2} \frac{dV_{n-1}}{db} + n V_{n-1} + \frac{b^n}{2} e^{-2b} .$$

Out of the last two equations we deduce the recurrent relation

$$V_n - \frac{1}{2} U_n = -\frac{b}{2} \frac{d}{db} [V_{n-1} - \frac{1}{2} U_{n-1}] + n [V_{n-1} - \frac{1}{2} U_{n-1}] + \frac{b^n}{2} e^{-2b} \dots (8)$$

by which we can reduce the evaluation of $V_n - \frac{1}{2} U_n$ to that of $V_0 - \frac{1}{2} U_0$.

Let us now determine the value of $V_0 - \frac{1}{2} U_0$. To this end we start from the equation (c); this becomes for $n = 0$

$$-\frac{1}{2b} \frac{d^2 V_0}{db^2} + \frac{1}{2b^2} \frac{dV_0}{db} = -2b \int_b^\infty e^{-x - \frac{b^2}{x}} \frac{dx}{x^2} - \frac{2}{b} e^{-2b} - \frac{1}{2b^2} e^{-2b}.$$

By substituting in this integral $\frac{b^2}{z}$ for x we find

$$\int_b^\infty e^{-x - \frac{b^2}{x}} \frac{dx}{x^2} = \frac{1}{b^2} \int_0^{\frac{b^2}{b}} e^{-z - \frac{b^2}{z}} dz = \frac{1}{b^2} (U_0 - V_0),$$

hence the preceding equation becomes

$$U_0 = \frac{1}{4} \frac{d^3 V_0}{db^3} - \frac{1}{4b} \frac{dV_0}{db} + V_0 - e^{-2b} \left(1 + \frac{1}{4b} \right).$$

By subtracting from this according to (5)

$$0 = \frac{1}{4} \frac{d^3 V_0}{db^3} - \frac{1}{4b} \frac{dV_0}{db} - V_0 - \frac{e^{-2b}}{4b},$$

we find

$$V_0 - \frac{1}{2} U_0 = \frac{1}{2} e^{-2b} \dots \dots \dots (9)$$

With the aid of equation (8) we get :

$$V_1 - \frac{1}{2} U_1 = \left(b + \frac{1}{2} \right) e^{-2b},$$

$$V_2 - \frac{1}{2} U_2 = \left(\frac{3b^2}{2} + 2b + 1 \right) e^{-2b},$$

$$V_3 - \frac{1}{2} U_3 = (2b^3 + 5b^2 + 6b + 3) e^{-2b},$$

$$V_4 - \frac{1}{2} U_4 = \left(\frac{5}{2} b^4 + 10b^3 + 21b^2 + 25b + 12 \right) e^{-2b},$$

in which we can easily trace the following law :

$$V_n - \frac{1}{2} U_n = \frac{1}{2} \left[\frac{(n+1)!}{n!} b^n + \frac{1!(n+2)!}{3!(n-1)!} b^{n-1} + \frac{2!(n+3)!}{5!(n-2)!} b^{n-2} + \dots + n! \right] e^{-2b} \dots (10)$$

Out of equation (8) and this one it is evident that $V_{n+1} - \frac{1}{2} U_{n+1}$ follows the same law ; so the relation (10) is proved.

Mathematics. — “An article on the knowledge of the tetrahedral complex.” By DR. Z. P. BOUMAN. (Communicated by Prof. JAN DE VRIES).

§ 1. When for an arbitrary ray out of a tetrahedral complex P_i represents the point of intersection with the face $A_k A_l A_m$ of the tetrahedron, then

$$R p_2 p_5 + p_3 p_6 = 0,$$

where R represents the given anharmonic ratio of the complex and p_i ($i = 1 \dots 6$) are the PLÜCKER coordinates of lines.

By using the condition necessary for each ray of the complex, namely

$$p_1 p_4 + p_2 p_6 + p_3 p_5 = 0$$

the equation of the complex becomes

$$A p_1 p_4 + B p_2 p_6 + C p_3 p_5 = 0,$$

where the anharmonic ratio is given by

$$R = \frac{B-A}{C-A}.$$

A given tetrahedral complex can always transform itself projectively into another one with the same anharmonic ratio in regard to the faces of the rectangular system of coordinates and the plane at infinity.

§ 2. After having executed this transformation we can examine whether a surface with two independent parameters can be found in such a manner that the normals to be erected in an arbitrary point on the ∞^1 number of surfaces passing through that point, are rays of the given tetrahedral complex.

To this end we make the two determining points to lie infinitely close to each other on each ray of the complex, so that each ray is determined by one point (x, y, z) and the direction (dx, dy, dz) in that point. The coordinates of lines now take the form:

$$\begin{aligned} p_1 &= x dy - y dx, & p_2 &= y dz - z dy, & p_3 &= z dx - x dz, \\ p_4 &= -dz, & p_5 &= -dx, & p_6 &= -dy. \end{aligned}$$

So the equation for the complex becomes:

$$A (x dy - y dx) dz + B (y dz - z dy) dx + C (z dx - x dz) dy = 0.$$

If now every ray of the complex is to be at right angles to a surface $z = f(x, y)$, then we have for each ray in each point of the surface:

$$dx : dy : dz = p : q : -1,$$

where $p = \frac{\partial z}{\partial x}$, $q = \frac{\partial z}{\partial y}$.

So the differential equation of the surface becomes :

$$-pqz(B - C) + yp(A - B) + xq(C - A) = 0$$

or

$$z - \frac{x}{p} \frac{1}{R-1} - \frac{y}{q} \frac{R}{1-R} = 0.$$

The complete integral with two parameters C and C_1 becomes :

$$z = \pm \sqrt{\frac{1}{R-1} \sqrt{x^2 - C}} \pm \sqrt{\frac{R}{1-R} \sqrt{y^2 - C_1}}.$$

It represents a surface of order four.

It is evident out of the equation that for $R = \frac{1}{R'}$ the surface remains the same; only the X - and the Y -axes have been interchanged. (This is geometrically immediately made clear). So we have but to examine the surface for, let us say, $R > 1$.

§ 3. It must be possible to find the equation of the cone of the complex in a definite point out of the equation of the surface because that cone is the locus of the normals to the ∞^1 number of surfaces, passing through the point under consideration. If α, β, γ represent the cosines of direction of a ray of the complex in the point x_1, y_1, z_1 then

$$p = -\frac{\alpha}{\gamma}, q = -\frac{\beta}{\gamma}.$$

Substituting this in the differential equation and eliminating α and β by means of the equations of the ray of the complex, namely

$$\frac{x-x_1}{\alpha} = \frac{y-y_1}{\beta} = \frac{z-z_1}{\gamma},$$

we find for the cone of the complex :

$$(R-1) z_1 (x-x_1) (y-y_1) - R y_1 (x-x_1) (z-z_1) + x_1 (y-y_1) (z-z_1) = 0.$$

The planes of the coordinates forming the singular surface of the complex, the cone of the complex must degenerate for each point of one of these planes. For the point $P(x_1, y_1 = 0, z_1)$ the cone breaks up into $y = 0$ and into $x_1 z + (R-1) z_1 x = R z_1 x_1$, i. e. a plane passing through P and parallel to the Y -axis. This plane is at

right angles to OP , if this line has for equation $z = \pm x \sqrt{\frac{1}{R-1}}$.

(Comp. § 4).

§ 4. The drawing of the surfaces to be found offers no difficulties.

For $R > 1$ (§ 2) we must take C_1 positive and then we have to distinguish the cases $C \begin{matrix} \geq \\ < \end{matrix} 0$.

So for $C > 0$ the surface consists of two separated parts connected by points forming parts of a double conic in the XOY -plane. The planes $x = \pm \sqrt{C}$ touch both parts according to equal ellipses and no points lie between with $z > 0$.

The section with the XOZ -plane consists of two hyperbolae with centres $\left(z = \pm \sqrt{\frac{RC_1}{R-1}} \right)$ on the Z -axis. At infinity they are connected twice, and intersect each other in the points of intersection of the double conic with the X -axis. The hyperbolae coincide in the planes $y = \pm \sqrt{C_1}$, where the common vertex of the double conic is lying.

C becoming smaller, the two parts of the surface approach each other and for $C = 0$ the conics meet in the planes $x = \pm \sqrt{C}$. The surface becomes a ruled surface, so it breaks up into two cylinders with axes in the XOZ -plane.

The axes have for equation $z = \pm x \sqrt{\frac{1}{R-1}}$. (Comp. § 3). The section perpendicular to these axes is a circle which is in accordance with the signification of the axes as found in § 3.

§ 5. It is known that the normals of a system of similar, concentric ellipsoids form a tetrahedral complex ¹⁾. So this system must be a particular integral of the above-mentioned differential equation.

Let us put $C = gC_1 + h$ (g and h being constants) and let us operate in the ordinary way; we find C and C_1 as functions of the variables out of:

$$y^2 - C_1 = R \frac{gy^2 + h - x^2}{g(g+R)},$$

$$x^2 - C = -g \frac{gy^2 + h - x^2}{g+R}.$$

Substitution in the complete integral furnishes:

$$z^2 \frac{g(1-R)}{g+R} - gy^2 + x^2 = h.$$

Let us put in this equation $g = -\frac{a^2}{b^2}$, and let c be the axis along the Z -axis; we shall then find if we take a^2 positively

¹⁾ Dr. J. DE VRIES: On a special tetrahedral complex. Proceedings of Febr. 25 1905, Vol. XIII, pages 572--577.

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2} = h', \text{ with } R = \frac{a^2 - c^2}{b^2 - c^2}.$$

Likewise $\left(g = -\frac{a^2}{b^2}, a^2 \text{ negative} \right)$ the system of hyperboloids with two sheets

$$\frac{z^2}{c^2} - \frac{x^2}{a^2} - \frac{y^2}{b^2} = h', \text{ with } R = \frac{a^2 + c^2}{b^2 + c^2}$$

and also $\left(g = \frac{a^2}{b^2}, a^2 \text{ positive} \right)$ the system of hyperboloids with one sheet

$$\frac{z^2}{c^2} + \frac{x^2}{a^2} - \frac{y^2}{b^2} = h', \text{ with } R = \frac{c^2 - a^2}{c^2 + b^2}.$$

§ 6. The “curves of a complex” are curves whose tangents are rays of the complex. The coefficients of direction (α, β, γ) in a definite point (x, y, z) must therefore be proportional to

$$p = \frac{\partial z}{\partial x}, q = \frac{\partial z}{\partial y}, -1,$$

of one of those surfaces through that point. From this ensues that $p = -\frac{\alpha}{\gamma}$ and $q = -\frac{\beta}{\gamma}$, whilst x, y, z, p and q must satisfy the equation :

$$z - \frac{x}{p} \frac{1}{R-1} - \frac{y}{q} \frac{R}{1-R} = 0.$$

So the quantities $x, y, z, \alpha, \beta, \gamma$ must satisfy :

$$\frac{z}{\gamma} - \frac{y}{\beta} \frac{R}{R-1} + \frac{x}{\alpha} \frac{1}{R-1} = 0.$$

Let a curve of the complex be given by :

$$x = f_1(s), \quad y = f_2(s), \quad z = f_3(s),$$

where s need not of necessity represent the length of the arc, then :

$$\frac{f_3(s)}{f_3'(s)} + \frac{f_2(s)}{f_2'(s)} \frac{R}{1-R} + \frac{f_1(s)}{f_1'(s)} \frac{1}{R-1} = 0.$$

Amongst others all curves for all values of p to be represented by

$$x = \lambda(l + s)^p, \quad y = \mu(m + s)^p, \quad z = \nu(n + s)^p$$

satisfy this equation if only

$$\frac{l-n}{m-n} = R,$$

which condition can be satisfied by putting $l = B, m = C, n = A$.

For $p = -1$ these are twisted cubics. If we bring these through a point (x_1, y_1, z_1) the ∞^1 curves all lie on the cone of the complex of this point. This holding for each point, the bisecants (and not only the tangents) are rays of the complex.

Indeed, all the twisted cubics pass through the vertices of our tetrahedron and the four planes passing through a bisecant and these four points have thus a constant anharmonic ratio. From this ensues that the bisecants intersect the four planes of coordinates in the same anharmonic ratio.

For $p = 1$ we have the rays of the complex themselves.

For $p = 2$ we have conics which can be nothing but conics of the complex, e.g. for $s = -l$ the curve touches the plane YOZ , etc.

For $p = 3$ we have twisted cubics whose bisecants are not rays of the complex, etc.

In general the tangents to the "curves of a complex" lie always in linear congruences belonging to the tetrahedral complex. For such a tangent namely we have

$$(l + s) \frac{dx}{x} = (m + s) \frac{dy}{y} = (n + s) \frac{dz}{z}.$$

From this ensues among others:

$$(n + s) \frac{dz}{z} = \frac{(l + s) dx + k(m + s) dx}{x + ky}. \quad (k \text{ an arbitrary constant.})$$

This is evidently always satisfied by rays of the complex, satisfying at the same time:

$$x dz - z dx = k(z dy - y dz) \quad \text{and} \quad k dy = -R dx,$$

for which we can write in coordinates of lines:

$$r_3 = k p_2 \quad \text{en} \quad -k p_3 = R p_5.$$

These satisfy the equations of the tetrahedral complex and lie in congruences; the two linear complexes determining such a congruence, are themselves special, and the position of their axes is evident from their equation.

§ 7. Finally it proves to be simple to bring in equation the curves which are drawn on an arbitrary surface in such a way that the cone of the complex touches the surface in each point of the curve.

Let the surface be $f(x, y, z) = 0$ and the ray of the complex $\frac{x - x_1}{\alpha} = \frac{y - y_1}{\beta} = \frac{z - z_1}{\gamma}$, passing through the point x_1, y_1, z_1 of the surface.

A ray of the complex in the tangential plane must satisfy

$$\alpha \frac{\partial f}{\partial x_1} + \beta \frac{\partial f}{\partial y_1} + \gamma \frac{\partial f}{\partial z_1} = 0,$$

and further according to the differential equation

$$(R - 1) z_1 \alpha \beta - R y_1 \alpha \gamma + x_1 \beta \gamma \text{ must be equal to } 0.$$

The two rays of the complex in the tangential plane have but to be made to coincide. The condition is:

$$- 4 R (R - 1) z_1 y_1 f_2 f_3 = [-(R - 1) z_1 f_3 + R y_1 f_2 + f_1 x_1]^2,$$

where f_1, f_2, f_3 represent the differential quotients of f according to x, y and z respectively, whilst analogous relations are easy to deduce.

From this ensues that the required curve is the intersection of

$$f(x, y, z) = 0$$

and

$$- 4 R (R - 1) z y f_2 f_3 = [-(R - 1) z f_3 + R y f_2 + f_1 x]^2.$$

Without entering into further details I only wish to observe that when $f(x, y, z) = 0$ represents a plane, the curve can be nothing but the conic of the complex. From the above mentioned equations we therefore find a parabola (the conic of the complex touches the tetrahedron plane at infinity) touching the three planes of coordinates of the rectangular system of axes.

Physiology. — “*On the excretion of creatinin in man*“. By C. A. PEKELHARING. Report of a research made by C. J. C. VAN HOOGENHUYZE and H. VERPLOEGH.

As the muscle tissue in herbivora as well as in carnivora always contains a not unimportant amount of creatin, and creatinin is daily excreted with the urine it may be concluded, that creatin is formed as a product of metabolism in the muscles, and having entered the blood is at least for a part excreted by the kidneys in the form of the anhydride, creatinin.

But no agreement has been obtained about the question whether the forming of creatin is bound to the labour, the contracting of the muscles. To answer that question, researches have been made whether the amount of creatinin excreted by the kidneys augments after muscular labour. Different investigators have obtained different results. VAN HOOGENHUYZE and VERPLOEGH have resumed the research anew, using a new method to determinate the amount of creatinin in the urine, which was published some time ago by FOLIN¹). The

¹) Zeitschr. f. Physiol. Chemie, Bd. XLI, S. 223.

method of FOLIN is founded on the reaction of JAFFÉ, which consists in adding picric acid and an excess of caustic soda to a solution of creatinin, whereat the liquid takes a brown colour, which cannot be discerned from the colour of a solution of bichromate of potassium. This reaction is employed in the following way: 5 cc. of urine is mixed with 15 cc. picric acid 1,2 % and 5 cc. of caustic soda 10 %. After 5 minutes water is added to a volume of 250 cc. This solution is compared by FOLIN in the colorimeter of DUBOSCQ with a $\frac{1}{2}$ normal solution of bichromate of potassium of which a column 8 mm. high shows exactly the same intensity of colour as a column 8,1 mm. high of a solution of 10 mgr. creatinin with 15 cc. picric acid solution and 5 cc. caustic soda diluted to 500 cc. Instead of the colorimeter of DUBOSCQ, VAN HOOGENHUYZE and VERPLOGH used a little instrument, constructed after their indication, which answered completely to their demands. Immediately after each determination each of them performed 5 readings of the height of the solution of creatinin at which its colour had just the same intensity as a column 8 mm. high of the solution of bichromate of potassium. The several readings of which the average was taken, never differed more than 0,2, only very seldom more than 0,1 mm.

It proved meanwhile that the temperature has influence on the reaction in that sense that the colour of the creatinin solution becomes deeper by increase of temperature. Therefore the water used for the diluting was always kept at a temperature scarcely differing from 15° C. The relation found by FOLIN was affirmed. A solution of 10 mgr. of pure creatinin in 500 c.c. treated in the indicated way produced as the average of 10 readings 8.14 m.m. (max: 8.2, min. 8.1) out of which a quantity of 9.951 instead of 10 mgr. would be deduced.

The results become less exact when the concentration of creatinin is much larger or smaller than 10 mgr. in 500 c.c. Therefore the determination was repeated when the readings became higher than 10.5 or lower than 5, with 10 c.c. urine, in the first case diluted to 250 in the second to 1000 c.c. The method of FOLIN had great advantages over the method of NEUBAUER used till now, in which the creatinin is precipitated out of an alcoholic extract of the urine by means of chloride of zinc and after that weighed. Not only that the method of FOLIN takes much smaller quantities of urine, so that it renders it easy to discern by the examination of different portions of urine the oscillations in the secretion in the course of the day, but it is also more reliable. With the method of NEUBAUER there is always some danger that under the influence of the alkaline reaction arising from the addi-

tion of milk of lime to separate the phosphates, a part of the creatinin is changed into creatin. This danger may be lessened but not wholly avoided by acidifying the filtrate before evaporation by means of hydrochloric acid, after which at the end the hydrochloric acid must be eliminated by addition of sodium acetate in order not to hinder the precipitation of creatinin zinc chloride. But there are other difficulties connected with the method of NEUBAUER which can never be totally removed. The urine is after the removal of the phosphates concentrated till it obtains the consistency of syrup and is then extracted with alcohol. In the mass of salts rendered hard by the contact with alcohol, a part of the creatinin may be retained undissolved. If in order to eliminate this difficulty the urine is not very much evaporated, there arises another source of error. The alcohol is diluted by the still resting water and the consequence is that now the creatinin-zincchloride crystallises only partially. For this compound is insoluble in absolute alcohol but not in alcohol containing water. A too small quantity of creatinin is therefore always found by the application of this method.

VAN HOOGENHUYZEN and VERPLOEGH have investigated the solubility of creatinin-zincchloride in alcohol by putting dried crystals, prepared from urine and purified as much as possible, in closed bottles under alcohol of different strength at the temperature of the room under repeated shaking and by determining afterwards, by means of FOLIN'S method, how much creatinin was dissolved in the alcohol. They found:

in 100 C.C. alcohol	99 %	trace of creatinin.
„ „ „ „	93 %	5.6 mgr. „
„ „ „ „	72 %	32.1 „ „
„ „ „ „	50 %	104.5 „ „

In connection with this they obtained out of urine more creatinin-zincchloride when the alcoholic extract before the addition of chlorid of zinc was again evaporated to almost dryness and then dissolved by strong alcohol, than with the usual method. They could still show creatinin in the liquid filtered off from the creatinin-zinc-chlorid as well by the reaction of WEYL as by that of JAFFÉ. So the method of NEUBAUER always gives a loss of which the amount cannot be estimated. One is therefore not entitled to attribute much value to the little oscillations in the output of creatinin found by applying this method.

By the method of FOLIN on the contrary such a source of uncertainty does not exist, when the time of the reaction — 5 minutes — is rightly observed, the liquid is brought to the exact volume with

water of the temperature of the room and when the determination is completed immediately afterwards.

VAN HOOGENHUYZE and VERPLOEGH have investigated by themselves whether increase of the secretion of creatinin in consequence of muscular labour could be observed. For that purpose in every series of experiments the urine was collected every day at appointed times namely in the morning, in the first series of experiments at 9, in the following at 8 o'clock, in the afternoon at 12 o'clock and at 4¹/₂ o'clock, at night at 11¹/₂ o'clock. Every portion was measured and divided into two equal halves. One of the halves was used for an estimation of creatinin, the other halves were mixed, after which the quantity of creatinin in the mixture was determined and moreover an estimation of nitrogen was performed after the method of KJELDAHL.

In this way the determination of creatinin was also controlled. In all the series of experiments the conformity of the figure of the total quantity of creatinin and the sum of the four portions was very gratifying. The quantity of urine of one day was that collected from 12 o'clock in the afternoon till the following morning 8 or 9 o'clock.

During each series of experiments a fixed amount of food was taken, every day the same. Only in the first series coffee and tea were still taken, in the later series only water.

I. From April the 8th—24th 1904, seventeen days at a stretch, food was taken which consisted of bread, butter, cheese, milk, oatmeal, sugar, meat, eggs, potatoes and rice, daily an equal portion of each.

The food contained:

for v. H.	118 gr.	proteid	146 gr.	fat,	326 gr.	carbohydrat.;	40,8 Cal.	p. Kg.
,, V.	115 ,,	,, ,,	81 ,,	,, ,,	327 ,,	,, ,,	38.6 ,,	,, ,,

On working days moreover both consumed 50 gr. sugar.

The 11th, the 16th and the 21th of April bicycle excursions were undertaken at which they rode steadily on for 2¹/₂ à 3 hours without resting. The other days were spent in the laboratory while the evenings were passed peacefully.

The excretion of creatinin underwent no perceptible change in consequence of the muscular labour. With both investigators it oscillated not unimportantly during the whole experiment. It amounted on an average to:

v. H.	14 days of rest	2.116 gr.	daily	(max. 2.401, min. 1.821 gr.)
V.	,, ,, ,, ,,	1.998 ,,	,, (,,	2.158 ,, 1.858 ,,)
v. H.	3 workingdays	2.147 ,,	,, (,,	2.325 ,, 1.925 ,,)
V.	,, ,, ,,	2.015 ,,	,, (,,	2.058 ,, 1.949 ,,)

The difference is so small that no value must be attached to it. On the days which followed on the muscular exertion the figures of the creatinin remained within the usual daily oscillations.

The secretion of nitrogen was rather irregular with both during the whole experiment.

From June the 22nd till July the 2nd 1904 (eleven days) the experiment was repeated with less food which in particular was less rich in proteid. It contained:

for v. H. 71.5 gr. proteid, 125 gr. fat, 351 gr. carbohydr.; 33.7 Cal. p. Kg.
 „ V. 80.5 „ „ 74.75 „ „ 358 „ „ 34.6 „ „ „

On July the 1st a bicycle excursion of three hours was undertaken (50 KM.).

The excretion of creatinin amounted on an average to:

	10 days of rest	Workingday
v. H.	1.983 (max. 2.042, min. 1.809 gr.)	1.997 gr.
V.	2.039 („ 2.174, „ 1.920 „)	2.049 „

On the days which followed the day of muscular labour the excretion of creatinin did not increase either.

III. Whereas till now meat was still taken, in the series of experiment II daily 50 gr., the experiment was now taken with food which contained no creatinin at all, moreover it was made poorer in proteid. The experiment lasted from July the 7th till the 29th 1904, 23 days at a stretch.

From July the 7th till 18th only bread, butter, cheese, rice and sugar were taken containing:

for v. H. 50 gr. proteid, 115 gr. fat, 344 gr. carbohydr.; 31.2 Cal. p. Kg.
 „ V. 50 „ „ 74 „ „ 344 „ „ 33.8 „ „ „

From July the 18th rice was partly replaced by potatoes and the quantity of butter was decreased so that the ration became:

for v. H. 47 gr. proteid, 98 gr. fat, 337 gr. carbohydr.; 29.5 Cal. p. Kg.
 „ V. 47 „ „ 64 „ „ 337 „ „ 30.1 „ „ „

On July the 28th and the 29th 5 eggs were daily added to this food.

On July the 15th, the 20th and the 23rd muscular labour was again performed while the other days were passed in the laboratory with occupations which exacted only little exertion of the muscles. On July the 15th a bicycle excursion was undertaken in which 54 K.M. were covered in three hours. On July the 20th and 23rd fatiguing indoors gymnastics were performed for 2½ hours at a stretch with halters of 10 K.G. and with the chest-expander and

the combined developer of SANDOW; care was taken that all the muscles of the body and the extremities were used.

When the first three days of the scanty diet, July the 7th, 8th and 9th, in which the secretion of nitrogen fell with v. H. from 14,562 to 9,045 gr. and with V. from 13,721 to 10,234 gr. are not counted, as belonging to a transition-period, and neither the last two days, July the 28th and 29th at which about 30 gr. more proteids daily were taken, it appears that the excretion of creatinin has amounted in 15 days of rest on an average every day to :

v. H. 1.836 gr. (max. 1.935, min. 1.693 gr.)
 V. 1.962 „ („ 2.079, „ 1.876 „)

while on the working days was found :

v. H. July the 15th 1.908, July the 20th 1.921
 and July the 23th 1.974 gr. creatinin.
 V. July the 15th 2.142, July the 20th 1.947,
 and July the 23rd 1.937 gr. creatinin.

Here then the figure with v. H. is always, with V. once above the average on the working day. Meanwhile the deviations do not surpass the oscillations, which are always found, also without important exertions of the muscles.

The figure found with V. on July the 15th does, it is true, surpass the maximum in the period of the days of rest, but the difference 0,063 gr. is so slight, that no value must be attached to that, in connection to the lower figures of the two other working days.

On the two last days of the series on which no muscular labour was performed, but on which more proteid was taken, the excretion of creatinin was :

v. H. July the 28th 1.955 gr., and July the 29th 1.959 gr.
 V. „ „ „ 2.053 „ „ „ „ „ 1.984 „

while with both the secretion of nitrogen increased from about 8 gr. to 11 gr. daily.

IV. In September 1905 a new experiment was taken, to examine firstly whether preceding muscular exercise might perhaps bring some change in the result, secondly to investigate the influence of excessive labour and thirdly to see whether the excretion of creatinin would be increased with excessive labour and totally insufficient food.

After performing daily for three weeks at a stretch indoor gymnastics after the method of SANDOW, the experiment was begun September the 26th with food of the same composition as was used July the 18th till the 27th, hardly sufficient and poor in proteid. This food was

taken nine days at a stretch till Oct. the 4th. On September the 29th exercises were performed with SANDOW'S implements for 2¹/₂ hours with short intervals. On October the 2nd excessive labour was done, consisting of a walk of 21 K.M. in the morning from 9 till 12 o'clock, a walk of 10 K.M. in two hours in the afternoon and working with halters for ¹/₂ hour in the evening. On the six days of rest between September the 27th and Oct. the 4th (on the first day Sept. the 26th the urine was not examined) there was excreted on the average every day :

v. H. 1.859 (max. 1.977, min. 1.755) gr. creatinin
 V. 1.925 („ 2.047, „ 1.860) „ „

while on Sept. the 29th there was found :

v. H. 2,001 V. 1.979, gr. creatinin
 On October 2nd „ 1.859 „ 1,945, „ „

That not too much importance for the influence of muscular labour on the secretion of creatinin must be attached to the somewhat high figure of v. H. on September the 29th becomes clear when the separate portions of that day are considered. In the first portion of that day, that is in the urine excreted in the morning between 8 and 12 o'clock, so before muscular exertion was begun, 0,404 gr. creatinin was already found to 0,331 gr. and 0,345 gr. in the corresponding portions of the preceding and the following day.

After ordinary food had been taken for nine days, food was taken in absolutely insufficient quantity for five days at a stretch, consisting of bread, potatoes, butter and cheese. It contained :

for v. H. 36.6 gr. proteid 43 gr. fat 186 gr. carbohydrate; 15 Cal p. Kg.
 „ V. 29.7 „ „ 34.7 „ „ 158 „ „ ; 15 „ „ „

On Oct. the 16th a bicycle ride of 42 K.M. in 2¹/₂ hours was undertaken in the morning. In the first hour 20 K.M. were done but after that they could progress but slowly from hunger and fatigue.

In the afternoon a walk of 16 K.M. was taken from 2 till 5 o'clock and afterwards in the evening they worked with halters. The result was that both felt still very tired the next day.

The calculation of the average has no value in this short experiment. The course of the excretion of the creatinin was as followed :

	v. H.	V.
Oct. the 14 th	2.020	1.908
„ „ 15 th	1.702	1.934
„ „ 16 th	1.775	1.899 workingday
„ „ 17 th	1.831	1.938
„ „ 18 th	1.861	1.868

Here too where the food was not sufficient for the organism to defray the costs of the muscular labour, as appeared also from the increase of the nitrogen secretion on the workingday, one can certainly not speak of distinct influence of muscular labour on the excretion of creatinin.

It is however different when no food is taken at all for days.

VAN HOOGENHUYZE and VERPLOEGH had an opportunity to make observations about this too on the "Hungerkünstlerin" FLORA TOSCA a strong, young woman, who lent herself for the investigation during a starving period at the Hague, in a room which was opened to the public night and day. The urine was collected every day in three portions, in the morning from 10 o'clock till 4 o'clock in the afternoon, from 4 o'clock in the afternoon till 10 o'clock in the evening and from 10 o'clock in the evening till 10 o'clock the next morning; it was sent every day at a fixed time to the Physiological Laboratory in Utrecht and was there examined at once.

In the morning of June the 10th 1905 the last food was taken; after that nothing but mineral water (Drachenquelle) till June the 25th. Besides creatinin several other constituents of the urine were determined daily; about this it will be sufficient to mention that from the course of the secretion of nitrogen, urea, uric acid and phosphoric acid it appeared sufficiently that no food was taken.

During the whole hunger-period of fourteen days complete bodily rest was observed as much as possible save on June the 17th when TOSCA during two hours with short rests, under direction of VERPLOEGH, was occupied with gymnastic exercises with halters of 1 KGr. 13 different movements were made, the first ten 20 times each, the last three 10 times each. The movements were so chosen that as many muscles as possible were set to work.

The examination of the urine showed now that in hungering the secretion of the creatinin as well as of the other products of metabolism steadily decreased. But the muscular labour suddenly produced an undeniable increase, not on the same day, but on the following. Still on the third day the influence was to be perceived, which however also was the case with connection to the total quantity of nitrogen. On the first day, when food was still taken, the quantity of creatinin amounted to 1,087 gr. Later on it decreased rapidly and rather regularly till on the 8th day. On June the 17th, the day of the muscular labour, it amounted only to 0,469 to rise the following day to 0,689. In the three days before the muscular labour 1,662 was secreted, in the three following days 2,006 gr. creatinin. After that the secretion decreased almost to 0,5 gr, daily, to remain rather constant then.

From the above mentioned it appears that even with perfectly regular food and with avoiding of all excessive muscular labour the daily secretion of creatinin, as was communicated already in 1869 by K. B. Hofmann¹⁾, undergoes rather important oscillations. This is not sufficiently taken into consideration by those authors who as Moitessier²⁾ and as Gregor³⁾ have deduced from their results with series of experiments of three, four or five days, where the creatinin was precipitated from the alcoholic extract of the urine as a compound of zincchloride, that the excretion of creatinin increased as a result of muscular labour. It seems therefore to me that more value may be attached to the conclusion, which v. Hoogenhuyze and Verploegh drew from their observations, that in man only then increase of excretion of creatinin is caused by muscular labour when the organism is forced, by abstaining from food, to live at its own costs.

If the creatinin which is found in the urine of normal and normally fed men and animals is not to be considered, even were it for a small portion, as a product set free by the contraction of the muscle fibre, the question arises what signification must be given to this constituent of the urine.

Since Meissner's researches⁴⁾ it is known that to make use of meat as a food must lead to the excretion of creatinin, as creatin and creatinin, brought into the blood either by resorption out of the intestinal canal or by injection under the skin completely or almost completely is excreted as creatinin by the kidneys.

The quantity of creatin in meat is rather important. It is usually mentioned as 0,2 à 0,3% of the fresh muscle substance⁵⁾. With the aid of Folin's method v. H. and V. have determined the amount of creatin in muscle. 500 gr. meat freed as carefully as possible of fat and tendons and minced was mixed with chloroform water and was pressed out after standing for some hours at the temperature of the room. This was repeated twice. After that the pressed out meat was boiled for two hours with water and after cooling pressed out anew. The filtrates were mixed, boiled at weak acid reaction to remove proteids, after cooling filled up to 4000 c.c. and then filtered. 500 c.c. of the filtrate was concentrated to 100 c.c. and filtered anew, 80 c.c. of this filtrate was boiled with 50 c.c. *n*

1) Virchow's Archiv. Bd. XLVIII S. 358.

2) Thèse Montpellier 1891.

3) Zeitschrift f. Physiol Chemie. Bd. XXXI S. 98.

4) Zeitschr. f. rat. Med. Bd. XXXI, 1868, S. 234.

5) Vorr. Zeitschr. f. Biol. Bd. IV, 1868. S. 77.

H_2SO_4 , 48 hours in the waterbath, to change all creatin into creatinin. After that the quantity of creatinin was determined colorimetrically. Every time a determination of the same kind of meat of different animals was made twice. So the following was found:

Beef	I	3.688	gr. creatinin:	4.378	gr. creatin	p.	Kg.	meat
	II	3.898	„ „	4.522	„ „	„ „	„ „	„
Mutton	I	3.499	„ „	4.059	„ „	„ „	„ „	„
	II	3.608	„ „	4.185	„ „	„ „	„ „	„
Pork	I	3.718	„ „	4.313	„ „	„ „	„ „	„
	II	4.070	„ „	4.721	„ „	„ „	„ „	„
Horse	I	3.244	„ „	3.763	„ „	„ „	„ „	„
	II	3.395	„ „	3.948	„ „	„ „	„ „	„

Even with an abundant use of meat or beef-tea the creatinin excreted by the kidneys (1,5 à 2 gr. or still more in 24 hours) can but for a part be derived from the food. It is moreover well-known and by the above mentioned researches proved anew that the secretion of creatinin sinks not or scarcely under the norm, when the food does not at all contain creatin or creatinin. The organism itself forms creatin as a product of metabolism from the proteids. It would be possible that the nature of the proteid taken up as food was of signification for the forming of creatin. In that case it was possible that especially such proteids would produce creatin, out of which by hydrolysis much arginin, a more complicated derivative of guanidin could be obtained. According to the researches of KOSSEL and his disciples, from gelatin twice as much arginin can be obtained as from casein; out of gelatin 9.3 %¹⁾, out of casein 4.8 %²⁾. VAN HOOGENHUYZE and VERPLOEGH have therefore examined by a new series of experiments whether the use of casein or gelatin increases the secretion of creatinin and if such is the case in what measure.

V. On April the 7th 1905 a beginning was made with the use of the same food as in series IV.

v. H. 47 gr. proteid, 98 gr. fat, 337 gr. carbohydr.; 29.5 Cal. p. Kg.

V. 47 „ „ 64 „ „ 337 „ „ 30 „ „ „

On April the 12th, 13th, 14th 50 gram casein was taken prepared after HAMMARSTEN from cow-milk, in the afternoon at 12 o'clock 25 gr. and in the evening at 6 o'clock once more 25 gr. To leave the total chemical energy of the food unchanged, so much fewer potatoes were taken on these days that the quantity of carbohydrates fell from 337 to 287. After that the food was taken as on April the

1) Zeitschrift f. Physiol. Chem. Bd. XXXI, S. 207.

2) Ibid. Bd. XXXIII, S. 356.

7th till April the 19th. April the 20th 21st and 22nd 50 gram commercial gelatin, well washed in water, was taken every time in two portions, each of 25 gr., just as the casein instead of 50 gr. carbohydrate. On April 23rd and 24th the first diet was again taken.

In 10 days in which the food daily taken contained 47 gr. proteid (the first two days April the 7th and the 8th, which were still under the influence of the food taken the preceding days, the urine was not examined) the secretion of creatinin amounted to:

v. H. on the average 1.813 gr. (max. 1.921 min. 1.706 gr.) daily
 V. „ „ „ 1.850 „ („ 1.990 „ 1.723 „) „

On the days on which casein or gelatin was taken the secretion of nitrogen increased but the secretion of creatinin not or scarcely. It amounted on the three casein-days to:

v. H. on an average 1.913 gr. (max. 2.009, min. 1.836 gr.) daily
 V. „ „ „ 1.897 „ („ 1.934 „ 1.834 „) „

and on the three gelatin-days:

v. H. on an average 1.800 gr. (max. 1.813, min. 1.783 gr.) daily
 V. „ „ „ 1.872 „ („ 1.811 „ 1.868 „) „

Just as in the series of experiments III as was mentioned above, where, after the daily addition of 5 eggs to food which contained 47 gr. proteid, only a too insignificant increase of the secretion of creatinin was found to attach any value to it, it appeared now that the addition of casein and gelatin had no important influence whatever, although the added proteid was daily resorbed and desintegrated in the body, as the determination of nitrogen taught.

A short time ago FOLIN has communicated ample researches about the constituents of human urine and has come to conclusions¹⁾ with which the observations of VAN HOOGENHUYZE and VERPLOEGH are quite in accordance.

In 1868 MEISSNER has drawn the conclusion from his observations that the origin of creatinin in the organism of mammals must be quite different from that of the urea with which most of the nitrogen is excreted from the body²⁾. FOLIN draws this conclusion anew and, in connection with his observations about the secretion of other nitrogen containing substances and sulphur-compounds, starts from this point in proposing a new theory about the desintegration of proteid in the animal body, which he puts in the place of the wellknown theories of VOIT and of PELÜGER. In considering the desintegration of proteids in the body, there has been, argues FOLIN, generally laid

¹⁾ Amer. Journ. of Physiol. Vol. XIII, p. 45. p. 66 p. 117.

²⁾ l. c. S. 295.

stress almost only on the total quantity of nitrogen excreted, in relation to the quantity taken up in the food, and not enough attention has been paid to the quantities of each of the different nitrogenous products of metabolism which are excreted with the urine.

When the quantity of proteid in the food is enlarged or diminished then the secretion of nitrogen increases or decreases till after a short time a condition of equilibrium has been again obtained when intake and output of nitrogen are alike. The variability of the metabolism of proteids does not manifest itself in connection with all nitrogenous substances but for the greater part with connection to the urea. The secretion of creatinin on the contrary and also in a less degree that of uric acid is apparently independent of the richness of the food in proteid. We must distinguish a desintegration of proteid variable under the influence of the food, on which depends in the first place the forming of urea and which according to FOLIN's conception takes place for the greater part if not wholly in the digestive organs — in the cavity and in the mucosa of the intestine and in the liver — and beside a much less variable desintegration of proteid in the different organs which does not immediately depend on the food but on the function of the tissues. In the tissues there arise undoubtedly nitrogenous products of desintegrating of different composition. To them belongs as has been stated by NENCKI, SALASKIN and their collaborators ammonia, which is changed into the harmless urea by the liver. Moreover urea is formed in the organism in other places than the liver. This product of metabolism proceeds thus for a part, as FOLIN expresses it "endogenously" in consequence of the rather regular metabolism of proteid in the tissues and for another part "exogenously" in larger or smaller quantities, as more or less proteid is taken up in the digestive canal. It is however not possible to distinguish these two parts from each other in the urine.

But on the contrary the secretion of creatinin, on which the digestion of the food when it contains no creatin has no direct influence, gives an indication about the intensity of the desintegration of proteid in the tissues. In this respect the muscular tissue, must be thought of in the first place, but not exclusively, as creatin is formed undoubtedly in other tissues too.

It does not seem necessary to accept that all the creatin which is formed in the tissues is excreted as creatinin. The observations of MEISSNER give already rise to the supposition that creatin must be considered as an "intermediate" product of metabolism, as has been stated by BURIAN and SCHUR for the uric acid. MEISSNER at least could not quite retrace in the urine the creatinin brought into the

circulation. He did find, it is true, that after injection of creatin under the skin, not only the whole injected quantity was excreted again with the urine, but also 20 mgr. creatinin with it, but it remained uncertain how much of it proceeded from the metabolism of the animal itself.

To obtain an insight into this v. H. and V. have made anew an experiment in which the same food was taken, with 47 gr. proteid daily, as in the preceding experiment.

VI. The experiment lasted from Aug. the 17th till the 28th 1905. On the first day the urine was not examined. The oscillations in the secretion of creatinin were very insignificant. In five days from Aug. the 18th till the 22nd there was secreted :

v. H. average 2.023 gr. (max. 2.029, min. 2.017 gr.) daily
 V. " 2.028 " (" 2.029, " 1.930 ") "

On Aug. the 23rd each of them took in one portion 500 mgr. pure creatinin dissolved in water. On the same day there was excreted :

v. H. 2.420 gr. and V. 2.508 gr. The next day :
 V. 2.030 " " " 2.073 " " "

On Aug. the 26th each of them took again 500 mgr. creatinin but divided into 10 portions, 50 mgr. every hour. Now also the creatinin was found back the same day for the greater part in the urine. The excretion amounted to :

v. H. Aug. the 25th 1.998 Aug. the 26th **2.425** Aug. the 27th 1.940
 Aug. the 28th 1.951 gr.
 V. Aug. the 25th 2.045 Aug. the 26th **2.467** Aug. the 27th
 2.035 Aug. the 28th 1.968 gr.

At least in three of the four determinations a part of the creatinin brought into the blood was not found back in the urine.

From this experiment, which has still to be completed with others, in which creatin will be taken instead of creatinin, it appears how distinctly every change of some importance in the excretion of creatinin can be shown with the aid of FOLIN's method. So it gives the more reason to trust the results of the above mentioned series of experiments, and the conclusion derived from them, that creatin is a product of metabolism which is not formed at the contraction of the muscle-fibre, but proceeds in muscles and other organs by the desintegration of proteid to which is bound the life of the cells, without regard to the developing of energy to which they are able in performing their peculiar functions. Only then when the organism is deprived of food and must therefore seek the power of performing

labour in itself, the material which the muscles want for contraction is taken from the proteids of the tissue; for this the tissues are forced to more vigorous life, of which an increased formation of creatin is the result.

Quite in accordance with the investigations and arguments of FOLIN, v. HOOGENHUYZE and VERPLOEGH also found that though the excretion of urea increases and decreases with the resorption of proteids, the excretion of creatinin is not directly dependent on it. There is dependence in so far that with total privation of food, the activity of the organs becomes as small as possible and that then with the intensity of the symptoms of life the secretion of creatinin becomes extraordinarily small. In connection with this a statement made on the last day of the hunger-period of Tosca is worth mentioning. June the 25th she took milk and eggs in the evening after ten o'clock. The urine which was collected the following morning at 10 o'clock contained 0.375 gr. creatinin, more than double the quantity which was excreted by her in the last days in that same period. This sudden increase can certainly not be put to the account of the food as such, as is shown by the very slight increase of the excretion of nitrogen in the same period, but must be attributed to the stimulation which the whole organism suffered by the putting into action of the digestive organs after such a long rest.

NOËL PATON investigated a short time ago with the aid of FOLIN'S method the excretion of creatinin of a dog which was fed with oatmeal and milk and moreover on one day with 5 eggs and which got no food at all on other days¹⁾. According to the author the results seem to indicate that in the dog there is a relationship between the production of creatinin and the intake of nitrogen.

The secretion of creatinin shows a somewhat too large irregularity in the communicated series to admit the making of conclusions. But if the impression of the author is right, there may be thought here also of a stimulating effect of the food on the whole organism.

Just as FOLIN, VAN HOOGENHUYZE and VERPLOEGH have observed not unimportant individual varieties in the excretion of creatinin with mixed food. Without doubt the quantity of meat which one is used to take, influences it. But with persons living pretty well under the same circumstances the difference seems to be less great when the weight of the body is considered. In 5 students a secretion of 26, 26.9, 27.4, 29.4 and 31.5 mgr. creatinin pro bodily weight of one Kgr. was found in 24 hours.

¹⁾ Journal of Physiol. Vol. XXXIII, p. 1.

VAN HOOGENHUYZE and VERPLOEGH have also examined the urine of some sucklings. Always creatinin could be shown, more distinctly with the reaction of JAFFÉ than with that of WEYL. On account of the small concentration and the trifling quantities of urine which could be collected an accurate colorimetric determination was not possible. In four cases however a sufficient quantity of urine (15—60 cc.) was obtained, to admit at least of a somewhat reliable determination. In 10 cc. urine which was diluted to 50 cc. after having been mixed with picric acid and caustic soda, there was found :

I child	8 days	old,	1.11	mgr.	creatinine
II	„	32	„	„	0.91
III	„	2 months	„	„	0.41
IV	„	2	„	„	1.7

It is remarkable that in case III which concerned a weak child which was fed exclusively on cowmilk, the quantity of creatinin was so much smaller than in the three other children who were all strong and brought up by human-milk.

