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 $G_{\nu}(A, B, C, D)$ , for which  $\lambda = \nu$ , is an  $F^4$  with the double points A, B, C, D, E, G passing through the quadruples of lines E(A,B,C,D) and G(A, B, C, D) and the edges of the tetrahedron ABCD. Of the total intersection  $\varrho^{16}$  of these surfaces, having A, B, C, D, E as fourfold points, the ten right lines connecting the points A, B, C, D, E two by two, separate; so has been proved what was asserted.

### Botanics. — "Preservatives on the stigma against the Germination of Foreign Pollen." By Dr. W. BURCK. (Communicated by Professor HUGO DE VRIES.)

It is well known that the pollen of many plants gets destroyed as soon as it comes into contact with water. The both coats (exine and intine) are then seen to burst, while the contents stream out vigorously  $^{1}$ ).

Further it is known that frequently pollen is successfully brought into germination in sugar solutions at different degrees of concentration, or also in gelatin, agar-agar, gum, dextrine etc., or in mixtures of these substances with sugar <sup>2</sup>).

For number of pollen species, however, there has not yet been found, hitherto, a solution in which germination was observed (many *Compositae*, *Umbelliferae*, *Urticaceae*, *Malvaceae*, *Ericaceae*, and many others).

The idea that chemical substances occurring in the moisture of the stigma would here play a part, has been frequently expressed, among others by MOLISCH<sup>8</sup>), in 1892, who inferred it from the fact

<sup>1)</sup> On the relation of pollen to water compare, among others, BENGT LIDFORSS, Zur Biologie des Pollens. Pringsheim's Jahrbucher Bd. XXIX, 1896, pag. 1-39.

HANSGIRG, Beiträge zur Biologie und Morphologie des Pollens. Sitzungsber. der K. Bohm. Gesellsch. 1897, XXIII.

BENGT LIDFORSS, Weitere Beitrage zur Biologie des Pollens. Pringsheim's Jahrb. Bd. XXXIII, 1899.

<sup>2)</sup> See, among others, VAN TRIGHEM, Recherches physiologiques sur la végétation libre du pollen et de l'ovule. Annales des sc. nat. Bot. 5e série, tom. XII, 1872.

L. KNY, Sitzungsber. d. botanischen Vereines d. Provinz Brandenburg XXIII, 1881. E. STRASBURGER, Neuere Untersuchungen uber den Befruchtungs-Vorgang bei den Phanerogamen etc. Jena 1884.

E. STRASBURGER, Ueber fremdartige Bestaubung. Pringsheim's Jahrb. für w. Botanik Bd. XVIII, 1886.

H. MOLISCH, Zur Physiologie des Pollens, mit besonderer Rucksicht auf die chemotropischen Bewegungen der Pollenschlauche. Sitzungsber. der math. naturw. Classe der K. Akademie der Wissensch. Wien Bd. CII, Abth. I, 1893.

<sup>&</sup>lt;sup>3</sup>) MOLISCH, I.c. pag. 429.

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that the pollen of *Azalea*, which could not be brought into germination in water, formed beautiful pollen-tubes when, together with the pollen, a stigma of *Azalea* was introduced into the drop of water.

To me, also, it has seemed probable, for years already, that pollen, which did not germinate in water or sugar solutions, wanted a special chemical stimulus to call forth the process of germination, and that in the either or not being present of such a chemical substance in the liquid of the stigma, in some cases the explanation might be found of the striking fact, that often the pollen cannot germinate on the stigma of a plant, which stands in close relationship to the plant producing the pollen, while it germinates very well on the stigma of a plant belonging to a systematically distant family <sup>1</sup>).

Already in 1889 I thought this might be inferred from the facts following. The pollen of Mussaenda rufinervis, M. frondosa, M. Teijsmanniana, M. Afzelii, M. Reinwardtiana and M. cylindrocarpa, belong to those species of pollen which resist the action of water and are not prejudiced by it, but which do not, however, pass into germination in it.

When now this pollen is introduced into a drop of destilled water, in which is at the same time put a stigma of the plant, nearly all the pollen-grains will begin, within the space of two hours, to form tubes, which rather quickly attain a considerable length.

It is not necessary therefore to use the whole of the stigma; the germination sets in as well if only a half, a fourth, or an eighth part is put in the drop of water, and I even saw distinct germination on addition of  $\frac{1}{16}$  part of the stigma.

The same experiment to make pollen germinate in the thus diluted stigma-liquid of the same plant, succeeded for many species of *Pavetta* and further for *Pentas carnea*, *Eriostemma floribunda*, four species of *Begonia*, for *Uvaria purpurea*, *U. hirsuta*, *Torenia Fournieri*, and for *Murraija exotica*, plants belonging to the *Rubiaceae*, *Begoniaceae*, *Anonaceae*, *Scrophulariaceae* and *Rutaceae*.

With a great many other plants, however, the experiment did not succeed.

Furthermore I had found that for *Mussaenda* it did not matter whether the stigma of the same species was used, or that of another species of the genus.