The above mentioned proves, as it appears to me, that the method of FOLIN is an acquisition of importance of which may be expected that it will aid in penetrating deeper than before into the knowledge of metabolism.

Physics. — “*On the theory of reflection of light by imperfectly transparent bodies.*” By Prof. R. SISSINGH. (Communicated by Prof. H. A. LORENTZ).

1. The laws of metallic reflection have been derived first by CAUCHY¹⁾, later by KETTELER²⁾ and VOIGT³⁾, while LORENTZ⁴⁾ has developed them from the electromagnetic theory of light. By different

¹⁾ CAUCHY, Compt. Rend. **2**, 427, 1836; **8**, 553, 658, 1839; **9**, 726, 1839; **26**, 86, 1848; Journ. de Liouv, (1), **7**, 338, 1839. CAUCHY gives only general remarks on the way followed by him. Derivations of the results have been given, inter alia by BEER, Pogg. Ann. **92**, 402, 1854; ETTINGSHAUSEN, Sitzungs-Ber. Akad. Wien, **4**, 369, 1855; EISENLOHR, Pogg. Ann., **104**, 368, 1858; LUNDQUIST, Pogg. Ann., **152**, 398, 1874.

²⁾ Pogg. Ann., **160**, 466, 1877; Wied. Ann., **1**, 225, 1877; **3**, 95, 1878; **22**, 204, 1884. KETTELER has, also in consequence of VOIGT's observations, modified his developments, and given a final form to them in the “Theoretische Optik”, 1885.

³⁾ Wied. Ann., **23**, 104, 554, 1884; **31**, 233, 1887; **43**, 410, 1891.

⁴⁾ On the theory of reflection and refraction of light, 1875; SCHLÖMILCH's Zeitschr. f. Math. u. Physik, **23**, 196, 1878.

ways these investigators arrive at exactly the same results. The relation inter se of the mechanic theories has been elucidated by DRUDE¹⁾. In 1892 LORENTZ²⁾ derived the laws of the refraction of light by metal prisms, which had already been given by VOIGT³⁾ and DRUDE⁴⁾, from a few simple principles. Concerning the nature of the vibrations of light no special hypothesis is introduced. This investigation of LORENTZ enables us to develop the theory of metallic reflection in a simple way.

2. The simplest disturbance in a metal is that represented by :

$$A e^{-px} \sin (ct - qx + s) \dots \dots \dots (1)$$

In this x is the distance from the bounding plane of the metal. This disturbance is caused when light falls perpendicularly on the metal. Here we meet with the particularity, that the planes of equal phase determined by the goniometric factor of (1) coincide with these of equal amplitude which follow from the exponential factor. From the assumption that the metal is isotropic and the deviation from the condition of equilibrium in the light disturbance is a vector determined by homogeneous linear differential equations, LORENTZ derives, what other disturbances are possible in the metal. Assume that the bounding plane of the metal is the YZ -plane, and that the plane wave-fronts are perpendicular to the XZ -plane. Then a disturbance is possible, represented by :

$$A e^{-Pl} \sin (ct - Ql_2 - s) \dots \dots \dots (2)$$

if

$$P^2 - Q^2 = p^2 - q^2 \dots \dots \dots (3)$$

$$PQ \cos (\alpha_1 - \alpha_2) = pq \dots \dots \dots (4)$$

are satisfied.

The planes of equal amplitude and phase are given by $l_1 = \text{const.}$, $l_2 = \text{const.}$ In this l_1 is the distance to the plane in which the amplitude is A , and l_2 that to the plane in which the phase has the value s . α_1 and α_2 are the angles of the normals of the planes of equal amplitude and phase with the X -axis.

3. From (3) and (4) the principal equations for the propagation of light in metals may be immediately obtained. If light penetrates from the surroundings into the metal, then the planes of equal amplitude are parallel to the bounding plane. The exponential factor

1) Göttinger Nachrichten 1892, 366, 393.

2) Wied. Ann., 46, 244. 1892.

3) Wied. Ann., 24, 144, 1885.

4) Wied. Ann., 42, 666, 1891.

in (2) passes into e^{-Px} and $\alpha_1 = 0$. In this case α_2 may be called the angle of refraction in agreement with what takes place for perfectly transparent bodies. Denote it by α , then (4) passes into :

$$PQ \cos \alpha = pq. \dots \dots \dots (5)$$

Let us now put $P = 2\pi k : \lambda$, where λ is the wave length in the air, and k the coefficient of absorption. In (2) we put $Q = 2\pi : \lambda_1$, where λ_1 represents the wave length in the metal. Be $\lambda : \lambda_1 = n$, then we may call the index of refraction of the metal n , in agreement with what happens in transparent bodies. In the same way $Q = 2\pi n : \lambda$. Let us call the values of l and n , when the light propagates in the metal perpendicularly to the bounding plane k_0 and n_0 . Then in (1) $p = 2\pi k_0 : \lambda$, $q = 2\pi n_0 : \lambda$.

Introducing these values into (3) and (5), we get :

$$k^2 - n^2 = k_0^2 - n_0^2 \dots \dots \dots (6)$$

$$kn \cos \alpha = k_0 n_0 \dots \dots \dots (7)$$

In order to bring our formulae for the disturbance in the metal at the bounding plane in harmony with those for the disturbance in the air, we must put $\sin i : \sin \alpha = \lambda : \lambda_1 = n$ or $\sin i = n \sin \alpha$, when i is the angle of incidence. It follows from (6) and (7) that both the index of refraction and the coefficient of absorption depend on the direction of propagation, i. e. on the direction of the normal of the planes with equal phase.

If (7) is written in the form :

$$k^2 n^2 \cos^2 \alpha = k^2 (n^2 - \sin^2 i) = k_0^2 n_0^2 \dots \dots \dots (8)$$

it follows from (6) and (8) that :

$$2n^2 = -k_0^2 + n_0^2 + \sin^2 i + \sqrt{(k_0^2 - n_0^2 + \sin^2 i)^2 + 4n_0^2 k_0^2} \dots \dots (9)$$

$$2k^2 = k_0^2 - n_0^2 + \sin^2 i + \sqrt{(k_0^2 - n_0^2 + \sin^2 i)^2 + 4n_0^2 k_0^2} \dots (10)$$

They denote in what way k and n depend on the angle which the direction of the propagation of the disturbance falling on the metal forms with the normal to the bounding plane ¹⁾.

For an opaque mirror of silver deposited on glass by a chemical

¹⁾ KETTELER was the first to derive these equations, (see inter alia Pogg. Ann., 160, 408, 1877) which, of course, also occur in VOIGT's theory. VOIGT puts the quantity corresponding to P equal to $2\pi k : \lambda_1$, so that VOIGT's nk corresponds to the coefficient of absorption k introduced here. It is not correct that CAUCHY already gave these equations, as DRUDE observes (Wied. Ann. 35, 515, 1888). They have not been given explicitly in this theory. This appears, indeed, from the fact that BEER (Pogg. Ann., 92, 412, 1854) substitutes other relations for them, which are not correct. Derivations of the principal equations were given by WERNICKE (Pogg. Ann. 159, 226, 1876) and KETTELER, Pogg. Ann. 160, 468, 1877. See also KETTELER, Wied. Ann., 49, 512, 1893 and Theoretische Optik, p. 198, § 85, Zur Geschichte der Hauptgleichungen.

way, and very firmly attached to the glass, the values $I = 72^{\circ}34'.8$, $H = 42^{\circ}21'.7$ were found for principal angle of incidence I and principal azimuth H^1) (H being the angle which the plane of polarization of the reflected light, being restored by compensation to plane polarization makes with the plane of incidence) from which follows for:

$i = 0^{\circ}$	20°	40°	60°	80°	90°
$n = 0,295$	0,450	0,800	0,928	0,990	1,03
$k = 2,88$	2,90	2,95	3,01	3,04	3,05

In the same way I found for a steel mirror ²⁾, $I = 77^{\circ}23'.5$, $H = 26^{\circ}34'$, so that for:

$i = 0^{\circ}$	$i = I$	$i = 90^{\circ}$
$n = 2,684$	2,794	2,799
$k = 3,404$	3,491	3,496

As follows from (9) and (10), k and n increase with the angle of incidence i . From (8) follows, that always $n^2 > \sin^2 i$. Media which absorb the light, can never reflect the light totally.

4. Normal to the planes of equal amplitude the amplitude decreases in ratio $1 : e^{-1}$ over a distance $\lambda : 2\pi k$. In the planes of equal phase the points whose amplitudes stand in the same ratio, lie at a distance $\lambda : 2\pi k \sin(\alpha_1 - \alpha_2)$.

According to (6) and (7) n depends on k . The velocity of propagation depends therefore on the way, in which the amplitude in a plane of equal phase varies. If $\alpha = 0$, it follows from (6) and (7) that $k = k_0$, $n = n_0$. The planes of equal phase and amplitude can therefore only coincide with a propagation normal to the bounding plane. If this took place in every direction, k would be zero according to (8), so the substance would have to be perfectly transparent.

When the planes of equal phase and amplitude are normal to each other, $\alpha = 90^{\circ}$. For light that penetrates into the metal from outside, the planes of equal amplitude are parallel to the bounding plane, so for $\alpha = 90^{\circ}$ those of equal phase are perpendicular to it. The propagation then takes place parallel to the bounding plane. This is in harmony with what follows from (7) and (8). According to (7) $k_0 n_0 = 0$ for $\alpha = 90^{\circ}$ and so according to (8) either $k = 0$ or $n = \sin i$. The first case leads us back to perfectly transparent media. For $n = \sin i$ there is total reflection. This however, can only be the case with light absorbing media, if $k_0 n_0 = 0$ or, as $n_0 > 0$, if

¹⁾ SINGH, Thesis for the doctorate, p. 88, 1885, Arch. Néerl., **20**, 207, 1886.

²⁾ SINGH, Verh. Akad. v. Wetensch., Amsterdam, deel 28, 1890; Wied. Ann., **42**, 132, 1891.

$k_0 = 0$. So the coefficient of absorption of the medium normal to the bounding plane had to be 0. For metals this is not the case, so that no total reflection can occur there, as has been observed above.

It is well known that with total reflection on perfectly transparent media the planes of equal phase and amplitude are normal to each other for the disturbance in the second medium which is propagated parallel to the bounding plane. VOIGT showed, that this case also occurs for a disturbance, which leaves a prism of a substance which absorbs light, when plane waves fall on it and the dimensions of the prism are large with respect to the wave length¹⁾.

From (6) and (7) we may derive $(k_0^2 - n_0^2) \cos \alpha = n_0 k_0 \left(\frac{k}{n} - \frac{n}{k} \right)$.

From this follows, that according as $k : n$ increases, α differs more from $\pi : 2$, with which we have got back a result of VOIGT's²⁾.

5. EISENLOHR³⁾ showed, that by the introduction of a complex index of refraction, we arrive at CAUCHY's results for metallic reflection.

In the following way it may be shown that for metals a complex quantity corresponds to the index of refraction of transparent bodies. With observance of the conditions (3) and (4), (2) is a possible disturbance. In this l_1 and l_2 are the distances from the point for which (2) holds, to the plane of equal amplitude, in which the amplitude is A and the plane of equal phase, in which the phase is s . We may also write for (2):

$$Ae^{-p_1x - p_2z} \sin (ct - q_1x - q_2z - s) \dots \dots \dots (11)$$

because the planes of equal phase and amplitude are normal to the XZ -plane. The normals from the point x, z on the two above mentioned of these planes are respectively $(p_1x + p_2z) : \sqrt{p_1^2 + p_2^2}$ and $(q_1x + q_2z) : \sqrt{q_1^2 + q_2^2}$, so that $P = \sqrt{p_1^2 + p_2^2}$, $Q = \sqrt{q_1^2 + q_2^2}$.

In the same way as (11) a possible disturbance is also:

$$Ae^{-p_1x - p_2z} \cos (ct - q_1x - q_2z - s).$$

The differential equations, which are supposed homogeneous and linear, are therefore also satisfied by:

$$Ae^{-p_1x - p_2z} \{ \cos (ct - q_1x - q_2z - s) \pm i \sin (ct - q_1x - q_2z - s) \}$$

or by

$$Ae^{\pm i \{ (ct - xq_1 \mp q_1) - z(q_2 \mp q_2) - s \}} \dots \dots \dots (12)$$

For a perfectly transparent medium $p_1 = p_2 = 0$. The velocity of propagation is then $v = c : \sqrt{q_1^2 + q_2^2}$, or c being $c = 2\pi : T$,

1) Wied. Ann., 24, 153, 1885.

2) Wied. Ann., 24, 150, 1885.

3) Pogg. Ann., 104, 368, 1858.

$v = 2\pi : T\sqrt{q_1^2 + q_2^2}$. Let the velocity of light in the air be V , the index of refraction of the perfectly transparent medium n , then:

$$n^2 = V^2 T^2 (q_1^2 + q_2^2) : 4\pi^2$$

From (12) follows, that for a metal $q_1 \mp \wp_1$ occurs instead of q_1 and the quantity $q_2 \mp \wp_2$ for q_2 . Let n_m be the quantity, which for a metal corresponds to the index of refraction n of the perfectly transparent medium, then

$$n_m^2 = \frac{V^2 T^2}{4\pi^2} \{-p_1^2 + q_1^2 - p_2^2 + q_2^2 \mp 2\iota(p_1 q_1 + p_2 q_2)\}.$$

The cosines of the angles formed by the normals of the planes of equal amplitude and phase with the X and Z -axis, are respectively:

$$p_1 : \sqrt{p_1^2 + p_2^2}, \quad p_2 : \sqrt{p_1^2 + p_2^2} \quad \text{and} \quad q_1 : \sqrt{q_1^2 + q_2^2}, \quad q_2 : \sqrt{q_1^2 + q_2^2}$$

With observance of the above given values of P and Q and introduction of the angle α between the planes of equal phase and amplitude $p_1 q_1 + p_2 q_2 = PQ \cos \alpha$. Thus:

$$n_m^2 = \frac{V^2 T^2}{4\pi^2} (-P^2 + Q^2 \mp 2\iota PQ \cos \alpha),$$

or according to (3) and (5):

$$n_m^2 = \frac{V^2 T^2}{4\pi^2} \{-p^2 + q^2 \mp 2\iota pq\}.$$

Hence the so-called complex index of refraction of a metal is $n_m = (\iota \pm q) \frac{VT}{2\pi}$. Let λ_0 be the wave length in the metal for light entering normally, then according to (1) $q = 2\pi : \lambda_0 = 2\pi n_0 : \lambda$ and $p = 2\pi k_0 : \lambda$, so $n_m = n_0 \mp \iota k_0$.

6. It follows from what precedes, that in accordance with EISENLOHR¹⁾ we can deduce the expressions determining the amplitudes for the metallic reflection from those for the reflection on transparent bodies, if we replace n by $n_0 \mp \iota k_0$. Let the incident beam of light have the intensity 1 and let it be polarized in the plane of incidence. The reflected disturbance may be represented by the real part of $\frac{\sin(i-r)}{\sin(i+r)} e^{\pm \iota(ct+z)}$. Here $\sin r = \sin i : n$. Put $n = n_0 \mp \iota k_0$, then $\frac{\sin(i-r)}{\sin(i+r)}$ passes into $A e^{\pm \iota B}$. The disturbance reflected by metals is the real part of $A e^{\pm \iota(ct+z-B)}$, in which A is the amplitude and B the difference of phase with the incident ray. In this way we arrive at the well known expressions for the metallic reflection. I may be

¹⁾ Cf. also LORENTZ, Theorie der Terugkaatsing en Breking, p. 163, SCHLÖMILCH's Zeitschr., 23, 206, 1878.

allowed to place them here side by side, after which I shall give some expressions which enable us to determine the optical constants of a metal from the quantities measured, and also some approximative formulae for the calculation of the principal angle of incidence I and principal azimuth H from n_0 and k_0 .

Light polarized // plane of incidence.

Incident light	Reflection by	
	transparent bodies	metals
	Intensity	
	Reflected light	
1	$\frac{\sin^2(i-r)}{\sin^2(i+r)}$	$R_p^2 = \frac{(\cos i - \sqrt{n^2 - \sin^2 i})^2 + k^2}{(\cos i + \sqrt{n^2 - \sin^2 i})^2 + k^2}$

Difference of phase with incident beam

$$180^\circ \qquad \qquad \qquad tg\varphi_p = -\frac{2k \cos i}{1 - n^2 - k^2}$$

Light polarized \perp plane of incidence

Incident light	Reflection by	
	transparent bodies	metals
	Intensity	
	Reflected light	
1	$\frac{tg^2(i-r)}{tg^2(i+r)}$	$R_l^2 = \frac{n^2 \cos^2(i-\alpha) + k^2 \cos^2 i}{n^2 \cos^2(i+\alpha) + k^2 \cos^2 i} R_p^2$

Difference of phase with incident beam

$$0^\circ \text{ for } 0^\circ < i < I \qquad \qquad \qquad tg\varphi = C$$

$$180^\circ \text{ ,, } I < i < 90^\circ$$

$$C = \frac{2k(k^2 + n^2 \cos^2 \alpha - \sin^2 i) \cos i}{(k^2 - n^2 \cos^2 \alpha - \sin^2 i) \cos^2 i - n^2 \cos^2 \alpha \cos 2i - k^2}$$

From this follows also:

$$tg(\varphi_l - \varphi_p) = \frac{2k \sin i \, tg \, i}{n^2 \cos^2 \alpha - tg^2 i \sin^2 i + k^2},$$

n and k apply to the disturbance in the metal, arising from plane waves, which fall on the metal with an angle of incidence i . The angle of refraction α is determined by $\text{Sin } \alpha = \text{Sin } i : n$.

7. The expressions obtained are in perfect harmony with those of CAUCHY. First the relations of § 6 may be brought to the same form as these. For this purpose we put in accordance with BEER¹⁾:

$$n \cos \alpha = \sqrt{n^2 - \text{Sin}^2 i} = U \cos u, \quad k = U \text{Sin } u \quad . \quad . \quad (13)$$

Substituting this we get

$$R_p^2 = \frac{\cos^2 i + U^2 - 2U \cos i \cos u}{\cos^2 i + U^2 + 2U \cos i \cos u}.$$

Put

¹⁾ BEER, Pogg. Ann. **92**, 413, 1854.

$$\operatorname{tg} f = \frac{\cos^2 i + U^2}{2U \cos i \cos u},$$

then

$$R_p^2 = \operatorname{tg} \left(f - \frac{\pi}{4} \right).$$

From the value of f follows also

$$\cot f = \cos u \sin \left(2 Bg \operatorname{tg} \frac{\cos i}{U} \right) (14)$$

Further we get:

$$\operatorname{tg} \varphi_p = \sin u \operatorname{tg} \left(2 Bg \operatorname{tg} \frac{\cos i}{U} \right).$$

Be $R_l : R_p = \operatorname{tg} h$, then

$$\operatorname{tg}^2 h = \frac{n^2 \cos^2 (i - \alpha) + k^2 \cos^2 i}{n^2 \cos^2 (i + \alpha) + k^2 \cos^2 i}.$$

In the corresponding expression of CAUCHY the value of $\operatorname{Cos} 2h$ is given. From the value of $\operatorname{tg}^2 h$ follows, as

$$\cos 2h = (1 - \operatorname{tg} 2h) : (1 + \operatorname{tg} 2h), \quad \cos 2h = \frac{2n \cos \alpha \sin^2 i \cos i}{(n^2 \cos^2 \alpha + k^2) \cos^2 i + \sin^4 i}.$$

According to (13) this passes into

$$\cos 2h = \cos u \sin \left(2 Bg \operatorname{tg} \frac{\sin i \operatorname{tg} i}{U} \right) (15)$$

In the same way becomes

$$\operatorname{tg} (\varphi_l - \varphi_p) = \sin u \frac{2U \sin i \operatorname{tg} i}{U^2 - \sin^2 \operatorname{tg}^2 i} = \sin u \operatorname{tg} \left(2 Bg \operatorname{tg} \frac{\sin i \operatorname{tg} i}{U} \right) . (16)$$

The expressions (14), (15), (16) have the same form as the corresponding ones of CAUCHY, only according to LORENTZ's notation $\sigma\varrho$ stands for U , the angle $\tau + \omega$ for u .¹⁾

Just as from i , U and u the quantities R_p , R_l , φ_p , and φ_l may be derived, which determine the reflected beam of light, U and u may be calculated from i and two of these four quantities. U and u depend therefore in exactly the same way on the angle of incidence and the optical properties of the metal as CAUCHY's corresponding quantities $\sigma\varrho$ and $\tau + \omega$. At the same time it appears that two constant quantities suffice for the determination of the optical behaviour of metals. They are here n_0 and k_0 , which have a definite physical meaning, with CAUCHY σ and τ , whose meaning is not so obvious. Whatever

¹⁾ LORENTZ, Theorie der terugkaatsing en breking, p. 166. According to EISENLOHR's notation (loc. cit. p. 369, 370) $U = c \mathfrak{D}$, $u = \varepsilon + u$. As R_p and R_l : R_p , φ_p and $\varphi_l - \varphi_p$ have the same form as CAUCHY's equation, this holds also for R_l and φ_l .

system of two determining quantities is chosen, however, the amplitudes and phases of the two components of the reflected light polarized in and normal to the plane of incidence, whether calculated in one way or in the other, will have the same values. The two systems of formulae are therefore identical.

CAUCHY ¹⁾ calls the so-called complex index of refraction $\sigma e^{i\tau}$. This quantity being represented here by $n_0 + ik_0$, $\sigma \cos \tau = n_0$, $\sigma \sin \tau = k_0$. The auxiliary quantities ρ and ω have been introduced by CAUCHY for the determination of the so-called imaginary angle of refraction r , determined by $\sin r = \sin i : (n_0 + ik_0)^2$. In order to express ρ and ω in the quantities used above, it may be observed that:

$$\cos^2 r \sin^2 i : \sin^2 r = \cos^2 r (n_0 + ik_0)^2 = (n_0 + ik_0)^2 - \sin^2 i$$

or with the aid of (6) and (7):

$$\cot r \sin i = n \cos \alpha + ik.$$

As CAUCHY gives:

$$\cos r = \rho e^{i\omega} \text{) and } n_0 + ik_0 = \sigma e^{i\tau}, \quad n \cos \alpha + ik \text{ is equal to } \rho \tau e^{i(\tau+\omega)}$$

or

$$n \cos \alpha = U \cos u = \rho \sigma \cos (\tau + \omega) \quad . \quad . \quad . \quad (17)$$

$$k = U \sin u = \rho \sigma \sin (\tau + \omega) \quad . \quad . \quad . \quad . \quad (18)$$

The equations (17) and (18) allow us to deduce our auxiliary quantities from those of CAUCHY and reversely ³⁾.

8. According to § 7:

$$\cos 2h = \cos u \frac{2U \sin i \operatorname{tg} i}{U^2 + \sin^2 i \operatorname{tg}^2 i}, \quad \operatorname{tg} (\varphi_l - \varphi_p) = \sin u \frac{2U \sin i \operatorname{tg} i}{U^2 - \sin^2 i \operatorname{tg}^2 i}.$$

These two equations may serve to determine U and u , and from this the optical constants n_0 and k_0 with the aid of (13), (6) and (7).

From the values of $\cos 2h$ and $\operatorname{tg} (\varphi_l - \varphi_p)$ follows:

$$\sin 2h \cos (\varphi_l - \varphi_p) \frac{U^2 - \sin^2 i \operatorname{tg}^2 i}{U^2 + \sin^2 i \operatorname{tg}^2 i}$$

or

$$1 - \sin 2h \cos (\varphi_l - \varphi_p) = \frac{2 \sin^2 i \operatorname{tg}^2 i}{U^2 + \sin^2 i \operatorname{tg}^2 i} \quad . \quad . \quad . \quad (19)$$

From (19) and the value of $\cos 2h$ follows:

$$U \cos u = \frac{\sin i \operatorname{tg} i \cos 2h}{1 - \cos (\varphi_l - \varphi_p) \sin 2h} \quad . \quad . \quad . \quad . \quad (20)$$

¹⁾ LORENTZ, l.c. Theorie der terugkaatsing en breking, p. 164, SCHLÖMILCH's Zeitschr., **23**, pg. 206. EISENLOHR, p. 369.

²⁾ See note 1 on the preceding page.

³⁾ Cf. also KETTELER, Wied. Ann. **1**, 242, 1877; **22**, 212, 1884. Formulae for the calculation of r and ω are given by LORENTZ, Theorie der Terugkaatsing en Breking, p. 164, 165, EISENLOHR, Pogg. Ann., **104**, 370, 1858.

Further

$$\sin 2h \sin (\varphi_l - \varphi_p) = \frac{2U \sin u \sin i \operatorname{tg} i}{\sqrt{U^2 + \sin^2 i \operatorname{tg}^2 i}}$$

From this and from the value of $\operatorname{tg} (\varphi_l - \varphi_p)$ follows

$$U \sin u = \frac{\sin i \operatorname{tg} i \sin (\varphi_l - \varphi_p) \sin 2h}{1 - \cos (\varphi_l - \varphi_p) \sin 2h} \dots \dots (21)^1$$

So from the restored azimuth h and the difference of phase $\varphi_l - \varphi_p$ at an arbitrary angle, $U \cos u$ and $U \sin u$ or $n \cos \alpha$ and k are to be derived for that angle. As $n \cos \alpha = \sqrt{n^2 - \sin^2 i}$, we get afterwards n_0 and k_0 with the aid of (6) and (7). By means of them we can calculate $\varphi_l - \varphi_p$ and h for every angle.

9. As a rule we introduce the principal angle of incidence I , for which $\varphi_l - \varphi_p = \pi : 2$. The restored azimuth at this angle is called the principal azimuth H . As well from (20) and (21), as from 15) and (16) we may derive, when we add the index I to the values of all the quantities for the principal angle of incidence :

$$U_I = \sin I \operatorname{tg} I \quad , \quad \cos u_I = \cos 2H \dots \dots (22)$$

According to (13)

$$k_I = U_I \sin u_I = \sin I \operatorname{tg} I \sin 2H \dots \dots (23)$$

$$(n^2 \cos^2 \alpha)_I = n_I^2 - \sin^2 I = \sin^2 I \operatorname{tg}^2 I \cos^2 2H$$

or

$$n_I^2 = \operatorname{tg}^2 I (1 - \sin^2 I \sin^2 2H) \dots \dots (24)$$

We may also write (24) :

$$n_I^2 + k_I^2 = \operatorname{tg}^2 I^2) \dots \dots (25)$$

The optical constants n_0 and k_0 are obtained from :

$$n_0^2 - k_0^2 = n_I^2 - k_I^2 = \operatorname{tg}^2 I (1 - 2 \sin^2 I \sin^2 2H)$$

or

$$n_0 k_0 = (n \cos \alpha)_I k_I = \frac{1}{2} \sin^2 I \operatorname{tg}^2 I \sin 4H \dots \dots (26)$$

10. When n_0 and k_0 have been given, we find by elimination of n_I and k_I from the two first members of the two equations (26) and (25) an equation of the sixth degree for the determination of I . There may be given also approximating formulae for the determination of I and H from n_0 and k_0 . From $n_I^2 - k_I^2 = n_0^2 - k_0^2$ and $k_I \sqrt{n_I^2 - \sin^2 I} = n_0 k_0$ follows

$$2n_I^2 = \sin^2 I + n_0^2 - k_0^2 + \sqrt{(\sin^2 I - n_0^2 - k_0^2)^2 + 4k_0^2 \sin^2 I}$$

Substituting this in $n_I^2 + k_I^2 = \operatorname{tg}^2 I$, we get :

¹⁾ This equation was already given by KETTELER, Wied. Ann., 1, 241, 1877.

²⁾ KETTELER calls this equation an analogon of the law of BREWSTER, Wied. Ann 1, 242, 1877.

$$\sin^4 I + 2\sin^2 I(k_0^2 - n_0^2) + (k_0^2 + n_0^2)^2 = \sin^4 I \operatorname{tg}^4 I \quad . \quad (27)$$

With metals $n_0^2 + k_0^2$ is comparatively large compared to the two first terms of the first member of (27). By approximation we get therefore:

$$\sin^2 I \operatorname{tg}^2 I = k_0^2 + n_0^2,$$

from which follows with the same degree of approximation

$$\sin^2 I = 1 - \frac{1}{k_0^2 + n_0^2}.$$

Introducing this in (27), we get:

$$\sin I \operatorname{tg} I = \sqrt{k_0^2 + n_0^2} \left\{ 1 + \frac{1}{4} \frac{2(k_0^2 - n_0^2) - 1}{(n_0^2 + k_0^2)^2} \right\} \quad . \quad (28)$$

In the following way we get an approximate value for H . From (23) and (24) follows:

$$n_I^2 - k_I^2 = n_0^2 - k_0^2 = \sin^2 I + \sin^2 I \operatorname{tg}^2 I \cos 4H,$$

so

$$\cos 4H = \frac{n_0^2 - k_0^2 - \sin^2 I}{\sin^2 I \operatorname{tg} I}$$

From this follows, as $\operatorname{tg}^2 2H = \frac{1 - \cos 4H}{1 + \cos 4H}$, after substitution of the approximate value

$$\sin^2 I \operatorname{tg}^2 I = (n_0^2 + k_0^2) \left\{ 1 + \sin^2 I \frac{k_0^2 - n_0^2}{k_0^2 + n_0^2} \right\}$$

which follows from (27),

$$\operatorname{tg} 2H = \frac{k_0}{n_0} \left\{ 1 + \sin^2 I \frac{1}{n_0^2 + k_0^2} \right\} \quad . \quad . \quad . \quad (29)^1$$

11. Finally it may be observed that the relations hold for any value of k . The reflection on perfectly transparent bodies is therefore a limiting case for the metallic reflection.²⁾

Chemistry. — “*On the chlorides of maleic acid and of fumaric acid and on some of their derivatives.*” By Dr. W. A. VAN DORP and Dr. G. C. A. VAN DORP.

(This communication will not be published in these Proceedings).

¹⁾ Corresponding approximate formulae were given by DRUDE in WINKELMANN, Physik II. 1, p. 823, 824.

²⁾ Cf. VOIGT, Wied. Ann., 24, 146, 147, 1885.

(October 25, 1905).

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM.

PROCEEDINGS OF THE MEETING
of Saturday October 28, 1905.

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Afdeling van Zaterdag 28 October 1905, Dl. XIV).

C O N T E N T S.

H. DE VRIES: "Central Projection in the space of LOBATSCHESKY", (1st Part). (Communicated by Prof. J. CARDINAAL), p. 389.

H. J. HAMBURGER: "A method for determining the osmotic pressure of very small quantities of liquid", p. 394.

EUGEN FISCHER: "On the primordial cranium of *Tarsius spectrum*". (Communicated by Prof. A. A. W. HUBRECHT), p. 397.

H. A. LORENTZ: "On the radiation of heat in a system of bodies having a uniform temperature", p. 401.

H. ZWAARDEMAKER: "On the ability of distinguishing intensities of tones. Report of a research made by A. DEENIK", p. 421.

Erratum, p. 426.

The following papers were read:

Mathematics. — "*Central Projection in the space of LOBATSCHESKY*".
(1st part). By Prof. H. DE VRIES. (Communicated by Prof. J. CARDINAAL).

(Communicated in the meeting of September 30, 1905).

1. Let an arbitrary plane τ be given in hyperbolic space; let the perpendicular be erected in an arbitrary point O_1 of τ , and let finally an arbitrary point O be taken on this perpendicular. We can now ask what we can notice if we project the figures of space out of O as a centre of projection on τ as a plane of projection or picture plane, and inversely, how the exact position and situation of the figures in space can be determined by means of their projections.

In the following a few observations will be given on these two questions.

Let us suppose an arbitrary plane ε through the line OO_1 , standing therefore at right angles to τ ; in that plane we can draw through O two straight lines p_1, p_2 parallel to the line of intersection e of ε and τ passing through O_1 , therefore also parallel to τ itself. The angles formed by p_1 and p_2 with OO_1 are equal; they are both acute, and their amount is a function of the distance $OO_1 = d$. LOBATSCHESKY has called each of these two angles the *parallel angle*¹⁾ belonging to the distance d , and has indicated them by $\Pi(d)$; if d is given, the parallel angle is found out of the relation

$$\operatorname{tg} \frac{1}{2} \Pi(d) = e^{-d},$$

in which for the number e the basis of the natural logarithmic system may be taken, if only the unity of length by which OO_1 is measured be taken accordingly²⁾. As far as the range of values of $\Pi(d)$ is concerned, I only observe that the parallel angle $= \frac{1}{2} \pi$ for $d = 0$, decreasing and tending to 0 if d increases and tends to ∞ .

If the plane ε rotates round OO_1 , then p_1 and p_2 will describe a cone of revolution round OO_1 as axis; this cone is the locus of all straight lines through O parallel to τ , and distinguishes itself in many respects, in form and properties, from the cone of revolution of Euclidian Geometry; the plane τ is an asymptotic plane, to which its surface tends unlimited, and from the symmetry with respect to O follows easily that another plane τ^* like this exists, also placed perpendicularly on OO_1 , but in the point O_1^* situated symmetrically to O_1 with respect to O . So the cone is entirely included between the two planes τ and τ^* , and these two planes having not a single point in common (neither at finite nor at infinite distance), are *divergent*; however, they possess the common perpendicular $O_1O_1^*$, and their shortest distance is $2d$. The cone discussed here will be called for convenience, sake the parallel cone \varkappa belonging to the point O .

2. The parallel cone divides the space into three separate parts; let us call those two parts, inside which is the axis OO_1 , the interior of the cone, the remaining part the exterior; it is then easy to see that the points of space behave differently with respect to their projectability according to their lying inside or outside the cone; for a point P inside the cone the projecting ray OP forms with

1) F. ENGEL: „N. I. LOBATSCHESKY. Zwei geometrische Abhandlungen“. Leipzig, TEUBNER, 1899, p. 167.

2) F. ENGEL, l. c. p. 214.

OO_1 ¹⁾ an acute angle smaller than the parallel angle, from which ensues that OP (or perhaps the prolongation of PO over O) must meet the picture plane; the point of intersection P' is the central projection of P . However, for P outside the cone the acute angle between OP and OO_1 is greater than the parallel angle; so now OP is divergent with respect to τ , from which ensues that points outside the cone possess no projections at all; points on the cone on the contrary do, but these projections lie at infinity.

From the fact that points outside the parallel cone are not projectible we need not infer that these points cannot be determined by Central Projection; if such a point is regarded let us say as the point of intersection of two straight lines, and if these *can* be projected by Central Projection, their point of intersection will also be determined in this indirect way.

3. Let a straight line l be at right angles to τ in a point D of τ . As the line OO_1 is also perpendicular to τ , it is possible to bring a plane through l and OO_1 , the trace of which connects O_1 with D . This plane will intersect the cone α in two generatrices, p_1, p_2 ; we now assume that l cuts these two lines in two points P_1 and P_2 , and — to fix our thoughts — that P_1 lies between D and P_2 . The line l possesses two points at infinity, $V_{1\infty}, V_{2\infty}$, which both lie inside the parallel cone; let us suppose that $V_{1\infty}$ lies under the picture plane and $V_{2\infty}$ above it, then the succession of the points on l is this: $V_{1\infty}, D, P_1, P_2, V_{2\infty}$.

The projecting ray $OV_{1\infty}$ cuts τ in a point V'_1 of e lying between D and O_1 ; we shall call it the first *vanishing point* of l . In like manner the ray $OV_{2\infty}$ prolonged over O will cut the line e in a point V'_2 lying in such a way that O_1 lies between V'_1 and V'_2 ; we shall call V'_2 the second vanishing point of l . The point O_1 does not lie in the middle between V'_1 and V'_2 , on the contrary it is closer to V'_1 ; if namely we let down the perpendicular OS out of O to l a quadrangle is formed with three right angles, namely at O_1, D and S , and from this ensues that the fourth $\angle SOO_1$ is acute. Now OS is the bisectrix of $\angle V_{1\infty}OV_{2\infty}$, and therefore the perpendicular in O on OS the bisectrix of $\angle V'_1OV'_2$; this perpendicular must be placed, as $\angle SOO_1$ is acute, between OO_1 , and OV'_2 , and from this ensues $\angle V'_1OO_1 < \angle V'_2OO_1$. If we now let the rectangular triangle V'_1OO_1 rotate about the side OO_1 till it lies on the triangle V'_2OO_1 , then we can immediately find that $O_1V'_1 < O_1V'_2$.

1) By OO_1 we understand the straight line prolonged at both ends unlimitedly, by OP however a semi-ray starting from O .

It is clear that the central projection l' of l coincides with the trace e of the projecting plane $Ol \equiv \varepsilon$, and at the same time that l is determined by its point of intersection and by *one* of the two vanishing points; the second will be found by letting down the perpendicular OS out of O to l , and by setting off at the other side of OS an angle equal to the parallel angle, formed by OS and the only existing ray parallel to l . But further can be remarked that l is also determined by its two vanishing points, or what comes to the same by its two points at infinity; to find l we should but have to bisect the angle formed by the two projecting parallel rays of l , to mark on the bisecting line a segment OS corresponding to $\frac{1}{2} \angle V_{1\infty} O V_{2\infty}$ as parallel angle, and to erect the perpendicular in S on OS .

The line l is divided into four segments by its two points at infinity, its point of intersection and its two points P_1, P_2 (whose projections lie at infinity), and l' in like manner by its points at infinity $P'_{1\infty}, P'_{2\infty}$, the point D , and the two vanishing points V'_1, V'_2 of l ; the connection between these different segments of l and l' is as follows. To the infinite segment $V_{1\infty} D$ corresponds the finite segment $V'_1 D$, and to the finite segment DP_1 the infinite segment $DP'_{1\infty}$; to the points between P_1 and P_2 no projections correspond, because the projecting rays of these points are divergent with respect to τ ; to the infinite segment $P_2 V_{2\infty}$ on the contrary a segment of l' again corresponds, namely the infinite segment $P'_{2\infty} V'_2$. There now remain on l' only the points between the two vanishing points, to which also belongs O_1 ; to these no points of l correspond, their projecting rays being divergent with respect to l .

§ 4. If a line $l \perp \tau$ is to cut the surface of the parallel cone in two points, the length of DO_1 may not exceed a certain upper limit, so that the results just found do not hold for *all* lines $l \perp \tau$. Let us again suppose through OO_1 an arbitrary plane ε , and let us now first regard OO_1 itself. If we let down out of O_1 on to p_2 the perpendicular $O_1 T$, then because p_2 is parallel to e , the angle $TO_1 P'_{2\infty}$ is the parallel angle belonging to $O_1 T$, and therefore angle $TO_1 O$ is smaller than this parallel angle, because $O_1 O$ cuts the line p_2 (namely in $\angle O$); and $OO_1 P'_2$ being equal to 90° , the parallel angle $TO_1 P'_{2\infty} > 45^\circ$, and angle $TO_1 O < 45^\circ$. If in ε we move l , first coinciding with OO_1 , in such a way that it remains in D perpendicular to e , namely towards the side of $P'_{1\infty}$ (therefore from $P'_{2\infty}$), then the perpendicular DT on p_2 becomes continually greater, and so (see N^o. 1) the parallel angle $TD P'_{2\infty}$ continually smaller; as soon as the perpendicular DT has attained such a length that the

parallel angle corresponding to it is precisely 45° , the complement becomes 45° too, and therefore l parallel to p_2 , but on the other side of DT compared to e ; l will still intersect p_1 in a finite point P_1 , for as it enters the triangle $OO_1P'_{1\infty}$ at D , does of course not contain the point $P'_{1\infty}$, and is divergent with reference to OO_1 , it can leave the triangle only in a finite point of p_1 ; but it will cut p_2 in an point at infinity $P_{2\infty}$, being at the same time $V'_{2\infty}$. So its projection consists of the segment of the line e of V'_1 over D to $P'_{1\infty}$, and the isolated point $P'_{2\infty}$ is equal to $V'_{2\infty}$; now too it is determined by two of the three points D , V'_1 , $V'_{2\infty}$.

The point D lies at a certain distance r from O_1 ; if we describe a circle in τ about O_1 as centre and with r as radius, and if we erect in all points of that circle the perpendiculars on τ , a surface appears which may be called a cylinder of revolution, of which the circle just mentioned is the gorge line; the lines l (1τ) lying inside that cylinder have two different vanishing points (with the exception of OO_1 , whose projection is a single point), the lines l on the cylinder have a finite and an infinite vanishing point, and the lines l outside the cylinder miss the second vanishing point.

As for the shape of the cylinder it is easy to see, that the plane τ^* (see N^o. 1) is an asymptotic plane; and τ itself being evidently a plane of orthogonal symmetry, the plane τ^{**} normal to OO_1 in the point O_1^{**} symmetrical to O_1^* with respect to τ will be a second asymptotic plane; so the distance of these two planes is $4d$.

5. In Euclidean Geometry the lines 1τ are at the same time those which are parallel to OO_1 , but in Hyperbolic Geometry this is different; here we have to regard the lines having in common with OO_1 the point $V_{1\infty}$ lying under the picture plane at infinity, and those having with OO_1 in common the point $V_{2\infty}$ lying above τ . A line l of the former kind lying in the vicinity of OO_1 has a picture point D , two points P_1, P_2 , and a second point at infinity lying inside the cone \varkappa ; its first vanishing point coincides with O_1 , whilst the second lies on DO_1 in such a way, that O_1 lies between D and that point.

If the perpendicular OS let down out of O to l becomes continually larger, the first particularity appearing here is that l becomes parallel to the generatrix p_2 of cone \varkappa lying in the plane Ol ; then it is at right angles to the bisectrix of the obtuse angle formed by p_2 and OO_1 . All lines having this property form an asymptotic cone of revolution ¹⁾ with vertex $V_{1\infty}$, whilst τ^* is an asymptotic plane;

1) H. LIEBMANN, "Nichteuklidische Geometrie", Collection Schubert XLIX, page 63.

as base circle we can obtain a circle with finite radius in τ . For the generatrices of this cone the second point P_2 coincides with the second point at infinity; so the projection consists of the infinite segment $O_1DP'_{1\infty}$ and the isolated second point at infinity of this line.

For lines l outside this cone this isolated point vanishes, and on account of this the second vanishing point; for its determination remain however D , and the first vanishing point O_1 . Now however, the perpendicular OS still increasing, l can become parallel to p_1 , and hence parallel to e or to τ ; it is then at right angles to the bisectrix of the acute angle between p_1 and OO_1 , as well as to that of the right angle between e and O_1V_{1x} , which bisectrices are respectively divergent. All lines showing this property form a second asymptotic cone of revolution, for which however τ is now the asymptotic plane; they have a picture point at infinity, but are no less determined by this point and the first vanishing point O_1 .

If l also lies outside this second cone, it becomes divergent with respect to τ , so it loses its picture point D ; but now its second point at infinity lies again inside the cone α , which makes it projectible, so that in this case l has two vanishing points but no picture point; however, the two vanishing points are sufficient for its determination (see N^o. 3). The originals at infinity corresponding to it are both under the picture plane; in connection with the preceding it would be preferable, in order to avoid confusion, to say that l has in this case two "first points at infinity" and therefore also two "first vanishing points".

The lines containing the second point at infinity $V_{2\infty}$ of OO_1 behave in like manner; we again find two asymptotic cones of revolution, one with the asymptotic plane τ , a second with the asymptotic plane τ^* , and we terminate with lines with two "second vanishing points" and without picture point.

Delft, September 1905.

Physiology. — "*A method for determining the osmotic pressure of very small quantities of liquid.*" By Prof. H. J. HAMBURGER.

It not unfrequently happens that one wishes to know the osmotic pressure of normal or pathological somatic fluids of which no more than $\frac{1}{2}$, or $\frac{1}{4}$ cc. are available. I recently had such a case when an oculist asked me what should be the concentration of liquids used for the treatment of the eye. It seemed to me to be rational — and the investigations of MASSART¹⁾ justified this opinion — to prescribe

¹⁾ MASSART, Archives de Biologie 9 1889, p. 335.

concentrations of the same osmotic pressure as the natural medium of the cornea and conjunctiva, namely the lachrymal fluid.

Until now, however, this pressure had not been measured, at any rate by a direct method, probably on account of the difficulty of obtaining a quantity of that fluid, sufficient for the customary methods, viz. the freezing-point and the blood corpuscles method.

So I tried to find a method with which $\frac{1}{2}$ cc., if necessary $\frac{1}{4}$ cc. of liquid should be sufficient. I succeeded in finding such a method.

It is based on the already known principle that the volume of blood corpuscles is greatly dependent on the osmotic pressure of the solution containing them. ¹⁾

This principle has been applied here in the following manner. The fluid to be examined is put into a small, funnel-shaped glass tube, the cylindrical neck of which is formed by a calibrated capillary, closed below. ²⁾ Let this quantity be $\frac{1}{2}$ cc. Into other similar funnel-shaped tubes of the same size are put solutions of Na Cl of different concentration (0.8 ‰, 0.9 ‰, 1 ‰, 1.1 ‰, 1.2 ‰, 1.3 ‰, 1.4 ‰, 1.5 ‰, 1.6 ‰) and to each of these 0.02 cc. of blood is added. After half an hour — during which time the corpuscles are sure to have found osmotic equilibrium with their surroundings — the tubes are centrifuged until the sediments no longer alter their volumes. It is obvious that the osmotic pressure of the fluid under examination will be equal to that of the Na Cl solution in which the sediment of blood corpuscles is the same as in the fluid examined. We passingly remark that this solution of Na Cl in the case of lachrymal fluid contained 1.4 ‰.

A few remarks must be added.

Firstly it may be asked whether the blood which is added to the fluid to be examined does not appreciably alter the osmotic pressure of that fluid.

Assuming that the blood used contains 60 pCt. of serum, 0.02 cc. of blood will contain 0.012 cc. of serum. If the quantity of fluid was $\frac{1}{2}$ cc., the total quantity of fluid will now be $0.012 + 0.5 = 0.512$ cc. If the fluid to be examined had an osmotic pressure of a 1.2 pCt. Na Cl solution and the serum that of a 0.9 pCt. Na Cl solution, dilution of the fluid with the serum will have produced a liquid with an osmotic pressure of $\frac{0.012 \times 0.9 + 0.5 \times 1.2}{0.012 + 0.5} = 1.19$ pCt. Na Cl. The osmotic pressure of the fluid is consequently reduced

¹⁾ HAMBURGER, Centralblatt f. Physiologie, 17 Juni 1893.

²⁾ HAMBURGER, Journal de Physiol. norm. et pathologique 1900 p. 889.

by 0.01 pCt Na Cl by the addition of 0.02 cc. of serum, a difference which cannot even be detected with the BECKMANN apparatus.

If instead of 1/2 cc. of fluid only 1/4 cc. has been used, a similar calculation shows that the osmotic pressure of the fluid under examination is diminished by a 0.014 pCt. Na Cl solution, corresponding to a depression of scarcely 0.0084°, a difference of depression, lying near the limit of accuracy of BECKMANN'S determination of the freezing point.

However, if the difference were greater, this could be no objection to the method, since also the Na Cl solutions are mixed with the same quantity of blood.

The second remark concerns the pipette and the tubes.

In order to measure accurately, the bore of the pipette must be narrow and accordingly the instrument itself long. The column of 0.02 cc. of blood has a length of 143 mm. The same remark applies to the funnel-shaped tubes. The calibrated capillary part has a length of 57 millimetres and a volume of 0.01 cc. and is divided into 100 equal parts, which can easily be observed with the naked eye, fractions being estimated with a magnifying glass.

The use of funnel-shaped tubes of the same length, but with a still smaller volume of the capillary part than 0.01 cc., which would enable us to make determinations of the osmotic pressure of much smaller quantities of liquid than 1/4 cc., would give rise to technical difficulties, on which I will not dwell here. No more shall I mention here the special precautions in experimenting, necessary for obtaining accurate figures. This subject will be dealt with elsewhere.

In order to give an idea of the reliability of the method, a table follows, containing two series of parallel experiments. (See p. 397).

The agreement between the figures (each division represents $\frac{0.01}{100} = 0.0001$ cc.) is seen to be very satisfactory.

A third remark concerns the possibility of making one or more additional determinations with the same fluid, for checking the result obtained. All one has to do is to drain off the liquid above the sediment by means of a finely drawn tube or pipette and to convey it into another funnel-shaped tube, to add again 0.02 cc. of blood and to centrifuge in the same way. The liquids in the NaCl-tubes are treated in the same way. Undoubtedly one changes the osmotic pressure of the liquids a little by again introducing 0.02 cc. of blood, but this is done with all the liquids and so the alteration

Salt solutions.	Volumes of the sediments after centrifuging for.				
	$\frac{1}{2}$ hour.	$\frac{1}{2}$ hour.	$\frac{1}{2}$ hour.	$\frac{1}{2}$ hour.	15 min.
Na Cl 0.9 %	74	69	68	68	68
» »	73	69	68	68	68
Na Cl 1.1 %	71	65	64	64	64
» »	68	64	64 $\frac{1}{2}$	64 $\frac{1}{2}$	64 $\frac{1}{2}$
Na Cl 1.2 %	68	65	63	61 $\frac{1}{2}$	61 $\frac{1}{2}$
» »	69	65 $\frac{1}{2}$	63	62	62
Na Cl 1.3 %	67	62	60	59	59
» »	67	62	60	59	59
Na Cl 1.4 %	69	62	58 $\frac{1}{2}$	57	57
» »	67	62 $\frac{1}{2}$	58	57 $\frac{1}{2}$	57 $\frac{1}{2}$
Na Cl 1.5 %	62	58	55	55	55
» »	64	59	56	56	56
lachrymal fluid	78	63	59 $\frac{1}{2}$	57	57
the same lachr. fl.	76 $\frac{1}{2}$	64	60	57	57

has no influence on the result, as would be the case if fresh solutions of NaCl were taken each time.

A last remark concerns the applicability of the method. It cannot be used so generally as the freezing point method: It cannot be applied with gall since this fluid contains substances causing haemolysis; it also fails for urine, since this fluid contains a relatively large quantity of urea which contributes considerably to the osmotic pressure but has no influence on the volume of the blood corpuscles.

For a number of other fluids, as blood serum, lymph, cerebrospinal fluid, saliva, lachrymal fluid, etc., the method can be successfully applied. It does not matter whether the fluids are coloured, for the determination only depends on the volume occupied in the fluid by the blood corpuscles.

Zoology. — "*On the primordial cranium of Tarsius spectrum*".

By Prof. Dr. EUGEN FISCHER of Freiburg i. B. (Preliminary paper). Communicated by Prof. A. A. W. HUBRECHT.

An investigation of the primordial cranium of *Tarsius spectrum* seemed particularly interesting to me as it might fill up a gap I had found when making a comparative study of the cartilaginous skull of apes and man on one hand, and of lower mammals (the mole) on the other ¹⁾. So I was exceedingly happy when Prof. HUBRECHT,

¹⁾ FISCHER E. Das Primordialcranium von *Talpa europae*. Anat. Hefte Bd. 17, 1901 and: zur Entwicklungsgeschichte des Affenschädels. Zeitschr. f. Morph. und Anthropol. Bd. 5, 1903.

with generous kindness, placed at my disposal, out of his rich and valuable collection of embryos, such stages as were proper for this investigation.

In what follows a brief description will be given of the form and development of the chondrocranium as it appears at the height of development; this description is based on the reconstructed waxmodel which I made of the skull of an embryo of 34 mm. length. Other details of this embryo are shown in KEIBEL's Normentafel ¹⁾.

Since an extensive and illustrated description will follow elsewhere, I shall be very brief here and give no detailed information as to literature and comparisons. For the first and also for the nomenclature used and the meaning of many only shortly mentioned details I refer to GAUPP's brilliant comparative of the development history of the vertebrate cranium in HERTWIG's Handbuch ²⁾.

The basal plate is broad behind and well developed; anteriorly it delimits the foramen magnum. It is perforated by the hypoglossus. Laterally it has a fixed connection with the ear-capsule. This connection, however, is pierced by the narrow and long, almost slit-shaped foramen jugulare. Behind it, starting from the junction of the basal plate and the ear-capsule the cartilaginous plate develops which upwards represents the parietal plate, backwards and inwards the tectum synoticum. This tectum is a very narrow strap. So in this respect *Tarsius* resembles the young foetus of monkeys and man (cf. BOLK, Petr. Camp. II) and differs from the other mammals, where a broad plate is found.

Further forwards the basal plate itself becomes very remarkably narrow, so that here it consists only of a thin, round projection. At the same time it is separated by long slits from the two ear-capsules, with the anterior parts of which it only coalesces again in the region of the sella. This thin projection rises rather steeply, and in the sella region it becomes quite considerable with its two processus clinoides posteriores. The two slits terminate close by, after having grown very narrow. Their existence seems to be very rare in mammals; they are defects which may be compared with the fenestra basicranialis posterior of Reptiles (GAUPP).

The ear-capsules themselves showed no peculiarities; they are

¹⁾ HUBRECHT und KEIBEL, Normentafeln zur Entwicklung von *Tarsius spectrum* und *Nycticebus tardigradus*. Jena 1906. Tabelle N^o. 36. Fig. 20 a.—c.

I am also greatly indebted to Prof. KEIBEL for enabling me to use the splendid series of sections of HUBRECHT's *Tarsius* embryos on which his own investigations were effectuated.

²⁾ GAUPP, Die Entwicklung des Kopfskelettes. Hertwig's Handbuch 1905. Cap 6 p. 573.

moderately erect, the fossa subarcuata is only indicated. The foramen acousticum and higher upwards the foramen Nervi facialis mark the border of the vestibular and cochlear parts; to the former are attached above the parietal plates; they are very small and insignificant. A foramen jugulare spurium perforates its base. Frontally they send out a very short processus marginalis posterior, exactly as in the monkey skull. On the exterior of the ear-capsules lie, in exactly the same way as I described for the mole and embryos of apes, the cartilaginous stirrup, anvil and hammer, passing into MECKEL'S cartilage.

The orbito-temporal part is characterised by its relatively phenomenal length. The continuation of the cranial trabecle from the saddle groove, where it had much broadened, is a narrow high ridge, a true septum interorbitale (GAUPP) still more extended than I found it with apes, although not so high as there. So the cranium is clearly tropibasical. By this long septum, which in front of course passes into the nasal septum, the nasal capsule is far separated from the brain capsule; it lies far in front of it, exactly as with Reptiles. The relatively large eyes of *Tarsius* are probably the cause of the survival of this extremely primitive formation.

Where the described cartilaginous beam broadens into the hypophysis groove it sends out, fairly deep towards the base, a round stalk at each side, bearing the small ala temporalis, which tapers in the same way as with the foetus of man and ape. It does not serve as a cranial wall yet, and has no Foramina rotunda and ovalia yet. Above it starts with two roots the large ala orbitalis. Between the roots the two foramina optica, the right and left one, are very close together, so that only the thin septum mentioned separates them. The orbital wings, themselves large plates, are neither bent upwards so strongly as with the lower mammals (the mole), nor do they extend laterally in such a perfect plane as with ape and man, but their shape is exactly between the two extremes, they slant sideways and upwards. Also the circumstance that their posterior end lengthens out into a real, although very thin taenia marginalis, which nearly reaches the parietal plate (there remains a very small gap), shows a similar transitional stage between the Primates and the other mammals. The anterior parts of the alae orbitales are not connected with the nasal capsule as usual (also in the sheep e. g. this connection is wanting according to DECKER). Below the sphenoid beam are, isolated from it, the roundish pterygoid cartilages, quite independent.

Proximally the septum interorbitale, as has been stated, passes

into the nasal septum. The nasal capsule has a remarkable resemblance with that of the Primates; there is no trace of the double tube form of other mammals.

The two apertures for the olfactory nerves are both simple, without any formation of cribrosa.

This part of the future nasal root is relatively broad, which is especially conspicuous with regard to the completed cranium.

Basally the whole nasal capsule has a slit-shaped opening, i. e. the bottom (lamina transversalis post. and ant.) is lacking, this being also characteristic for man and partly for apes, with whom I still found an indication of the bottom (*Semnopithecus*). About the yet slightly developed conchae, the cartilages of JACOBSON, the alar cartilage enclosing the nasal entrance, nothing particular can be mentioned.

MECKEL's cartilage proceeds well developed as far as the point of the chin and here has a continuous connection, without any trace of a suture, with that of the other side. REICHERT's cartilage proceeds continuously to the tongue bone.

On the dermal bones I will not dwell here; besides the upper squama of the occipital, resp. interparietal, all membrane-bones are present; the annulus tympanicus is only $\frac{2}{3}$ of a ring; frontal and parietal extend as yet to such a small height that the top of the skull is mostly covered with skin only.

When we now survey the whole cranium, as sketched above, we find two important characteristics. On one hand appears the exceedingly close relationship of the developing cranium of *Tarsius* and that of ape and man. In spite of clear specific peculiarities, it evidently stands much nearer to these than to the other known mammalian crania. This affords a new proof for the correctness of HUBRECHT's opinion as to the position of *Tarsius* in the system. At the same time an investigation of the primordial cranium of true Lemurs becomes necessary and promises important results. This investigation will shortly follow.

Secondly the resemblance between this type of skull and that of Reptiles is striking; like the skull of monkeys, so that of *Tarsius* in its cartilaginous stage, pleads unmistakably for unity of plan and origin of the Reptilian and Mammalian skull (cf. GAUPP's various articles). In our case the position of the nasal capsule, the septum interorbitale, a series of details in the arrangement of the foramina, the cartilaginous straps, etc. point clearly in that direction.

The study of each single form may in this way contribute to the solution of the problem of phylogenesis.

Freiburg i. B., October 1905.

Physics. — “*On the radiation of heat in a system of bodies having a uniform temperature*”. By Prof. H. A. LORENTZ.

(Communicated in the meetings of September and October 1905).

§ 1. A system of bodies surrounded by a perfectly black enclosure which is kept at a definite temperature, or by perfectly reflecting walls, will, in a longer or a shorter time, attain a state of equilibrium, in which each body loses as much heat by radiation as it gains by absorption, the intervening transparent media being the seat of an energy of radiation, whose amount per unit of volume is wholly determinate for every wave-length. The object of the following considerations is to examine somewhat more closely this state of things and to assign to each element of volume its part in the emission and the absorption. Of course, the most satisfactory way of doing this would be to develop a complete theory of the motions of electrons to which the phenomena may in all probability be ascribed. Unfortunately however, it seems very difficult to go as far as that. I have therefore thought it advisable to take another course, based on the conception of certain periodic electromotive forces acting in the elements of volume of ponderable bodies and producing the radiation that is emitted by these elements. If, without speaking of electrons, or even of molecules, we suppose such forces to exist in a matter continuously distributed in space, and if we suppose the emissivity of a black body to be known as a function of the temperature and the wave-length, we shall be able to calculate the intensity that must be assigned to the electromotive forces in question. The result will be a knowledge, not of the real mechanism of radiation, but of an imaginary one by which the same effects could be produced.

§ 2. For the sake of generality we shall consider a system of aeolotropic bodies. As to the notations used in our equations and the units in which the electromagnetic quantities are expressed, these will be the same that I have used in my articles in the *Mathematical Encyclopedia*. We may therefore start from the following general relations between the electric force \mathfrak{E} , the current \mathfrak{C} , the magnetic force \mathfrak{H} and the magnetic induction \mathfrak{B}

$$\text{rot } \mathfrak{H} = \frac{1}{c} \mathfrak{C}, \quad (1)$$

$$\text{rot } \mathfrak{E} = - \frac{1}{c} \dot{\mathfrak{B}}, \quad (2)$$

In these formulæ c denotes the velocity of light in the aether.

In the greater part of what follows, we shall confine ourselves to cases, in which the components of the above vectors and of others we shall have occasion to consider, are harmonic functions of the time with the frequency n . Then, the mathematical calculations can be much simplified if, instead of the real values of these components, we introduce certain complex quantities, all of which contain the time in the factor e^{int} and whose real parts are the values of the components with which we are concerned. If $\mathfrak{A}_x, \mathfrak{A}_y, \mathfrak{A}_z$ are complex quantities of this kind, relating in one way or another to the three axes of coordinates and in which the quantity e^{int} may be multiplied by complex quantities, the combination $(\mathfrak{A}_x, \mathfrak{A}_y, \mathfrak{A}_z)$ may be called a complex vector \mathfrak{A} and $\mathfrak{A}_x, \mathfrak{A}_y, \mathfrak{A}_z$ its components.

By the real part of such a vector we shall understand a vector whose components are the real parts of $\mathfrak{A}_x, \mathfrak{A}_y, \mathfrak{A}_z$. It will lead to no confusion, if the same symbol is used alternately to denote a complex vector and its real part. It will also be found convenient to speak of the rotation and the divergence of a complex vector, and of the scalar product $(\mathfrak{A}, \mathfrak{B})$ and the vector product $[\mathfrak{A}, \mathfrak{B}]$ of two complex vectors \mathfrak{A} and \mathfrak{B} , all these quantities being defined in the same way as the corresponding ones in the case of real vectors. E. g., we shall mean by the scalar product $(\mathfrak{A}, \mathfrak{B})$ the expression $\mathfrak{A}_x\mathfrak{B}_x + \mathfrak{A}_y\mathfrak{B}_y + \mathfrak{A}_z\mathfrak{B}_z$.

It is easily seen that, if $\mathfrak{E}, \mathfrak{H}, \mathfrak{C}$ and \mathfrak{B} are complex vectors, satisfying the equations (1) and (2), their real parts will do so likewise. The denominations electric force, etc. will be applied to these complex vectors as well as to the real ones.

One advantage that is gained by the use of complex quantities lies in the fact that now, owing to the factor e^{int} , a differentiation with respect to the time amounts to the same thing as a multiplication by in ; in virtue of this the relation between \mathfrak{E} and \mathfrak{C} and that between \mathfrak{H} and \mathfrak{B} may be expressed in a simple form. Indeed, we may safely assume that, whatever be the peculiar properties of a ponderable body, the components of \mathfrak{C} are connected to those of \mathfrak{E} by three linear equations with constant coefficients, containing the components and their differential coefficients with respect to the time. In the case of the complex vectors, these equations may be written as linear relations between the components themselves; in other terms, one complex vector becomes a linear vector function of the other. A relation of this kind between two vectors \mathfrak{A} and \mathfrak{B} can always be expressed by three equations of the form

$$\begin{aligned} \mathfrak{B}_x &= v_{11} \mathfrak{A}_x + v_{12} \mathfrak{A}_y + v_{13} \mathfrak{A}_z, \\ \mathfrak{B}_y &= v_{21} \mathfrak{A}_x + v_{22} \mathfrak{A}_y + v_{23} \mathfrak{A}_z, \\ \mathfrak{B}_z &= v_{31} \mathfrak{A}_x + v_{32} \mathfrak{A}_y + v_{33} \mathfrak{A}_z, \end{aligned}$$

which we shall condense into the formula

$$\mathfrak{B} = (\nu) \mathfrak{A}.$$

According to this notation we may put $\mathfrak{C} = (\rho) \mathfrak{E}$, or, as is more convenient for our purpose,

$$\mathfrak{C} = (\rho) \mathfrak{C}, \dots \dots \dots (3)$$

the symbol (ρ) containing a certain number of coefficients ρ which are determined by the properties of the body considered. As a rule, these coefficients are complex quantities, whose values depend on the frequency n .

As to the relation between \mathfrak{B} and \mathfrak{H} , we shall put

$$\mathfrak{B} = (\mu) \mathfrak{H},$$

or

$$\mathfrak{H} = (q) \mathfrak{B} \dots \dots \dots (4)$$

We have further to introduce an electromotive force which will be represented by a vector \mathfrak{E}_e , or by the real part of a complex vector \mathfrak{E}_e . The meaning of this is simply that the current \mathfrak{C} is supposed to depend on the vector $\mathfrak{C} + \mathfrak{E}_e$ in the same way in which it depends on \mathfrak{C} alone in ordinary cases, so that

$$\mathfrak{C} + \mathfrak{E}_e = (\rho) \mathfrak{C} \dots \dots \dots (5)$$

Similarly, we may assume a magnetomotive force \mathfrak{H}_e , replacing (4) by

$$\mathfrak{H} + \mathfrak{H}_e = (q) \mathfrak{B} \dots \dots \dots (6)$$

This new vector \mathfrak{H}_e however, does not correspond to any really existing quantity; it is only introduced for the purpose of simplifying the demonstration of a certain theorem we shall have to use.

As to the coefficients we have taken together in the symbols (ρ) and (q) , we shall suppose them to be connected with each other in the way expressed by

$$p_{12} = p_{21}, p_{23} = p_{32}, p_{31} = p_{13}, \dots \dots \dots (7)$$

and

$$q_{12} = q_{21}, q_{23} = q_{32}, q_{31} = q_{13} \dots \dots \dots (8)$$

The only case excluded by this assumption is that of a body placed in a magnetic field.

For isotropic bodies we may write, instead of (5) and (6),

$$\mathfrak{C} + \mathfrak{E}_e = p \mathfrak{C}, \dots \dots \dots (9)$$

$$\mathfrak{H} + \mathfrak{H}_e = q \mathfrak{B}, \dots \dots \dots (10)$$

with only one complex coefficient p and one coefficient q .

§ 3. Before coming to the problem we have in view, it is necessary to treat some preliminary questions. In the first place, we shall examine the vibrations that are set up in an unlimited homogeneous and isotropic body subjected to given electromotive and magnetomotive forces, changing with the frequency n . This problem is best treated by using the complex vectors.

We may deduce from (1)

$$\text{rot rot } \mathfrak{H} = \frac{1}{c} \text{rot } \mathfrak{E},$$

or

$$\text{grad div } \mathfrak{H} - \Delta \mathfrak{H} = \frac{1}{c} \text{rot } \mathfrak{E} \dots \dots \dots (11)$$

and similarly from (2)

$$\text{grad div } \mathfrak{E} - \Delta \mathfrak{E} = -\frac{1}{c} \text{rot } \mathfrak{H} \dots \dots \dots (12)$$

Again, always using the equations (1), (2), (9) and (10), we find

$$\begin{aligned} \text{div } \mathfrak{H} &= 0, \quad \text{div } \mathfrak{E} = 0, \\ \text{div } \mathfrak{H} &= -\text{div } \mathfrak{H}_e, \quad \text{div } \mathfrak{E} = -\text{div } \mathfrak{E}_e, \\ \text{rot } \mathfrak{E} &= \frac{1}{p} (\text{rot } \mathfrak{E} + \text{rot } \mathfrak{E}_e) = -\frac{1}{pc} \mathfrak{H} + \frac{1}{p} \text{rot } \mathfrak{E}_e \\ &= -\frac{1}{pqc} (\mathfrak{H} + \mathfrak{H}_e) + \frac{1}{p} \text{rot } \mathfrak{E}_e, \\ \text{rot } \mathfrak{H} &= \frac{1}{q} (\text{rot } \mathfrak{H} + \text{rot } \mathfrak{H}_e) = \frac{1}{qc} \mathfrak{E} + \frac{1}{q} \text{rot } \mathfrak{H}_e \\ &= \frac{1}{pqc} (\mathfrak{E} + \mathfrak{E}_e) + \frac{1}{q} \text{rot } \mathfrak{H}_e, \end{aligned}$$

so that (11) and (12) become

$$\begin{aligned} \Delta \mathfrak{H} - \frac{1}{pqc^2} \mathfrak{H} &= -\text{grad div } \mathfrak{H}_e + \frac{1}{pqc^2} \mathfrak{H}_e - \frac{1}{pc} \text{rot } \mathfrak{E}_e, \\ \Delta \mathfrak{E} - \frac{1}{pqc^2} \mathfrak{E} &= -\text{grad div } \mathfrak{E}_e + \frac{1}{pqc^2} \mathfrak{E}_e + \frac{1}{qc} \text{rot } \mathfrak{H}_e. \end{aligned}$$

The solution of these equations may be put in a convenient form by means of two auxiliary vectors \mathfrak{A} and \mathfrak{B} . If these are determined by

$$\Delta \mathfrak{A} - \frac{1}{pqc^2} \mathfrak{A} = -\mathfrak{E}_e, \dots \dots \dots (13)$$

$$\Delta \mathfrak{B} - \frac{1}{pqc^2} \mathfrak{B} = -\mathfrak{H}_e, \dots \dots \dots (14)$$

we shall have

$$\mathfrak{H} = \text{grad div } \mathfrak{B} - \frac{1}{pqc^2} \mathfrak{B} + \frac{1}{pc} \text{rot } \mathfrak{A}, \dots \dots \dots (15)$$

$$\mathfrak{E} = \text{grad div } \mathfrak{U} - \frac{1}{pqc^2} \ddot{\mathfrak{U}} - \frac{1}{qc} \text{rot } \dot{\mathfrak{Q}} \quad \quad (16)$$

Finally, putting

$$v^2 = i p q n c^2, \quad \quad (17)$$

we get instead of (13) and (14)

$$\Delta \mathfrak{U} - \frac{1}{v^2} \ddot{\mathfrak{U}} = - \mathfrak{E}_e,$$

$$\Delta \mathfrak{Q} - \frac{1}{v^2} \ddot{\mathfrak{Q}} = - \mathfrak{H}_e,$$

for the solution of which we may take

$$\mathfrak{U} = \frac{1}{4\pi} \int \frac{1}{r} \mathfrak{E}_e \left(t - \frac{r}{v} \right) dS, \quad \quad (18)$$

$$\mathfrak{Q} = \frac{1}{4\pi} \int \frac{1}{r} \mathfrak{H}_e \left(t - \frac{r}{v} \right) dS. \quad \quad (19)$$

Here dS denotes an element of volume situated at a distance r from the point for which we wish to calculate \mathfrak{U} and \mathfrak{Q} , and the index $\left(t - \frac{r}{v} \right)$ means that, in the expressions representing \mathfrak{E}_e and \mathfrak{H}_e

for that element of volume, t is to be replaced by $t - \frac{r}{v}$.

The algebraic sign of v is left indeterminate by (17). We shall choose it in such a way that our formulae represent a propagation of vibrations *issuing* from the elements of volume in which \mathfrak{E}_e and \mathfrak{H}_e are applied.

For aether we have $q = 1$ and, as may easily be shown $\frac{1}{p} = in, v = c$.

§ 4. We have next to establish the equation of energy. The calculations required for this purpose, as well as those we shall have to perform later on, may be much simplified, if we replace all discontinuities at the limit of two bodies by a gradual transition from one to the other; this may be done without loss of generality, because, in our final results, the thickness of the boundary layers may be made to become infinitely small. A further simplification is obtained by leaving out of consideration the imaginary magnetomotive forces, and by supposing the coefficients μ and q to be real. The coefficients p_{11}, p_{12} etc. however will always be considered as complex quantities. We shall decompose them into their real parts, which we shall denote by α_{11}, α_{12} , etc., and their imaginary parts, for which we shall write $-i\beta_{11}, -i\beta_{12}$, etc., so that $p_{11} = \alpha_{11} - i\beta_{11}$, etc.

The equation (5) now becomes

$$\mathfrak{E} + \mathfrak{E}_e = (\alpha) \mathfrak{E} - i(\beta) \mathfrak{E}, \dots \dots \dots (20)$$

or, if we define a new vector \mathfrak{D} by means of the equation

$$\mathfrak{E} = \mathfrak{D}, \dots \dots \dots (21)$$

$$\mathfrak{E} + \mathfrak{E}_e = (\alpha) \mathfrak{E} + n(\beta) \mathfrak{D} \dots \dots \dots (22)$$

In the deduction of the equation of energy we have to understand by \mathfrak{E} , \mathfrak{E}_e , \mathfrak{H} and \mathfrak{D} the real vectors. For these we have the formulae (1), (2) and (21), and besides, since q , α and β are real, the relations (4) and (22).

From (1) and (2) we may draw immediately

$$c\{(\mathfrak{H} \cdot \text{rot } \mathfrak{E}) - (\mathfrak{E} \cdot \text{rot } \mathfrak{H})\} = -(\mathfrak{H} \cdot \mathfrak{B}) - (\mathfrak{E} \cdot \mathfrak{E}),$$

the left-hand member of which is

$$\text{div } \mathfrak{S},$$

if we define the vector \mathfrak{S} by the equation

$$\mathfrak{S} = c[\mathfrak{E} \cdot \mathfrak{H}], \dots \dots \dots (23)$$

i.e., if we understand by it the vector product of \mathfrak{E} and \mathfrak{H} , multiplied by c .

In the right-hand member we have in the first place

$$(\mathfrak{H} \cdot \mathfrak{B}) = \frac{1}{2} \frac{\partial}{\partial t} (\mathfrak{H} \cdot \mathfrak{B}),$$

as may be seen from (4), if (8) is taken into account, and further, in virtue of (7), (21) and (22),

$$(\mathfrak{E} \cdot \mathfrak{E}) = ((\alpha) \mathfrak{E} \cdot \mathfrak{E}) + \frac{1}{2} n \frac{\partial}{\partial t} ((\beta) \mathfrak{D} \cdot \mathfrak{D}) - (\mathfrak{E}_e \cdot \mathfrak{E}).$$

Our equation therefore takes the following form, in which the meaning of the different terms is at once apparent,

$$(\mathfrak{E}_e \cdot \mathfrak{E}) = ((\alpha) \mathfrak{E} \cdot \mathfrak{E}) + \frac{1}{2} n \frac{\partial}{\partial t} ((\beta) \mathfrak{D} \cdot \mathfrak{D}) + \frac{1}{2} \frac{\partial}{\partial t} (\mathfrak{H} \cdot \mathfrak{B}) + \text{div } \mathfrak{S}.$$

The first member represents the work done by the electromotive force per unit of volume and unit of time; in the second member

$$w = ((\alpha) \mathfrak{E} \cdot \mathfrak{E}) \dots \dots \dots (24)$$

is the expression for the quantity of heat that is developed per unit of space and unit of time. Further, $\frac{1}{2} (\mathfrak{H} \cdot \mathfrak{B})$ is the magnetic and

$\frac{1}{2} n ((\beta) \mathfrak{D} \cdot \mathfrak{D})$ the electric energy, both reckoned per unit of volume.

The vector \mathfrak{S} denotes the flow of energy, so that the amount of energy an element of volume dS loses by this flow is given by $\text{div } \mathfrak{S} dS$.

§ 5. We may now pass to a theorem which I have formerly proved in a somewhat more cumbersome and less general way. In order to arrive at it, we have to use the complex vectors, supposing at the same time the existence of magnetomotive forces; we have therefore to apply the formulae (5) and (6).

We shall consider *two* different states with the same frequency n , both of which can exist in the system of bodies. The symbols \mathfrak{E} , \mathfrak{H} , etc. will be used for one state and the corresponding symbols, distinguished by accents, for the other. We shall proceed in a way much like the operations of the last paragraph, with this difference however, that we shall now combine quantities relating to one state with quantities belonging to the other.

We shall start from the relation

$$c \{ (\mathfrak{H}' \text{ rot } \mathfrak{E}) - (\mathfrak{E} \text{ rot } \mathfrak{H}') \} = - (\mathfrak{H}' \cdot \mathfrak{B}) - (\mathfrak{E} \cdot \mathfrak{E}').$$

Here the expression on the left is equal to

$$c \operatorname{div} [\mathfrak{E} \cdot \mathfrak{H}']$$

and on the other side we may put

$$\begin{aligned} (\mathfrak{H}' \cdot \mathfrak{B}) &= \operatorname{in} (\mathfrak{H}' \cdot \mathfrak{B}) = \operatorname{in} ((q) \mathfrak{B}' \cdot \mathfrak{B}) - (\mathfrak{H}'_e \cdot \mathfrak{B}), \\ (\mathfrak{E} \cdot \mathfrak{E}') &= ((p) \mathfrak{E} \cdot \mathfrak{E}') - (\mathfrak{E}_e \cdot \mathfrak{E}'), \end{aligned}$$

so that we find

$$c \operatorname{div} [\mathfrak{E} \cdot \mathfrak{H}'] = - \operatorname{in} ((q) \mathfrak{B}' \cdot \mathfrak{B}) - ((p) \mathfrak{E} \cdot \mathfrak{E}') + (\mathfrak{H}'_e \cdot \mathfrak{B}) + (\mathfrak{E}_e \cdot \mathfrak{E}').$$

The theorem in question is a consequence of this formula and the corresponding one that is got by interchanging the quantities belonging to the two states; we have only to subtract one equation from the other. Since, by (8) and (7)

$$((q) \mathfrak{B}' \cdot \mathfrak{B}) = ((q) \mathfrak{B} \cdot \mathfrak{B}') \text{ and } ((p) \mathfrak{E} \cdot \mathfrak{E}') = ((p) \mathfrak{E}' \cdot \mathfrak{E}),$$

we find in this way

$$c \{ \operatorname{div} [\mathfrak{E} \cdot \mathfrak{H}'] - \operatorname{div} [\mathfrak{E}' \cdot \mathfrak{H}] \} = (\mathfrak{H}'_e \cdot \mathfrak{B}) - (\mathfrak{H}_e \cdot \mathfrak{B}') + (\mathfrak{E}_e \cdot \mathfrak{E}') - (\mathfrak{E}'_e \cdot \mathfrak{E}).$$

We shall finally multiply this by an element of volume dS , and take the integral of both sides over the space within a closed surface σ . If we denote by n the normal to the latter, drawn outward, the result will be

$$c \int \{ [\mathfrak{E} \cdot \mathfrak{H}']_n - [\mathfrak{E}' \cdot \mathfrak{H}]_n \} d\sigma = \int \{ (\mathfrak{H}'_e \cdot \mathfrak{B}) - (\mathfrak{H}_e \cdot \mathfrak{B}') + (\mathfrak{E}_e \cdot \mathfrak{E}') - (\mathfrak{E}'_e \cdot \mathfrak{E}) \} dS \quad (25)$$

§ 6. There are a number of cases in which the first member of this equation is zero.

a. E. g. we may suppose the system to be limited on all sides in such a way that it cannot exchange rays with surrounding bodies; we can realize this by enclosing the system in an envelop that is

perfectly reflecting on the outside. If, under these circumstances, the surface σ surrounds that envelop, we may put in every point of it $\mathfrak{E} = 0, \mathfrak{E}' = 0, \mathfrak{H} = 0, \mathfrak{H}' = 0$.

b. If the envelop is made of a perfectly conducting material, both the electric force \mathfrak{E} and the force \mathfrak{E}' will be normally directed in every point of its inner surface. Consequently, if the latter is chosen for the surface σ , we shall have

$$[\mathfrak{E} \cdot \mathfrak{H}']_n = 0 \text{ and } [\mathfrak{E}' \cdot \mathfrak{H}]_n = 0.$$

c. Finally we may conceive a system lying in a finite part of space and surrounded by aether, into which it emits rays travelling outwards to infinite distance. Taking in this case for σ a sphere of infinite radius, we shall show that for each element $d\sigma$ the factor by which it is multiplied in the equation (25) vanishes. The direction of the axes of coordinates being indeterminate, it will suffice to prove this proposition for the point P in which the sphere is cut by a line drawn from the centre O in the direction of the axis of x .

Now, if we confine ourselves to those parts of $\mathfrak{E}, \mathfrak{H}, \mathfrak{E}'$ and \mathfrak{H}' which are inversely proportional to the first power of OP , as may obviously be done, we may consider the state of things near the point P as a propagation of vibrations in the direction OP , the electric and magnetic force being perpendicular to that direction and to each other. Denoting by a and b , a' and b' certain complex quantities, we may write

$$\begin{aligned} \mathfrak{E}_x &= 0, \mathfrak{E}_y = ae^{int}, & \mathfrak{E}_z &= be^{int}, \\ \mathfrak{H}_x &= 0, \mathfrak{H}_y = -be^{int}, & \mathfrak{H}_z &= ae^{int}, \\ \mathfrak{E}'_x &= 0, \mathfrak{E}'_y = a'e^{int}, & \mathfrak{E}'_z &= b'e^{int}, \\ \mathfrak{H}'_x &= 0, \mathfrak{H}'_y = -b'e^{int}, & \mathfrak{H}'_z &= a'e^{int}, \end{aligned}$$

and we have at the point P , since in it the normal to the spherical surface is parallel to the axis of x ,

$$[\mathfrak{E} \cdot \mathfrak{H}']_n - [\mathfrak{E}' \cdot \mathfrak{H}]_n = (\mathfrak{E}_y \mathfrak{H}'_z - \mathfrak{E}_z \mathfrak{H}'_y) - (\mathfrak{E}'_y \mathfrak{H}_z - \mathfrak{E}'_z \mathfrak{H}_y) = 0.$$

These considerations show that in many cases the equation (25) reduces to

$$\int \{(\mathfrak{E}'_e \cdot \mathfrak{E}) - (\mathfrak{H}'_e \cdot \mathfrak{H})\} dS = \int \{(\mathfrak{E}_e \cdot \mathfrak{E}') - (\mathfrak{H}_e \cdot \mathfrak{H}')\} dS \quad . \quad (26)$$

§ 7. It is particularly interesting to examine the effects produced by an electromotive or a magnetomotive force which is confined to an infinitely small space S . Let P be any point of this region, \mathfrak{a} a real vector having everywhere the same direction h and the same magnitude $|\mathfrak{a}|$, and let us apply in all points of S an electromotive force $\mathfrak{a} e^{int}$. Then we shall say that there is an "electromotive

action" at the point P in the direction h . We may represent it by the symbol

$$a S e^{int}$$

and we may consider its intensity and its phase to be determined by the real part of $|a| S e^{int}$.

In a similar sense we can also conceive a "magnetomotive action" existing in some point of the system.

These definitions being agreed upon, equation (26) leads to the following remarkable conclusions.

a. Let there be, in the first of the two cases we have distinguished in the preceding paragraph, an electromotive action $a S e^{int}$ at the point P in the direction h , and in the second case an electromotive action $a' S' e^{int}$ at the point P' in the direction h' , there being in neither case a magnetomotive force. Then the integrals in (26) are to be extended to the infinitely small spaces S' and S and the result may be written in the form

$$(a' \cdot \mathfrak{C}_{P'}) S' = (a \cdot \mathfrak{C}'_P) S,$$

if we represent by $\mathfrak{C}_{P'}$ the current produced in P' in the first case and by \mathfrak{C}'_P the current existing in P in the second.

Hence, assuming the equality

$$|a| S = |a'| S',$$

we conclude that

$$\mathfrak{C}_{h'P'} = \mathfrak{C}'_{hP} \dots \dots \dots (27)$$

The full meaning of this appears, if we write the two quantities in the form

$$\mathfrak{C}_{h'P'} = \mu e^{i(nt+\nu)} \quad \text{and} \quad \mathfrak{C}'_{hP} = \mu' e^{i(nt+\nu')}.$$

Indeed, (27) requires that

$$\mu = \mu', \nu = \nu',$$

and we have the theorem:

If an electromotive action applied at a point P in the direction h produces in a point P' a current whose component in an arbitrarily chosen direction h' has the amplitude μ and the phase ν , an equal electromotive action taking place at the point P' in the direction h' will produce a current in P , whose component in the direction h has exactly the same amplitude μ and the same phase ν .

b. Without changing anything in the circumstances of the first case, we shall now assume, that in the second the vibrations are excited not by electromotive forces, but by a magnetomotive action $a' S' e^{int}$, at the point P' in the direction h' . We then find

$$-(a' \cdot \mathfrak{B}_{P'}) S' = (a \cdot \mathfrak{C}'_P) S,$$

and, if we put

$$|\alpha| S = |\alpha'| S',$$

$$- \mathfrak{H}_{KP'} = \mathfrak{E}'_{hP}, \dots \dots \dots (28)$$

a theorem similar to the former.

§ 8. The absorption of rays being measured by the amount of heat developed, the expression (24), in which \mathfrak{E} is the real current, will be often used in what follows. It may be replaced by

$$w = (\mathfrak{F} \cdot \mathfrak{E}),$$

if we write \mathfrak{F} for the vector (α) \mathfrak{E} , so that

$$\mathfrak{F}_x = \alpha_{11} \mathfrak{E}_x + \alpha_{12} \mathfrak{E}_y + \alpha_{13} \mathfrak{E}_z, \text{ etc. } \dots \dots \dots (29)$$

Now, by a well known theorem, the axes of coordinates may always be chosen in such a way that the coefficients $\alpha_{12}, \alpha_{23}, \alpha_{31}$ in these equations become zero. Denoting the remaining coefficients by $\alpha_1, \alpha_2, \alpha_3$, we have for the relation between \mathfrak{F} and \mathfrak{E}

$$\mathfrak{F}_x = \alpha_1 \mathfrak{E}_x, \quad \mathfrak{F}_y = \alpha_2 \mathfrak{E}_y, \quad \mathfrak{F}_z = \alpha_3 \mathfrak{E}_z,$$

and for the development of heat

$$w = \alpha_1 \mathfrak{E}_x^2 + \alpha_2 \mathfrak{E}_y^2 + \alpha_3 \mathfrak{E}_z^2. \dots \dots \dots (30)$$

The directions we must give to the axes in order to obtain these simplifications, may properly be called the *principal directions*; in general, they will not be the same for different frequencies. This is due to the fact that the coefficients in (29) depend on the value of n .

It is also to be noticed that by this choice of the axes of coordinates, the coefficients $\beta_{12}, \beta_{23}, \beta_{31}$, and p_{12}, p_{23}, p_{31} will not, in general, be made to become zero.

In the case of an isotropic body we may take as principal directions any three directions perpendicular to each other.

§ 9. Thus far we have only prepared ourselves for our main problem. In the next paragraphs we shall first consider the absorption by a very thin plate surrounded by aether on both sides, and receiving in the normal direction a beam of rays. Combining the result with the ratio between the emissivity and the coefficient of absorption of a body, we shall be able to determine the amount of energy, radiated by the plate in a normal direction, and our next object will be to calculate the intensity we must ascribe to electromotive forces acting in the plate (§ 1), in order to account for that radiation. This will lead us to a general hypothesis concerning the electromotive forces acting in the elements of volume of a ponderable body and we shall conclude by showing that, if these electromotive forces were applied, the condition required for the equilibrium of radiation would always be fulfilled.

§ 10. Let the plate be homogeneous, with its faces parallel to the first and the second principal direction. We shall take these for the axes of x and y , placing the origin O in the front surface of the plate, i. e. in the surface exposed to the rays, and drawing the axis of z toward the outside. As has already been said, the absorption will be calculated by means of the formula (30); it will therefore be determined by the components of \mathfrak{C} and by those of \mathfrak{E} , on which they depend. Now, our problem is greatly simplified, if we suppose the thickness Δ of the plate to be infinitely small and if, in calculating the absorption, we confine ourselves to quantities of the first order of magnitude with respect to Δ . The quantity w relating to unit volume, we may then neglect all infinitely small terms in \mathfrak{C} and \mathfrak{E} ; consequently, we need not attend to the changes of these vectors in the plate along a line perpendicular to its faces. Moreover, in virtue of the well known conditions of continuity, the values of \mathfrak{E}_x and \mathfrak{E}_y within the plate will be equal to those existing in the aether immediately before it; also, \mathfrak{E}_z will be 0, because it is so in the aether. For \mathfrak{E}_x and \mathfrak{E}_y we may even take the values, existing in the incident beam, the reason for this being that the values belonging to the reflected rays, (the vibrations reflected at the two sides being taken together) are proportional to the thickness, if the plate is infinitely thin.

It is seen by these considerations that in the case of a given incident motion, \mathfrak{E}_x , \mathfrak{E}_y , \mathfrak{E}_z are the only unknown quantities in the three equations connecting the components of \mathfrak{E} and \mathfrak{C} . We need not, however, work out the solution of these equations.

Finally, it must be kept in mind that, in the case of harmonic vibrations, the mean value of w for a lapse of time comprising many periods is given by

$$w = \frac{1}{2} \{ \alpha_1 (\mathfrak{E}_x)^2 + \alpha_2 (\mathfrak{E}_y)^2 + \alpha_3 (\mathfrak{E}_z)^2 \}, \quad \dots \quad (31)$$

if (\mathfrak{E}_x) , (\mathfrak{E}_y) , (\mathfrak{E}_z) are the *amplitudes* of the components of the current.

§ 11. We shall in the first place assume that in the incident rays the electric force is parallel to the axis of x . Let its amplitude be a . Then, an element ω of the front surface will receive an amount of energy

$$\frac{1}{2} ca^2 \omega \quad \dots \quad (32)$$

per unit of time.

Within the plate, there will be electric currents in the directions of x and y . These will have amplitudes proportional to a , and for which we may therefore write:

$$(\xi_x) = f a \quad , \quad (\xi_y) = g a$$

denoting by f and g two factors, which it will be unnecessary to calculate. From (31) we deduce for the heat developed in the part $\omega \Delta$ of the plate,

$$\frac{1}{2} (\alpha_1 f^2 + \alpha_2 g^2) a^2 \omega \Delta$$

and, dividing this by (32), for the coefficient of absorption

$$A = \frac{1}{c} (\alpha_1 f^2 + \alpha_2 g^2) \Delta \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

Our next step must be to obtain a formula for the emission. For this purpose we fix our attention on a surface-element ω' parallel to the plate and situated at a large distance r from it, at a point of OZ . The electric vibrations issuing from the plate may be decomposed in the first place into vibrations of different frequencies and in the second place into components parallel to OX and OY .