<sup>1)</sup> STRASBURGER, Ueber fremdartige Bestäubung l.c.

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The pollen of *M. rufinervis* germinates as well in the dilute liquid of *M. frondosa* and *M. cylindrocarpa* as in that of its own species, and pollen of *M. frondosa* could also be brought into gérmination in the stigma-liquid of *M. rufinervis* and *M. cylindrocarpa*, whilst the pollen of *M. cylindrocarpa*, *M. Reinwardtiana* and *M. Teijs*manniana, germinated besides in the stigma-liquid of *M. rufinervis*.

For the different species of *Pavetta* this was otherwise.

I succeeded indeed in causing the pollen of Pavetta javanica to germinate in destilled water in the presence of a stigma of P. javanica and P. fulgens, but not in the dilute stigma-liquid of P. longipes, P. grandiflora, P. coriacea and P. pauciflora.

The pollen of *Pavetta grandiflora* germinated only in presence of a stigma of its own species and of *P. fulgens*, but not with a stigma of *P. javanica*, *P. longipes*, *P. coriacea* and *P. pauciflora*.

That of *Pavetta coriacea* could not be brought into germination at all in this way, not even when using the stigma of *P. coriacea* itself.

It was also proved that the pollen of Mussaenda cylindrocarpa did not germinate in the dilute stigma-liquid of Pavetta grandiflora and the pollen of Mussaenda rufinervis not in that of Gardenia curvata, etc. All this points to the presence in the fluid of the stigma of substances which possess the power to bring about the process of germination, and gives also cause to suppose that for distinct genera and also for distinct species of the same genus, those substances may be distinct too. Since I occupied myself with this investigation, the pollen has repeatedly been the object of interesting researches, as well with regard to its relation to water (KERNER, LIDFORSS, HANSGIRG), and to the negative aerotropism, which may be observed in pollen-tubes (MOLISCH), as to the chemotropical action exerted by the stigma and by special chemical compounds on the pollen-tubes.

It is not impossible that sometimes the same substances which exert a chemotropical influence on the *once formed* pollen-tube, also possess the faculty to excite the latent germinal power of the pollengrains, but certain it is not; in any case, it has not yet been proved to be so.

If a stigma of *Narcissus Tazetta* is passed into a drop of sugargelatin solution, together with some pollen of this plant, then, as MOLISCH has pointed out, the tubes formed are attracted by the stigma and also by the section-face of the style, but the germination of the pollen itself is not influenced by the stigma; the process of germination is accomplished also without a stigma, if only the Narcissus-pollen is introduced into the 7 pCt. sugar solution referred to  $^{1}$ ).

The influence of the stigma is first felt when the tubes are formed, and after all appearance the curving towards the stigma, in this case at least, reposes on a growth towards the nutrient source (trophotropism) of a pollen-tube, formed from the reservesubstances of the pollen-grain.

The last research of LIDFORSS<sup>2</sup>) proved that the stigma can in this experiment be replaced by organs of foreign plants, for instance by bits of *Allium*-root, which made him suppose that a substance, largely spread in the vegetable kingdom, was here concerned. Fragments of diastase act in the same way and, as was nearer indicated, it is not the diastase as such, the starch-converting principle, but the albumen occurring in the preparations, from which goes out the chemotropical influence.

So, these things should not be confounded; the chemical substances possessing the faculty to call forth the process of germination are not, — at least not here — the same that occasion a chemotropical curvation of a once formed pollen-tube.

An investigation of chemotropical curvations under the influence of a stigma was not in my way. Nor was the way in which the germination experiments were performed, — namely in a medium in which the soluble constituents easily diffunded from the stigmamoisture, adapted to observations in this direction.

My object was exclusively to examine in how far pollen, not passing into germination in water or in sugar solutions, required a special chemical substance to call forth the germination. For I put myself the question whether STRASBURGER's opinion that on the stigma no preservatives were present to prevent the germination of foreign pollen, was not taken in too general a sense?

After the said preliminary experiments had pointed out the presence in the stigma-fluid of special chemical compositions, under whose influence the germination was brought about, I tried to find a substance able to exert on the pollen of these different plants, the same influence as the stigma-fluid.

This research has led to the following results:

It lay at hand first of all to think of some organic acid, not only because the stigmas react feebly acidly, but in particular on

<sup>&</sup>lt;sup>1</sup>) Molisch l. c. p. 427.

<sup>&</sup>lt;sup>2</sup>) Bot. Centralbl. No. 11, 1900, p. 373.

account of the well-known influence of organic salts and acids on the spermatozoids of ferns and of *Selaginella*<sup>1</sup>).

All my efforts, however, to find a solution of tartaric acid, oxalic acid, or malic acid, able to make the pollen of *Mussaenda rufinervis* germinate, remained unsuccessful <sup>2</sup>).