After having effected this decomposition, we may attend to the amount of energy travelling across ω' per unit of time, in so far as it belongs to vibrations having the first of the two directions and to frequencies lying between the limits n and $n + dn$. Now, if the plate were removed, and if instead of it a perfectly black body of the same temperature were placed behind an opaque screen with an opening coinciding with the element ω , the radiation might be represented by

$$\frac{k \omega \omega' dn}{r^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)$$

an expression which may also be regarded as indicating the ratio between the emissivity of a body of any kind under the said circumstances and its coefficient of absorption. The experimental investigations of these last years have led to a knowledge of the coefficient k for a wide range of temperatures and frequencies.

By KIRCHHOFF'S law, the flow of energy across the element ω' , originated by the part

$$\omega \Delta = S$$

of the plate, in so far as it is due to vibrations of the said direction and frequency, is found by multiplying (34) by (33). Its amount is therefore

$$\frac{k S (\alpha_1 f^2 + \alpha_2 g^2) \omega' dn}{c r^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

and we have now to account for this radiation by means of suitable electromotive forces applied to the plate.

§ 12. We shall first put the question what must be the amplitude a_1 of an electromotive force acting in the direction of OX with the frequency n , if this force is to produce, on account of the electric vibrations parallel to OX , a flow of energy

$$\frac{k S a_1 f^2 \omega' dn}{c r^2} \dots \dots \dots (36)$$

across the element ω' at the point P . Since this flow may be represented by

$$\frac{1}{2} c b^2 \omega',$$

if b is the amplitude of \mathfrak{E}_x at the point P , we must have

$$b = \frac{f}{cr} \sqrt{2k S a_1 \bar{a}n}.$$

The amplitude of the current $\mathfrak{C}_x = \dot{\mathfrak{E}}_x$ must therefore be

$$\frac{nf}{cr} \sqrt{2k S a_1 dn} \dots \dots \dots (37)$$

At this stage of our reasoning we may avail ourselves of the theorem of § 7, *a*. Indeed, if the electromotive force \mathfrak{E}_{ex} in the part S of the plate must have the amplitude a_1 in order to call forth at the point P a current \mathfrak{C}_x whose amplitude has the value (37), a_1 will also be the amplitude we must give to an electromotive force \mathfrak{E}_{ex} , acting in an element of volume S of the aether near P , if we wish to bring about by its action a current with the amplitude (37) in the plate. This is the condition by which we shall determine the value of a_1 .

§ 13. The solution is readily obtained by means of the formulae (18) and (16). If, in an element of volume S of the aether, $\mathfrak{E}_{ex} = a_1 e^{int}$, $\mathfrak{E}_{ey} = 0$, $\mathfrak{E}_{ez} = 0$, we shall have

$$\mathfrak{A}_x = \frac{a_1 S}{4 \pi r} e^{in\left(t - \frac{r}{c}\right)}, \mathfrak{A}_y = 0, \mathfrak{A}_z = 0, \mathfrak{Q} = 0$$

and

$$\mathfrak{E}_x = \frac{\partial^2 \mathfrak{A}_x}{\partial x^2} + \frac{n^2}{c^2} \mathfrak{A}_x,$$

as may be easily seen, if the equations

$$p = \frac{1}{in}, \quad q = 1, \quad \dot{\mathfrak{A}}_x = in \mathfrak{A}_x$$

are taken into account.

In the differential coefficients of \mathfrak{A}_x we may omit all terms containing the square and higher powers of $\frac{1}{r}$. Hence, in a point of the

axis of z , which passes through the point P , $\frac{\partial^2 \mathfrak{A}_x}{\partial x^2} = 0$.

In this way, the electric force in the aether immediately before the plate is found to be

$$\mathfrak{E}_x = \frac{a_1 n^2 S}{4 \pi c^2 r} e^{in\left(t - \frac{r}{c}\right)}$$

Its amplitude is

$$\frac{a_1 n^2 S}{4 \pi c^2 r} \dots \dots \dots (38)$$

and that of the current \mathfrak{C}_x within the plate

$$\frac{a_1 n^2 S f}{4 \pi c^2 r}$$

This must be equal to the expression (37). The solution of our problem is therefore

$$a_1 = \frac{4 \pi c}{n} \sqrt{\frac{2 k a_1 dn}{S}} \dots \dots \dots (39)$$

In the preceding formulae S means the volume of the portion of the plate we have considered. Now, after having decomposed this portion into a large number of elements of volume \mathbf{s} , we may bring about just the same radiation by applying in each of these an electromotive force in the direction of OX with the amplitude

$$a_1 = \frac{4 \pi c}{n} \sqrt{\frac{2 k a_1 dn}{\mathbf{s}}}, \dots \dots \dots (40)$$

provided only we suppose the electromotive forces in all these elements \mathbf{s} to be independent of each other, so that their phases are distributed at random over the elements.

Indeed, from the fact that the force whose amplitude is (39), acting in the space S , gives rise to a radiation represented by (36), we may conclude that an electromotive force with the amplitude (40), when applied to the element \mathbf{s} , will produce a flow of energy

$$\frac{k \mathbf{s} a_1 f^2 \omega' dn}{c r^2}$$

across the element ω' . A similar expression holds for each element \mathbf{s} and, on account of the circumstance that the vibrations due to the separate elements have all possible phases, we may add to each other all these expressions. We are thus led back to the result contained in (36).

§ 14. Whatever be the nature of the processes in the interior of an element of volume, by which the radiation is caused, they can

undoubtedly be considered as determined by the state of the matter contained within the element; for this reason an electromotive force equivalent to those processes can only depend on quantities determined by that state; it cannot be altered by changing the state of the system outside the element considered, or the form and magnitude of the whole body. The formula (40), which indeed is determined by the state of things within the element \mathbf{s} , must therefore be applied to an element of volume of all ponderable matter. It will be clear also that we have to add the following formulae for the amplitudes of the electromotive forces in the directions of y and z ,

$$a_2 = \frac{4\pi c}{n} \sqrt{\frac{2k\alpha_2 dn}{\mathbf{s}}} , \quad a_3 = \frac{4\pi c}{n} \sqrt{\frac{2k\alpha_3 dn}{\mathbf{s}}} . . . \quad (41)$$

As to the phases of the three electromotive forces, we shall suppose them not only to change irregularly from one element to another, but also to be mutually independent in one and the same element, so that the phase-differences between the three forces have very different values in neighbouring infinitely small spaces. In virtue of this assumption the intensities of the radiation due to the different causes may be added to each other.

Till now we have only accounted for the flow of energy (36), a part of the total flow represented by (35). We shall show in the next paragraph that the remaining part

$$\frac{k S \alpha_2 g^2 \omega' dn}{c r^2} \quad (42)$$

is precisely the radiation brought about by the electromotive forces we have supposed to exist in the direction of OY , and that the forces acting in that of OZ cannot give rise to a radiation across the element ω' . After having proved these propositions, we may be sure that, as far as the electric vibrations parallel to OX are concerned, the plate has exactly the emissivity that is required by KIRCHHOFF'S law. Of course, the same will be true for the vibrations in the direction of OY .

§ 15. It may be immediately inferred from the theorem of § 7, *a* that the electromotive forces applied to the plate in the direction of OZ , i. e. perpendicularly to the surfaces, cannot contribute anything to the radiation we have considered. Indeed, we know already that an electromotive force \mathfrak{E}_{ex} existing in the aether at the point P can produce no current \mathfrak{E}_z in the plate; consequently, an electromotive force \mathfrak{E}_{ez} in the plate cannot cause a current \mathfrak{E}_x at the point P .

As to the effect produced by the electromotive force with the

amplitude a_2 acting in the direction of OY , this may be found by a reasoning similar to that we have used in §§ 12 and 13. Let us suppose for a moment an electromotive force of the same direction and intensity to exist in an element of volume \mathbf{s} of the aether near the point P . The amplitude of the electric force \mathfrak{E}_x in the aether immediately before the plate will then be (cfr. 38)

$$\frac{a_2 n^2 \mathbf{s}}{4\pi c^2 r},$$

and that of the current \mathfrak{E}_y in the plate

$$\frac{a_2 n^2 \mathbf{s} g}{4\pi c^2 r}.$$

It follows from this that, if the element \mathbf{s} in the plate is the seat of an electromotive force \mathfrak{E}_{ey} , with amplitude a_2 , the current $\mathfrak{E}_x = \dot{\mathfrak{E}}_x$ at the point P will have this same value. The amplitude of the electric force \mathfrak{E}_x will be

$$b' = \frac{a_2 n \mathbf{s} g}{4\pi c^2 r} = \frac{g}{cr} \sqrt{2k \mathbf{s} a_2} dn$$

and the corresponding radiation across the element ω'

$$\frac{1}{2} c b'^2 \omega' = \frac{k \mathbf{s} a_2 g^2 \omega' dn}{c r^2}.$$

This leads immediately to the expression (42).

§ 16. We are now in a position to form an idea of the state of radiation in a system of bodies of any kind. After having divided them into elements of volume \mathbf{s} , and after having determined the principal directions at every point, we conceive in each element the electromotive forces whose amplitudes are determined by (40) and (41), the phases of all these forces being wholly independent of each other. In representing to ourselves the state of things obtained in this way, we must keep in mind:

1st. that the principal directions and the coefficients a_1 , a_2 , a_3 will, in general, change from point to point and will depend on the frequency n .

2^{ndly}. that for each frequency n or rather for each interval dn of frequencies, we must assume electromotive forces of the intensity we have defined in what precedes, all these forces existing simultaneously.

We shall now show that, if the temperature is uniform throughout the system, the condition for the equilibrium of radiation will be fulfilled in virtue of our assumptions. Of course, it will suffice to prove this proposition for a single interval of frequencies dn .

Let \mathbf{s} and \mathbf{s}' be two elements of volume, arbitrarily chosen, h one of the principal directions of the first element, h' one of the principal directions of the other, a_h and $a_{h'}$ the coefficients relating to these directions.

In virtue of the electromotive force \mathfrak{E}_{eh} acting in \mathbf{s} in the direction h , there will be in \mathbf{s}' in the direction h' a current $\mathfrak{C}_{h'}$ with a certain amplitude ($\mathfrak{C}_{h'}$); by (31) the development of heat corresponding to this current will be per unit of time

$$\frac{1}{2} a_{h'} (\mathfrak{C}_{h'})^2 \mathbf{s}' \dots \dots \dots (43)$$

Similarly, we may write

$$\frac{1}{2} a_h (\mathfrak{C}'_h)^2 \mathbf{s} \dots \dots \dots (44)$$

for the heat developed in \mathbf{s} on account of the current \mathfrak{C}'_h produced in this element in the direction h by the electromotive force acting in \mathbf{s}' in the direction h' .

Since each of the three electromotive forces in \mathbf{s} calls forth a current in the element \mathbf{s}' in each of its principal directions, there will be in all nine expressions of the form (43). These must be added to each other, as may be seen by observing that the total development of heat, represented by (31), is the sum of three parts, each belonging to one of the components of the current and that the three electromotive forces in \mathbf{s} are mutually independent. The sum of the nine quantities will be the total amount of heat \mathbf{s}' receives from \mathbf{s} , and in the same way we must take together nine quantities of the form (44), if we wish to determine the amount of heat transferred from \mathbf{s}' to \mathbf{s} . We shall have proved the equality of the mutual radiations between the two elements, if we can show that for any two principal directions, the expressions (43) and (44) have the same value.

Let us call a_h and $a_{h'}$ the amplitudes of the electromotive forces originating the currents whose thermal effects have been represented by (43) and (44). Then, in accordance with (40) and (41),

$$a_h = \frac{4 \pi c}{n} \sqrt{\frac{2 k a_h dn}{\mathbf{s}}}, a_{h'} = \frac{4 \pi c}{n} \sqrt{\frac{2 k a_{h'} dn}{\mathbf{s}'}} \dots (45)$$

Now, by the general theorem of § 7, a the amplitudes ($\mathfrak{C}_{h'}$) and (\mathfrak{C}'_h) in (43) and (44) are proportional to $a_h \mathbf{s}$ and $a_{h'} \mathbf{s}'$. Taking into account the formula (45), we infer from this

$$(\mathfrak{C}_{h'})^2 : (\mathfrak{C}'_h)^2 = a_h^2 \mathbf{s}^2 : a_{h'}^2 \mathbf{s}'^2 = a_h \mathbf{s} : a_{h'} \mathbf{s}'$$

an equation, which leads directly to the equality of (43) and (44).

If the system of bodies is entirely shut off from its surroundings, the equality of the mutual radiation between any two elements implies that the state is stationary.

In order to show this, we fix our attention on one particular element \mathbf{s} , denoting all other elements by \mathbf{s}' . By what has been said, the sum w_1 of all quantities of heat which \mathbf{s} receives from the elements \mathbf{s}' will be equal to the sum w_2 of the quantities of heat it gives up to them. But, if the system is isolated from other bodies, each quantity of energy lost by \mathbf{s} will be found back in one of the elements \mathbf{s}' ; w_2 is therefore the total amount of energy radiating from \mathbf{s} and the equality $w_1 = w_2$ means that \mathbf{s} gains as much heat as it loses.

§ 17. We shall finally assume that the system contains a certain space which is occupied by an isotropic and homogeneous body L , perfectly transparent to the rays; we shall examine the electromagnetic state existing in this medium, if all bodies are kept at the same temperature. To this effect, we must begin by a discussion of the radiation that would take place, if the body L extended to infinity, and if it were subjected to an electromotive or magnetomotive action (§ 7) at a certain point O .

A perfectly transparent body is characterized by the absence of all thermal effects. This means that the coefficient α is zero, as appears by (30). We have therefore

$$p = -i\beta, \dots \dots \dots (46)$$

the coefficient q being real and positive, and the equation (17) becomes

$$v = c\sqrt{\beta q n}, \dots \dots \dots (47)$$

I shall take here the positive value.

Let us first apply to an element of volume S at the point O , which I shall take as origin of coordinates, an electromotive force $\mathfrak{E}_{ex} = \alpha e^{int}$, but no magnetomotive force. Then

$$\mathfrak{A}_x = \frac{\alpha S}{4\pi r} e^{i n \left(t - \frac{r}{v} \right)}, \mathfrak{A}_y = 0, \mathfrak{A}_z = 0, \mathfrak{Q} = 0.$$

What we want to know, is the amount of energy radiating from O , i. e. the flow of energy through a closed surface surrounding this point. In calculating this flow, the form and dimensions of the surface are indifferent; we shall therefore consider a sphere with O as centre and with an infinite radius r .

Then we may omit all terms in \mathfrak{E} and \mathfrak{H} containing the square and higher powers of $\frac{1}{r}$, and we find from (15) and (16), attending

to (46) and (47) and taking the real parts

$$\begin{aligned} \mathfrak{E}_x &= \frac{a S n^2}{4 \pi r v^2} \cdot \frac{r^2 - v^2}{r^2} \cos n \left(t - \frac{r}{v} \right), \\ \mathfrak{E}_y &= -\frac{a S n^2}{4 \pi r v^2} \cdot \frac{xy}{r^2} \cos n \left(t - \frac{r}{v} \right), \quad \mathfrak{E}_z = -\frac{a S n^2}{4 \pi r v^2} \cdot \frac{vz}{r^2} \cos n \left(t - \frac{r}{v} \right), \\ \mathfrak{H}_x &= 0, \quad \mathfrak{H}_y = \frac{a S n}{4 \pi r \beta c v r} z \cos n \left(t - \frac{r}{v} \right), \quad \mathfrak{H}_z = -\frac{a S n}{4 \pi r \beta c v r} y \cos n \left(t - \frac{r}{v} \right). \end{aligned}$$

The electric and magnetic force being known, the flow of energy through the sphere may be calculated by means of (23). Its value is

$$\frac{a^2 S^2 n^3}{12 \pi \beta v^3} \cdot \dots \dots \dots (48)$$

If we perform a similar calculation in the assumption of a magnetomotive force with amplitude a , acting in the space S , the result is

$$\frac{a^2 S^2 n^4}{12 \pi q v^3} \cdot \dots \dots \dots (49)$$

§ 18. Let P be a point of the body L mentioned at the beginning of the preceding paragraph, l an arbitrarily chosen direction and let us seek the amplitude (\mathfrak{E}_l) of the electric current, or rather the square of the amplitude, produced by the radiating bodies, confining ourselves to the interval of frequencies dn .

We shall divide the bodies into elements of volume \mathbf{s} and we shall denote, for one of these elements lying at the point Q , by h one of the principal directions, by α_h the coefficient relating to it, and by a_h (cfr. (45)) the amplitude of the electromotive force acting in that direction.

The amplitude (\mathfrak{E}_l) produced by this force at the point P is equal to the amplitude of the current \mathfrak{E}_h , existing in the element \mathbf{s} , if an electromotive force \mathfrak{E}_{el} , having the amplitude $\frac{a_h \mathbf{s}}{S}$ is applied to an element of volume S of the aether near P . In order to express myself more briefly, I shall understand by A the radiation that would be excited by an electromotive action at the point P in the direction l of such intensity that the product (\mathfrak{E}_{el}) S has the value 1. The amplitude (\mathfrak{E}_l) in P , of which we have just spoken, will be found if we multiply by $a_h \mathbf{s}$ the value which, in that state, (\mathfrak{E}_h) would have in the element \mathbf{s} . Hence

$$\begin{aligned} (\mathfrak{E}_{lP})^2 &= a_h^2 \mathbf{s}^2 (\mathfrak{E}_{hQ})^2 = \frac{32 \pi^2 c^2 k \alpha_h \mathbf{s} dn (\mathfrak{E}_{hQ})^2}{n^2} \\ &= \frac{64 \pi^2 c^2 k dn}{n^2} w_h^\Lambda, \quad (50) \end{aligned}$$

if we write w_h^A for the development of heat in the element \mathbf{s} , which, in the state A, is due to the current in the principal direction h .

Now, starting from the expression (50), we shall obtain the total value of $(\mathfrak{E}_{lP})^2$ by an addition, in which all elements \mathbf{s} , each with its three principal directions, must be taken into account. In a system, completely shut off from surrounding bodies, $\sum w_h^A$ will be the total amount of energy, emitted by P in the state A; we can therefore determine it by the formula (48), putting $a S = 1$. This leads to the result

$$(\mathfrak{E}_{lP})^2 = \frac{16 \pi k c^2 n dn}{3 \beta v^3}.$$

In the same way, using the theorem of § 7, b and the expression (49), I find

$$(\mathfrak{B}_{lP})^2 = \frac{16 \pi k c^2 n^2 dn}{3 q v^3}.$$

These results being independent of the place of the point P and the choice of the direction l , we come to the conclusion that the state of things is the same in all parts of the medium L and that both the electric and the magnetic vibrations take place with equal intensities in all directions. The amount of the electric and magnetic energy per unit of volume is now easily found. According to § 4 the first is

$$\frac{1}{4} n \beta [(\mathfrak{D}_x)^2 + (\mathfrak{D}_y)^2 + (\mathfrak{D}_z)^2],$$

for the value of which one finds

$$\frac{4 \pi k c^2 dn}{v^3},$$

by remembering that for every direction l ,

$$(\mathfrak{D}_l)^2 = \frac{1}{n^2} (\mathfrak{E}_l)^2.$$

The magnetic energy may likewise be determined. Referred to unit volume it has the value

$$\frac{1}{4} q [(\mathfrak{B}_x)^2 + (\mathfrak{B}_y)^2 + (\mathfrak{B}_z)^2],$$

and this is easily calculated, since for every direction l ,

$$(\mathfrak{B}_l)^2 = \frac{1}{n^2} (\mathfrak{B}_l)^2.$$

The result is that the two kinds of energy are distributed over the body l with equal densities. This has been known for a long

time, as has also been the rule implied in our formulae, that these densities are inversely proportional to the cube of the velocity of propagation v . It must further be noticed that, if the medium L is aether, the density of the energy of the radiation becomes

$$\frac{8 \pi k \cdot dn}{c}.$$

This agrees with the meaning we have originally attached to the coefficient k (§ 11).

§ 19. There is one point in the foregoing considerations that may at first sight seem strange, viz. that the intensity of the electromotive forces we have imagined should depend on the magnitude of the elements of volume \mathbf{s} . It must be kept in mind however, that these forces have no real existence, and that we do not pretend to have found something concerning the causes by which the phenomena are produced. That the magnitude of the electromotive forces must be taken inversely proportional to the square root of the volume of \mathbf{s} is simply a consequence of our assumption that the force has the same phase in all points of such an element. For a given amplitude of the electromotive force, the radiation would therefore be proportional to \mathbf{s}^2 , and we had to make such assumptions concerning that amplitude, that the radiation became proportional to \mathbf{s} itself.

In connection with these remarks it must be observed that we have no reasons for ascribing to the dimensions of the elements of volume some particular value. These dimensions are indifferent as long as we consider only the radiation at finite distances and the transfer of energy between neighbouring molecules lies outside the theory I have here developed.

Physiology. — *“On the ability of distinguishing intensities of tones”*.

By Prof. H. ZWAARDEMAKER. (Report of a research made by A. DEENIK.)

The “Unterschiedsschwelle” for impulsive sounds (dropping bullets and hammers) has been studied frequently and many-sidedly, but regarding the “Unterschiedsschwelle” for intensities of tone we have had at our disposal till now only some information communicated by M. WIEN in his thesis.

M. WIEN found the value of the “Unterschiedsschwelle” for the three tones, to which he limited his investigation to be as follows: for a average 22.5% (with 18.2 and 27 for extremes) for e' 17.6%.

(one determination) for a' average 14.4% (with 10.8 and 22.5 for extremes). It appeared desirable to perform such an investigation through the whole scale and to establish it in other regards also on larger foundations. At my request Mr. A. DEENIK has executed a very great number of observations of this kind, and I take the liberty to communicate his results here in short, and refer the reader to an ample description in a thesis on this subject by Mr. DEENIK which will soon be published.

Experiments with the tuning-fork.

A tuning-fork kept vibrating by electro-magnetism is started in a room at the side of the sound-free cabinet of the physiological laboratory and is kept vibrating at a fixed amplitude. This amplitude may be measured microscopically by means of the triangle of GRADENIGO. Normal to the axis of this tuning-fork a circle divided into grades is placed, to which two hearing-tubes are attached in such a way, that their radial prolongations cut the axis of the tuning-fork in the tuning-centre. These hearing-tubes can be moved along the whole circumference of the scale, and can be brought at pleasure into the interference-planes of KIESSLING, in the planes of maximum-sound or between.

The hearing-tubes are led into the interior of the sound-free cabinet by means of thick-walled caoutchouc tubes which were still further acoustically isolated. There by means of a T—tap alternately the one or the other of the tubes may be listened at or perfect acoustic rest can be obtained by bringing the tap into a closed position.

An assistant now displaces one of the hearing-tubes, while the other hearing-tube is fixed in the plane of maximum sound, every time through some grades at a time into the direction to the interference plane of KIESSLING till a distinct difference has been signalled by the investigator (descending method). After the position of the tube has been read this is pushed on and then brought back in the same way till the investigator observes that the existing difference in intensity becomes indistinct (ascending method). Again the position of the tube is read off and the average is taken.

The observations take place in the above mentioned way “unwisentlich” and at five succeeding times. From the ten figures obtained in this way the average is taken at last, which indicates in grades of the scale a lowest “Unterschiedsschwelle” for the concerned amplitude.

To be able to transpose these angle-values into absolute values,

in the sound free cabinet, which has been internally covered with trichopiese, the greatest distance at which sound is still perceptible is determined for the intensity of sound in the maximum plane and for that in the discovered "Unterschiedsschwelle" plane. If we accept that in case of absence of reverberations, as we may suppose here, the sound intensities decrease proportionate to the quadrates of the distances, the sound intensities stand mutually in the same proportion as the quadrates of those distances. If we call the distance at which the tone sound is perceptible in the plane of maximum sound r and that for the somewhat weaker sound r_u , then the quotient $\frac{r^2 - r_u^2}{r_u^2}$ represents evidently the "Unterschiedsschwelle", which in this case may be indicated as "untere Unterschiedsschwelle" because the stimulation distinguished from the chief is taken weaker than the chief stimulation.

TABLE I. Experiments with the tuning-fork.

Tone level.	Amplitude in microns	$\frac{\Delta r}{r}$	'Unterschiedsschwelle' (average).
c^1	640	0.29589	33.2 %
	800	0.34429	
	1040	0.35657	
c^2	20	0.22698	29.3 %
	40	0.26932	
	70	0.29825	
	100	0.30835	
	150	0.31003	
	200	0.31540	
	300	0.32006	
c^3	2	0.23435	19.5 %
	2	0.20243	
	2	0.14865	

Experiments with organ-pipes.

An accurately tuned, wide, covered, wooden organ-pipe is placed in a felt tent in a room at the side of the soundfree cabinet in such

a way that the sound may be listened to through a caoutchouc tube in the cabinet. This organ-pipe is permanently blown by air which was supplied by a pressump driven by water and afterwards dried with chloride of calcium. The supply of this air takes place along a long system of leaden tubes, which shows inside the cabinet a division into two parts and afterwards a reunion. To this two separate branches by micrometer screws removable diaphragm openings of AUBERT are attached, which may be widened or narrowed at pleasure. The reunion takes place in a T-tap, which may also be directed by the investigator, and down the current are placed the necessary measuring apparatus for determining the pressure and volume of the air passing to the organ-pipe. These measuring apparatus are placed within the reach of the investigator, so that he himself can do the reading off.

The investigator arranges in the first place the width of the two diaphragm-openings in such a way that the sound may be called equal in the two positions of the tap. Then he enlarges one of the diaphragmata (the other remains constant) till a distinct difference is perceived (ascending method). This he does five times. After this the difference between the two tone intensities, which were alternately listened to, was enlarged and the diaphragm position was ascertained by descending at which the difference became indistinct (descending method). This again was done five times. The same takes place conformally in narrowing the diaphragm-openings. So the first series leads to a "obere" the second to an "untere Unterschiedsschwelle". The determinations which were made for each tone with two chief intensities have evidently taken place "wissentlich" in this way. At last a pressure and volume determination of the supplied air is made for the found diaphragm widths. The first takes place by means of a watermanometer, which for increasing sensibility has been put sloping; the second with an aerodromometer¹⁾. The energy offered to the organ-pipe could be calculated with the usual formula $e = \text{air-volume} \times \text{pressure} \times 981$. This number, multiplied by a constant factor, different for each pipe, indicates the acoustic energy.

As in the expression of the "prozentische Unterschiedsschwelle" $\frac{\Delta R}{R}$ the constant factor occurs both in the numerator and the denominator, the constant factor of the organ-pipe falls away from the further calculation and we can also come to a trustworthy result of the "prozentische Unterschiedsschwelle" without its preceding

¹⁾ Arch. f. (Anat. u.) Physiologie 1902 supplement. p. 417.

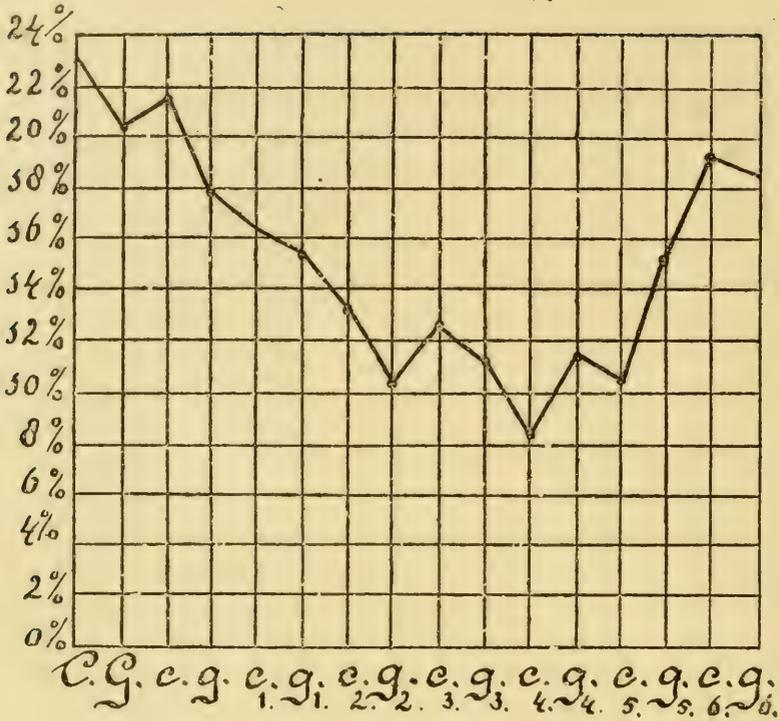
determination. The final result for each tone is in this way the average from 40 determinations.

T A B L E II.

Tone level	Relative intensity of the chief stimulation ¹⁾	Unterschiedsschwelle.			
		$\frac{\Delta r^o}{r}$	$\frac{\Delta r^u}{r^u}$	$\frac{\Delta r}{r}$	in %
<i>C</i>	1392.408	0.237	0.219	} 0.232	23.2
	1120.55	0.236	0.237		
<i>G</i>	1560.168	0.199	0.199	} 0.204	20.4
	1243.35	0.211	0.210		
<i>c</i>	1213.63	0.201	0.221	} 0.218	21.8
	861.798	0.224	0.227		
<i>g</i>	1412.200	0.183	0.179	} 0.179	17.9
	788.97	0.173	0.184		
<i>c</i> ₁	107.112	0.162	0.158	} 0.163	16.3
	86.129	0.166	0.168		
<i>g</i> ₁	132.411	0.142	0.152	} 0.154	15.4
	104.725	0.157	0.166		
<i>c</i> ₂	140.800	0.143	0.108	} 0.131	13.1
	114.444	0.137	0.134		
<i>g</i> ₂	139.96	0.098	0.112	} 0.105	10.5
	101.152	0.108	0.105		
<i>c</i> ₃	135.976	0.104	0.132	} 0.125	12.5
	101.764	0.126	0.138		
<i>g</i> ₃	134.552	0.114	0.108	} 0.112	11.2
	98.424	0.120	0.108		
<i>c</i> ₄	251.01	0.077	0.082	} 0.085	8.5
	139.438	0.081	0.101		
<i>g</i> ₄	332.072	0.117	0.122	} 0.117	11.7
	230.888	0.107	0.121		
<i>c</i> ₅	424.636	0.108	0.114	} 0.107	10.7
	280.908	0.100	0.107		
<i>g</i> ₅	295.68	0.160	0.155	} 0.154	15.4
	218.621	0.157	0.145		
<i>c</i> ₆	260.100	0.188	0.200	} 0.192	19.2
	183.272	0.204	0.178		
<i>g</i> ₆	580.190	0.164	0.191	} 0.188	18.8
	480.720	0.171	0.229		

¹⁾ For the calculation of the absolute intensity the number of the second column must still be multiplied by a constant factor which however falls away in the calculation of the "Unterschiedsschwelle" and is of no consequence.

Differences
of intensities.



Smallest perceptible difference of intensity by the scale.

CONCLUSION.

1. From the results of the experiments with the tuning-fork proceeds that the law of WEBER is valuable, when taken in a general way, but not exactly for the investigated middle-strong and weak intensities.

2. From the results of the organ-pipes proceeds that the most favourable "Unterschiedsschwelle" is found with c^4 and that from there to the ends the power of distinguishing differences in intensities decreases rather regularly.

E R R A T U M.

p. 380 line 7 for 0,990 1,03 read 1,02 1,04.

(November 22, 1905).

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM.

PROCEEDINGS OF THE MEETING
of Saturday November 25, 1905.

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Geology. — "*The geographical and geological signification of the Hondsrug, and the examination of the erratics in the Northern Diluvium of Holland.*" By Prof. EUG. DUBOIS. (Communicated by Prof. K. MARTIN).

(Communicated in the meeting of September 30, 1905).

To those who do not know the Hondsrug from a personal visit the name generally suggests an imposing hilly ridge, or perhaps even a small mountain range. Visiting it for the first time, one is disappointed in finding it to be no more than a nearly imper-

ceptible undulation of the ground, which only in some parts scarcely deserves the name of hill. Before one is aware of it, its "summit" has been reached, and it is probably only owing to the rather steep slope of the Drenthe plateau towards the valley of the Hunze and the extensive Bourtangher marsh, that this part of the country has received its peculiar name. Without these the "ridge" would possibly be passed unnoticed. However, the fact remains that there is a slight, irregular elevation of the ground, rising at the most but a few meters above the country on its western borderline, which, running from the South-East to the North-West, is almost entirely confined to the Province of Drenthe and has its Northern end a short distance beyond the town of Groningen.

From a geological point of view, the Hondsrug is interesting on account of the numerous erratics found there, several shiploads of which are yearly collected. This, however, is a peculiarity not limited to the Hondsrug: until recently similar boulders were also met with, in as large numbers, in other parts of Drenthe and Friesland, but in the more inhabited districts of these provinces they have, for the greater part, already been dug out. Another point which until lately lent a certain importance to the Hondsrug, was the generally accepted notion of it being a terminal moraine. This interpretation, first started by Prof. VAN CALKER, and especially based on his exploration of the northern termination of the Hondsrug, in the town of Groningen and in its vicinity, has successively been adopted. By a number of papers, dealing with the Hondsrug in Groningen, published during the last twenty years Prof. VAN CALKER has not a little contributed to give to this insignificant ridge a rather prominent geological importance. Almost from the outset of his investigations, VAN CALKER expressed his positive conviction that the Hondsrug is a terminal moraine. As early as 1889, he writes¹⁾: "Seit meinen ersten einschlägigen Untersuchungen stand meine Ansicht fest, dass der Hondsrug eine Endmoräne repräsentire, eine Moränenablagerung, welche einem längeren Stagniren im Rückzuge des Gletschers, vielleicht bei einer gleich gerichteten Bodenwelle entspricht. Und mein Vermuthen, dass diese eine weitere südöstliche Erstreckung habe, wurde bestätigt, als ungefähr 38 K.M. südöstlich von hier bei Buinen in Drenthe beim Aufgraben von Geschieben auch solche mit abgeschliffener und geschrammter Oberfläche zum Vorschein kamen und noch etwa 26 K.M. weiter südöstlich von dort, bei Nieuw-Amsterdam solche von mir selbst gesammelt wurden, und ich an letzterer Localität die Grundmoräne constatiren konnte."

¹⁾ Zeitschr. der Deutschen Geologischen Gesellschaft. 1889, p. 351.

But when we compare the descriptions of Prof. VAN CALKER with those of the terminal- and bottom moraines of other countries, it appears doubtful whether even that part of Groningen examined by VAN CALKER, notwithstanding its "tremendous accumulation of stones and large boulders", deserves the name of terminal moraine, and may not in fact rather be considered as a bottom-moraine¹⁾. It can only have been the shape and direction of the Hondsrug and the presence of the numerous erratics found *at its surface*, which induced Prof. VAN CALKER and others to regard this steep ridge of the Drenthe plateau as a terminal moraine. Of its internal structure, except for the portion which terminates in Groningen, no notice had been taken.

However in 1891, LORIÉ, after his exploration of the high peat-moss of Schoonoord, already expressed the opinion that those who had really visited and explored the Hondsrug were not justified in calling it a terminal moraine. He considers it to be the border of the Drenthe plateau, slightly folded back by the moving ice-sheet²⁾.

A few years ago I had several opportunities of visiting those parts and making the exploration alluded to by LORIÉ. To me it became quite evident that the Hondsrug in Drenthe is not a terminal moraine. Its geological structure, which I investigated more closely over the Southern half of its length in Drenthe and but partially over its Northern half, entirely refutes this interpretation. I found its nucleus not composed of morainic material, but to be of fluvial origin and to consist of Rhenish Diluvium³⁾. At the same time I also observed that this fluvial nucleus — although but slightly — was distinctly vaulted. The second problem therefore to be solved, was to find the cause of this vaulting, about which I could not agree with LORIÉ, who ascribes it to the motion of land-ice from the North-East. I could not admit the possibility of the ice-sheet folding the soil without perceptibly disturbing the nucleus of the fold, for the contortions do not enter deeply into this nucleus; its stratification has, in general, been well preserved. Basing my deductions on the phenomena observed in the ice-sheet of Greenland, to which the diluvial land-ice may be most aptly compared, I proposed several possibilities which might account for this peculiarity. I suggested the possibility of the ice having moved in the longitudinal direction

¹⁾ F. J. P. VAN CALKER, De ontwikkeling onzer kennis van den Groninger Hondsrug gedurende de laatste eeuw. Bijdragen tot de kennis van de provincie Groningen, etc. p. 217. Groningen. 1901.

²⁾ Handelingen van het Derde Nederl. Natuur- en Geneeskundig Congres, 1891. pp. 347 and 349.

³⁾ These Proceedings, V, p. 93—114.

over the Hondsrug, a certain elevation of the soil underneath it at the same time having taken place from some cause or other. I supposed, as one possibility, the mean pressure of the ice to have been somewhat lessened, or its progress to have been easier just above the present ridge. I imagined the change in the direction of the ice-stream to have been occasioned by the Northern ice-sheet being pushed back by the British ice-sheet in the German Ocean.

Recently, Dr. H. G. JONKER, one of Prof. VAN CALKER's youngest pupils, has refuted my views in these Proceedings¹). Though, from a few lines at the end of his paper, it appears that he agrees with me on the main point, — namely, that, as to its geological composition, the Hondsrug in Drenthe consists of a fluvial nucleus, covered with a glacial deposit, and that on this account it cannot possibly be considered a terminal moraine. But on the other hand, he advances numerous arguments to disprove the probability of a change in the direction of the ice-stream, and one of the ways in which I conceived the raising of that ridge could have been effected.

In the first place I wish to refute, as briefly as possible, the objections raised by Dr. JONKER to the explanation of the last-named point suggested by me.

As mentioned before, the results of my investigation principally related to the portion of the Hondsrug situated in the Southern part of Drenthe, about half of its entire length in that province. I myself mentioned several spots where the glacial covering does not consist of sand but of loam. This circumstance however is not inconsistent with the statement that the ridge, *in general*, is less rich in clay than its Western borderland. Neither does it exclude a freer movement of the ice-sheet over the Hondsrug, which I suggested as a probable agency in the formation of this ridge.

As far as I am able to judge from the few excavations I visited in the Northern portion of the Hondsrug, it seems to me that, in general, its structure does not differ from that of the Southern part.

Dr. JONKER further mentions a few spots in the North of Drenthe where the glacial cover of the Hondsrug consists of boulder-clay, viz. in the neighbourhood of Gasselte and Zuidlaren. Of the latter locality and also of some places near the town of Groningen, where much boulder-clay is found, Dr. JONKER himself says that the hilly character of the Hondsrug is less distinctly to be recognized, and that the Hondsrug is hardly noticed there. These spots therefore may be left out of account.

With regard to Dr. JONKER's reference to the borings of the Dutch

¹) Vol. VIII (1905), p. 96—104.

Society for the Reclaiming of Heaths, I make the following remark. Through the kindness of the Direction I was enabled to consult the original registers together with the maps, relating to the borings, and afterwards controlled these *in situ*. I ascertained, by many controlling borings, that the borings of the Society are lying too far apart to give an approximately exact idea of the presence and distribution of the loam; besides that it is decidedly incorrect to state that "red clay especially occurs on the Hondsrug and chiefly in its highest parts".

The other solution, which I suggested, in a second paper dealing with the Hondsrug, as a possible explanation for the origin of the longitudinal vaulting of the ridge (an explanation which is independent of the distribution of the boulder-clay and boulder-sand and which at the same time throws some light on the origin of the strange, round hill "Brammershoop"), which Dr. JONKER leaves unnoticed.

I believe to I have given already sufficient reasons for the opinion I hold, that, generally speaking, boulder-clay and boulder-sand have been, from the first, two distinct kinds of deposits, and that the latter has not proceeded from the former. I will only add, that to Dr. JONKER's statements "that the percentage of stones in the boulder-clay *increases very much* towards the surface", I can oppose the results of other and, I believe, more extensive statements, where either the reverse was the case, or the stones were uniformly distributed. This disparity is easily explained from the great local difference in that quantity, justly observed by Dr. JONKER.

The vanishing of limestone-boulders does not prove the washing-out of the loam, for it may have been occasioned by solution alone, without washing; calcareous pebbles, originally present in clay or sand, may disappear when the underground-water is not saturated with bicarbonate of lime, and they may be preserved when this is indeed the case. I willingly allow that the reason why, for instance, the clay of the Mirdum-Cliff is especially rich in absolutely unmodified calcareous stones (the finest scratchings have been preserved), and that on the contrary, in other parts, not a single calcareous pebble is found in similar clay, need not be attributed to local differences in the original composition of the ground-moraine. But this cannot be said with regard to the flints, and especially not in respect of the clay itself. Clay of the tough kind, called boulder-clay, is a very resistant substance. Experience in the field teaches that there can be no question of a wash-out of particles of clay from a similar mass. The motion of the water through the clay is far too slow for it. If Dr. JONKER had more frequent opportunities of studying boulder-clay and sand abroad, especially in England, he would, undoubtedly, have modified his

opinion on this head. I do not in the least question Dr. JONKER's assertion, that in some places he "can decidedly conclude from the relief whether we have to do with boulder-sand or with clay", because there is such a large difference in the resistance which boulder-clay and sand offer to erosion; but in most parts of Drenthe it is *impossible* to judge from the appearance of the surface, whether the ground underneath is sand or clay: this I learnt from consulting the mentioned register of borings and also from numerous small borings on my own account. The parts of the bottom-moraine from which, in the opinion of Dr. JONKER, the boulder-clay has "disappeared", and the "intermediate stages between original boulder-clay, and altogether washed-out boulder-clay", therefore undoubtedly, have been varieties existing from the beginning.

With regard to the occurrence of flint, which among our erratics has been rather disregarded, there really exists an important difference between boulder-clay and boulder-sand. This I learned especially too through the "comparative mechanical analysis", recommended by Dr. JONKER. Further I recollect that among the stones found in the sand on the Hondsrug, I did not come across a single flint; on the other hand I met with flint in all the clay-pits in the neighbourhood, and, taking also into account the small fragments, I found it even largely represented. The single exception which Dr. JONKER observed in a pit of loamy sand near Groningen, is no proof against this general experience. Besides, the bed was only loamy sand, not boulder-clay. He too found flint in several clay pits on the Hondsrug in Drenthe. In the fact, that on the whole (for it is necessary to compare places lying outside the Drenthe Hondsrug as well, because our Northern diluvium is generally considered as belonging to one and the same glacial epoch) there is, with regard to the presence of flint, an evident difference between boulder-clay and boulder-sand, I find another proof in favour of my opinion that, generally speaking, the one has not proceeded from the other by a wash-out. Neither the occasional absence of flints from boulder-clay nor the occasional presence of these stones in boulder-sand, are proofs against the general tendency of my argument.

In the preceding I have endeavoured to give a succinct refutation of the objections raised by Dr. JONKER against one of the solutions I proposed to account for the vaulting of the Hondsrug, — a question which is only of secondary importance.

But I gladly avail myself of the opportunity to discuss a point of far greater importance, on which Dr. JONKER has expressed an

opinion, namely, the direction of motion of that part of the ice-sheet which reached our country.

From an examination of sedimentary-rock erratics from the Groningen part of the Hondsrug, the results of which he stated in his dissertation, which appeared last year, Dr. JONKER came to the same conclusion as SCHROEDER VAN DER KOLK had arrived at from the examination of igneous-rock erratics, especially from the Eastern parts of the country, and as others too, namely "that the glacial flow which has produced the glacial diluvium in the North of the Netherlands was a *Baltic* one." He even thinks it possible to trace exactly the course taken by the glacial flow which "has created the Groningen-diluvium". To these statements I have to make serious objections.

For long years, neglecting the available direct means of tracing the direction of the glacial flow, such as the examination *in situ* of the *Quetschsteine* — a study already recommended fourteen years ago by our ever-lamented SCHROEDER VAN DER KOLK — it has been a custom in the Netherlands to be guided, in the determination of the direction of the glacial flow, exclusively by the solid rocks from which the stones carried towards us by the ice were derived. It was not taken into account, and indeed was not at all known in former time, that the great Ice Age, during which the Northern Diluvium of our country was deposited, was preceded by another glacial epoch, of lesser importance, it is true, for the Northern ice-sheet did not reach our country then, but which was notwithstanding the first real glacial epoch, by which the Pleistocene period was introduced. In that first glacial epoch, the *Scanian Epoch* of Prof. JAMES GEIKIE, there lived in the North Sea the arctic fauna of the Weybourn Crag, and, during the melting period of the Alpine ice, our country received the Rhenish Diluvium.

In that same epoch, in Scandinavia and in the uplands to the East of the Baltic, on the plateau called Fennoscandia, an ice-sheet was formed which, following the slope of the land, terminated in the North Sea as drift ice, and, on the other side, descended into the basin of the Baltic, as the first Baltic glacier. It is well known that the sculpture of the Scandinavian peninsula and of Finland has been accomplished almost entirely during the Tertiary period, at a time of a much higher level of those countries. The ice, which afterwards repeatedly passed over these parts, removed principally only the loose material, smoothing the surface. Thus the *first* ice-sheet found all the superficial deposits, accumulated on the rocky land-surface in the preceding long period of erosion, both on that highland and in the basin of the Baltic with its other environments.

Doubtless, already in the first glacial period, a transport of stones, on a large scale and over considerable distances from the solid rocks, has taken place, to the North Sea and especially in the basin of the Baltic. The earliest Baltic glacier has been traced as far as Schleswig. When at the later, much more considerable accumulation of ice, the North Sea also was filled up with inland ice¹⁾, it may be reasonably inferred that the British portion of it has carried along with it the erratics which at that earlier glacial epoch dropped from the drift-ice to the bottom of the sea.

In this manner we account for the finding of erratics of Scandinavian origin on the coast of East-Anglia. They are however not so plentiful in those parts as Dr. JONKER supposes. Among thousands of stones of British origin, occasionally one Scandinavian stone is met with. I believe that indeed not a single geologist in England is of opinion that the Scandinavian inland ice ever reached the shores of Britain.

Undoubtedly the inland ice of that second or great glacial epoch, which brought to our country the Northern diluvium, largely swept up and transported the morainic débris deposited in the basin of the Baltic, especially in its Western parts, during the preceding glacial epoch. A large percentage, perhaps even the majority, of the erratics thus again taken up and carried much further by the ice, must originally have come from a direction entirely different from that which would answer to the glacial flow, by which they were then carried along. Consequently, the presence of numerous stones of Baltic origin in the bottom-moraine at the town of Groningen and in its neighbourhood, is no reason why we should assume that the course of the glacial flow has been from the Northern and Eastern parts of the Baltic towards Groningen.

The abundance of flints in our Northern diluvium and the direction of the glacial striae in the southern parts of Sweden, indicated on the well-known map of NATHORST, rather suggest a more westerly origin. Moreover it appears questionable if on more extensive study of our erratics — those found in the bottom-moraine of Texel and Wieringen have been almost entirely neglected — the Baltic character of those stones found in the Diluvium of the northern parts of our country can be maintained. Considering the great local differences existing in the composition of the ground-moraines the erratics of such a small spot as the Hondsrug in Groningen, prove but little.

I may here be allowed to mention a few other facts distinctly

¹⁾ There are good reasons for not admitting here pack-ice, as does the well-known American geologist SALISBURY.

supporting the conception that the coalescence in the North Sea of the Northern ice-stream with another coming from Britain, may have caused a deflection in its course over the northern parts of our country, and changed its direction into one from North-West to South-East. Owing to this meeting of Scandinavian and British glacial flows, an enormous ice mass filled up the North Sea, in connection with the ice-sheet extending over Holland, North Germany and the British islands, the edge of which, as a high wall, faced the South. According to KLOCKMANN, WAHNSCHAFFE, RUTOT and others, between this wall of ice and the mountains of Middle Germany, Belgium, France and the southern parts of England, the melting water rose several hundreds of meters high, and in this water the deposition of the löss took place. With regard to our country, I entirely agree with this view. The structure of the löss in the South of Limbourg decidedly shows, in several places, its origin as a sediment deposited by very slowly running water containing a large amount of drift-ice, an opinion formerly advocated by Dr. A. ERENS. In several localities of the Limbourg chalk-plateau (in the adjacent parts of Belgium even as high as 300 M. above sea-level) erratics of Southern origin are found in or were excavated from the löss, especially veined quartzites from the Ardennes, sometimes measuring 2 M. and even more.

If thus we have to admit such an extensive and powerful ice-sheet with considerable accumulation in the North Sea, — and at the same time infer from the direction of the glacial striae on the rocky subsoil in North Germany, that one and the same glacial flow, owing to local conditions, has taken at the same or contingent points very different directions, deflecting even more than 90° , — I do not consider it impossible that in its course over the Hondsrug, and in general over the northern parts of our country, the direction of the glacial flow may have deviated entirely from that of the flow passing over the North of Germany.

Taking into consideration the still very limited knowledge we possess of our erratics, and in view of the arguments in favour of a secondary transport of perhaps the greater part of these stones, I consider the suppositions which I advanced before, and which I have now somewhat more developed, as to a possible modification of the direction of motion of the Northern ice-sheet over our country, not only warranted but necessary as a working-hypothesis for further investigation. I doubt whether Dr. JONKER himself will now still adhere to his belief that, “in case this conception is the right one a great number of researches into our ““Scandinavian diluvium”” would become doubtful and it would be advisable at once to begin a revision”. That Diluvium

will in every case remain Scandinavian, or rather Northern. At the same time I would recommend a closer study of the Diluvium in Texel and Wieringen, in order to ascertain, whether it contains erratics, the origin of which may be traced to other parts than of those which are found in the eastern parts of our country.

What I consider to be very "doubtful" indeed, is the right to trace the direction which the Northern glacial flow is supposed to have taken, solely from the examination of erratics, found at such a large distance from the rocks of their origin. In reference to this matter, I would strongly recommend "revision" and would especially suggest a wider field of investigation than the Hondsrug in Groningen.

Mathematics. -- "HUYGENS' *sympathic clocks and related phenomena in connection with the principal and the compound oscillations presenting themselves when two pendulums are suspended to a mechanism with one degree of freedom.*" By Prof. D. J. KORTEWEG.

(Communicated in the meeting of October 28, 1905).

Introduction.

1. When in February 1665 CHRISTIAAN HUYGENS was obliged to keep his room for some days on account of a slight indisposition he remarked that two clocks made recently by him, and placed at a distance of one or two feet, had so exactly the same rate that every time when one pendulum moved farthest to the left the other deviated at that very moment farthest to the right¹⁾. Yet when the clocks were removed from each other one of them proved to gain daily five seconds upon the other.

At first HUYGENS ascribed this "sympathy" to the influence of the motion of the air called forth by their pendulums; but he soon discovered the real cause — the slight movability of the two chairs

¹⁾ „Ce qu'ayant fort admiré quelque temps"; he writes: „j'ay enfin trouvé „que cela arrivoit par une espèce de sympathie: en sorte que faisant battre les „pendules par des coups entremeslez; j'ay trouvé que dans une demieheure de „temps, elles se remettoient tousiours a la consonance, et la gardoient par apres „constamment, aussi longtemps que je les laissois aller. Je les ay ensuite éloignées „l'une de l'autre, en pendant l'une à un bout de la chambre et l'autre à quinze „pieds de là: et alors j'ay vu qu'en un jour il y avoit 5 secondes de difference „et que par consequent leur accord n'estoit venu auparavant, que de quelque „sympathie". *Journal des Sçavans du Lundy 16 Mars 1665. Oeuvres de CHRISTIAAN HUYGENS, Tome V. p. 244.*

over the backs of which rails had been placed with the clocks suspended to them ¹⁾).

¹⁾ „J'ay ainsi trouvé que la cause de la sympathie . . . ne provient pas du mouvement de l'air mais du petit branslement, du quel estant tout a fait insensible je ne m'estois par apperceu alors. Vous scaurez donc que nos 2 horologes, chacune attachée a un baston de 3 pouces en quarré, et long de 4 pieds estoient appuïées sur les 2 mesmes chaises, distantes de 3 pieds. Ce qu'estant, et les chaises estant capables du moindre mouvement, je demonstre que necessairement les pendules doivent arriver bientost à la consonance et ne s'en departir apres, et que les coups doivent aller en se rencontrant et non pas paralleles, comme l'experience desia l'avoit fait veoir. Estant venu a la dite consonance les chaises ne se meuvent plus mais empeschent seulement les horologes de s'écarter par ce qu'aussi tost qu'ils tachent a le faire ce petit mouvement les remet comme auparavant”. Letter to MORAY of March 6th 1665. *Oeuvres*, T. V. p. 256.

Compare *Journal des Sçavans du Lundy 23 Mars 1665*, *Oeuvres* T. V. p. 301, note (4), where HUYGENS withdraws his first explanation to replace it by the correct one and likewise his “*Horologium Oscillatorium*” where his experiments and his explanation are developed on one of the last pages of “*Pars prima*”.

A somewhat more detailed account of those observations is moreover found in one of his manuscripts, from which we derive the diagrams found here and the explanation HUYGENS deemed he could give of the phenomenon :

Fig. 1a

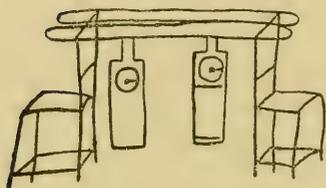
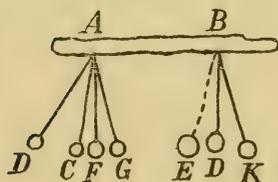


Fig. 1b



„Utrique horologio pro fulcro erant sedes duae, quarum exiguus ac plane invisibilis motus pendulorum agitatione exitatus sympathiae praedictae causa fuit, coegitque illa ut adversis ictibus semper consonarent. Unumquodque enim pendulum tunc cum per cathetum transit maxima vi fulera secum trahit, unde si pendulum B sit in BD catheto cum A tantum est in AC, moveatur autem B sinistram versus et A dextram versus, punctum suspensionis A sinistram versus impellitur, unde acceleratur vibratio penduli A. Et rursus B transiit ad BE quando A est in catheto AF, unde tunc dextrorsum impellitur suspensio B, ideoque retardatur vibratio penduli B. Rursus B pervenit ad cathetum BD quando A est in AG, unde dextrorsum trahitur suspensio A, ideoque acceleratur vibratio penduli A. Rursus B est in BK, quando A rediit ad cathetum AF, unde sinistrorsum trahitur suspensio B, ac proinde retardatur vibratio penduli B. Atque ita cum retardetur semper vibratio penduli B, acceleretur autem A, necesse est ut brevi adversis ictibus consonent, hoc est ut simul ferantur A dextrorsum et B sinistrorsum, et contra. Neque tunc ab ea consonantio recedere possunt quia continuo eadem de causa eodum rediguntur. Et tunc quidem absque ullo fere motu manere fulcro manifestum est, sed si turbari vel minimum incipiat concordia, tunc minimo motu fulcrum restituitur, qui quidem motus sensibus percipi nequit, ideoque errori causam dedisse mirandum non est”.

We give this explanation for what it is. HUYGENS, who never published it, will probably himself, at all events later on, not have been entirely satisfied by it.

2. Although HUYGENS' observations were published in the *Journal des Sçavans* of 1665, and are moreover mentioned in his "Horologium oscillatorium", they seem to have been forgotten when in 1739 correlated phenomena were discovered by JOHN ELLICOTT ¹⁾. What he observed at first was this: of two clocks N^o. 1 and N^o. 2 placed in such a way that their backs rested against the same rail ²⁾, one, always N^o. 2, took over the motion of the other, so that after a time N^o. 1 stopped even if at first N^o. 2 had been in rest and N^o. 1 exclusively was set in motion. Later on he found that the mutual influence was greatly increased by connecting the backs of the clocks by a piece of wood ³⁾. He also made *both* clocks go on indefinitely by giving their pendulums the greatest possible motion, when alternately they took over a part of the motion from each other, according to a period becoming longer as the clocks being placed without connection with each other had a more equal rate ⁴⁾. At the same time he observed that both clocks when connected with each other in the way described above assumed a perfectly equal rate lying between those which they had each separately.

3. Since then different mechanisms where suchlike phenomena

Indeed, it is nothing but the friction which can finally cause that of the three possible principal oscillations only *one* remains. Every explanation in which friction does not play a part must thus from the outset be regarded as insufficient.

1) *Phil. Trans.* Vol. 51, p. 126—128: "An Account of the Influence which two Pendulum Clocks were observed to have upon each other," p. 128—135: "Further Observations and Experiments concerning the two Clocks above mentioned."

2) "The two Clocks were in separate Cases, and . . . the Backs of them rested "against the same Rail."

3) "I put Wedges under the Bottoms of both the Cases, to prevent their bearing "against the Rail; and stuck a Piece of Wood between them, just tight enough "to support its own Weight."

4) "Finding them to act thus *mutually* and *alternately* upon each other, I set "them both a going a second time, and made the Pendulums describe as large "Arches as the Cases would permit. During this Experiment, as in the former, I "sometimes found the one, and at other times the contrary Pendulum to make the "largest Vibrations. But as they had so large a Quantity of Motion given them "at first, neither of them lost so much during the period it was acted upon by "the other as to have its Work stopped, but both continued going for several "Days without varying one Second from each other" . . . "Upon altering the Lengths "of the Pendulums, I found the Period in which their Motions increased and "decreased, by their mutual Action upon each other, was changed; and would be "prolonged as the Pendulums came nearer to an Equality, which from the Nature "of the Action it was reasonable to expect it would." Later on we shall see that there was probably an error in these observations. The continual transmissions of energy and the perfectly equal rate of the clocks exclude each other to my opinion.

of sympathy may appear have been investigated theoretically and experimentally; among others by EULER¹⁾ the case of two scales of a balance of which DANIEL BERNOULLI²⁾ had observed that they in turns took over each other's oscillations; by POISSON³⁾, by SAVART⁴⁾ and by RÉSAL⁵⁾ the case of two pendulums fastened with POISSON to the extremities of a horizontal elastic rod, or with SAVART and RÉSAL to the horizontal arms of a T-shaped elastic spring; by W. DUMAS⁶⁾ the case of a pendulum, beating seconds, with movable horizontal cross rails, on which other pendulums were hung; by LUCIEN DE LA RIVE⁷⁾ and EVERETT⁸⁾ the case of two pendulums joined by an elastic string; whilst finally CELLÉRIER, FURTWÄNGLER and others developed the theory of the motion of two pendulums of about equal length of pendulum, placed on a common elastic stand, in order to determine experimentally, and to take into account in this way the influence exercised by the small motions of such a stand on the period of the oscillations⁹⁾.

However, we see that the more recent investigations, with the exception of the work of W. DUMAS, who does not purposely mention the phenomena of sympathy, relate to mechanisms where elasticity plays a part; whilst it seems probable that this was not the case or at least in only a slight degree in the experiments of HUYGENS and ELLICOTT.

¹⁾ *Novi commentarii Ac. Sc. Imp. Petropolitanae*, T. 19, 1774, p. 325—339. ROUTH, *Dynamics of a system of rigid bodies, Advanced part, Chapt. II, Art. 94*, giving the right solution, has justly pointed out an error in EULER's solution and likewise in the one signed D. G. S. appearing in *The Cambridge math. Journ.* of May 1840, Vol. 2, p. 120—128. EULER's treatment of the phenomenon of the transmission of energy is also defective, as he does not lay stress upon the necessity of the two almost equal periods, in this case of his quadratic equation admitting a root nearly equal to the length of the mathematical pendulum by which he replaces the scales.

²⁾ *Nov. Comm.* l. c. preceding note, p. 281.

³⁾ *Connaissance des tems pour l'an 1833, Additions*, p. 3—40. Theoretical. This memoir was indicated to me after the publication of the Dutch version of this paper.

⁴⁾ *L'Institut*, 1^e Section, 7^e Année, 1839, p. 462—464. Experimental.

⁵⁾ *Compt. Rend.* T. 76, 1873, p. 75—76; *Ann. Éc. Norm.* (2), II, p. 455—460. Theoretical.

⁶⁾ "Ueber Schwingungen verbundener Pendel", *Festschrift zur dritten Säcularfeier des Berlinischen Gymnasiums zum grauen Kloster*. Berlin, WEIDMANN'sche Buchhandlung. 1874. The investigations themselves are according to this paper from the year 1867. Theoretical and experimental.

⁷⁾ *Compt. Rend.* T. 118, 1894, p. 401—404; 522—525; *Journ. de phys.* (3), III, p. 537—565. Experimental and theoretical.

⁸⁾ *Phil. Mag.* Vol. 46, 1898, p. 236—238. Theoretical.

⁹⁾ See for this the *Encyclopädie der mathematischen Wissenschaften*, Leipzig, Teubner, Band IV, I, II, Heft 1, § 7, p. 20—22.

So it seemed worth while looking at the question from another side, and studying the behaviour of a very generally chosen mechanism ¹⁾ with one degree of freedom, and with two compound pendulums attached to it; noting particularly the case that both pendulums have about equal periods of oscillation, whilst at the same time for the application of the phenomena of sympathy of clocks the influence of the motive works will have to be paid attention to.

Moreover it is worth noticing that the results obtained in this way will also be applicable to the case that the connection between the two pendulums is brought about by means of an elastic mechanism, every time when practically speaking only one of the infinite number of manners of motion is operating which such a mechanism can have. Such a manner of motion will have a definite time of oscillation for itself, which will play the same part in the results as if it belonged to a non-elastic mechanism with one degree of freedom.

Deduction of the equations of motion.

4. Let ζ represent for any point of the mechanism with one degree of freedom, to be named in future the "frame", the linear displacement out of the position of equilibrium common to frame and pendulums; let $\zeta^{(m)}$ be its maximum value for a definite oscillation to be regarded as equal on both sides for small oscillations; let ζ_1 and ζ_2 be its values for the suspension points O_1 and O_2 of the pendulums; let M be the mass of the frame; let m_1 and m_2 be that of the pendulums; a_1 and a_2 the radii of gyration of the pendulums about their suspension points; φ_1 and φ_2 their angles of deviation from the vertical position of equilibrium; x_1, y_1 and x_2, y_2 the horizontal and the vertical coordinates of O_1 and of O_2 , h the vertical coordinate of the centre of gravity of the frame; taking all these vertical coordinates opposite to the direction of gravitation.

So we begin by introducing for the frame a suitable general coordinate u , for which we choose the quantity determined by the relation

$$Mu^2 = \int \zeta^2 dm, \dots \dots \dots (1)$$

where the integration extends to all the moving parts of the frame; this quantity might therefore be called the mean displacement of the particles of the frame.

¹⁾ We assume with respect to this mechanism no other restriction than that the motions of each of its material parts just as those of the two pendulums take place in mutually parallel vertical planes, i.o.w. we restrict ourselves to a problem in two dimensions.

For small oscillations of the frame we can put: $u = nu^{(m)}$, $\zeta = n\zeta^{(m)}$, where n is a function of time, but the same for all the points of the frame.

So we have for such vibrations:

$$Mu^2 = M(\dot{nu}^{(m)})^2 = \int (\dot{n}\zeta^{(m)})^2 dm = \int \dot{\zeta}^2 dm ;$$

so that $\frac{1}{2}Mu^2$ proves to represent the vis viva of the frame.

For the vis viva of the first pendulum we find, if k_1 denotes the distance between its suspension point O_1 and its centre of gravity, and if φ_1 is reckoned (like φ_2) in such a way that a positive value of φ_1 increases the horizontal coordinate of the centre of gravity :

$$\begin{aligned} & \frac{1}{2} [m_1 \dot{\zeta}_1^2 + 2 m_1 k_1 \dot{x}_1 \dot{\varphi}_1 + m_1 a_1^2 \dot{\varphi}_1^2] = \\ & = \frac{1}{2} m_1 \left[\left(\frac{d\zeta_1}{du} \right)^2 \dot{u}^2 + 2 k_1 \dot{\varphi}_1 \frac{dx_1}{du} \dot{u} + a_1^2 \dot{\varphi}_1^2 \right] ; \end{aligned}$$

therefore for the entire vis viva of the whole system:

$$\begin{aligned} T = \frac{1}{2} \left[M + m_1 \left(\frac{d\zeta_1}{du} \right)^2 + m_2 \left(\frac{d\zeta_2}{du} \right)^2 \right] \dot{u}^2 + \frac{1}{2} m_1 a_1^2 \dot{\varphi}_1^2 + \frac{1}{2} m_2 a_2^2 \dot{\varphi}_2^2 + \\ + m_1 k_1 \frac{dx_1}{du} \dot{u} \dot{\varphi}_1 + m_2 k_2 \frac{dx_2}{du} \dot{u} \dot{\varphi}_2 ; \dots \dots \dots (2) \end{aligned}$$

and further for the potential energy¹⁾

$$V = \frac{1}{2} g \left[M \frac{d^2 h}{du^2} + m_1 \frac{d^2 y_1}{du^2} + m_2 \frac{d^2 y_2}{du^2} \right] u^2 + \frac{1}{2} m_1 g k_1 \varphi_1^2 + \frac{1}{2} m_2 g k_2 \varphi_2^2 . (3)$$

5. To simplify further we introduce the new variable u' determined by:

$$M' u'^2 = \left[M + m_1 \left(\frac{d\zeta_1}{du} \right)^2 + m_2 \left(\frac{d\zeta_2}{du} \right)^2 \right] u^2 = Mu^2 + m_1 \zeta_1^2 + m_2 \zeta_2^2 ; (4)$$

where

$$M' = M + m_1 + m_2 , \dots \dots \dots (5)$$

represents the entire mass of the whole system; this variable u' is proportional to u , because for small vibrations $\frac{d\zeta_1}{du}$ and $\frac{d\zeta_2}{du}$, as indeed all such derivatives appearing in the formulae, may be regarded as constant.

¹⁾ Indeed that potential energy amounts to $Mgh + m_1 g y_1 + m_2 g y_2 - m_1 g k_1 \cos \varphi_1 - m_2 g k_2 \cos \varphi_2 +$ a constant. By developing according to u , taking note that on account of the equilibrium $M \frac{dh}{du} + m_1 \frac{dy_1}{du} + m_2 \frac{dy_2}{du}$ is equal to 0 and by proper choice of constant, we can easily deduce (3) from it.

Out of this proportionality follows easily :

$$M' \dot{u}'^2 = \left[M + m_1 \left(\frac{d\mathfrak{S}_1}{du} \right)^2 + m_2 \left(\frac{d\mathfrak{S}_2}{du} \right)^2 \right] \dot{u}^2 = M\dot{u}^2 + m_1 \dot{\mathfrak{S}}_1^2 + m_2 \dot{\mathfrak{S}}_2^2 . \quad (6)$$

which proves that $\frac{1}{2} M' \dot{u}'^2$ represents the vis viva of what we shall call the *reduced system*, which system consists of the frame and of the masses of the pendulums each transferred to the corresponding suspension point O_1 or O_2 .

If now likewise we introduce the vertical coordinate h' of the centre of gravity of the reduced system, so that $M'h' = Mh + m_1 y_1 + m_2 y_2$, the first term of (3) transforms itself into $\frac{1}{2} g M' \frac{d^2 h'}{du'^2} u'^2$, for which, however, on account of the mutual proportionality of u and u' we may write : $\frac{1}{2} g M' \frac{d^2 h'}{du'^2} u'^2$.

So for the reduced system it holds that $T' = \frac{1}{2} M' \dot{u}'^2$ and $V' = \frac{1}{2} g M' \frac{d^2 h'}{du'^2} u'^2$; if now we write for this system the equations of motion, and if we then introduce the length l' of the simple pendulum which is synchronic to this system¹⁾ we shall easily find :

$$\frac{d^2 h'}{du'^2} = (l')^{-1} \quad (7)$$

Thus we finally may write for (2) and (3) :

$$T' = \frac{1}{2} M' \dot{u}'^2 + \frac{1}{2} m_1 a_1^2 \dot{\varphi}_1^2 + \frac{1}{2} m_2 a_2^2 \dot{\varphi}_2^2 + m_1 k_1 \frac{dx_1}{du'} \dot{u}' \dot{\varphi}_1 + m_2 k_2 \frac{dx_2}{du'} \dot{u}' \dot{\varphi}_2 ; \quad (8)$$

$$V' = \frac{1}{2} g M' (l')^{-1} u'^2 + \frac{1}{2} m_1 g k_1 \varphi_1^2 + \frac{1}{2} m_2 g k_2 \varphi_2^2 . . . \quad (9)$$

Application of the equations of LAGRANGE and substitution of the expressions :

$$u' = u^{(m)} \sin \sqrt{\frac{g}{\lambda}} t ; \varphi_1 = \alpha_1 \sin \sqrt{\frac{g}{\lambda}} t ; \varphi_2 = \alpha_2 \sin \sqrt{\frac{g}{\lambda}} t . . \quad (10)$$

leads further easily to the equations

$$M' (l' - \lambda) u^{(m)} + m_1 k_1 l' \frac{dx_1}{du'} \alpha_1 + m_2 k_2 l' \frac{dx_2}{du'} \alpha_2 = 0 ; . . \quad (11)$$

$$\frac{d^2 \alpha_1}{du'} u^{(m)} + \left(\frac{a_1^2}{k_1} - \lambda \right) \alpha_1 = 0 ; . . \quad (12)$$

$$\frac{d^2 \alpha_2}{du'} u^{(m)} + \left(\frac{a_2^2}{k_2} - \lambda \right) \alpha_2 = 0 . . . \quad (13)$$

1) Should the reduced system be in indifferent equilibrium as was probably the case in ELLICOTT'S experiments l' is infinite; if it were in unstable equilibrium this would correspond to a negative value of l' . We shall again refer to these cases in the notes. In the text we shall always consider l' positive, hence the reduced system stable.

where α_1 and α_2 denote the maximum deviations of the pendulums and λ the length of the pendulum synchrone to one of the principal vibrations.

6. In order to put these equations still more simply, we first introduce the lengths of pendulum $l_1 = \frac{a_1^2}{k_1}$ and $l_2 = \frac{a_2^2}{k_2}$ of the two suspended pendulums, secondly the maximum deviations in horizontal direction of their suspension points:

$$\xi_1^{(m)} = \frac{dx_1}{du_1} u'^{(m)} \quad \text{and} \quad \xi_2^{(m)} = \frac{dx_2}{du_2} u'^{(m)} .$$

It is then easy to find the following system of equations equivalent to the equations (11), (12) and (13), namely:

$$F(\lambda) \equiv (l' - \lambda)(l_1 - \lambda)(l_2 - \lambda) - c_1^2 l' l_1 (l_2 - \lambda) - c_2^2 l' l_2 (l_1 - \lambda) = 0 ; \quad (14)$$

$$\alpha_1 = \frac{\xi_1^{(m)}}{\lambda - l_1} ; \quad \alpha_2 = \frac{\xi_2^{(m)}}{\lambda - l_2} ; \quad \quad (15)$$

where :

$$c_1^2 = \frac{m_1}{M'} \cdot \frac{k_1}{l_1} \cdot \frac{(\xi_1^{(m)})^2}{(u'^{(m)})^2} ; \quad c_2^2 = \frac{m_2}{M'} \cdot \frac{k_2}{l_2} \cdot \frac{(\xi_2^{(m)})^2}{(u'^{(m)})^2} . . \quad (16)$$

We must notice here that c_1 and c_2 are numerical coefficients, the first of which depends only on the first pendulum and its manner of suspension, the second on the second pendulum.

Taking note of the signification of u' and ξ_1 , and observing that for instance $\xi_1^{(m)} : u'^{(m)} = \xi_1 : u'$ on account of the supposed smallness of the vibrations, we can write for the above after some reducing:

$$c_1^2 = \frac{m_1 \xi_1^2}{m_1 \zeta_1^2 + m_2 \zeta_2^2 + \int \xi^2 dm} \cdot \frac{k_1}{l_1} , \quad c_2^2 = \frac{m_2 \xi_2^2}{m_1 \zeta_1^2 + m_2 \zeta_2^2 + \int \xi^2 dm} \cdot \frac{k_2}{l_2} \quad (17)$$

holding at any moment of the oscillation, where ξ denotes the horizontal, ζ the linear deviation out of the position of equilibrium of an arbitrary point of the frame, and where the indices relate to the suspension points O_1 and O_2 , whilst the integrations must be extended over the whole frame.

If we finally remark that the relation between every ξ and every ζ is the same as that of the fluxions, we can give the signification of c_1^2 and c_2^2 also in the following words:

c_1^2 is equal to the proportion, remaining constant during the motion, between on one side the vis viva of the horizontal motion of the suspension point O_1 in which the mass of the first pendulum is con-

centrated and on the other side the entire vis viva of the reduced system multiplied by the distance between suspension point and centre of gravity of the first pendulum and divided by its length of pendulum; and in the same way c_2^2 .

Discussion of the general case.

7. Passing to the discussion of equation (14) we notice that in the supposition $l_1 > l_2$ we have: $F(+\infty)$ neg.; $F(l_1)$ pos.; $F(l_2)$ neg.; $F(0) = l_1 l_2 (1 - c_1^2 - c_2^2)$, and therefore with reference to (17) where $k_1 : l_1$ and $k_2 : l_2 < 1$, $F(0)$ always positive.

So there are three principal oscillations. The slowest, which we shall call the *slow principal one* has a synchronic length of pendulum greater than the greatest length of pendulum of both suspended pendulums; of the *intermediate principal one* the length of pendulum lies between that of these two pendulums; of the *rapid principal one* it is shorter than the shorter of the two ¹⁾. Further we can note that when $l' > l_1 > l_2$ the length of pendulum of the slow principal one is greater than l' and that for $l_1 > l_2 > l'$ the rapid principal one has a smaller length of pendulum than l' .

The following graphic representation gives these results ²⁾ for the case $l' > l_1 > l_2$, practically the most important.

¹⁾ This is the case for l' positive and this proves that when the reduced system is stable, this must also be the case for the original system with the two suspended pendulums. If l' is infinite, thus the reduced system at first approximation in indifferent equilibrium, then the slow principal oscillation has vanished or rather has passed into an at first approximation uniform motion of the entire system, which would soon be extinguished by the friction. The two other principal ones remain and their lengths of pendulum are found out of the quadratic equation:

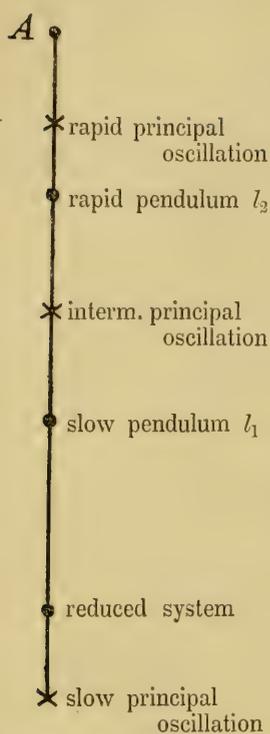
$$(l_1 - \lambda)(l_2 - \lambda) - c_1^2 l_1 (l_2 - \lambda) - c_2^2 l_2 (l_1 - \lambda) = 0.$$

For l' negative $F(0)$ becomes negative too, but $F(-\infty)$ positive, so then always one of the principal lengths of pendulum is negative. From this ensues that when the reduced system is unstable, this is also the case for the original one.

²⁾ Of course these results are in perfect harmony with and partly reducible from the well-known theorem according to which when removing one or more degrees of freedom by the introduction of new connections the new periods must lie between the former ones. To show this we can 1. fix the frame, 2. bring about two connections in such a way that the pendulums are compelled to make a translation in a vertical direction when the frame is moved. In the latter case it is easy to see that the time of oscillation of the reduced system must appear.

For the rest these same results are found back in the main, extended in a way easy to understand for more than two suspended pendulums, in the work of W. DUMAS, quoted in note 6, page 439 which I did not get until I had finished my investigations. By him also the length of pendulum of the reduced system is introduced. However, he has not taken so general as we have done the mechanism of one degree of freedom, on which the pendulums were suspended.

Fig. 2.



8. With respect to the manner of oscillating of the two suspended pendulums we shall call it the *antiparallel* mode when the simultaneous greatest deviations are on different sides as was the case in the observations of HUYGENS, in the reverse case we shall call it the *parallel* mode.

It is easy to see then from (15) that the following three possible combinations will always appear, namely: for one of the three principal oscillations the mode of oscillating of the pendulums is the antiparallel one, for the two other ones the parallel one, but in such a way that for a definite greatest deviation of the pendulums in a given sense the frame takes for each of these two other principal oscillations an opposite extreme position¹⁾.

If thus for instance $\xi_1^{(m)}$ and $\xi_2^{(m)}$ have equal signs as was certainly the case in the mechanism used by HUYGENS (see fig. 1a) and also in that of ELLICOTT, the antiparallel mode of oscillation observed by HUYGENS

belongs to the intermediate principal one.

9. For the application to the behaviour of two clocks connected in the manner described we first consider l_1 and l_2 as very different from each other, and that neither c_1 nor c_2 is small. In that case it is evident from the values of $F(l_1)$ and $F(l_2)$ differing greatly from naught that neither of the principal lengths of pendulum nearly corresponds to l_1 or l_2 ; however from (15) then ensues that the oscillations of the frame are of the same order as those of the pendulums at every possible mode of oscillating.

Now it is of course not at all impossible that the principal oscillations or certain combinations of them once set moving, might remain sustained by the action of one or of both motive works under favourable circumstances with sufficiently powerful works and when means have

¹⁾ DUMAS has: „dass, wenn . . . die Aufhängepunkte der Nebenpendel tiefer als die Drehungsaxe des Hauptpendels liegen, alle Nebenpendel von kürzerer als der zu erzielenden [principalen] Schwingungsdauer in gleichen Sinne mit dem Hauptpendel Schwingen müssen, alle anderen im entgegengesetzten Sinne“. This too follows immediately from the formulae (15) which, indeed, correspond essentially to those of DUMAS.

been taken to decrease sufficiently the frictions in the frame. However in such a case the behaviour of the two clocks would differ greatly from what was observed concerning the phenomena of sympathy; and in the more probable supposition that the motive works will prove to be unable to sustain a considerable motion of the frame, which motion would absorb a great part of the energy, each of the principal oscillations as well as each combination of them will after a certain time have to come to a stop.

So we shall leave this general case, and pass to the discussion of three special cases, which are more important for the consideration of the phenomena of sympathy, namely *A* the case that l_1 and l_2 differ rather much, but where c_1 and c_2 are small numbers, *B* the case, that l_1 and l_2 differ but little, but c_1 and c_2 are not small, *C* the case where l_1 and l_2 differ but little and c_1 and c_2 are both very small. In all these discussions we shall suppose $l' > l_1 > l_2$ and l' differing considerably from l_1 and l_2 . The treatment of other special cases, e.g. c_1 small but c_2 not, will not furnish any more difficulties if such a mechanism were to present itself¹⁾.

A. Discussion of the case that l_1 and l_2 differ rather much but where c_1 and c_2 are small²⁾.

In this case $F(l')$, $F(l_1)$ and $F(l_2)$ are all very small, from which is evident that each of the three roots of equation (14) is closely corresponding to one of these three quantities, so that the graphic representation of Fig. 2 looks as is indicated in Fig. 3.

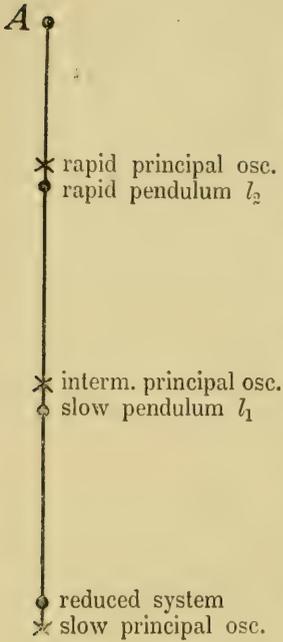
From this then ensues according to (15) that for the rapid principal oscillation the oscillations of the rapid pendulum are much wider than of the slow one³⁾, and that for the intermediate principal oscillation

¹⁾ Also the case $l' = \infty$ differs in nothing, as far as the results are concerned, from the cases treated here but by the vanishing of the slow principal oscillation.

²⁾ The smallness of each of these coefficients may according to (16) be due to three different causes, namely 1. to the smallness of $k_1 : l_1$ which will not easily appear in clocks, 2. to the fact that the masses of the pendulums are small with respect to that of the frame, 3. to the fact that the pendulums are suspended to points of the frame whose horizontal motion is a slight one compared to that of other points of that frame. It is remarkable that this difference of cause has hardly any influence on the considerations following here, and therefore on the phenomena which will present themselves.

³⁾ Then still when in (15) $\xi_2^{(m)}$ might prove to be very small compared to $\xi_1^{(m)}$; for as a first approximation for $l_2 - \lambda$ we find: $c_2^2 l' l_2 : (l' - l_2)$, and therefore $\kappa_2 = -M(l' - l_2)(l'^{(m)})^2 : m_2 k_2 l' \xi_2^{(m)}$. So the motion of the frame determined by $u^{(m)}$ is slight compared to that of the rapid pendulum and consequently κ_1 is small compared to κ_2 .

Fig. 3.



the opposite is the case. For the slow principal oscillation the oscillations of both pendulums are either of the same order as those of the frame or smaller still; the latter is the case when the third cause mentioned in note 2 of page 446 is at work.

Suppose now π' , π_1 and π_2 to be small oscillations belonging respectively to each of the three types of the principal oscillations, namely the slow one, the intermediate one and the rapid one, each having the same small quantity of total energy $\varepsilon = T + V$; then every compound oscillation can be represented by $\omega \equiv K'\pi' + K_1\pi_1 + K_2\pi_2$ and its total energy will be equal to $(K'^2 + K_1^2 + K_2^2)\varepsilon$.

Let us then start from an arbitrary compound oscillation for which K' , K_1 and K_2 have moderate and mutually comparable values; it is then clear that the motion of one clock, namely the one with the rapid pendulum will be dependent almost exclusively on the rapid principal oscillation, that of the other clock on the intermediate one. It is true, that slight periodical deviations in the amplitudes will present themselves, which are due to the two other principal oscillations, but these can have no influence of any importance on the periods according to which the motive works regulate their action; so that therefore one of the motive works will be able to contribute to the sustenance of the motion $K_1\pi_1$, the other to the motion $K_2\pi_2$, but neither of them to the sustenance of the motion $K'\pi'$. So this will vanish first.

What takes place furthermore will depend on the power of the motive works, and on the frictions presenting themselves during the motion of the frame. If those powers are great enough to conquer the frictions when the pendulums deviate sufficiently to keep the motive works in movement, a motion $K_1\pi_1 + K_2\pi_2$ will remain, where the values of K_1 and K_2 , thus also of their proportion, will finally depend exclusively on the power of those motive works and on the frictions. A theorem the proof of which we shall put off to § 14, to be able to give it at once for all cases, shows that in general such a motion can be sustained rather easily; it is the theorem that for principal oscillations whose λ differs but slightly from l_1 or l_2 whatever may be the cause, the kinetic energy of the motion of the frame

will be small compared to that of the corresponding pendulum. For such a motion $K_1 \alpha_1 + K_2 \alpha_2$ remaining in the end, the two clocks will each have their own rate¹⁾ whilst however slight periodic variations in their amplitudes are noticed, caused by the cooperation of the two remaining principal oscillations whose periods differ considerably if l_1 and l_2 are sufficiently unequal.

11. Let us now however suppose that l_1 and l_2 , differing at first considerably, are made to correspond more and more, for instance by displacement of the pendulum weights. The chief consequence will have to be that, according to equation (15), the amplitudes of both pendulums will become more and more comparable to each other, for $K_1 \alpha_1$ as well as for $K_2 \alpha_2$, in consequence of which to obtain their motion for the compound oscillation $K_1 \alpha_1 + K_2 \alpha_2$ we shall finally have to compose for each of them two oscillations with comparable amplitudes, and whose periods of oscillation differ but slightly. As is known this leads for both pendulums alternately, to periods of relatively greater and smaller activity, i. o. w. to the phenomenon of transference of energy of motion from one pendulum to another and back again; the period in which this alternation of activity takes place will be the longer according as l_1 and l_2 differ less²⁾.

Now however a suchlike behaviour of the two pendulums according as it gets more and more upon the foreground when l_1 and l_2 approach each other, becomes less and less compatible with the regular action of the two clockworks. For, during the period of smaller activity of one of the pendulums the motive work corresponding to it will finally, when the remaining activity has become much smaller than the normal, come to a stop. Then one of the two will take place: *either* the principal oscillation which is sustained particularly by this work is powerful enough to keep on till the period of greater activity has been entered upon, and this will be deferred the longer according as l_1 and l_2 differ less, *or* it is not so. In the first case the clock can keep going with alternate periods in which it ticks and in which it does not tick, which phenomenon may of course present

1) Both rates however a little more rapid than for independent position.

2) These phenomena remind us of what ELLICOTT observed later on (see note (4) p. 438). However the correspondence is not complete, as in the case treated here both clocks retain their different rate, whilst ELLICOTT mentions emphatically that the two clocks did not differ a second for many days. We shall therefore have to again refer to these observations at case C.

itself in both clocks¹). In the second case the clockwork stops entirely; the corresponding principal oscillation vanishes, and the pendulum performs only passively the slight motion which is its due in that principal oscillation, which can now be sustained indefinitely by the other motive work.

This is the phenomenon remarked by ELLICOTT in his first experiment when the clock n^o 2 regularly made n^o 1 stop.

We have now gradually reached case *C* where c_1 and c_2 are small and where l_1 and l_2 differ but slightly; this case demands, however, separate treatment, for which reason we shall discuss it later on.

B. *Discussion of the case that l_1 and l_2 differ but very little, but where c_1 and c_2 are not small²).*

Before passing to the case *C* we shall treat the simpler case now mentioned which will lead us to phenomena corresponding to those found by HUYGENS.

To this end we put $l_1 = l_2 + \Delta$, and substitute this in the cubic equation (14). Then by writing for one of the roots of that equation $l_2 + \sigma$ and by treating Δ and σ as small quantities we shall easily find for the length of pendulum of the intermediate principal oscillation the value

$$l_2 + \frac{c_2^2}{c_1^2 + c_2^2} \cdot \Delta, \quad (18)$$

from which is evident that this length of pendulum divides the distance between l_1 and l_2 in ratio of $c_1^2 : c_2^2$.

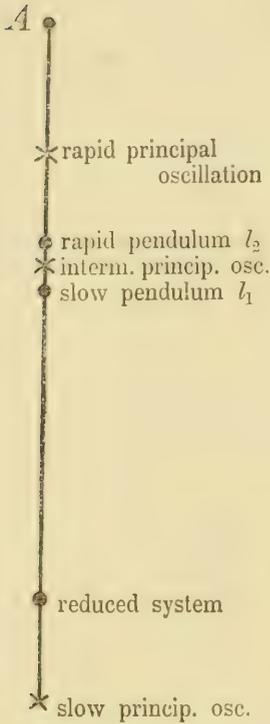
The two other roots satisfy approximately the quadratic equation:

$$(l' - \lambda)(l_2 - \lambda) - (c_1^2 + c_2^2) l' l_2 = 0 \quad (19)$$

¹) This was really observed by ELLICOTT (l. c. p. 132 and 133) for both clocks, however only temporarily, for at last the work of the first clock came entirely to a stop. Compare for the rest the experiment of DANIEL BERNOULLI with the two scales mentioned in § 3.

²) If l_1 is perfectly equal to $l_2 = l$, then of course (14) has a root $\lambda = l$ for whose principal oscillation according to (15) the frame remains in rest. The remaining roots are found by means of the quadratic equation $(l' - \lambda)(l - \lambda) - (c_1^2 + c_2^2) l' l = 0$. One of them will nearly correspond to l if c_1 and c_2 are both small fractions. All this in accordance with ROUTH's solution (l. c. note (1) page 439) which refers exclusively to this case and also to that of EULER (barring what is remarked in that note).

Fig. 4.



They correspond to the slow and the rapid principal oscillation differing considerably in general in length of pendulum from l' and l_2 ¹⁾ and therefore by reason of (15) giving rise to oscillations of the frame which are of the same order of magnitude as those of the pendulums.

So unless special measures are taken with respect to the decrease of the friction of the frame, these oscillations will have to stop, the more so as they are not sustained by the action of the motive works.

So the only oscillation which will be able to continue for some time is the intermediate principal one whose length of pendulum is lying between l_1 and l_2 ; entirely in accordance with the observations of HUYGENS²⁾ and also with those of ELLICOTT described in note (4) p. 438 when for the latter we overlook for a moment the observed periodic transference of energy.

C. *Discussion of the case that l_1 and l_2 differ but very little and that at the same time c_1 and c_2 are small numbers.*

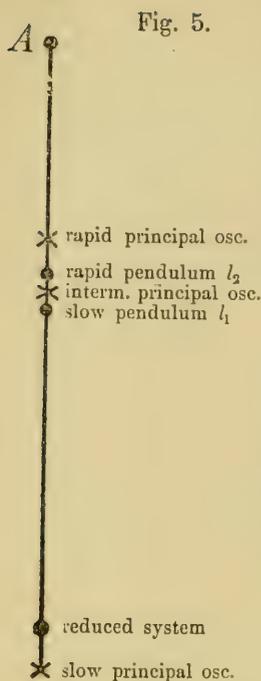
13. The remarkable thing in this case is that now the remaining quadratic equation (19) is also satisfied by a root differing but little from l_2 . So there are now *two* roots of the original cubic equation situated in the vicinity of l_2 , one found just now and expressed by (18) and the other which is likewise easily found by approximation and represented by the expression

$$l_2 - \frac{(c_1^2 + c_2^2) l' l_2}{l' - l_2} \dots \dots \dots (20)$$

This root is, at first approximation, independent of $\Delta = l_1 - l_2$; so when the lengths of the pendulums approach each other sufficiently, it is, though small, yet many times larger than Δ . These

1) See the graphic representation of Fig. 4.

2) See however note (3) p. 452; from which is evident that the case which really presented itself in HUYGENS' experiments is probably not the one discussed here, but the more complicated case C.



conditions are represented by Fig. 5, where we have moreover to notice that the third root belonging to the slow principal oscillation differs but little from l .

We can now show that for the rapid principal oscillation as well as for the intermediate one, *although not in the same measure*, the oscillations of the frame remain small compared with those of the pendulums.

Generally this is already directly evident from the equations (15); this is however not the case when the pendulums are suspended to points of the frame whose horizontal motion is an exceptionally slight one¹⁾. In that case we refer to the general theorem to be proved in the following paragraph, and from which what was assumed ensues immediately.

Let us note before continuing that now for the rapid as well as for the intermediate principal oscillation the two pendulums possess amplitudes which are mutually of the same order of magnitude.

14. The indicated theorem can be formulated as follows: *when the length of pendulum of a principal oscillation approaches closely to l_1 of l_2 then the vis viva of the reduced system, thus a fortiori of the frame alone, is continually small with respect to that of the pendulum corresponding to l_1 or l_2 .*

To prove this we compare in formula (8) the three terms: $\frac{1}{2} M' \dot{u}'^2$; $m_1 k_1 \frac{dx_1}{du'} \dot{u}' \dot{\varphi}_1$ and $\frac{1}{2} m_1 a_1^2 \dot{\varphi}_1^2$. For the proportion of the

second to the third can be written $2 \frac{dx_1}{du'} \dot{u}' : l_1 \dot{\varphi}_1$, or on account

of equation (10), $2 \frac{dx_1}{du'} u'^{(m)} : l_1 x_1 = 2 \check{s}_1^{(m)} : l_1 x_1 = 2 (\lambda - l_1) : l_1$. The

second is therefore, when λ approaches l_1 closely, small with respect to the third, which can thus be regarded in such a case to represent at first approximation the vis viva of the first pendulum.

¹⁾ That is to say, when the third cause mentioned in note (2) p. 446 has given rise to the smallness of c_1 and c_2 .

For the proportion of the vis viva of the reduced system to that of the pendulum referred to we can write ¹⁾:

$$\begin{aligned} M' \dot{u}'^2 : m_1 a_1^2 \dot{\varphi}_1^2 &= M' (u^{(m)})^2 : m_1 a_1^2 \alpha_1^2 = \\ &= M' (u^{(m)})^2 (l_1 - \lambda)^2 : m_1 a_1^2 (\xi_1^{(m)})^2 = (l_1 - \lambda)^2 : c_1^2 l_1^2. \quad (21) \end{aligned}$$

If now c_1 is not small, as in case B , then we have in this manner already proved what was put. In case A we substitute $\lambda = l_1 - \delta$ in the cubic equation (14) after which we find easily at first approximation, c_2 being likewise small ²⁾, $\delta = l_1 - \lambda = c_1^2 l_1 : (l' - l_1)$, by which what was put is likewise proved.

In case C finally, which occupies our attention at present, ensues from (20) for the rapid principal oscillation $l_2 - \lambda = (c_1^2 + c_2^2) l_2 : (l' - l_2)$; from which is evident after substitution of l_2 and c_2 for l_1 and c_1 in (21) the correctness of the theorem also for this principal oscillation, hence *a fortiori* for the intermediate one; unless c_1 be small but yet much larger than c_2 , which restriction does not exist for the intermediate principal oscillation.

15. From these results must be inferred that in the case C under consideration the rapid principal oscillation as well as the intermediate one when once set in motion will each be able to maintain themselves under the influence of the motive works, when the conditions of friction in the frame are not too unfavourable. However, the intermediate principal oscillation will have, if the difference in rate between the two clocks was originally very slight, a considerable advantage on the rapid one, the motion of the frame being much slighter still in the former case than in the latter. And this will probably be the reason that in the experiments of HUYGENS as well as in the later ones of ELLICOTT evidently the intermediate principal oscillation exclusively ³⁾ or at least chiefly ⁴⁾ presented itself.

¹⁾ According to (10), (15) and (16) taking at the same time note of the signification of l_1 , a_1 and k_1 .

²⁾ For c_1 small and c_2 not, the proof runs in the same way, although the expression for δ becomes a little less simple.

³⁾ With HUYGENS. In his experiments the masses of the pendulums were certainly slight with respect to those of the frame, so that without doubt c_1 and c_2 were small and the case C was present.

⁴⁾ With ELLICOTT, where at least at first according to the observed transferences of energy also the rapid principal oscillation must have been present. Although ELLICOTT used according to his statement very heavy pendulums, we have probably also the case C with him. If we do not assume this then it is more difficult still to make the perfectly equal rate of his clocks tally with the observed transferences of energy. The presence of two principal oscillations evident from these would have been continued indefinitely in case B , so the clocks would have retained an unequal rate.

SAVART on the contrary has effected with the aid of his T-shaped spring at whose ends almost equal pendulums were attached both principal oscillations ¹).

But besides these two principal oscillations which deviate in their periods of oscillation, and moreover by the circumstance that the pendulums will move in a parallel mode for one and in an antiparallel mode for another, there is still a third manner of motion which must be able to continue indefinitely.

16. To prove this let us again start from an arbitrary compound oscillation $\omega = K'\pi' + K_1\pi_1 + K_2\pi_2$; then unless the friction in the frame be extremely slight the oscillation $K'\pi'$ will soon disappear. When however in the remaining motion K_2 is much smaller than K_1 , it is clear that as the intermediate principal oscillation is then the chief one for the motion of the two pendulums, the motive works of *both* clocks will regulate themselves according to it, so that they will not be able to contribute to the sustenance of the principal oscillation $K_2\pi_2$ which will thus likewise have to die away, so that finally only a pure oscillation $K_1\pi_1$ will be left, for which both clocks will follow the rate of the intermediate principal oscillation.

If on the contrary after the disappearance of the slow principal oscillation K_1 is much smaller than K_2 , it will have to be the intermediate principal oscillation, which dies away, whilst the rate of the clocks will finally regulate itself entirely according to the rapid one.

But in the intermediate case, when the proportion of K_1 to K_2 lies within certain limits, also a manner of motion will be able to appear under favourable circumstances where both principal oscillations are sustained for indefinite time, whilst each of them will govern the behaviour of one of the two clocks; for from the equations (15) it is easy to deduce that in general the proportion between the amplitudes α_1 and α_2 is different for both principal oscillations ²). Then the values of K_1 and K_2 and so also their proportion will in the long run be entirely governed by the power of the motive works,

¹) *l.c.* note (4) page 439. SAVART had however $l' < l_1 = l_2$; therefore with him it is the *slow* principal oscillation which plays the part given here in the supposition $l' > l_1 > l_2$ to the rapid one.

²) By substitution of the value (18) for λ we find for the intermediate principal oscillation $\alpha_1 : \alpha_2 = c_1^{-2} \xi_1^{(m)} : c_2^{-2} \xi_2^{(m)}$; whilst the substitution of (20) furnishes for the rapid principal oscillation

$$\alpha_1 : \alpha_2 = \left[\Delta + \frac{(c_1^2 + c_2^2)l'l_2}{l' - l_2} \right]^{-1} \xi_1^{(m)} : \left[\frac{(c_1^2 + c_2^2)l'l_2}{l' - l_2} \right] \xi_2^{(m)} ;$$

so for very small values of Δ we have for this one $\alpha_1 : \alpha_2 = \xi_1^{(m)} : \xi_2^{(m)}$.

connected with the frictions presenting themselves, i. e. these values will be independent of the initial condition. At the same time the two clocks will show a different rate ¹⁾, of which clocks one therefore will have to sustain the rapid principal oscillation, the other the intermediate one. Periodic transference of energy will then take place.

Probably it will not be easy to realize this condition, characterizing itself particularly by the fact, that one of the clocks goes considerably faster than would be the case when placed independently ²⁾. The initial conditions will then have to be chosen in such a manner that from the very beginning one oscillation will predominate for one clock, the other for the other clock. And this will become all the more difficult as c_1 and c_2 become more and more equal, therefore according as the two clocks become more and more alike and are suspended in a more symmetric way. For, so much smaller will, according to what was mentioned in note (2) p. 453 be the difference in proportion of the amplitudes x_1 and x_2 at each of the oscillations. ³⁾

17. Finally we wish to point out how we must represent to our-

¹⁾ So this differs again from what ELLICOTT observed in his last experiments, so that these cannot be regarded as the realisation of this case, though they have the transferences of energy in common with it. However, between the fact of those transferences and the assurance that both clocks have entirely the same rate exists a contradiction, as we have already seen, which is not to be solved. Indeed, those transferences can be explained by interference only, so they require the cooperation of two oscillations of different periods; but these oscillations must both be sustained if the state is really to continue indefinitely, and then each of them by one of the motive works where the oscillation referred to will predominate the other one. See also the last note.

To me it seems most probable that with ELLICOTT the transferences of energy existed only at first indicating the *temporary* presence of the rapid principal oscillation. ELLICOTT's wording is not emphatically against this conviction.

²⁾ The difference from case *A* is of course only quantitative. In both cases the clocks go faster than when placed independently, but in case *C* the acceleration of the quickest clock becomes much greater than that of the less rapid one (see § 13). A gradual transition presents itself then, and the case of ELLICOTT was probably situated on that transition-line.

³⁾ The idea that perhaps each of the motive works might be able to take over one principal oscillation and the other in turns had to be set aside after a closer investigation. If we compose in the well-known graphical way two oscillations of unequal amplitudes and of periods of oscillation differing but little, it is evident that the motive work will go alternately somewhat quicker and somewhat slower than will correspond to the period of oscillation of the greatest amplitude, but this can never go so far that the rate of the smaller amplitude is taken over, not even for a short time.

selves the transition of case *A* into case *C*. In case *A* in which the rate of the clocks differs greatly, the manner of motion which is most difficult to realize in case *C*, namely the one, where the clocks have each their own rates, is the normal one. Yet the two other manners of motion also are possible, i. e. those where exclusively *one* of the principal oscillations appears; however in these cases, the pendulum of the least active of the two clocks will still perform a slight oscillation though not sufficient to set its motive work in motion.

If now starting from case *A* we reach case *C*, i. e. if the rate of the clocks is taken more and more equal, the state of motion with mutually different rate of the clocks becomes continually more difficult to realize, finally perhaps impossible; whilst for the two other possible manners of motion the pendulum of the second clock too keeps performing greater and greater deviations till these deviations are finally sufficient to set its motive work also in motion, so that both clocks go quite alike, either with the rate belonging to the rapid principal oscillation or, what is more easily realized, with that of the intermediate one.

Chemistry. — “*The different branches of the three-phase lines for solid, liquid, vapour in binary systems in which a compound occurs.*” By Prof. H. W. BAKHUIS ROOZEBOOM.

(Communicated in the Meeting of October 28, 1905)

A chemical compound, formed from two components, need not to be regarded as a third component, when this compound is somewhat dissociated, at least when it passes into the liquid or gaseous state. Instead of the triple point we then get a series of triple points, the three-phase line, indicating the co-related values of temperature and pressure at which the compound can exist in presence of liquid and vapour of varying compositions ¹⁾ This was advanced for the first time in 1885 by VAN DER WAALS. The equation for that line was deduced by him ²⁾ and shortly afterwards ³⁾ applied by me in a few instances where it was always admitted that the vapour tension of the liquid mixtures gradually diminished from the side of the most volatile (*A*) towards that of the least volatile component (*B*).

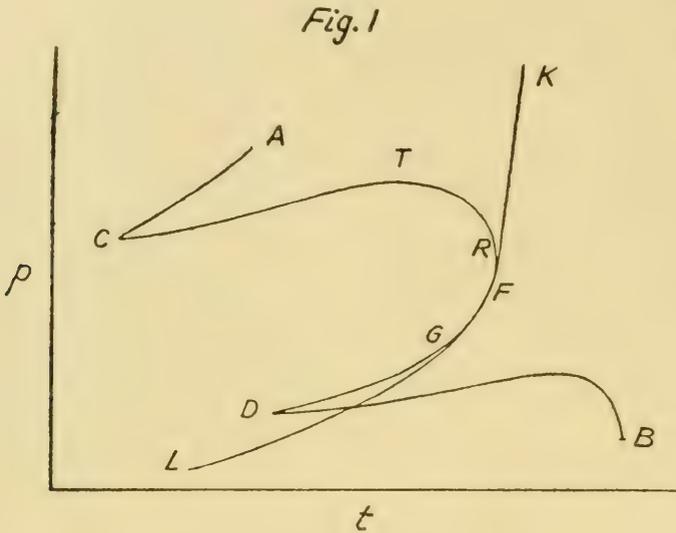
In the first considerations as to the course of the three-phase line

¹⁾ There exist several other three-phase lines which are not considered here.

²⁾ Verslag Kon. Akad. 28 Febr. 1885.

³⁾ Rec. Tr. Chim. 5, 334 (1886)

and the parts which could be realised in different binary systems, the line was generally divided by me into two branches according as the coexisting liquid contained more *A* or more *B* than the compound.



In figure 1 branch 1: *CTRF* represents liquids with more *A* and branch 2: *FD* liquids with more *B*.

At the commencement, special attention was called to the important fact that in the first branch a maximum pressure occurs at *T* where the heat of transformation of the three phases passes through zero. Less attention was paid to the fact that the maximum temperature *R* does not completely coincide with the point *F*, where the composition of the liquid becomes the same as that of the compound, but is situated either on branch 1, if the compound expands when melting, or on branch 2 if the reverse is the case; this may be best understood if one remembers that the melting point line of the compound *FK* meets the three-phase line in the point *F*. Although indicated in the first publication of VAN DER WAALS and in my more extended paper ¹⁾ this point remained in the background because, practically, the difference in temperature between *F* and *R* is very small. Afterwards ²⁾, VAN DER WAALS worked it out more carefully and only recently SMITS ³⁾ has fully considered the peculiarities of the *p, x*-figures between *F* and *R*, after these had become important

¹⁾ Rec. 5, 339, 340, 356, 1886.

²⁾ Verslag Kon. Akad. April 1897.

³⁾ These Proc. June 1905.

from the point of view of the hidden equilibria which continuously connect with each other the lines of the liquids and vapours coexisting with the solid phase.

In the systems which formerly came most to the front, the difference in volatility between the two components was so large — such as with water and salts — that on the whole three-phase line no vapour occurred which had the same composition as the compound.

If however, the difference in volatility is less pronounced, a case may occur where the equality in composition between vapour and compound is attained somewhere. VAN DER WAALS foresaw that possibility in 1885, but not until 1897 did he point out how such a point, occurring on the three-phase line below the point F , indicates the maximum temperature at which the compound may still evaporate in its entirety, and how in that point the subliming line of the compound meets the three-phase line. Such a point is indicated in fig. 1 by G , the subliming line by GL .

It was, however, thought very desirable to elucidate the manner in which, in such a case, the equilibria solid-vapour, solid-liquid and liquid-vapour join each other on the three-phase line by a representation in which is also shown the change of the concentrations of liquid and vapour along the three-phase line of the compound with increasing temperature.

Dr. SMITS ¹⁾ recently gave a representation of this by working out a connected series p, x -sections of a spacial figure, which in the case of a binary compound takes the place of my spacial figure, where only the components occur as solid phases.

A good example may be found in STORTENBEKER's ²⁾ research on the system chlorine + iodine. There it is found that both the compounds JCl and JCl_3 yield at their melting point a vapour containing more Cl , but at a lower temperature they have a point on their three-phase line where the vapour becomes the same as the compound. STORTENBEKER had noticed this fact during his research, but had not followed the matter up. After I had completed in 1896 my p, t, x -figure for binary mixtures, I also projected the spacial representation for this case, and I had then already come to the view, by graphical methods, that the point G is the highest temperature at which a compound can exist near vapour of equal composition.

BANCROFT ³⁾, in consequence of VAN DER WAALS' publication, tried to elucidate the case of JCl by a representation of partial pressures,

¹⁾ These Proc. June 1905.

²⁾ Rec. Trav. Chim. 7. 183. 1888.

³⁾ Journ. Phys. Chemistry 3. 72. 1899.

which appears to me less suitable, to survey the connection of the phase-equilibria. The representation now worked out by SMITS (see his communication fig. 4) is a p, x -projection of my own spacial figure with p, t, x as coordinates which, however, had not yet been published.

This representation is well suited to explain at once which are the transformations which take place on the different parts of the three-phase line, owing to change in pressure or temperature, and finally lead to the disappearance of one of the three phases.

Those transformations are dominated first of all by the connection of the compositions of the three-phases.

From the figure it will be seen at once that, if we indicate the solid compound by S , the coexisting liquid by L , and the vapour by G , the order of the compositions of the phases commencing with one richest in the volatile component A , is as follows :

on branch $CTRF$: GLS
 „ „ FG : GSL
 „ „ GD : SGL .

The only transformation which can take place between three phases is such that one is converted into two others, or reversely. That one must then necessarily be the middlemost in composition, consequently successively L, S, G .

The most rational division of the three-phase line is obtained when this takes place according to the transformation which occurs between the phases, and we will, therefore, call in future the branches on which L, S or G are the middle-bodies, the branches 1, 2, 3.

The transformation of 1 into 2, therefore, takes place in the point F where $S = L$, that of 2 into 3 in the point G where $S = G$.

If now we observe in what direction that transformation takes place, for instance on applying heat, we have

on branch 2 : $S \rightarrow G + L$
 „ „ 3 : $S + L \rightarrow G$

on the other hand on branch 1 we have :

on the part TRF : $S + G \rightarrow L$ branch Ia
 „ „ „ CT : $L \rightarrow S + G$ „ Ib

whilst in the point T itself, both transformations are without heat effect. The reversal of the direction of the transformation causes retrograde phenomena, on increasing or lowering the temperature.

A reversal of the direction of the transformation caused by a change in pressure also takes place on either side of the point F on branch 1, or on branch 2 if the compound melts with contraction,

and in this way retrograde phenomena by variation in pressure become possible.

On the branches 2 and 3 a reversal of the direction of the transformation caused by heat supply is as a rule not probable, as this always consists in the evaporation of the solid matter, coupled with melting of the same, or evaporation of the liquid, processes which generally want a supply of heat ¹⁾. The readiness of the reversal on branch 1 is, therefore, closely connected with the fact that the liquid phase is here the middle body.

If we consider in an analogous manner the character of the three-phase line on which the most volatile component *A* occurs as solid phase, the order of the phases is here *SGL*, therefore the line *AC* represents branch 3; in the point *A*, *G* and *L* become simultaneously equal to *S*; consequently, there exists no branch corresponding with branch 2 of the compound. On the three-phase line *DB* where the least volatile compound *B* is the solid phase, the order is *GLS*, therefore *DB* corresponds with branch 1.

In the previously studied binary compounds the volatility of the one component was so much smaller than that of the other, that on the three-phase line only the branches 1 and 2 were noticed; if the second constituent is sufficiently volatile branch 3 may be met ²⁾ with as in the case of *JCl* and *JCl₂*.

Such is the state of affairs in the case that the vapour tension of the liquid mixtures gradually decreases from 100 % *A* to 100 % *B*.

If now, however, a minimum or a maximum occurs in the vapour tensions the possibility may arise that, somewhere on the three-phase line of a compound, the liquid and vapour phases, which coexist with the solid phase, become equal in composition; and the question arises what significance this fact possesses for the division of the three-phase line.

In his communication cited Dr. SMITS has for the first time given the three-phase lines for both cases and also the *p*, *x*-projections of the appertaining spacial figure but has not further investigated the character of the different parts of the three-phase line.

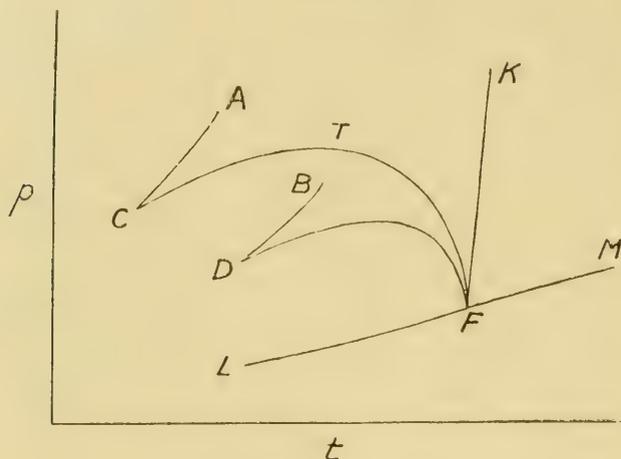
Let us first take the case that a minimum occurs in the *p*-*x*-lines for liquid-vapour. If the compound in liquid and gaseous state was

¹⁾ The special cases where reversal might take place will not be considered here.

²⁾ If branch 3 is wanting because on branch 2, *S* nowhere becomes equal to *G*, there is still a possibility that this occurs somewhere on the three-phase line which the compound with the least volatile component as solid phase and vapour gives below the point *D*. This we cannot further enter into.

not at all dissociated, that minimum would coincide with the composition of the compound.

Fig. 2



The three-phase lines would then appear about as shown in Fig. 2. Instead of one continuous line for the compound, there would be two branches sharply meeting in F , CF and DF , both exhibiting the character of branch 1, and therefore the order GLS of the three phases, and both becoming tangent in F , to the melting point line.

The sharp meeting in F is caused by the fact that there is no continuity between liquids or vapours containing an excess of A or of B , if the compound itself on its transformation into liquid or vapour, that is in F , remains totally undissociated and therefore contains no trace of A or B in the free state. In this case F is a triple point for the compound.

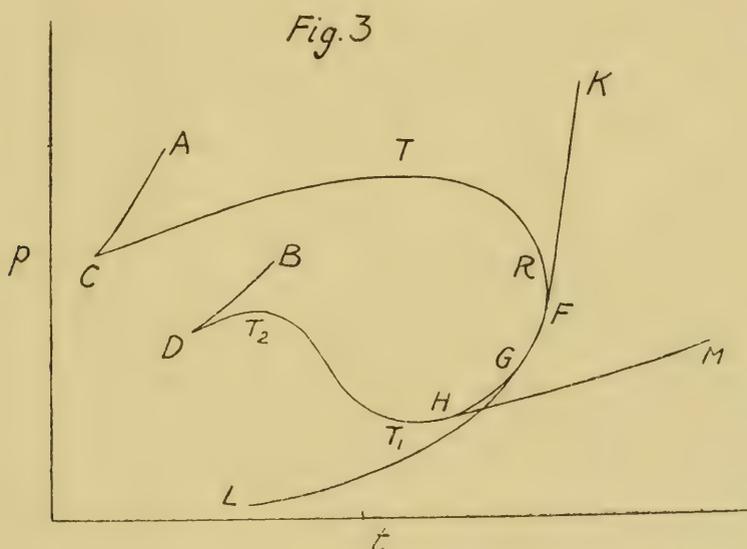
In case of the least trace of dissociation we, however, get continuity and the branches CF and DF unite to one three-phase line of the compound, which therefore assumes the general form deduced by SMITS, and is represented in fig. 3. The minimum in the vapour and liquid line now, however, shifts towards a composition differing from that of the compound, generally all the more as the volatility of A and B differs more and the dissociation is greater. Unless special influences¹⁾ decidedly modify the partial pressures of the components in the liquid phase, the minimum will generally be situated at the side of B . From the p, x -representation deduced for this case by SMITS, it will be easily seen that, proceeding along

¹⁾ Such as the existence of several compounds.

branch CF of the three-phase line and continuing over FD , the order in which two of the three phases become equal in composition is as follows:

- point F : $L = S$
 point G : $G = S$
 point H : $L = G$.

From this it follows firstly that, if somewhere on the three-phase line of the compound liquid and vapour become identical (point H), there is certainly also a point G where vapour and solid become equal, as G is situated between H and F .



Let us now consider the character of the different parts of the three-phase line. From C to H , the state of affairs is just the same as in Fig. 1. CF is, therefore, again branch 1 with the order GLS for the composition of the phases, FG branch 2 with the order GSL and GH branch 3 with the order SGL .

Whilst however in Fig. 1 the character of branch 3 continued up to D , a change occurs at H because $L = G$. It is easy to deduce from Dr. SMITS'S p, x -figure that the continuation HD of the three-phase line again exhibits the character of branch 1, the order of the phases is just as on CTF : GLS , with this difference that G is now the richest in the component B whilst on branch CTF the vapour was richest in A . Because in H the compositions of L and G become equal, a transformation in that point of the three-phase line

only occurs between those two and, therefore, the tangent HM to the three-phase line must be the line indicating the p, t values for the series of liquids and vapours having equal composition.

Just as in F occurs as tangent to the three phase line the melting point line FK , which is the extreme limitation of the equilibria between solid and liquid, and in G the subliming line GL , which is the extreme limitation for the equilibria solid and vapour, the tangent in H is the line HM , which is the boiling point line of the liquids with a constant boiling point, and also the extreme limitation for the equilibria liquid-vapour ¹⁾.

The points F G and H are, therefore, points of strictly related significance; they are the points where the order of the phases suddenly changes.

Let us now further consider branch HD . In fig. 3 occurs a point of maximum pressure T_2 and of minimum pressure T_1 . The first point is quite comparable with the maximum T in the branch CTF , the part DT_2 is again Ib on which, on heating, the transformation $L \rightarrow S + G$ takes place, the part $T_2 T_1$ is branch Ia , to which belongs the reverse transformation, whilst in T_2 itself the heat of transformation passes through zero.

Owing to the continuous connection of $DT_2 T_1$ to HG , we necessarily get a small rising part $T_1 H$ of branch 1, after the line has passed through a minimum T . The possibility of this minimum may be explained as follows:

Just beyond T_2 , the amount of heat necessary to convert $S + G$ into L can at first increase, because L and G both approach in composition to S , so that the quantity of G concerned in the said transformation diminishes with regard to S . But as we approach on the three-phase line the point H , L and G approach each other more than they approach S (for point H , where $L = G$, is reached sooner than G , where $S = G$); consequently the ratio of the phases G/S , which transform themselves in L , becomes again larger and the heat required for this again smaller until it finally becomes zero at T_1 and beyond this point negative, in other words the transformation again becomes $L \rightarrow S + G$; the small part $T_1 H$ again represents Ib and keeps on doing so up to the point H where the transformation in branch 3 takes place.

As the minimum T_1 does *not* coincide with the point H where $L = G$, a small modification must be made in the p, x -projection of

¹⁾ In the figure the lines HM and LG intersect. In the spacial figure this is however, a crossing.

the spacial figure given by Dr. SMITS in his fig. 5. His three-phase strip, which I will rather call two-phase strip because it is formed by the

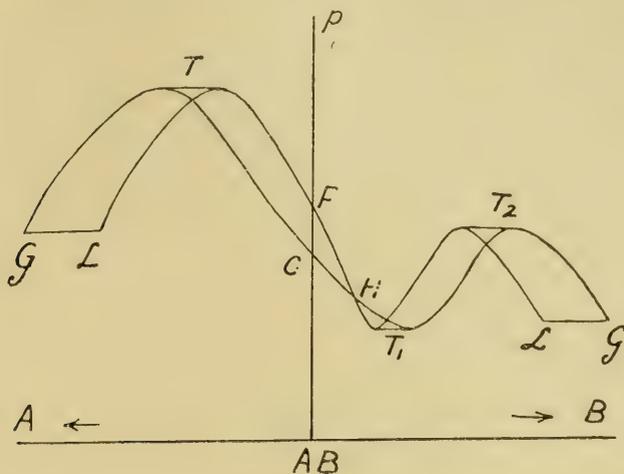


Fig. 4

lines indicating the liquid and vapour existing by the side of the compound, assumes the form of fig. 4, in which the particular points of the three-phase line fig. 3 with which this figure corresponds are indicated by the same letters. The line is extended so far that it also includes the maxima T and T_2 , and so shows in which respects it differs from the case corresponding with fig. 2, and of which the strips have been indicated by SMITS in his fig. 2.

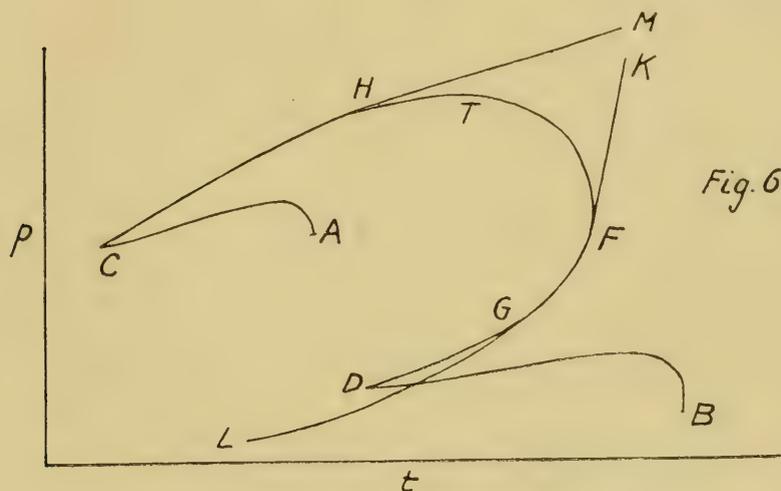
If the minimum in the liquid-gas surfaces should be very little pronounced, another type of the three-phase line may be expected, which is represented in fig. 5 in which both minimum and maximum have disappeared in branch HD , the whole line having the character of branch Ib .

In fig. 4 this would result that beyond the point H vapour and liquid lines keep on a downward course, which may be the case if the composition of L and G , which coexist with the compound, shifts but little with the temperature so that the increase in pressure which would occur owing to the shifting towards the side of B is more than compensated by the decrease in pressure caused by the fall in temperature.

Up to the present not a single example has been studied where a three-phase line of the type fig. 3 or 5 made its appearance. Still it is not difficult to see that both must frequently exist in the case of dissociable compounds with sufficient volatility of the two com-

of the fourth hydrate at the side of the solutions richer in HBr — in no case, therefore, on the ice line.

Let us further consider the case where liquid and vapour become equal at a maximum pressure. Here, this point will lie generally on the side of the most volatile component and as the compound becomes more dissociated and the difference in volatility of its components greater, the chances are that the composition of liquid and vapour at which they become equal, differs more from the compound.



From this originates a form of the three-phase line which is in general indicated by Fig. 6. The point H is now shifted to the top branch at the left side of the maximum T in branch 1. The part HC now exhibits the character of branch 3. The line HM , which indicates the maximum pressures of the series of liquids and vapours having an equal composition, is tangent in H to the three-phase line and forms the extreme limitation of the equilibria between liquid and vapour. The three-phase lines for solid A and solid B both exhibit the character of branch 1.

Owing to the non-coincidence of the points H and T a similar correction must be applied to the p, x -projection of the two-phase strip given by Dr. SMITHS as has been done by me in Fig. 5 in the case of the minimum.

The type fig. 6 will, presumably, not frequently occur, as a combination between two bodies is as a rule accompanied by a reduction in pressure and therefore, the occurrence of a maximum

pressure in the series of the liquid-vapour equilibria is but little probable. At the moment there only seems an indication that the case occurs with PH_4Cl .

If the line HM is situated much more towards the side of A it might then also happen that the point H did not occur on the three-phase line of the compound, but on that of the compound A , so that branch 3 on this line follows on branch 1 and disappears from the three-phase lines of the compound.

In a future communication I will discuss the boiling phenomena of the saturated solutions corresponding with the said branches of the three-phase lines.

Crystallography. — “On *Diphenylhydrazine, Hydrazobenzene and Benzylaniline, and on the miscibility of the last two with Azobenzene, Stilbene and Dibenzyl in the solid state.*”

By DR. F. M. JAEGER. (Communicated by Prof. BAKHUIS ROOZEBOOM).

(Communicated in the meeting of October 28, 1905).

The following research was undertaken to furnish a new contribution to the knowledge of the relation of the crystal-symmetry of organic compounds and their power of yielding crystallised mixed phases with each other¹⁾. Originally, it only aimed at the investigation of *Hydrazobenzene* and *Benzylaniline* in their connection with the series, investigated by BRUNI, GARELLI, CALZOLARI and GORNI, of *Azobenzene, Stilbene, Tolane, Dibenzyl* and *Benzylideneaniline*, but afterwards, *Diphenylhydrazine*, which is isomeric with *Hydrazobenzene* was also included.

Diphenylhydrazine.

$(\text{C}_6\text{H}_5)_2\text{N}-\text{NH}_2$; melting point: 44°C .

This compound, which I obtained through the kindness of Prof. S. HOOGEWERFF of Delft, crystallises from ligroine in the form of colourless, large, lustrous crystals, which exhibit a rather varying aspect. On exposure to light they rapidly assume a brown colour.

¹⁾ Compare F. M. JAEGER, These Proc. VII. p. 658.

Triclino-pinacoidal.

$$a : b : c = 0,7698 : 1 : 0,5986.$$

$$A = 89^{\circ}13\frac{1}{2}' \quad \alpha = 89^{\circ}24'$$

$$B = 137^{\circ}28' \quad \beta = 137^{\circ}28\frac{1}{2}'$$

$$C = 89^{\circ}29' \quad \gamma = 90^{\circ}4\frac{1}{2}'$$

The approach to *monoclinic* symmetry is very plain.

Forms observed: $b = \{010\}$, broad and lustrous; $m = \{110\}$, somewhat narrower and reflecting less sharply; $p = \{\bar{1}\bar{1}0\}$, very lustrous and broad; $c = \{001\}$, well developed and yielding fairly sharp reflexes; $o = \{\bar{1}\bar{1}1\}$, very lustrous and well developed. The crystals are mostly flattened towards p , or they may be developed isometrically with a slight elongation along the c -axis. It is peculiar that in the vertical zone the co-related parallel planes of the forms m , p and b are generally very unevenly developed. Perhaps we may have here a new example of the presence of an acentric crystal; the nature of the surface of the parallel planes is also often different on a plane and its corresponding contreplane. Etched figures could not be obtained.

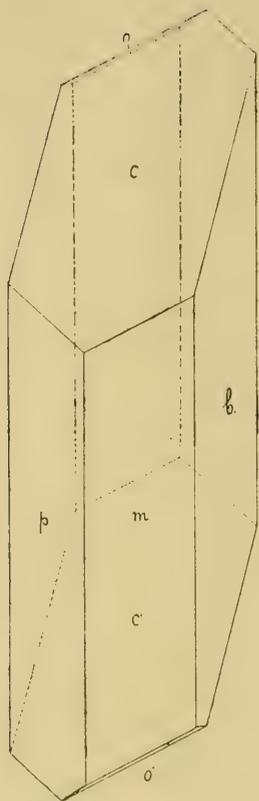


Fig. 1.

(Diphenylhydrazine).

No distinct plane of cleavage.

	<i>Measured :</i>	<i>Calculated :</i>
$b' : p = (0\bar{1}0) : (1\bar{1}0) =$	$62^{\circ}6'$	—
$b : m = (010) : (110) =$	$62\ 54\frac{1}{2}$	—
$b' : c = (0\bar{1}0) : (001) =$	$89\ 13\frac{1}{2}$	—
$p : c = (\bar{1}\bar{1}0) : (001) =$	$48\ 53$	—
$o : m' = (\bar{1}\bar{1}1) : (\bar{1}\bar{1}0) =$	$73\ 38$	—
$m : c = (110) : (001) =$	$49\ 24$	$49^{\circ}28'$
$o : c = (\bar{1}\bar{1}1) : (001) =$	$56\ 54$	$56\ 54$
$p : o = (\bar{1}\bar{1}0) : (\bar{1}\bar{1}1) =$	$78\ 42$	$78\ 36$
$o : b' = (\bar{1}\bar{1}1) : (0\bar{1}0) =$	$58\ 45\frac{1}{2}$	$58\ 43$
$p : m = (\bar{1}\bar{1}0) : (110) =$	$54\ 59\frac{1}{2}$	$54\ 59\frac{1}{2}$

In the vertical zone the situation of the optical elasticity axes was almost parallel to the direction of the c -axis; but on b the angle of inclination amounted to about 10° , on m only about 1° . An axial image could not be observed.

The sp. gr. of the crystals is 1,190 at 16°; the equivalent volume 154,62. Topical axes $\chi : \psi : \omega = 6,0956 : 7,9182 : 4,7399$.

Hydrazo-Benzene.

$C_6H_5 \cdot NH-NH \cdot C_6H_5$; melting point: 125° C.

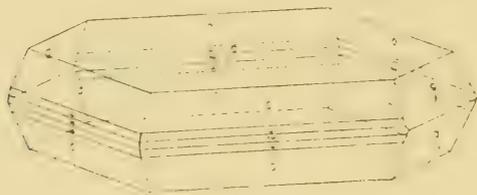


Fig. 2.
(Hydrazobenzene).

When recrystallised from a mixture of alcohol and ether, the compound forms small, thin, colourless, square plates.

Rhombic-bipyramidal.

$$a : b : c = 0,9787 : 1 : 1,2497.$$

Forms observed: $c = \{001\}$, strongly predominant and very lustrous; $o = \{111\}$, sharply reflecting; $q = \{021\}$, lustrous, always very small developed; $\omega = \{221\}$, narrow; $m = \{110\}$ very narrow and often wanting altogether. Thin-tabled towards c .

	<i>Measured :</i>	<i>Calculated :</i>
$c : o = (001) : (111) =^* 60^\circ 46'$		—
$o : o = (111) : (\bar{1}\bar{1}1) =^* 75^\circ 14'$		—
$c : q = (001) : (021) = 68^\circ 11'$		$68^\circ 12'$
$o : \omega = (111) : (221) = 13^\circ 45'$		$13^\circ 36'$
$\omega : m = (221) : (110) = 15^\circ 27'$		$15^\circ 38'$
$c : m = (001) : (110) = 89^\circ 56'$		$90^\circ 0'$
$\omega : \omega = (221) : (2\bar{2}1) =$ —		$84^\circ 41'$
$m : m = (110) : (\bar{1}\bar{1}0) = 88^\circ 36'$		$88^\circ 46'$
$\omega : \omega = (221) : (2\bar{2}\bar{1}) = 30^\circ 58'$		$31^\circ 16'$

Very completely cleavable along $\{001\}$.

On c the situation of the directions of extinction is orientated towards the side $c : q$. An axial image could not be observed.

Sp. gr. = 1,158 at 16° C.; the equivalent volume is 158,89.

Topical axes : $\chi : \psi : \omega = 4,9567 : 5,0645 : 6,3291$.

Benzylaniline.

$C_6H_5 \cdot CH_2-NH \cdot C_6H_5$; melting point: $36\frac{1}{2}^\circ C$.

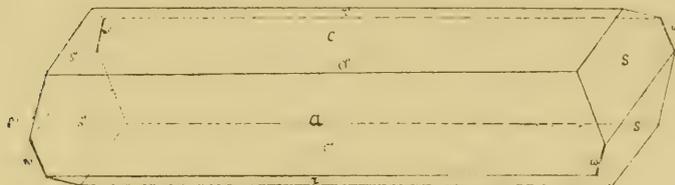


Fig. 3.
(Benzyl-Aniline).

From ether or alcohol the compound crystallises in large colourless crystals flattened towards a which, however, never exhibit measurable end planes. The best crystals are obtained from methyl alcohol. They are then mostly twins towards $\{100\}$ or sometimes parallel-crystallisations. The end planes are generally curved and unsuitable for measurement. With some of the better developed crystals more accurate measurements could be executed.

Monoclinic-prismatic.

$$a : b : c = 2,1076 : 1 : 1,6422.$$

$$\beta = 76^\circ 36\frac{1}{2}'.$$

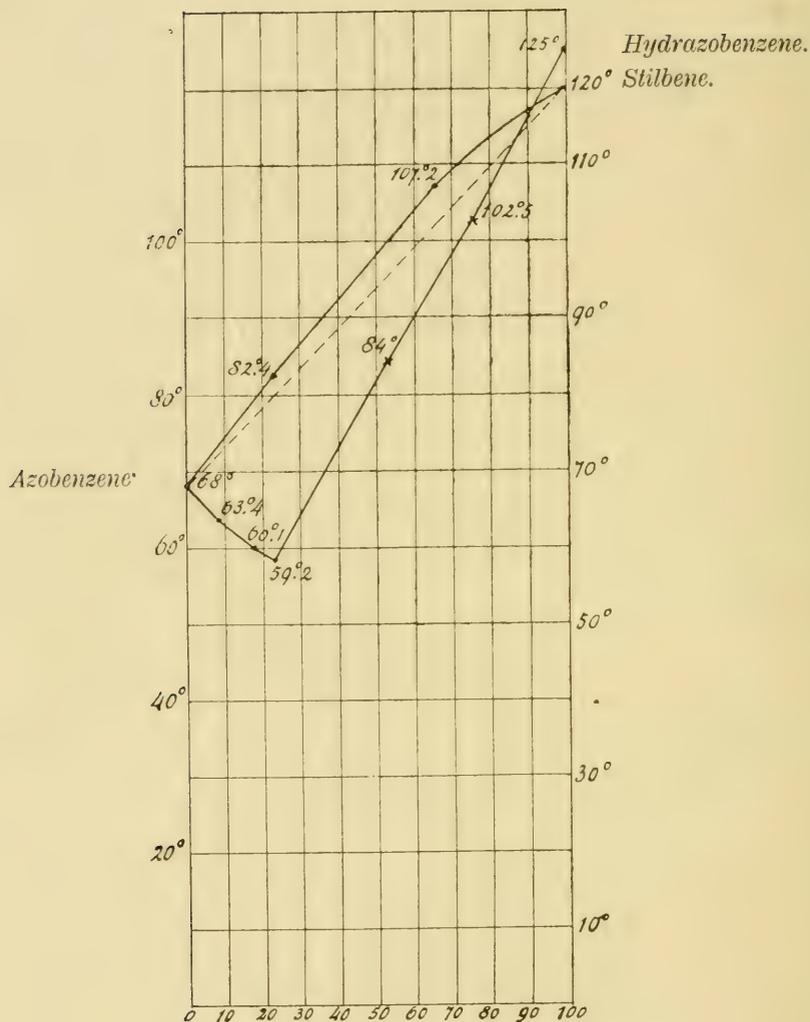
Forms observed: $a = \{100\}$, most broadly developed of all and strongly lustrous; $c = \{001\}$, somewhat narrower and strongly lustrous; $s = \{021\}$, bent and curved, sometimes less opaque and flat; $r = \{\bar{2}03\}$, well developed and lustrous; $\omega = \{\bar{2}4 2 1\}$, indicated as extremely narrow vicinal form, mostly wanting.

<i>Measured :</i>	<i>Calculated :</i>
$a : c = (100) : (001) =^* 76^\circ 36\frac{1}{2}'$	—
$a : r = (100) : (\bar{2}03) =^* 73 31\frac{1}{2}'$	—
$c : s = (001) : (021) =^* 72 37\frac{1}{4}'$	—
$s : s = (021) : (02\bar{1}) = 34 45\frac{1}{2}'$	$34^\circ 45\frac{1}{2}'$
$a : s = (100) : (021) = 93 58$	93 58
$r : s = (\bar{2}03) : (02\bar{1}) = 75 1$	$74 59\frac{1}{2}'$
$c : r = (001) : (\bar{2}03) = 29 53$	29 52

Very completely cleavable towards $\{001\}$ and $\{100\}$. Twins towards $\{100\}$.

In the zone of the b -axis orientated extinction everywhere; the optical axial plane is $\{010\}$. On a and c a black hyperbola is visible in convergent light; one axis forms with the normal on a an angle

Fig. 4



Binary meltingpoint lines of Azobenzene + Stilbene
and of Azobenzene + Hydrazobenzene.

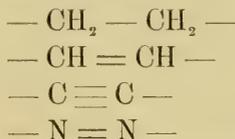
of about 12° . The apparent axial angle in α -monobromonaphthalene amounts to about 90° . Strong, inclined dispersion with $\varrho > \nu$.

The Sp. Gr. = 1,149 at 14° C.; equivalent vol. = 159,25.

Topical axis: $\chi : \psi : \omega = 7,6220 : 3,6164 : 5,9389$.

As regards *Hydrazobenzene* and *Benzylaniline* the following observations must be made.

Some time ago, BRUNI and CIAMICIAN¹⁾, and GARELLI and CALZOLARI²⁾ concluded, on account of cryoscopic abnormalities, to a formation of mixed phases in the solid state between, *Dibenzyl*, *Stilbene*, *Tolane* and *Azobenzene*, and to the *isomorphogenous* substitution in aromatic molecules of the atomic-combinations:



According to BRUNI and GORNI³⁾, *Benzylideneaniline*: $\text{C}_6\text{H}_5 \cdot \text{CH} = \text{N} \cdot \text{C}_6\text{H}_5$ may also form mixed crystals with *Stilbene* and *Azobenzene* so that according to them the atomic combination: $\text{--- CH} = \text{N ---}$ ought to be included in the above series. The question now arises whether the combining forms: --- NH---NH--- and $\text{--- CH}_2 \text{--- NH ---}$ which find in *Hydrazobenzene* and *Benzylamine* their most simple representatives, analogous with the above derivatives, belong to this isomorphogenous series or no.

The important question, however, arose whether we have really the right to speak here of an isomorphism, as we are not allowed to conclude at once that an isomorphism exists merely on account of the power of mixing in the solid state only.

BOERIS³⁾, however, demonstrated that the four firstnamed substances exhibit such a close form relationship that this is practically indistinguishable from true isomorphism.

Dibenzyl: $\text{C}_6\text{H}_5 \cdot \text{CH}_2 \text{--- CH}_2 \cdot \text{C}_6\text{H}_5$.

Monoclinoprismatic $a : b : c = 2,0806 : 1 : 1,2522$; $\beta = 64^\circ 6'$

Stilbene: $\text{C}_6\text{H}_5 \cdot \text{CH} = \text{CH} \cdot \text{C}_6\text{H}_5$.

Monoclinoprismatic $a : b : c = 2,1701 : 1 : 1,4003$; $\beta = 65^\circ 54'$

Tolane: $\text{C}_6\text{H}_5 \cdot \text{C} \equiv \text{C} \cdot \text{C}_6\text{H}_5$.

Monoclinoprismatic $a : b : c = 2,2108 : 1 : 1,3599$; $\beta = 64^\circ 59'$

Azobenzene: $\text{C}_6\text{H}_5 \cdot \text{N} = \text{N} \cdot \text{C}_6\text{H}_5$.

Monoclinoprismatic $a : b : c = 2,1076 : 1 : 1,3312$; $\beta = 65^\circ 34'$

Here, however, we meet with differences in aspect, optical orien-

¹⁾ BRUNI and CIAMICIAN, Soluzioni solide e miscele isomorfe fra i composti a catena aperta saturi e non saturi; Rendic. Lincei (1899). 8. I. 575; Gazz. Chimic. Ital. (1899). 29. 149.

²⁾ GARELLI and CALZOLARI, Sul comportamento erioscopico di sostanze aventi i costituzione simile a quella del solvente; Rendic. Lincei (1899). 8. I. 585; Gazz. Chim. Ital. (1899). 29. (2). 258; Rendic. Lincei R. Accad. (1900). 9. (1). 382.

³⁾ BRUNI and GORNI, Gazz. Chim. Ital. (1899). 1. 55.

³⁾ BOERIS, Atti Società Ital. di Sc. Natur, Milano. (1900). 39. 111—123. Abstract Z. f. Kryst. 34. 298.

ation etc. which are greater than is allowed in strictly isomorphous substances, so that it is better to speak of isomorphotropism instead of isomorphism.

Now according to GARELLI and CALZOLARI, *Dibenzyl* and *Benzyl aniline* form mixed crystals; also *Azobenzene* and *Benzylaniline*¹⁾. This in connection with the results previously obtained by MUTHMANN²⁾ according to which the *Terephthalic-methyl-ether* is isomorphotropous with $\Delta_{1,4}$ —, and $\Delta_{1,3}$ — *Dihydroterephthalic-dimethyl-ether* and the $\Delta_{1,3}$ — and $\Delta_{1,5}$ — *Dihydroterephthalic-diethyl-ethers* are isomorphotropous with the Δ_1 — *Tetrahydroterephthalic-diethyl-ether*, whilst, in addition the *p-Dioxyterephthalic-ethers* behave in an analogous manner to the *p-Dioxydihydroterephthalic-ethers* and are capable of forming with these mixed phases in the solid state, the Italian investigators believe they are justified in coming to the conclusion that *if two aromatic substances can form mixed crystals, their hydro-products can do the same.*

The universal application of this rule is at once upset by *Hydrazobenzene* and *Dibenzyl*, which, cryoscopically, behave quite normally but differ in their crystalline form as shown above.

It was, therefore, to be expected that *Azobenzene* and *Hydrazobenzene* would form no mixed crystals. Experiments taught me indeed that from their mixed solution in ether *Hydrazobenzene* is deposited first in colourless, perfectly pure crystals. Afterwards these are accompanied by pure red crystals of *Azobenzene*; they were verified by the melting point.

I have also determined the melting point line of mixtures of the two substances. This line has two branches and an ordinary eutecticum situated at 59°.25 and corresponding with a concentration in *Azo-compound* of 76.2 mol %.

Here are a few data:

<i>Azobenzene</i>		melts at 67°.8 C.
„ + 9.6 %	<i>Hydrazobenzene</i>	„ „ 63°.4 C.
„ + 17.7 %	„	„ „ 60°.1 C.
„ + 23.8 %	„	„ „ 59°.25C.
„ + 47.0 %	„	„ „ 84° C.
„ + 70.5 %	„	„ „ 102°.5 C.
<i>Hydrazobenzene</i>		„ „ 125°.2 C.

1) BRUNI, Ueber feste Lösungen. Samml. chem. techn. Vorträge. Bd. VI. (1901). p. 48.

2) MUTHMANN, Z. f. kryst, 15. 60; 17. 460: 19. 357.

According to my research there is here no question of an isomorphism with an appearing hiatus.

All this is quite in accord with the deviating crystalline form of *Hydrazobenzene*.

It deserves attention that BILLOWS¹⁾ has investigated *p-Azotoluene* and *p-Hydrazotoluene*. He finds:

p-Azotoluene (143° C.)-Monoclinic-prismatic

$$a : b : c = 0,5687 : 1 : 1,7105; \beta = 89^{\circ}.44'$$

p-Hydrazotoluene (128° C.)-Monoclinic-prismatic

$$a : b : c = 0,6279 : 1 : 2,0287; \beta = 89^{\circ}.49'$$

Notwithstanding these deviations, also that one where {001} of the first substance plays the role of {100} at the second he declares these compounds to be "isomorphous"! Of more than a mere morphotropic relation there can be no question here, and the so called isomorphogenous replacement of —N=N— by —NH—NH— does not help us here.

As *Dibenzyl* and *Benzylaniline* can yield mixed crystals and as according to BRUNI the latter yields mixed crystals with *Azobenzene* an analogy in form is to be suspected here. This may indeed be brought to light by assigning to BOERIS' forms in *Azobenzene*: {100}, {001}, {110}, $\{\bar{2}01\}$, $\{\bar{4}03\}$ respectively the symbols: {100}, $\{\bar{1}01\}$, {410}, {101}, {103}, that is to say by calling the form which should be $\{\bar{1}01\}$ with BOERIS, {001}.

Then we have:

$$\textit{Azobenzene}: a : b : c = 2,1076 : 1 : 1,4220; \beta = 76^{\circ}.32'$$

$$\textit{Benzylaniline}: a : b : c = 2,1076 : 1 : 1,6422; \beta = 76^{\circ}.36\frac{1}{2}'$$

Therefore, a relation which, having the *same* ratio *a:b* and an equal angle β , looks as if it ought to be considered as a case of isomorphotropism bordering on isomorphism.

It must, however, be pointed out immediately that this explanation is not a *rational one* as the other forms of *Azobenzene* observed by BOERIS obtain in this way very complicated symbols.

It must also be observed that the meltingpoint of *Benzylaniline* (36½° C.) is lowered by addition of small quantities of *Azobenzene*.

Whilst the *Benzylaniline* used melted at 36½° C. and the *Azobenzene* at 68° C., the following melting points *t* were found for mixtures:

¹⁾ BILLOWS, *Rivista di Mineral. e Cristall. Ital.* (1903). **30**. 34—48. Abstract *Z. f. Kryst.* **41**. 273.

93½ %	<i>Benzylaniline</i>	+	6½ %	<i>Azobenzene</i> ,	$t = 35^{\circ}$	C.
88 %	„		12 %	„	$t = 32\frac{1}{2}^{\circ}$	C.
48,6 %	„		51,4 %	„	$t = 49^{\circ}$	C.
23,7 %	„		76,3 %	„	$t = 61\frac{1}{2}^{\circ}$	C.

On crystallisation of the two compounds from a joint solution in alcohol + chloroform, small aggregated orange-coloured needles were obtained which were unsuitable for further investigation. But it seems that solid solutions are formed here.

As regards *Azobenzene* and *Stilbene* with which *Dibenzyl* forms solid solutions, I have tried to determine, in mixtures of the two substances, the points of initial and final solidification in the usual manner. It appeared that these two substances whose isomorphotropism is almost indistinguishable from real isomorphism, also agree with real isomorphous substances in this respect that they can form a continuous series of mixed phases from 0 % to 100 %. The lower branch of the continuously-rising melting point curve is situated so close to the higher one that a sharp determination was quite impossible.

The following melting points were found:

Azobenzene melts at 68° C.

„ + 22,9 % *Stilbene* melts at $82^{\circ}.4$ C.

„ + 66,94 % „ „ „ $107^{\circ}.2$ C.

Stilbene melts at 120° C.

The melting point of *Azobenzene* is therefore raised by addition of *Stilbene*. The lowering of the melting point of *Stilbene* is not proportional to the number of molecules of added *Azobenzene* (incorrect rule of KÜSTER) but takes place more slowly.

The mixed crystals obtained from mixed solutions were homogeneous and of a bright red colour. They crystallise beautifully. The mixture being sublimed the vapour deposits mixed crystals as is also observed by BRUNI.

Finally, we wish to observe that *Hydrazobenzene*, notwithstanding the difference in symmetry, shows in its parameters some degree of analogy with *Azobenzene* if we take $o = \{211\}$, $\omega = \{421\}$ and $m = \{210\}$.

Azobenzene: $a : b : c = 2,1076 : 1 : 1,4220$ $\beta = 76^{\circ},32'$.

Hydrazobenzene: $a : b : c = 1,9574 : 1 : 1,2497$ $\beta = 90^{\circ}$.

In the case of *Diphenylhydrazine*, notwithstanding its great similarity to the monoclinic system, there is no question of such a distant analogy.

Chemistry. — “*The amides of α and β -aminopropionic acid.*”. By
 Prof. A. P. N. FRANCHIMONT and Dr. H. FRIEDMANN.

(Communicated in the meeting of October 28, 1905).

Some time ago, I was asked for information as to a substance isolated in 1873 by BAUMSTARK from some urines. He describes it as white prisms some millimetres long and resembling hippuric acid not only in form but also in lustre. It is fairly readily soluble in boiling water, with difficulty in cold water and spirit of wine, insoluble in absolute alcohol and ether, and suffers no decomposition when heated to 250° . It is a neutral substance which, however, yields with acids, hygroscopic compounds difficult to crystallise, and gives a precipitate with mercuric nitrate. The analysis led to the formula $C_3H_8ON_2$. By means of nitrous acid he obtained from it a liquid acid and from this he prepared a zinc salt, which in zinc and water content corresponds with the zinc salt of sarcosylactic acid. This zinc salt was very soluble in water and in spirit of wine, and from this he concluded that it really consisted of zinc sarcosylactate. He also showed that under the influence of alkalis, one nitrogen atom is readily converted into ammonia and the other into ethylamine, carbon dioxide being also formed.

From this he concluded that his substance was the amide of α -aminopropionic acid or, as he called it, the diamide of lactic acid.

BELSTEIN in his text-book, mentions BAUMSTARK's substance as the amide of α -aminopropionic acid but adds a point of interrogation, and rightly so, for BAUMSTARK has tried to control the conclusion drawn from his analytical research by synthetically preparing the diamides of the lactic acids, or amides of the amino-propionic acids, and comparing them with his substance from the urine; from those experiments he drew the opposite conclusion, and declared the previous idea to be incorrect.

But if we look at the synthetical methods applied by BAUMSTARK, it is at once evident that he could obtain nothing else but mixtures, which he has not separated but seems to have regarded as pure substances whose properties were totally different from that of his substance from urine.

Moreover, many, particularly physical properties such as melting point, solubility, neutrality etc. of the substance from urine, are not those which we might reasonably expect of the amides of the amino-propionic acids.

None of the amides of the aminopropionic acids being known, I

instructed Dr. FRIEDMANN to prepare both by a method leading to pure products, in order to end the present uncertainty.

The α -aminopropionic acid (commercial alanine) was converted in the usual manner into the hydrochloric methyl ester, which melted at 158° . By the action of silver oxide or aqueous caustic soda, in presence of ether, the *free methyl ester* was prepared, which is very volatile, and under a pressure of 15 m.m. passes over between 38° and 41° as a colourless liquid (spec. gr. $13,5^\circ = 1,0309$), which however, after some days changes into a solid mass (alanine anhydride), presumably owing to the interaction of the two functions — amine and organic ester. A nitrogen determination in the liquid gave figures corresponding with those required by the amino ester $\text{CH}_3\cdot\text{CHNH}_2\cdot\text{CO}_2\text{CH}_3$. The amino ester was mixed with a saturated methylalcoholic ammonia and left to itself for a few days. A distillation at 35° at a pressure of 20 mm. removed the ammonia and alcohol and left as residue a colourless oily liquid of a strongly alkaline reaction which is but little soluble in ether and benzene and solidifies in a dessiccator. After being recrystallised from alcohol, the substance on analysis appeared to be pure. It crystallises in needles, is very soluble in alcohol, very hygroscopic and melts at 62° . On prolonged heating ammonia is set free and alanine anhydride is formed, as was indeed to be expected. The *α -aminopropionic amide* $\text{CH}_3\cdot\text{CHNH}_2\cdot\text{CO}\cdot\text{NH}_2$ gives also a well-crystallised compound with hydrogen chloride, a fine crystallised orange-red chloroplatinate, which is readily soluble in water, but little so in alcohol, and a bright yellow picrate, little soluble in water, which on being recrystallised from alcohol melts at 199° . Thus we have sufficiently characterized this amide for the present. It seems to be decomposed already at ordinary temperature in an exsiccator.

The β -aminopropionic acid was prepared but with a slight modification, according to HOOGEWERFF and VAN DORP from succinimide¹). Like the α -compound it was converted into the hydrochloric methyl ester, which melts at 95° .

From this was prepared in the manner described above the free *β -aminopropionic methyl ester*, which under 18 m.m. pressure distills at 57° — 59° as a colourless liquid and is pure as follows from analysis. After a few hours it is decomposed with formation of crystals. By direct treatment with methylalcoholic ammonia the amide was at first obtained as an oily liquid, which was purified by repeated

¹) This was simply prepared like many other amides (when they and their acids can resist a fairly high temperature) by heating the acid in a current of ammonia until no more water is expelled.

solution in methyl alcohol and precipitation with ether, when it gave good analytical results. On being cooled, it became solid, and on inoculation with a trace of the solid material, it yielded beautiful crystals, melting at 41°. The β -aminopropionic amide $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$ is very hygroscopic, very soluble in alcohol, with difficulty in ether, has a strongly alkaline reaction, absorbs carbon dioxide from the atmosphere and yields a well-crystallised hydrochloride.

Both aminopropionic amides are, therefore, now known and not identical with the substance obtained by BAUMSTARK from urine.

Physics. — “Remarks concerning the dynamics of the electron.”

By Prof. J. D. VAN DER WAALS JR. (Communicated by Prof. J. D. VAN DER WAALS).

The theory of electrons is usually deduced from the following equations :

$$\text{div } \mathfrak{d} = \rho \quad (I)$$

$$\text{rot } \mathfrak{h} = \frac{1}{c} (\dot{\mathfrak{d}} + \rho \mathfrak{v}) \quad (II)$$

$$\text{rot } \mathfrak{d} = -\frac{1}{c} \dot{\mathfrak{h}} \quad (III)$$

$$\text{div } \mathfrak{h} = 0 \quad (IV)$$

$$\mathfrak{f} = \mathfrak{d} + \frac{1}{c} [\mathfrak{v} \mathfrak{h}] \quad (V)$$

The units and notations used are those of LORENTZ'S article on the “Elektronentheorie” in the “Encyclopädie der Mathematischen Wissenschaften” V 14.

The equations (I) . . . (IV) determine the field, the motions of the electrons being given. Equation (V) will be independent of the former four, and determine the motion of the electron in the electromagnetic field, $\rho \mathfrak{f}$ representing the force exercised by the field on the electric charge. The application of equation (V) is however attended by peculiar difficulties. If in mechanics a body is given its mass is also supposed to be known ; then if we know the force, the acceleration, and the law according to which it will move may be calculated. Now if in forming \mathfrak{f} we take into account all the forces also those excited by the electron itself, then the case that we ascribe a “real” or “material” mass to the electron offers no fundamental difficulty. For the case, however, in which the electron has no real mass the equation (V) assumes the form :

$$\text{force} = 0$$

without a term with $\frac{dv}{dt}$ in the righthand member which enables us to determine the acceleration. If on the other hand in forming \mathfrak{f} we take into account only the external forces, we may introduce the electromagnetic mass m' and write :

$$\text{force} = m' \frac{dv}{dt}.$$

The mass m' , however, is not known, and we can only calculate it if we know already the law according to which the electron moves. But then of course we need not make use of equation (V) any more.

ABRAHAM¹⁾, accordingly, does not make any use of equation (V) for determining the motion of the electron. He does use an equation which in LORENTZ'S notation, the integrals being taken throughout infinite space, may be written as follows:

$$\iiint \varrho (\mathfrak{d} + \frac{1}{c} [\mathfrak{v} \mathfrak{h}]) dS = \frac{1}{c} \iiint \frac{\partial [\mathfrak{d} \mathfrak{h}]}{\partial t} dS.$$

But this equation is deduced from the equations (I) . . . (IV) and so it is not equivalent to equation (V) which must be independent of them. The only use which is made of equation (V) is the introduction of the name force for the quantity $\varrho \left(\mathfrak{d} + \frac{1}{c} [\mathfrak{v} \mathfrak{h}] \right)$, of

the name momentum for $\frac{1}{c} [\mathfrak{d} \mathfrak{h}]$, and of the name electric mass for the quotient of the so defined force and the acceleration. But the real problem: how will an electron with given shape and charge move in a given field, must be solved beforehand independently of this nomenclature.

Yet it is evident that the equations (I) . . . (IV) will in general be insufficient for the determination of the motion of an electrical system. In the case that we ascribe a real mass to the electron, it is obvious that we must know the force acting on it. But also on the supposition that the electron has no real mass — and in what follows we will confine ourselves to this case — another set of equations is required for the determination of the motion. For equation (II) enables us to determine \mathfrak{d} if \mathfrak{v} is always known, and inversely to determine \mathfrak{v} if we know \mathfrak{d} , but it does not enable us to determine both these quantities. The assumption that the motion is quasi stationary is equivalent to a relation between \mathfrak{v} and \mathfrak{d} .

¹⁾ ABRAHAM, "Dynamik des Elektrons." *Ann. der Physik* IV. B. 13, 1904, bl. 105.

For such a motion the equations (I) . . . (IV) are therefore sufficient to determine the motion. If the motion is not quasi stationary then the equations (I) . . . (IV) are not sufficient, and we must make use of equation (V), which may be written:

$$\iiint \varrho \left\{ \delta + \frac{1}{c} [(v + [g r]) h] \right\} dS = 0 \quad . \quad (Va)$$

the integral being taken throughout the electron.

If we wish to state the meaning of this formula with the aid of the conceptions force and mass, we may say: the real mass of the electron being zero, it is impossible that a force should act on it. We may, however, set these conceptions aside, and simply state: the electron places itself and moves in the electric field in such a way, that the relation (Va) is permanently satisfied.

It is true, this equation has the form: force = 0 without $m \frac{dv}{dt}$ in the righthand member. Yet it may serve to determine the motion. This is owing to the fact that the expression of the force itself contains the velocity v and the angular velocity g . In general we may choose such values for these quantities that the equation (Va) is satisfied. To some extent therefore we return with the dynamics of an electron to the standpoint of mechanics before GALILEI: the forces do not determine the acceleration but the velocity. If we might assume δ and h to be given throughout all space and at all times, δ and g would be determined by the place of the electron, and we should get a differential equation of the first order for the determination of the motion of the electron.

The question is in reality less simple, because δ and h depend on the former motion of the electron. This causes a time-integral of a function of v and g to occur in the equation of motion of the electron. So we get integral equations as SOMMERFELD has used in his treatises "Zur Elektronentheorie I, II and III".¹⁾ In some cases the integrations may be effected, and then we get functional equations.

If the electron moves rectilinearly without rotation, and if it moreover has an axis of symmetry the direction of which coincides with the direction of the translation, then the terms of equation (Va) which contain v or g disappear and the equation reduces to:

$$\iiint \varrho \delta dS = 0 .$$

In this case it is no longer possible to satisfy the equation by

¹⁾ Göttinger Nachrichten 1904, p. 99 and 363 and 1905 p. 201.

means of a suitable choice of the value of v and g , and now it is the *place* of the electron which must be such that the equation is satisfied. If the electron stood still the equation would cease to be satisfied in a following moment because of the propagation of the field-forces, it must therefore suffer a displacement in such a way that the relation *continues* to be satisfied. So the equation determines the velocity, though the velocity itself does not occur in it.

This remark may perhaps serve to elucidate the results of SOMMERFELD concerning the motion with a velocity greater than that of light, and this is principally my aim with this communication. In the following I shall denote a velocity, greater than that of light, with \mathfrak{B} and one smaller with v .

We see at once that the supposition of SOMMERFELD that the velocity of an electron moving with \mathfrak{B} will suddenly decrease to v when the external force is suddenly suppressed, cannot be accurate. For if we take \mathfrak{d} to be the sum of two parts \mathfrak{d}_1 the external field and \mathfrak{d}_2 the field of the electron itself, then we have at the moment t before the suppression of the external field:

$$\iiint \varrho (\mathfrak{d}_1 + \mathfrak{d}_2) dS = 0.$$

But as v requires an external force, $\iiint \varrho \mathfrak{d}_1 dS$ is not zero, so neither can $\iiint \varrho \mathfrak{d}_2 dS$ be zero. This last quantity is independent of the velocity at the moment t itself, and so it cannot be made to disappear by any choice of the velocity, and there is no possible way in which equation (Va) can be satisfied.

If we imagine the velocity of an electron moving with \mathfrak{B} momentarily to decrease to v , then the required external force will not suddenly become zero, but at the first instant it remains unchanged, and only gradually it varies in accordance with the new mode of motion. This thesis applies to every discontinuity in the velocity provided the motion be rectilinear and the electron have the required symmetry. For the case that the initial velocity is zero it follows from SOMMERFELD'S complete calculation of the force. We see again the conformableness of the dynamics of an electron with a theory of mechanics in which no inertia is assumed: the force required for a discontinuous change in the velocity is not only not infinite, but even zero; the force, which acts before the discontinuity, remains unchanged at the moment of the discontinuity.

We cannot be astonished at the fact that we do not find a possible

way of motion for an electron moving with \mathfrak{B} , when the external force is suddenly suppressed. The same applies to an electron moving with \mathfrak{v} ; if the motion is accelerated, and so if a force acts on the electron, and if this force is suddenly suppressed, the equation (Va) cannot be satisfied in any way. This is because the momentary disappearance of the external force is an impossible supposition. Even an infinite acceleration would not satisfy equation (Va) . The internal force namely depends only on the former motion of the electron, and not on the velocity or the acceleration at the moment itself. SOMMERFELD's conclusion that a motion with $\frac{\partial \mathfrak{v}}{\partial t} = \infty$ does not

require an external force holds only if the initial velocity is \mathfrak{v} , and is nothing else but a statement in other words of the fact that the force acting on an electron whose velocity is at the moment t momentarily — i. e. with infinite acceleration — brought from \mathfrak{v} to \mathfrak{B} , is zero at the moment t . If however we begin with a constant velocity \mathfrak{B}_1 , and change the velocity at the moment t suddenly to \mathfrak{B}_2 , then the force is not zero at the moment t , though the acceleration be infinite, but it has that value which corresponds with a constant velocity \mathfrak{B}_1 .

It may however be asked what will happen, if the force acting on an electron with \mathfrak{B} does not suddenly decrease to zero, but gradually. SOMMERFELD says about this case only that the sudden fall to \mathfrak{v} , which he expects from a sudden suppression of the force, will make room for a gradual fall. But as his expectation concerning the case of a sudden suppression of the force appeared to be inaccurate, we might suppose that also this expectation will appear not to be satisfied. The more so because SOMMERFELD found a negative value for the electric mass of an electron moving with \mathfrak{B} . We might therefore expect that a decrease of the force would cause an acceleration. This, however, is not the case, and here we see how risky it is to introduce the conception of mass in the theory of the motion of electrons, to which it is essentially strange.

The negative mass, which SOMMERFELD ascribes to the electron means nothing else, but that in order to move with a given \mathfrak{B}_1 the electron requires a greater force when in the active interval the velocity was on an average greater than \mathfrak{B}_1 , a smaller force when it was less. By active interval is meant the time during which the electron emitted the fieldforces, which at the moment t act on the electron. The greater the velocity during the active interval, the greater the force, and inversely the smaller the velocity the smaller

the force¹⁾. But it does not follow from this that also a greater force is required if the retardation exists only in the future. On the contrary when the velocity has decreased to $\mathfrak{B}_2 < \mathfrak{B}_1$, the velocity during the active interval has been smaller than \mathfrak{B}_1 on an average, and so also the force required will be smaller than that which corresponds to a constant velocity \mathfrak{B}_1 . So with a gradual decrease of the velocity corresponds a gradual decrease of the force. The reverse of this thesis is not always true: if $\frac{d\tilde{\delta}}{dt}$ is a continuous function of t then the

velocity will also vary continuously. If on the other hand $\frac{d\tilde{\delta}}{dt}$ is discontinuous though $\tilde{\delta}$ be continuous then v will vary discontinuously.

A diminution of the force is therefore accompanied by a diminution of the velocity, and inversely. The behaviour of an electron moving with \mathfrak{B} corresponds in this respect with that of a body with a positive mass. If the force acting on the electron decreases gradually to zero, the velocity will fall to v .

Though it seems to me that there is no reason to doubt whether the behaviour of an electron has been described here accurately though only in general outlines, and though a complete calculation of the motion is not practicable in consequence of the great intricacy of the formulae, I will show in one simple case that the force required for a given motion agrees with the above description. I imagine to that purpose an electron which for some time moves with a constant velocity \mathfrak{B} . At the instant t the motion is suddenly accelerated with a constant acceleration p . In order to render the calculation possible we will assume that we may apply the formulae for quasi stationary motion. We will calculate the force at an instant t in the first interval²⁾, so $t > \tau'$. The calculation does not present any difficulties, and can be carried out in the way indicated by SOMMERFELD. After introduction of the approximation for the quasi stationary motion we may everywhere separate the terms as they would be for a constant velocity \mathfrak{B} , (we call the sum of these terms $\tilde{\delta}_1$) and the supplementary terms which depend on the acceleration, and whose sum will be denoted by $\tilde{\delta}_2$. In this way we find:

1) This rule is given by SOMMERFELD though his calculations show that it does not hold good with perfect generality. In most cases and also in the present one it will give a true idea in general outlines of the value which the force must assume.

2) SOMMERFELD III p. 206.

$$\begin{aligned}
& - \frac{32\pi a^4}{3\varepsilon^2} \delta = - \frac{32\pi a^4}{3\varepsilon^2} \delta_1 - \frac{8}{5} \frac{av^2}{v^2} \frac{pt^2}{4} \\
& + p \frac{c}{2v^2(v+c)} \int_0^{x_1} \left(2\varphi + x \frac{d\varphi}{dx} \right) x dx - p \frac{c}{v^3} \int_0^{x_1} \varphi x dx \\
& - pt \frac{c}{v^2} \int_0^{x_1} \left(2\varphi + x \frac{d\varphi}{dx} \right) dx + pt \frac{c(v-2c)}{v^3} \int_0^{x_1} \varphi dx \\
& - pt^2 \frac{c(v+c)}{2v^2} \int_{x_1}^{2a} \left(2\varphi + x \frac{d\varphi}{dx} \right) \frac{1}{x} dx + pt^2 \frac{c^2(v+c)}{v^3} \int_{x_1}^{2a} \varphi \frac{1}{x} dx
\end{aligned}$$

+ six other integrals which are obtained by substituting $-c$ for c and x_2 for x_1 in the above.

The signification of the symbols is as follows: a is the radius of the spherical electron which is supposed to be charged with homogeneous cubic density; ε is the charge of the electron, c the velocity of light, v the numeric value of \mathfrak{B} ; φ the function $2a - x + \frac{1}{20} \frac{x^3}{a^3}$; x_1 is $(v+c)t + \frac{1}{2} pt^2$ and $x_2 = (v-c)t + \frac{1}{2} pt^2$. In the expressions for x_1 and x_2 the term $\frac{1}{2} pt^2$ may, however, be neglected.

Without performing the integrations completely we may draw the following conclusions:

1st. All the terms of δ_2 contain t as a factor. So we have $\delta = \delta_1$ if t vanishes. No sudden increase of the force is therefore required if the motion is suddenly accelerated, as is the case with a body with positive mass; neither a sudden diminution of the force as would be the case with a body with negative mass. The force remains unchanged.

2nd. No terms with the first power of t occur in δ_2 , therefore $\frac{d\delta}{dt_{(t=0)}} = 0$. Even the derivative $\frac{d\delta}{dt}$ is therefore continuous at the point $t=0$. This agrees with our remark that a discontinuity in the derivative of δ only occurs if the velocity changes discontinuously.

3rd. For establishing the sign of δ_2 for $t =$ very small, we have only to take into account the terms with t^2 . There are also terms with $t^2 l(t)$ but the sum of their coefficients is zero. If we perform the integrations as far as is required we find:

$$\left\{ + \frac{1}{3} \frac{c^2}{v^2} + \frac{c^2(v^2-c^2)}{v^3} l \frac{v+c}{v-c} \right\} 2 a p t^2 .$$

+ \mathfrak{F} representing the force of the field of the electron itself, — \mathfrak{F} is the external field required for the motion. So we see that the sign of the external force — \mathfrak{F}_e agrees with that of p , and that therefore acceleration requires increase, retardation decrease of the external force.

We conclude that the behaviour of an electron moving with \mathfrak{B} , though in many respects it differs considerably from that of an ordinary body, does not show at all that paradoxal character, to which we should conclude from the expression *negative mass*. Nothing prevents us from assuming that electrons really can behave in such a way. Accordingly I do not see any reason for assuming with WIEN¹⁾ that a moving electron must suffer a deformation in order that the possibility of a motion with \mathfrak{B} , as it requires an infinite amount of energy, will be precluded.

Finally a remark concerning the series of the emission spectra of elements. The equations of motion of the electron are integral or functional equations, and may be developed into differential equations of an infinitely high order. An infinite number of constants occur accordingly in the solution. If the equations are linear, these constants represent the amplitudes and phases of harmonic vibrations; the system may therefore vibrate with an infinite number of periods²⁾. We are inclined to think that the periods of the lines of a spectral series are the solutions of such an equation. We have then the great advantage that we need not ascribe to the electron a degree of freedom for each line in the spectrum. A degree of freedom in the atom is then not required for each line, but only for each series of lines.

SOMMERFELD tries to account for the spectral series by means of the vibrations an electron performs when it is not subjected to external forces. The periods which he finds, do not agree with those of light. It seems to me that we might have expected this a priori. For the vibrations of light are not emitted by isolated electrons but they are characteristic for atoms or positive ions, and are influenced by the forces by which the electron is connected to the other parts of the atoms or ions. But also with the aid of these forces we cannot account for the spectral series without a much better insight into

1) W. WIEN. Über Elektronen. Vortrag gehalten auf der 77. Versammlung Deutscher Naturforscher und Ärzte in Meran p. 20.

2) Comp. also these Proceedings March 1900 p. 534. Then however, I thought erroneously that the solution obtained in this way was different from that, which I had first developed with the aid of integrals of FOURIER.

the way in which these forces act, and of the properties of the electron, than we have as yet obtained. If e. g. we introduce the so called quasi-elastic force into the equations of motion of the electron, then this does not bring us any nearer to our aim. In order to show this we may write the equations for translation of an electron in the form of a differential equation as LORENTZ has done in equation 73 p. 190 of his article "Elektronentheorie" in the *Encycl. der Math. Wiss.* V 14. If we introduce the quasi-elastic force $-f'x$ we may write the equation as follows:

$$f'x + A_1 \frac{d^2x}{dt^2} + A_2 \frac{d^3x}{dt^3} + A_3 \frac{d^4x}{dt^4} + \dots = 0$$

As it is only my aim to determine the order of magnitude I have not determined the coefficients (A_1 and A_2 have been determined by LORENTZ). The only thing we have to know is that the order of magnitude of the ratios of two successive coefficients is $\frac{A_{n+1}}{A_n} = \frac{a}{c}$. The solution of this equation is $x = \sum e^{st}$ where s is a root of the equation:

$$f' + A_1 s^2 + A_2 s^3 + A_3 s^4 \dots = 0$$

This equation has two kinds of roots, namely 1st two roots for which the other terms are small compared with $f' + A_1 s^2$; these will represent the light vibrations; 2nd an infinite number of roots for which s is so large that f' may be neglected compared with the other terms. For these s must be of the order $\frac{c}{a}$, and the period of the order $\frac{a}{c}$. The appearance of the term f' has little influence on the value of these roots, the periods of these vibrations are therefore nearly independent of the quasi-elastic force, and an isolated electron might have executed vibrations with nearly the same periods. We might have expected a priori that we should find periods of the order $\frac{2a}{c}$: it represents the time required for the propagation of an electric force over the diameter of the electron. The periods of these vibrations are of the same order as those of the rotatory vibrations the periods of which have been accurately calculated in the interesting treatises of HERGLOTZ¹⁾ and SOMMERFELD.

The lines of the spectral series are not accounted for in this way. Yet the periods of the rotation and translation vibrations of the isolated electron must have a physical interpretation. Perhaps we should see them appear if we succeeded in forming the spectrum of RÖNTGEN radiation.

¹⁾ HERGLOTZ, *Gött. Nachr.*, 1903.

Physics. — “*Derivation of the fundamental equations of metallic reflection from CAUCHY’s theory*”. By Prof. R. SISSINGH. (Communicated by Prof. H. A. LORENTZ).

1. It has been pointed out in a previous paper¹⁾ that the theories of metallic reflection drawn up by CAUCHY, KETTELER and VOIGT and that by LORENTZ lead to identical results. It must therefore also be possible in the theory of CAUCHY to derive the two relations which the three last theories furnish between index of refraction and coefficient of absorption for normal and oblique incidence of the light that penetrates into a metal, the so-called fundamental equations. These fundamental equations may first be obtained by paying regard to the connection of the quantities which the theory of CAUCHY and the other theories introduce for the description of the phenomenon. CAUCHY determines the so-called complex angle of refraction r by $\sin r = \sin i : \sigma e^{\tau}$ and $\cos r = \rho e^{i\omega}$ ²⁾. From this follows $1 - \frac{\sin^2 i}{\sigma^2 e^{2i\tau}} = \rho^2 e^{2i\omega}$, so that:

$$\sigma^2 \cos 2 \tau = \rho^2 \sigma^2 \cos 2 (\tau + \omega) + \sin^2 i \quad (1)$$

$$\sigma^2 \sin 2 \tau = \rho^2 \sigma^2 \sin 2 (\tau + \omega) \quad (2)$$

If we pay regard to the relations between σ , τ and n_0 and k_0 , index of refraction and coefficient of absorption for normal incidence, and to the equations (17) and (18) of the preceding paper²⁾, the equations (1) and (2) appear to be nothing but the fundamental equations, given in equation (6) and (7) of the previous paper.

2. On account of the close connection between the theories of metallic reflection it must, however, be also possible, to derive these fundamental equations from CAUCHY’s theory without paying attention to the connection with the others. The fundamental idea of CAUCHY’s theory is the introduction of a complex index of refraction. Denote this again by $n_0 + ik_0 = \sigma e^{\tau}$, so that

$$n_0 = \sigma \cos \tau \quad , \quad k_0 = \sigma \sin \tau \quad (3)$$

and

$$\sin r = \sin i : \sigma e^{\tau} \quad (4)$$

while we put

$$\cos r = \rho e^{i\omega} \quad (5)$$

Let the XZ -plane of a rectangular system of coordinates be the plane of incidence of the light penetrating into the metal, and the YZ -plane the bounding plane of the metal, the X -axis being directed

1) SISSINGH, These Proc. VIII p. 377.

2) Loc. cit. p. 385.

from the surrounding medium to the metal. Assume plane waves to fall on the metal. The vector of light in the refracted ray is then determined by :

$$A \sin 2\pi \left\{ \frac{t}{T} - \frac{x \cos r + z \sin r}{\lambda} (n_0 + ik_0) \right\} (6)$$

In this λ is the wave-length in the air ¹⁾. The phase is determined with respect to a point in the bounding plane.

With the aid of (4) and (5) equation (6) passes into

$$A \sin 2\pi \left\{ \frac{t}{T} - \frac{x \varrho e^{i\omega} + z \sin i e^{-\sigma} : \sigma}{\lambda} (n_0 + ik_0) \right\} (7)$$

(7) satisfies also the differential equations for the vector of light in the metal which are supposed homogeneous and linear, if the sine is replaced by a cosine.

If the arc occurring in (7) is called φ , also

$$A \cos \varphi - i A \sin \varphi^2$$

satisfies.

The light-vector in the metal can therefore be represented by

$$A e^{-2\pi a} \times e^{-2\pi i \left(\frac{t}{T} - b \right)} (8)$$

In this :

$$a = \left(\varrho x \sin \omega - z \sin i \frac{\sin \tau}{\sigma} \right) \frac{n_0}{\lambda} + \left(\varrho x \cos \omega + z \sin i \frac{\cos \tau}{\sigma} \right) \frac{k_0}{\lambda} . (9)$$

$$b = \left(\varrho x \cos \omega + z \sin i \frac{\cos \tau}{\sigma} \right) \frac{n_0}{\lambda} - \left(\varrho x \sin \omega - z \sin i \frac{\sin \tau}{\sigma} \right) \frac{k_0}{\lambda} . (10)$$

3. From (8) follows, that the planes of equal amplitude are represented by :

$$a = p_1 x + q_1 z = C (11)$$

In this is, according to (9)

$$q_1 = - \sin i \frac{\sin \tau n_0}{\sigma \lambda} + \sin i \frac{\cos \tau k_0}{\sigma \lambda} .$$

As from (3) follows

$$n_0 : k_0 = \cot \tau , \text{ we have } q_1 = 0 .$$

¹⁾ LORENTZ showed that, also when a complex index of refraction is introduced, at the bounding plane the values of the light vector in the two media harmonize. Cf. Theorie der terugkaatsing en breking, 1876, p. 160.

²⁾ It appears from § 5 of the previous paper (loc. cit. p. 381), that if the index of refraction is put $n_0 \pm ik_0$, this expression is $A \cos \varphi \mp i A \sin \varphi$.

and the planes of equal amplitude run parallel to the bounding plane. This is necessary as it is assumed that the light enters the metal from the outside.

The planes of equal phase are represented by:

$$b = p_2 x + q_2 z = C \dots \dots \dots (12)$$

If we introduce again $n_0 : k_0 = \cot \tau$, then according to (10)

$$p_2 = \frac{\varrho}{\lambda} k_0 \frac{\cos(\tau + \omega)}{\sin \tau} \dots \dots \dots (13)$$

$$q_2 = \frac{k_0 \sin i}{\sigma \lambda \sin \tau} \dots \dots \dots (14)$$

4. Let α be the angle between the normals of the planes of equal amplitude and phase. The former running parallel to the bounding plane or the YZ -plane, α is the angle of the normal of the planes of equal phase with the X -axis. Thus $\cos \alpha = p_2 : \sqrt{p_2^2 + q_2^2}$ or if we introduce the values p_2 and q_2 from (13) and (14):

$$\cos \alpha = \varrho \cos(\tau + \omega) : \sqrt{\varrho^2 \cos^2(\tau + \omega) + \frac{\sin^2 i}{\sigma^2}} \dots (15)$$

From this follows:

$$\sin \alpha = \frac{\sin^2 i}{\sigma^2} : \left[\varrho^2 \cos^2(\tau + \omega) + \frac{\sin^2 i}{\sigma^2} \right] \dots \dots (16)$$

α being the angle of refraction corresponding to plane waves with an angle of incidence i (see § 2 of the preceding paper), we get:

$$n^2 = \sin^2 i : \sin^2 \alpha = \sigma^2 \varrho^2 \cos^2(\omega + \tau) + \sin^2 i \dots (17)$$

Let the coefficient of absorption belonging to n be k . Normal to the planes of equal amplitude the amplitude decreases over a distance x in ratio 1 to $e^{-2\pi kx} : \lambda$. As $q_1 = 0$, we get according to (8) and (9):

$$\frac{2\pi kx}{\lambda} = \frac{2\pi \varrho x}{\lambda} (n_0 \sin \omega + k_0 \cos \omega)$$

from which again follows, when $\cot \tau$ is substituted for $n_0 : k_0$:

$$k = k_0 \varrho \sin(\tau + \omega) : \sin \tau$$

or on account of (3):

$$k = \sigma \varrho \sin(\tau + \omega) \dots \dots \dots (18)$$

5. The fundamental equations follow immediately from the values found for the index of refraction and the coefficient of absorption. The equations (17) and (18) lead immediately to:

$$n^2 - k^2 = \sigma^2 \varrho^2 \cos 2(\tau + \omega) + \sin^2 i.$$

According to (1) the second member of this equation is equal to $\sigma^2 \cos 2\tau$ or according to (3) to $n_0^2 - k_0^2$. In this way the first fundamental equation is obtained.

Further follows from (15), (17) and (18):

$$n k \cos \alpha = \frac{1}{2} \sigma^2 \rho^2 \sin 2(\tau + \omega).$$

According to (2) the second member is equal to $\sigma^2 \sin 2\tau$ and so according to (3) to $n_0 k_0$, and thus the second equation has also been derived.

To conclude we may remark, that here the reversed course has been taken from that by which in the preceding paper the occurrence of the so-called complex index of refraction was derived from the two fundamental equations¹⁾.

Mathematics. — “*A tortuous surface of order six and of genus zero in space Sp_4 of four dimensions.*” By Prof. P. H. SCHOUTE.

1. We begin by putting the following question:

“In space Sp_4 are given three planes $\alpha_1, \alpha_2, \alpha_3$ and in these are “assumed three projectively related pencils of rays. We demand the “locus of the common transversal of the triplets of rays corresponding “to each other.”

Notation. We indicate the vertices of the rays of pencils by O_1, O_2, O_3 , three corresponding rays and their transversal by l_1, l_2, l_3 and l , the points of intersection of l and l_1, l_2, l_3 by S_1, S_2, S_3 and the pencils of rays by $(l_1), (l_2), (l_3)$. Let further P_{23}, P_{13}, P_{12} indicate the points of intersection of the planes $\alpha_1, \alpha_2, \alpha_3$ two by two, and α the plane P_{23}, P_{13}, P_{12} which has a line in common with each of the planes $\alpha_1, \alpha_2, \alpha_3$, namely with α_1 the line $P_{13}, P_{12} = \alpha_1$, with α_2 the line $P_{12}, P_{23} = \alpha_2$, with α_3 the line $P_{23}, P_{13} = \alpha_3$. We take for granted that not one of the three vertices O_1, O_2, O_3 coincides with one of the points P_{23}, P_{13}, P_{12} .

2. The answering of the given question offers no more difficulties, as soon as the locus of point S_1 in α_1 is known; so we shall first find this. Each ray l_1 of pencil (l_1) furnishing a single point S_1 , it is a rational curve, whose degree surpasses the number of times a transversal l passes through O_1 with unity. Now two transversals l pass through O_1 . For the pencil of planes (O_1, l_2) with (O_1, α_2) as bearing space and O_1, O_2 as axis marks on the line of intersection m of (O_1, α_2) with α_3 , a series of points (P) projectively related to the pencil of rays (l_3) , from which ensues that there are two rays l_3 passing through their corresponding point P and that therefore there

¹⁾ See loc. cit. § 5.

are two lines O_1P cutting the corresponding line l_3 , i.e. that two transversals l pass through O_1 . So the locus of S_1 is a cubic curve s_1^3 having O_1 as node, and so we find for the loci of S_2 and S_3 in α_2 and α_3 in the same way rational curves s_2^3 and s_3^3 with O_2 and O_3 as nodes.

3. To determine the degree of the scroll of the lines l we first investigate what this scroll has in common with an arbitrary space through α_1 . Each point Q lying outside α_1 which this space has in common with the scroll gives a line l having two points in common with that space, therefore lying entirely in that space. So that space can contain besides s_1^3 only a certain number of generatrices l of the scroll. As the line of intersection of α_2 with the assumed space through α_1 has three points in common with s_2^3 the number of generatrices to be found is three and the scroll, having a system of lines of order six in common with the assumed space, must be a tortuous surface O^6 of order six. So it is cut by an arbitrary space according to a twisted curve of order six; this section in general not degenerating is rational, its points corresponding one by one to the lines l and therefore to the rays of each of the pencils $(l_1), (l_2), (l_3)$. So the surface is of genus zero.

We call the locus just found — however not yet what was meant in the title — a surface, to show by this that the number of points is twofold infinite; by the predicate “tortuous” we express that it is not situated in a three-dimensional space.

4. By considering the three projective series of points $(A_1), (A_2), (A_3)$ marked by the three projective pencils of rays $(l_1), (l_2), (l_3)$ on $\alpha_1, \alpha_2, \alpha_3$ we easily prove that the plane α contains three generatrices of O^6 . For it happens, we know, three times that three corresponding points A_1, A_2, A_3 of the projective series of points $(A_1), (A_2), (A_3)$ lie in a same right line, which then becomes a generatrix l of O^6 ; for, the conics enveloped by the lines A_1A_2 and A_1A_3 connecting each point A_1 with the corresponding points A_2 and A_3 have besides α_1 still three common tangents.

To the rule that the tangents in a point of O^6 drawn to O^6 are situated in a plane, the points of intersection of two non-successive generatrices l form an exception. In such a point, through which the surface passes twice, a tangential plane will belong to each of the two lines l ; so it can be called a “biplanar node”. From the above is evident that O^6 possesses six biplanar nodes, the three points O_1, O_2, O_3 and the three points of intersection of the genera-

trices lying in α ; moreover we shall see directly that the number of those nodes is in general six, becoming infinite when it surpasses six, as takes place in the surface to be considered presently and which is indicated in the title.

5. We point out the fact, that the found surface O^6 is determined by the projective correspondence of the curves s_1^3 and s_2^3 in α_1 and α_2 , and we now show that this correspondence, characterised by the particularity of the corresponding triplets lying on α_1 and α_2 , is not the most general one can think of. To that end we take two rational curves s_1^3 and s_2^3 in two planes α_1 and α_2 , which planes for convenience' sake we assume for the present to be lying in our space, and which curves with the nodes O_1 and O_2 we suppose to be brought into projective correspondence in the most general manner. Are there then — we ask — to be found on s_1^3 three collinear points to which on s_2^3 three likewise collinear points correspond? The answer runs affirmatively; what is more: each point of s_1^3 forms one time a part of such a triplet and the bearing lines form a pencil of rays. If namely the point A_2 of s_2^3 corresponds to the point A_1 taken arbitrarily on s_1^3 , and if the central involution of the points B_1, C_1 of s_1^3 collinear with A_1 is represented by $(B_1 C_1)$, the non-central involution of the corresponding points B_2, C_2 of s_2^3 by $(B_2 C_2)$ and the central involution of the points B_2', C_2' of s_2^3 collinear with A_2 by $(B_2' C_2')$, then the two involutions $(B_2 C_2), (B_2' C_2')$ have a pair of points in common. If B_2°, C_2° is this pair and B_1°, C_1° on s_1^3 the pair corresponding to it, then $A_1, B_1^\circ, C_1^\circ$ and $A_2, B_2^\circ, C_2^\circ$ are two corresponding collinear triplets. If now Q_1 is the point of intersection of two such like lines l_1', l_1'' in α_1 and Q_2 the point of intersection of the corresponding lines l_2', l_2'' in α_2 , then the triple involution $(A_1 B_1 C_1)$ marked by the lines through Q_1 in s_1^3 must correspond to the triple involution $(A_2 B_2 C_2)$ marked by the lines through Q_2 in s_2^3 , with which we have proved what was asserted above.

With the aid of the preceding it is easy to show in how far the particularity of the corresponding triplets lying on α_1 and α_2 is a real one or an apparent one. With respect to the planes α_1 and α_2 placed in our space it is evidently an apparent one; for not one time but an infinite number of times it happens that three collinear points of s_1^3 correspond to three likewise collinear points of s_2^3 . If the planes α_1 and α_2 are placed in Sp_4 in such a way that an arbitrary point P_1 of α_1 coincides with an arbitrary point P_2 of α_2 , then however the three points in which s_1^3 is cut by the line $P_1 Q_1$ will correspond to three collinear points of s_2^3 , but the line through Q_2 ,

bearing the last three points will in general not pass through $P_2 = P_1$. So then there are no lines a_1 and a_2 to be drawn through the point of intersection P_{12} of the planes α_1 and α_2 cutting s_1^3 and s_2^3 in corresponding triplets.

6. We shall now consider the more general case of two projectively related curves s_1^3 and s_2^3 lying in such a way in α_1 and α_2 that through the point of intersection P_{12} no triplets of corresponding points bearing lines a_1 and a_2 are to be drawn. The argument leading to the order of the scroll, which is the locus of the line connecting the corresponding points of those curves, retains here its force. So we have but to determine the number of nodes. Of course O_1 and O_2 are nodes. If furthermore A_1A_2 and B_1B_2 are two generatrices cutting each other outside α_1 and α_2 , then A_1B_1 and A_2B_2 pass through P_{12} , as they must cut each other. So we consider the central triple involution $(A_1 B_1 C_1)$ marked by the pencil of rays with P_{12} as vertex in s_1^3 and the non-central triple involution $(A_2 B_2 C_2)$ of the corresponding triplets of s_2^3 ; then the latter furnishes as envelope of the sides of the triangles $A_2 B_2 C_2$ a definite curve of involution which makes us acquainted by the number of its tangents through P_{12} with the number of nodes not lying in α_1 and α_2 of the new surface O^6 . Now the class of the indicated curve of involution is four; for evidently four tangents pass through the node O_2 of s_2^3 . If to the two points of s_2^3 coinciding in O_2 the points M_1, N_1 on s_1^3 correspond, and if $P_{12}M_1$ and $P_{12}N_1$ cut the curve s_1^3 still in the point M_1', M_1'' and N_1', N_1'' , then the lines connecting P_{12} with the corresponding points M_2', M_2'', N_2', N_2'' are the only tangents of the curve of involution passing through P_{12} . So O^6 has here also six nodes.

7. It is now easy to see that the first surface O^6 of the three projective pencils of rays is found back, if the correspondence of the curves s_1^3 and s_2^3 is given in such a way that through the point of intersection P_{12} of α_1 and α_2 lines a_1 and a_3 pass bearing two triplets of corresponding points. The plane $\alpha_1\alpha_2$ is then again a plane a through three generatrices of O^6 and the line a_2 represents three of the four tangents to be drawn through P_{12} to the above found curve of involution, whilst the fourth tangent causes us to find a node not lying in α_1, α_2 or a . If we now cut the surface by the space determined by a and this node, the section will consist of the three generatrices in a and a curve of order three with a node, i. e. a rational plane cubic curve. The plane of that curve is then

the plane α_3 , the node of that curve the point O_3 of the first generation.

8. We now ask what arises when the planes α_1 and α_2 are placed in such a way in Sp_4 , that the points Q_1 and Q_2 coincide and therefore each line drawn through the point of coincidence P_{12} in α_1 is to be regarded as line a_1 . We then find that to every line a_1 through P_{12} in α_1 a definite line a_2 through P_{12} in α_2 corresponds, so that there is an infinite number of planes α . The locus of these planes α is a quadratic conic space with P_{12} as vertex; for the pencils of rays of the lines a_1, a_2 through P_{12} corresponding to each other in α_1, α_2 are evidently projectively related. This quadratic conic space must contain, as it contains all generatrices of O^6 , this tortuous scroll itself.

Now that the generatrices of this particular surface O^6 , being the surface indicated in the title, group themselves into triplets lying in a plane, there must be a locus of nodes. This is of order four. If namely we project the surface O^6 by means of the just found quadratic conic space out of P_{12} on to an arbitrary space not containing P_{12} , the projection is a quadratic scroll having the projections of the planes α as a system of generatrices. Of this surface O^2 the projections of α_1 and α_2 form thus two lines of the other system; for each of those two planes has a line in common with each of those planes α and from this ensues that the sections of α_1 and α_2 with the space of projection must have a point in common with the sections of the planes α with that space of projection. So in that space of projection each plane through one of the two lines contains a line of the system corresponding to the planes α and therefore the projections of four nodes, namely one on the first line and three on the second. So the projection of the nodal curve out of P_{12} on to the assumed space of projection is a curve of order four lying on O^2 , which has *one* point in common with each of the generatrices of one system, and *three* points with each of the generatrices of the other system. So the nodal curve itself is a tortuous curve of order four; it is rational as its projection is.

Considering the surface O^2 we see at the same time that the surface O^6 admits of an infinite number of planes cutting it according to a rational cubic curve, namely each plane through P_{12} and one of the lines of the system to which the projections of α_1 and α_2 belong.

So we find the following theorem:

“If we assume in two planes α_1 and α_2 two projectively related “rational cubic curves, if in these planes we determine the vertices “ Q_1, Q_2 of the corresponding central triple involutions on those

“curves and if now we place those planes in S_4 in such a way that “ Q_1 and Q_2 coincide in the points of intersection P_{12} of the planes, “the locus of the line connecting the pairs of corresponding points of “the cubic curves forms a tortuous surface with the following properties :

a. “It is projected out of P_{12} by a quadratic conic space, on “which two systems of planes are lying;

b. “It is cut by each plane of one system according to a cubic “curve with a node, by each plane of the other system according “to three generatrices;

c. “The cubic curves in two planes of the first system have no “point in common, neither have the triplets of lines in two planes of “the second systems; each cubic curve, however, is cut by each “generatrix;

d. “The generatrices cause a mutual projective correspondence “among all cubic curves and the cubic curves among all the gene-
ratrices.”

9. From the preceding ensues immediately that the tortuous scroll with a nodal curve k^4 can be represented on a plane. If in a plane σ we assume arbitrarily two pencils of rays with different vertices T_1, T_2 , and if we allow three arbitrary rays a_1, b_1, c_1 of the former to correspond to three rational cubic curves $s_{(a)}^3, s_{(b)}^3, s_{(c)}^3$ of O^3 , three arbitrary rays a_2, b_2, c_2 of the second to three generatrices $l_{(a)}, l_{(b)}, l_{(c)}$ of O^3 , then to each rational cubic curve $s_{(p)}^3$ corresponds a definite ray p_1 of the first pencil, to each generatrix $l_{(q)}$ corresponds a definite ray q_2 of the second; so we can assign the point of intersection of $s_{(p)}^3$ and $l_{(q)}$ to the point of intersection of p_1 and q_2 . The elements of exception of that representation are immediately found. If to the line connecting the vertices of the pencils of rays counted with the first pencil the curve s^3 corresponds and counted with the second pencil the generatrix l , and if S is the point of intersection of s^3 and l , then to point T_1 corresponds the line l , to point T_2 the curve s^3 and reversely to point S the line $T_1 T_2$. To each point P of the nodal curve k^4 correspond two points P', P'' of σ collinear to T_1 , because in the correspondence of $s_{(p)}^3$ to $l_{(p)}$ the node of $s_{(p)}^3$ represents two different points and two points of $l_{(p)}$ correspond to this point. As T_1 forms part of two representing pairs, the pairs belonging to the nodes of the generatrix l belonging to T_1 , this point is node and the curve of order four. This is also evident when we consider the rays of the other pencil. On each ray q lie two points of the curve forming

part of pairs corresponding to the points of the nodal curve lying on $l_{(q)}$, whilst T_2 corresponding to the node of the curve s^3 is likewise node of the curve. So in σ to the nodal curve k^4 corresponds a curve $k'^4(T_1^2, T_2^2)$, having T_1 and T_2 as nodes and being of genus *unity*. And to the rational space sections k^6 of O^6 correspond in σ curves $k'^4(T_1, T_2^3)$ through T_1 with T_2 as triple point, which is found immediately when we remember that an arbitrary space has three points in common with each of the rational cubic curves of O^6 and one point with each generatrix of O^6 . As is proper each of those rational curves $k'^4(T_1, T_2^3)$ has with the representation $k'^4(T_1^2, T_2^2)$ of the nodal curve k^4 besides T_1 and T_2 four pairs of points in common, corresponding to the four points of the nodal curve lying in the selected space, whilst two curves $k'^4(T_1, T_2^3)$ cut each other besides in T_1 and T_2 in six points corresponding to the six points of intersection of O^6 with the plane of section of the two spaces.

10. The locus of the bisecants of a tortuous curve of order four is a curved space of order three having the indicated curve as nodal curve. For the twofold infinite number of bisecants furnishes a triple infinite number of points and three of these lie on an arbitrary right line l , because the curve projects itself out of l on to a plane not intersecting l as a rational curve of order four and this plane curve possesses three double points. If we apply this to the nodal curve k^4 of O^6 , taking into consideration that the generatrices of this scroll are all bisecants of k^4 , we find :

“The tortuous scroll O^6 with the nodal curve k^4 is the complete section of a quadratic conic space with a curved space of order three, of which the first passes once, the second twice through k^4 .”

Whilst the cubic space is the locus of the bisecants of k^4 , the quadratic conic space with P_{12} as vertex is the locus of the planes containing three points of k^4 and passing through P_{12} .

The tortuous surface O^6 with a nodal curve k^4 is determined by this curve and the point P_{12} . As P_{12} lies arbitrarily with respect to k^4 each tortuous curve k^4 in Sp_4 is nodal curve of a fourfold infinite number of surfaces O^6 .

11. We observe that the case just considered of the correspondence of the curves s_1^3 and s_2^3 , where a tortuous scroll with a double curve k^4 is formed, is not the most particular one that one can think of. If for instance — instead of starting from two rational curves s_1^3 and s_2^3 taken arbitrarily in α_1 and α_2 — we start by making the pointfields α_1 and α_2 to be in projective correspondence and then

continue to assume two rational curves s_1^3 and s_2^3 corresponding to each other in this manner, then of course to every three collinear points of s_1^3 correspond three likewise collinear points of s_2^3 , and therefore we can take for the above determined pair of points Q_1, Q_2 any corresponding pair of points of a_1, a_2 . In this special case a plane α through three generatrices will present itself already for arbitrary position in Sp_4 and the position, that an infinite number of those planes present themselves, will be able to be brought about in a twofold infinite number of different ways; in the last case however the three generatrices lying in a plane α pass through a point, as the series of points lying on the lines of intersection a_1, a_2 of this plane with a_1, a_2 are perspectively related, so that the locus of the nodes becomes a *conic* instead of a k^4 . In both cases surfaces O^6 are formed differing from the above also in this respect that they admit not only of a single but of a twofold infinite number of spaces through three generatrices.

12. Also when we start from two projective rational curves s_1^3, s_2^3 in not projectively related fields a great number of special cases are left for consideration. So the point of intersection P_{12} of the planes α_1, α_2 can lie

- a. on one of the curves s^3 ,
- b. on both curves s^3 ,
- c. on the two curves s^3 and correspond to itself,
- d. it can be the node of one of the curves s^3 ,
- e. it can be the node of one of the curves and lying on the other,
- f. it can be the node of one of the curves and forming on the other part of the two points corresponding to this node,
- g. it can be the node of both curves,
- h. it can be the node of both curves and in such a way that one pair of points coinciding in this node has a point in common with the other,
- i. it can be the node of both curves and in such a way that the pairs of points coinciding in this point correspond to each other.

Of course the number is still increased if we further permit the pointfields α_1, α_2 to be projectively related. We do not wish to investigate more closely all these special cases. Neither do we intend to investigate here the scrolls presenting themselves in both cases of projective or non-projective pointfields α_1, α_2 as the locus of the line P_1P_2 connecting corresponding points P_1, P_2 of *other* curves of the same genus and of the same order, which are projectively related. We only wish to observe that these scrolls will lie in the

case of the projectively related pointfields α_1, α_2 on the locus of the line $P_1 P_2$ connecting corresponding points P_1, P_2 of the planes α_1, α_2 , which is a quadratic or a cubic space according to the point of intersection P_{12} of α_1 and α_2 corresponding to itself or not.

13. We conclude with the deduction of the equations of the above found cubic and quadratic spaces which have in common the surface O^6 with the nodal curve k^4 and to this end we start from this curve. If the curve k^4 is given by the system of equations:

$$q x_i = \lambda^i, (i = 0, 1, 2, 3, 4). \quad (1)$$

— and in this way the simplex of coordinates can always be taken —, and if the point which is the vertex of the quadratic conic space with respect to that same simplex has the coordinates $(y_0, y_1, y_2, y_3, y_4)$, then the equations

$$\begin{vmatrix} x_0 & x_1 & x_2 \\ x_1 & x_2 & x_3 \\ x_2 & x_3 & x_4 \end{vmatrix} = 0, \quad \begin{vmatrix} x_0 & x_1 & x_2 & x_3 \\ x_1 & x_2 & x_3 & x_4 \\ y_0 & y_1 & y_2 & y_3 \\ y_1 & y_2 & y_3 & y_4 \end{vmatrix} = 0 \quad (2)$$

represent those two spaces. We see namely immediately that the first determinant by insertion of the relations (1) shows three equal rows, i.e. that the cubic space represented by the first equation must have the points of the curve k^4 as nodes, and must thus contain each bisecant of k^4 . Further it is equally clear that the second determinant by insertion of the relations (1) shows two equal rows and that, when substituting y_i for x_i , two pairs of equal rows appear, from which ensues that the quadratic space represented by the second equation passes through k^4 and has a node in y .

A more direct deduction of the equation of the locus of the bisecants of the curve k^4 was communicated formerly (*Proceedings* of the February meeting of 1899 vol. I, page 313). It is founded on the wellknown lemma, according to which the product of two matrices $M_1^{r,k}$ and $M_2^{r,k}$ with r rows and k columns, taken according to the rows, vanishes identically for $r > k$. This same lemma leads to the deduction of the equation of the locus of the planes containing three points of k^4 , and passing through $(y_0, y_1, y_2, y_3, y_4)$. An arbitrary point P of the plane $P_1 P_2 P_3$ through the points P_1, P_2, P_3 of k^4 corresponding to the parameter values $\lambda_1, \lambda_2, \lambda_3$ is represented by

$$q x_i = p_1 \lambda_1^i + p_2 \lambda_2^i + p_3 \lambda_3^i, (i = 0, 1, 2, 3, 4) \quad (3)$$

If the plane $P_1 P_2 P_3$ passes moreover through the given point $(y_0, y_1, y_2, y_3, y_4)$, also the relations

$$\sigma y_i = q_1 \lambda_1^i + q_2 \lambda_2^i + q_3 \lambda_3^i, \quad (i = 0, 1, 2, 3, 4) \dots (4)$$

hold, and now the equation sought for is found by eliminating the nine quantities $\lambda_1, \lambda_2, \lambda_3, p_1, p_2, p_3, q_1, q_2, q_3$ out of the ten equations (3) and (4). This takes place by inserting the values given by (3) and (4) in the left hand member of the second equation (2). For by this we find

$$Q^2 \sigma^2 \begin{vmatrix} x_0 & x_1 & x_2 & x_3 \\ x_1 & x_2 & x_3 & x_4 \\ y_0 & y_1 & y_2 & y_3 \\ y_1 & y_2 & y_3 & y_4 \end{vmatrix} = \begin{vmatrix} 1 & 1 & 1 \\ \lambda_1 & \lambda_2 & \lambda_3 \\ \lambda_1^2 & \lambda_2^2 & \lambda_3^2 \\ \lambda_1^3 & \lambda_2^3 & \lambda_3^3 \end{vmatrix} \cdot \begin{vmatrix} p_1 & p_2 & p_3 \\ p_1 \lambda_1 & p_2 \lambda_2 & p_3 \lambda_3 \\ q_1 & q_2 & q_3 \\ q_1 \lambda_1 & q_2 \lambda_2 & q_3 \lambda_3 \end{vmatrix} = 0.$$

We considered in the above cited communication equations forming the extension of the first of the equations (2) to the curve k^{2n} of the space Sp_{2n} . In connection with this we shall notice that the second of the equations (2) admits of corresponding extensions, in which those of the first are included. However, these will be developed elsewhere.

Mathematics. — “*The PLÜCKER equivalents of a cyclic point of a twisted curve.*” By W. A. VERSLUYS. (Communicated by Prof. P. H. SCHOUTE.

If a twisted curve C admits of a higher singularity (cyclic point) of order n , of rank r and of class m , it is to be represented according to HALPHEN¹⁾ in the vicinity of this singular point M by the following developments in series:

$$\begin{aligned} x &= t^n, \\ y &= t^{n+r} [t], \\ z &= t^{n+r+m} [t], \end{aligned}$$

where $[t]$ represents an arbitrary power series of t , starting with a constant term.

If n , r and m satisfy the conditions that

$$\begin{aligned} 1^\circ & \quad n \text{ and } r, \\ 2^\circ & \quad r \text{ and } m, \\ 3^\circ & \quad n \text{ and } r+m, \\ 4^\circ & \quad n+r \text{ and } m \end{aligned} \tag{A}$$

are mutually prime, then this higher singularity $M(n, r, m)$ for

¹⁾ Bull. d. l. Soc. Mat. d. France t. VI p. 10.

the formulae of CAYLEY-PLÜCKER and for the genus is equivalent to the following numbers of ordinary singularities :

$$\begin{aligned}
 & n-1 \text{ cusps } \beta, \\
 & \frac{(n-1)(n+r-3)}{2} \text{ nodes } H, \\
 & m-1 \text{ stationary planes } \alpha, \\
 & \frac{(m-1)(m+r-3)}{2} \text{ double planes } G, \qquad (B) \\
 & r-1 \text{ stationary tangents } \theta, \\
 & \frac{(r-1)(r+m-3)}{2} \text{ double generatrices } \omega_1, \\
 & \frac{(r-1)(r+n-3)}{2} \text{ double tangents } \omega_2.
 \end{aligned}$$

For a curve with only ordinary singularities we always have $\omega_1 = \omega_2$.

If the curve admits of higher singularities, then the tangents in these singular points will not have to count for as many double tangents to the curve as they must count for double generatrices of the developable belonging to the curve. The number ω will then be different for the formulae of CAYLEY-PLÜCKER, relating to a section and for those formulae relating to a projection, i. o. w. the singularity ω of a twisted curve appearing in a term $(x + \omega)$ is not always the same as the one appearing in the term $(y + \omega)$.

So the formula

$$y - x = v - \mu^1)$$

is no longer correct as soon as the curve has higher singularities for which order and class are unequal.

The above as well as the following results do not hold for a common cusp $\beta(2, 1, 1)$ and for a common stationary plane $\alpha(1, 1, 2)$, the conditions (A) not being satisfied for these cyclic points.

Through the singular point $M(n, r, m)$ pass

$$\frac{n(n+2r+m-4)}{2}$$

branches of the nodal curve of the developable O belonging to the curve C .

All these branches touch the curve C in M and have in M with the common tangent

$$\frac{(n+r)(n+2r+m-4)}{2}$$

coinciding points in common.

¹⁾ SALMON. 3 Dim. § 327.

These branches have in M the same osculating plane as C and with this osculating plane they have in M

$$\frac{(n+r+m)(n+2r+m-4)}{2}$$

coinciding points in common.

From the conditions (A) ensues that $(n+2r+m)$ is even, so that the three above numbers are integers.

The second polar surface of O according to an arbitrary point meets in the point $M(n, r, m)$ the cuspidal curve

$$(n+r-2)(n+r+m)$$

times and the nodal curve

$$\frac{n+2r+m-4}{2} (n+r-2)(n+r+m)$$

times.

Each point R , where the tangent in M still meets a sheet of the surface O , counts for

$$r^3 + rm - m - r$$

points of intersection of the nodal curve with the second polar surface.

In the equation of CREMONA ¹⁾ serving to determine λ (number of cusps of the nodal curve) we must add for every singular point $M(n, r, m)$ in the second member of the equation a term

$$(n+r-2)(n+r+m).$$

In the equation of CREMONA ²⁾, serving to determine τ (number of triple points of the nodal curve) we must add for every singular point to the second member of the equation a term

$$\frac{n+2r+m-4}{2} (n+r-2)(n+r+m)$$

and for the corresponding points R a term

$$(n+2r+m-4)(r+m)(r-1).$$

The decrease of λ and τ arising from the presence of a point $M(n, r, m)$ is not equal to the decrease of λ and τ caused by the ordinary singularities necessary to form a singularity $M(n, r, m)$. So the equivalence of the values expressed in (B) does not extend to numbers which are found by means of a second polar surface.

Delft, November 1905.

¹⁾ CREMONA-CURTZE, Oberflächen § 104.

²⁾ loc. cit. § 109.

Astronomy. — *“Preliminary Report on the Dutch expedition to Burgos for the observation of the total solar eclipse of August 30, 1905,”* communicated by Prof. H. G. VAN DE SANDE BAKHUYZEN, in behalf of the Eclipse Committee.

In March 1904 the Eclipse Committee determined to fit out on a small scale an expedition to Spain to observe the total solar eclipse of August 30, 1905. The means for it were found from some liberal gifts of private persons and of societies (Provinciaal Utrechtsch Genootschap, Teyler's Stichting, Utrechtsch Oud-Studentenfonds, Natuur en Geneeskundig Congres). As observers the same persons were appointed who had been sent to Sumatra in 1901: Messrs. W. H. JULIUS, J. H. WILTERDINK and the undersigned. The observations were to include the spectrography of the corona and of the sun's limb and, provided a fourth observer should offer himself to join as a volunteer, the radiation of heat of the corona.

A volunteer was soon found in the person of Mr. MOLL, assistant for physics at Utrecht, and so the entire programme could be worked out.

The outfit of the expedition consisted of:

- a siderostat with a coelostat apparatus;
- two slit-spectrographs, to be directed on the coelostat mirror;
- a prismatic camera, to be directed on the northern polar mirror;
- a heat actinometer;
- a pyrheliumeter;
- a sextant with accessories;
- three chronometers and other auxiliary apparatus.

As the principal instruments were also used for the eclipse of 1901, I refer for the description of them to previous publications (These Proc. III p. 529).

The sextant and two of the three chronometers were kindly placed at our disposal by His Excellency “de Minister van Marine” out of the collection of instruments at Leyden.

On the 13th of August the party arrived at Burgos. This town had been chosen for the observations not only on account of its favourable situation and other outward advantages, but also because, as far as was known at the time, it would not be visited by other expeditions. These advantages were lost through the visit of H.M. the King of Spain, on which occasion the town council of Burgos organised a series of festivities which seriously interfered with the astronomical work. For it is chiefly owing to those feasts that in spite of all

endeavours we could get no assistants from among the educated inhabitants of Burgos. At last one volunteer was found for the spectrographic observations, and fortunately on the day of the eclipse some assistants offered their help; without this help the measurements of the heat radiation especially would have been entirely impossible.

The eclipse has been observed under very untoward circumstances. The station of observation, the hill Lilaila, at 3 kilometers south east of Burgos (some 18 kilometers north of the central line) was a true desert of sand where clouds of dust and sand were blown up by the usually very strong wind, from which the tents, kindly lent us by the Spanish war administration could only partly protect the instruments.

Especially the siderostat, which as a matter of course could not be entirely covered, suffered very much from the sand-storm; although it had been cleaned on August 29, the wheelwork did not work properly on August 30. The piers once being erected, it was impossible to change the station of observation; moreover, Lilaila offered the advantage that we could make use of the determinations of time and geographical coordinates made by the Madrilian astronomers in whose camp our instruments were standing.

The weather on the eclipse day was very unfavourable. The 1st contact could not be observed owing to clouds, and though there were some bright moments between the 1st and 2nd contact, the observation of totality seemed hopeless. One minute before the 2nd contact the rain ceased, the caps of the siderostat mirror could be taken off, the clouds broke, and the corona was fairly visible during $3\frac{1}{2}$ minutes, sometimes even clearly visible.

Unfortunately totality began 20 seconds earlier than the computation had predicted, — it seems that also in Algiers and at other places in Spain a fairly large difference has been stated between observation and computation — so that the observers were taken by surprise by the phenomenon, much to the detriment of a smooth carrying out of the programme.

For a detailed description of the observations I refer to the annexed papers, which show that the results for some instruments, the very unfavourable circumstances considered, may be called satisfactory.

At the end of my report I wish to acknowledge thanks to the Madrilian astronomers, who hospitably made room for us in their camp and who were very obliging to us in all respects; to the Spanish civil and military authorities who kindly allowed us exemp-

tion from import-duties and placed some tents at our disposal; and lastly to the Compañía del Norte who forwarded the luggage of the eclipse party by express at reduced rates.

The Secretary of the Committee
A. A. NIJLAND.

Utrecht, November 1905.

SUPPLEMENT I. *Measurement of the heat produced by the integral radiation of the corona and of the solar disk, by Prof. W. H. JULIUS.*

The object of our heat observations was, as in 1901, 1st. to settle the question of the order of magnitude of the coronal radiation, and 2nd. to determine the curve of the total radiation from the first until the fourth contact, with the aim of deriving from it the distribution of the radiative power over the solar disk.

The investigation has been carried out with the same actinometer that had been constructed for the Sumatra eclipse ¹⁾; in it the rays are caught directly on a thermopile, without the intervention of lenses or mirrors. As long as the radiation was sufficiently intense, absolute determinations with ÅNGSTRÖM's pyrhelimeter were also made at intervals, in order to make sure whether the indications of our sensitive actinometer might be considered proportional to the received radiation. Such proving to be the case even for intense radiations, we were quite justified in assuming proportionality also to exist for the feeble radiation falling beyond the range of the pyrhelimeter.

The astronomers of Madrid had a small house built in the observation camp; they kindly allowed us to dispose of one of the rooms for setting up the galvanometer and performing the necessary laboratory work.

Four persons were required for manipulating the apparatus, two inside and two outside the room. Mr. W. J. H. MOLL, who has also had a prominent share in the preparation of the observations and the setting up of the instruments, was in charge of the absolute measurements and of noting down all the readings together with the corresponding times. The operations of directing and exposing the actinometer and the pyrhelimeter at signals, given by the observers inside the room, were performed very punctually by P. ELEUTERIO MARTINEZ S. J., phys. prof. at Valladolid, and P. ANTONIO DE

¹⁾ Total Eclipse of the Sun. Reports on the Dutch Expedition to Karang Sago, Sumatra, N^o. 4. Heat Radiation of the Sun during the Eclipse, by W. H. JULIUS.

MADARIAGA, S. J., theol. prof. at Burgos, to whom we express once more our sincere thanks for their very valuable assistance. I myself regulated the resistance in the circuit of the thermopile, and read the galvanometer deflections.

The conditions for measuring radiation were much more favourable now at Burgos than during the 1901 eclipse at Karang Sago; for then the phenomenon was permanently veiled by rather thin clouds of very variable transparency, covering the whole sky; this time heavy clouds caused the Sun to be indeed absolutely invisible now and then, but between the epochs of the first and the fourth contact there were intervals in which the phenomenon showed itself in perfectly clear patches of the firmament. The favourable periods have all been utilized; thus we were able to determine some parts of the radiation curve very sharply. After the results of the 81 observations had been plotted down on millimeter paper, we saw that the missing parts of the curve could be inserted with a fair chance of exactness.

Fortunately the time between second contact and 11 minutes after third contact was among the favourable periods. This period, however, had been preceded by full half an hour during which no observations could be made; and as the rift in the clouds, through which totality just became visible in our camp, came quite suddenly, we were not prepared and lost at least a minute after second contact in arranging our apparatus for highest sensitivity. Nevertheless we compared three times the radiation of the corona with that of a portion of the sky at a distance of about four degrees from the Sun. The observed deflections were 9, 13 and 33 scale divisions; then a sudden increase showed that totality was over. The effect produced by full sunshine corresponded to 1800000 divisions, when reduced to the same resistance of the circuit. So the smallest effect observed during the total eclipse was $\frac{1}{200000}$ of the radiation of the uneclipsed

Sun, or about $\frac{2}{5}$ of the radiation of the full Moon. This value must be considered as an upper limit to the radiation emitted by those parts of the corona, which were not screened by the Moon at the epoch of central eclipse. Indeed, the radiation must pass through a minimum about the middle of totality, and we are not sure that the first of the three observations above mentioned corresponded exactly to the central position. Moreover, since a few thin clouds may have traversed the compared fields, there is some uncertainty left.

An account of the observations made before and after totality and a copy of the resulting radiation curve will be found in the com-

plete report shortly to be published. The shape of the unshielded part of the solar disk being known for every moment, and the corresponding radiation being given by the ordinates of the curve, we have the data for calculating how the apparent emissive power increases from the limb unto the centre of the disk. This method avoids certain sources of error by which the results must be disturbed when the distribution of the energy is measured in an *image* of the Sun, viz.: the diffusion of rays by the Earth's atmosphere and by the optical train, as well as the consequences of variable radiation emitted by the apparatus. We find a greater difference between the heat from the limb and that from the central parts, than has been obtained by the other method. According to our measurements the decrease of the integral radiation from the centre to the limb follows nearly the same law that was found by H. C. VOGEL, with the spectrophotometer, to hold for rays of wave-lengths between 500 and 600 $\mu\mu$.

SUPPLEMENT II. *The prismatic camera.* By Prof. A. A. NIJLAND.

The prismatic camera was mounted above the northern polar mirror in such a manner that the dispersion direction is almost perpendicular to the expected crescents of the first and the second flash.

The programme was as follows:

- 1st flash: 5 exposures, each of $\frac{1}{2}$ second on one plate at intervals of 3 seconds;
- totality: 2 corona exposures, each of one minute and a half, at two different positions of the instrument so that the plate in the second position might show a part of the spectrum which did not occur on the first corona plate.
- 2nd flash: 5 exposures in the same manner as those of the 1st flash.

CADETT's spectrum plates were used.

As soon as we found that we could not count upon assistance of volunteers I had after some training acquired the necessary skill to carry out this programme, yet I disliked the prospect of having to do everything entirely by myself. Therefore I gladly accepted the help of Dr. J. KAPLAN (from St. Petersburg) who, having arrived at Burgos on August 29, immediately offered his assistance. I wish to express here my cordial thanks to him for his skillful aid.

The two corona negatives show traces of the corona rings λ 3987 and λ 5303. In consequence of the general cloudiness the plates are veiled, to which it is undoubtedly owing that the very bright green corona ring, which visually was so clearly visible, has produced such a faint image.

The plate taken of the second flash failed entirely because the end of totality took place 20 seconds earlier than had been computed, and took me by surprise while I changed the plates.

Also the first flash came 20 seconds before the time computed; fortunately through a window in the tent I observed the rapid approach of totality, and could start the series of 5 exposures long before the warning sign agreed upon was given. It later appeared that the second negative has caught about the second contact.

The second negative shows a great variety of details, which in the ultra violet have suffered so much from absorption that for those parts of the spectrum the first negative, taken 3 seconds before totality, forms a very welcome supplement. These two spectra together show between λ 470 and λ 367 350 crescents of very different length and brightness; in the discussion of the meaning of the observed particulars the three other negatives may also be used to advantage. This discussion is reserved, however, for a more detailed report; I only mention that the enigmatic doubling of the flash crescents of 18 May 1901 can, in the case considered here, occur only for wave-lengths above γ 434. Though from this it follows that the doubling may be partly due to the slanting position of the plate the possibility of the existence of double lines in the flash spectrum is noways excluded by this.

A closer consideration of this question is also reserved for a more detailed report.

SUPPLEMENT III. *Report on the operations with the two slit-spectrographs for the solar eclipse of August 30, 1905* by
J. H. WILTERDINK.

Operations at Leiden. The instruments, constructed for the solar eclipse of 1901 arrived here such a short time before they had to be sent off to Sumatra that a thorough investigation of them was then quite out of the question. This has been made now.

As had been decided upon the siderostat provided with a coelostat apparatus would serve to feed the three spectral apparatus, and in

order to render the mounting more simple, the coelostat mirror would be used for both slit-spectrographs instead of the southern siderostat mirror.

The Eclipse Committee had consented to an alteration of the clock-work of the coelosiderostat, so that the number of the wheels in outside gearing, of which some were very difficult to get at for cleaning, was reduced from 5 to 2; I had this constructed by Mr. GAUTIER. The clock-work was received here in the middle of July 1905. It has worked excellently.

The two spectrographs were carefully examined and cleaned.

I determined the zeros of the micrometer screws, indicating the slit-width, by means of diffraction observations, a method which allows of an accuracy of some microns. The adjustment of the slit in the principal focus of the collimator object glass, which could not be easily done with the desired accuracy in a direct way, was indirectly performed in the following manner. By photographs made according to the method of HARTMANN I determined the position of the photographic plate in the principal focus of the camera object glass. Then the collimator was placed as a source of light in front of the camera object glass, and the same photographs were made again. From the difference between the focus found now and the principal focus found before we could derive how much the slit had to be removed in order to bring it in the principal focus of the collimator object glass.

In this experiment it appeared however that both the collimator and the camera object glass of the large spectrograph had a very great spherical aberration, and with full aperture they were unfit to form sharp images, while a diaphragm would cause a loss of light which, with a view to our purpose, was inadmissible.

Therefore I ordered of STEINHEIL new object glasses; a single object glass with a field of sharp definition of 2° for the collimator and a compound one with a field of sharp definition of 15° for the camera.

Neither of them were in store and in the available time this firm could only supply object glasses of the first kind of which two pieces were sent to me.

Although their fields of sharp definition were too small for the camera I determined to try them also for this purpose, as the middle of the spectrum was of chief interest for the photograph intended. The spherical aberration was exceedingly small.

Meanwhile the Steamboat Company had sent word that everything had to be shipped 10 days earlier than had been agreed upon,

so that there remained no time for further experiments in Holland. The object glasses of ZEISS of the small spectrograph were found to be in excellent order, this instrument had produced very fine spectral photographs. In order to slide the photographic plate for this instrument during the flash phenomenon I put the clock-work in order which in Sumatra had served for the motion of the axis carrying the four photographic cameras. I devised an arrangement which let slip the cord, fastened to the plate-holder, with greater velocity than had been required in Sumatra.

As photographic plates I chose, after experiments for comparison with four different kinds of SCHLEUSSNER's plates, his "Sternwarte" and "orthochromatic" plate. At the last moment I fortunately obtained two kinds of plates of CADETT, known to be very good.

Operations at the camp. Besides the mounting of the different instruments, the operations at the camp included therefore also several experiments, as: tests for comparison of the old and new object glasses and tests of the German and English plates.

Owing to a delay in the construction of the pier, and because I had to take charge of two instruments, whereas according to the original plan of the expedition each spectral apparatus would be worked by a separate observer, and also owing to the continual disturbances from the side of the public, these operations did not get on at the desired speed, so that at the last moment a great many things remained to be done and the necessary calmness, which in America in 1900 and in Sumatra in 1901 so much contributed to regular proceedings, was entirely wanting.

After tests for comparison we chose for object glasses those of STEINHEIL, and for plates the English ones, especially as the orthochromatic plates gave a much more regular spectrum than the German plates of the same kind.

Assistance, so easily obtained at the previous expeditions was difficult to get here. Though several weeks before we had asked for it on all sides, a promise of assistance reached us only a few days before the critical moment. Not much could be expected from it, but I myself intended to work the small spectrograph with the sliding plate-holder and I hoped that the very simple operations with the large spectrograph would offer no difficulties. Joint rehearsals as were held for days together in America and Sumatra were quite out of the question owing to the above mentioned circumstances. Yet, though all things were so different from what we might wish them to be, I still hoped to obtain useful results.

This, however, has not been the case.

The day of the eclipse. Through the unfortunate concurrence of three entirely different disturbances, where two of them would not have been able to prevent success, the results of the two slit-spectrographs have come to nothing.

The first of these disturbances happened as follows. Some hours before the beginning of the eclipse, the steel band which transfers the motion of the siderostat axis to the coelostat axis was broken entirely without my fault through a movement which was altogether inadmissible for my part of the siderostat, which we used in common. At one end of this band, which was fixed between two copper plates by means of two steel screws, the two holes through which these screws passed were torn up. This effect could not possibly have been reached by a stress of 100 kilograms. The fact that this happened instead of the steel band simply sliding over the steel axis was the best refutation of the often quoted opinion that this way to transfer motion should not be reliable. The dust, inevitable in an eclipse camp, naturally heightened the friction of the band on the axis. Hence it is evident that the disturbance to be mentioned next would have had no effect on the instrument if it had been in the condition as it was before the fracture. Fortunately I had spare bands taken with me and a new one could be put on, which operation, however, cost three quarters of an hour of our time which began to grow more and more precious, nor did this incident contribute to the quietness so indispensable at an eclipse.

During the first part of the first partial phase, as often as the sun was visible through the clouds, we could control whether the image of the sun fell on the slit and it could be easily kept there.

Now, however, something happened which in America and in the East Indies would have been utterly impossible, but proved to be inevitable in Spain as experience had taught me during a fortnight. During the second half of the first partial phase, a little more than a quarter of an hour before the critical moment my assistant admitted several persons near my apparatus. Against this I was altogether powerless. It seems that one of these unwished for visitors has pushed against the coelostat mirror and thus disturbed it, from which may be inferred that the newly fastened band has more or less given way at its fastening points and the friction on the axis was not sufficient to prevent disturbance.

Had not over and above — the third disturbance — the sky been clouded and the sun for the rest of the time been invisible, I should

have detected the absence of the image by means of the controlling telescope and could have removed the mirror into its proper position, now, however, the absence of any image was quite accounted for by the clouds. As a few seconds before the beginning of totality the sun broke through the clouds the absence of the image was stated and the displacement of the mirror became manifest; yet without proper assistance it was impossible to put it in order.



(December 21, 1905).

Koninklijke Akademie van Wetenschappen
te Amsterdam.

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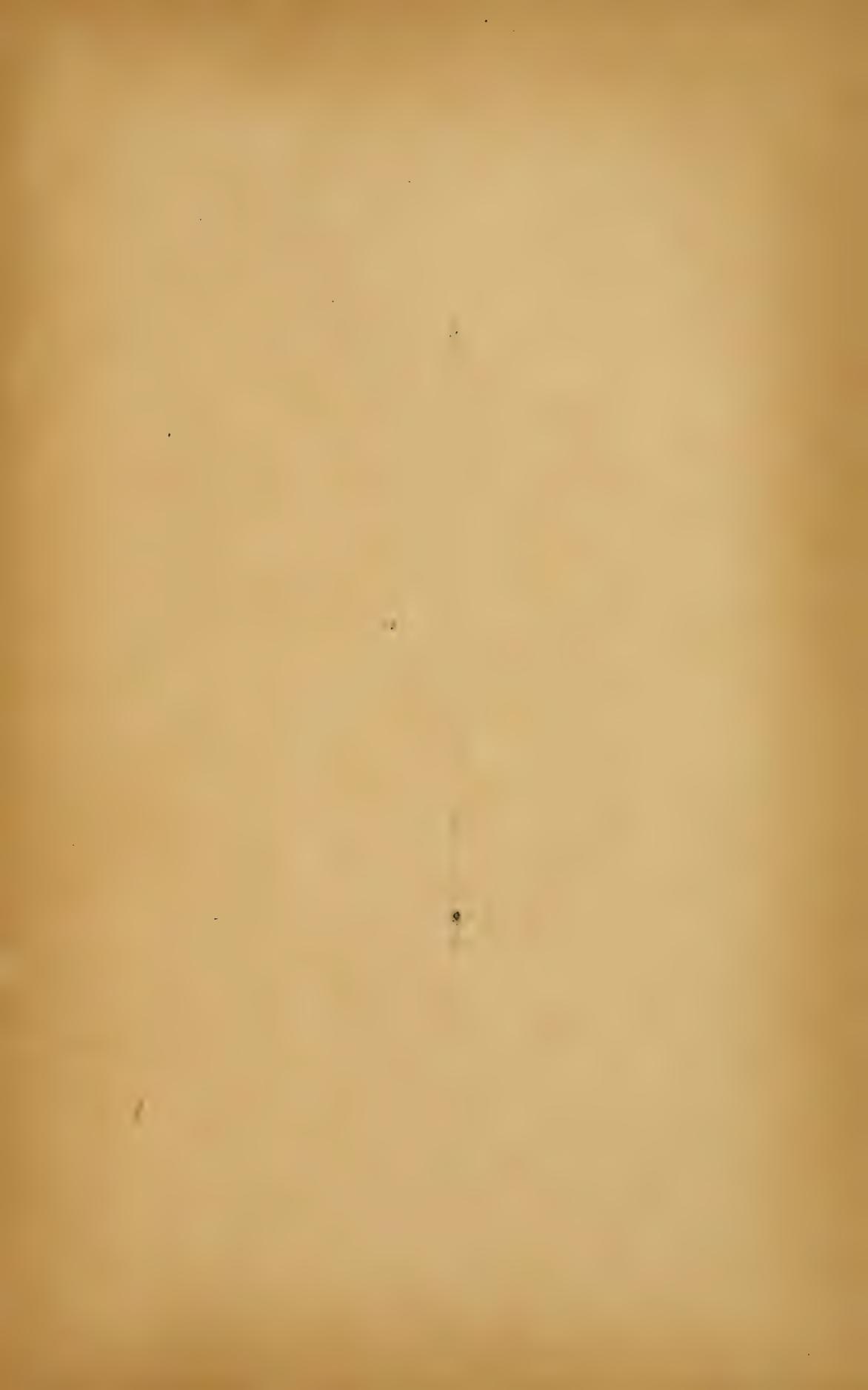
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