Since it is become known that MOLISCH, led by the same course of thought, tried in 1892, by means of organic acids and salts, to call forth the development of tubes in pollen of some *Compositae*, *Umbelliferae*, *Urticaceae*, *Malvaceae* and *Ericaceae*, which could not be caused to germinate in water, gelatin, sugar, glycerine, or gum, and that he indeed succeeded in so far as regards that of *Azalea indica*, *Rhododendron ponticum*, and *B. arboreum*. In solutions of 1-0,05 calcium malate and of 0.01 pCt. malic acid, germination was observed <sup>3</sup>).

The other pollen species were quite insensible to these stimuli.

As little as the pollen of *Mussaenda*, that of different species of *Pavetta*, *Begonia* and *Pentas carnea*, was to be brought into germination in acids or salts.

From the acids I turned to the sugars and allied substances and then it became evident that it was impossible to cause the *Mussaenda*pollen to germinate in solution of *saccharose*, whichsoever degree of concentration this solution might have. I used solutions of 0.05 pCt. mounting to 40 pCt.

No more were *Mannite* and *Dextrose* able to cause germination. Experiments with *Asparagine* and *Dextrine*, too, led to no results.

When, however, the slightest trace of levulose was added to the water, the process of germination set in within the time of two hours and soon the tubes proved as long and as beautiful as at the germination in dilute stigma-liquid.

Here it was perfectly indifferent whether *levulose* was added to the destilled water, or to the solutions of the said sugars in different degrees of concentration, or to a solution of gelatin. *Levulose* proved thus to exert the same influence on the pollen-grains as the stigma.

That the chemical substance which diffunds from the stigma-liquid in the drop of water should contain *levulose*, is, of course, not ascertained hereby; other substances also occurring in the stigma-liquid

<sup>1)</sup> PFEFFER, Locomotorische Richtungsbewegungen durch chemische Reize. Unters, aus dem bot. Institut zu Jubingen Bd. I, Heft 3.

<sup>&</sup>lt;sup>2</sup>) The experiments were performed with solutions of 0.2 pCt. to 0.0025 pCt.

<sup>&</sup>lt;sup>3</sup>) Molisch, l. c. p. 429.

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might exert the same influence on the pollen-grains of *Mussaenda*. Presently it will become evident, at the mentioning of a related experiment, that it is necessary to be cautious with such an identification.

The research showed further that the pollen of other species of Mussaenda behaved towards sugar solutions just in the same way as that of M. rufinervis; from the facility with which the pollen of these species germinated in each other's dilute stigma-liquid, this might be expected.

The pollen of *Begonia* corresponds, regarding its relation to sugar solutions, in many respects with that of *Mussaenda*, but in this genus important deviations occur with regard to the behaviour of the pollen to water.

That of *Begonia gorgocensis* namely, germinates already in destilled water, while that of *B. Deppii*, *B. semperflorens* and *B. imperialis* does not try to form tubes in water. Of all four examined species the pollen germinates, however, easily in the presence of a stigma in the drop of water. But here I should observe that it is not beforehand to be said with certainty whether newly collected pollen of *Begonia gorgocensis* will come into germination in destilled water or not.

Repeatedly in the germination experiments the phenomenon occurred that the pollen of this *Begonia*, having one day formed tubes in the drop of water, the next day did not manifest a trace of tube-development, although it was taken from the same plant.

This is a particularity which I later found not to be rare in other species of pollen neither.

All botanists who have occupied themselves with the germination of pollen, have likewise experienced that its relation to water is not always the same by far.

A slight difference in the humidity of the surrounding air can be the cause, not only that pollen which, under normal circumstances is resistent to the influence of water, when brought into contact with it bursts immediately, but also that pollen, which germinates in destilled water, cannot be brought into germination at a deviating humidity of the air. Elaborate informations thereabout have of late been given by BENGT LIDFORSS in PRINGSHEIM'S Jahrbücher, Bd. XXXIII, Heft 2, 1899, Cap. I en II. This is the reason that never any experiment can be performed concerning the germination of this pollen in any liquid without having first examined, — by control experiments, by preference with the pollen from the same anther, — whether it passes into germination in destilled water, either or not. If this precaution is neglected there is great risk to

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draw a wrong conclusion from the germination experiments. The pollen of this *Begonia*, for instance, I have repeatedly seen germinating in solutions of saccharose, dextrose and mannite of different degrees of concentration, but as often the same experiment did not succeed. Now one might be inclined herefrom to conclude, that in this species of pollen germination can be stirred by the said sugars; but this is by no means the case: to the solutions mentioned this pollen is perfectly indifferent. The divergent results are explained in this way, that the said pollen at one time germinates in water, at another time not. If it does *not* germinate in water the process cannot be called forth by saccharose, dextrose, mannite or asparagine, if it *does*, this also takes place in solutions of these substances, and so, this is to be taken in such a sense that saccharose, dextrose and mannite have not the power of preventing the germination.

In presence of a stigma of the own plant it invariably germinates and likewise if the liquid contains a trace of levulose, indifferently whether the levulose is added to the destilled water, or to a solution of saccharose, dextrose, mannite or asparagine.

The three other species of *Begonia*, *B. semperflorens*, *B. Deppii* and *B. imperialis*, behave towards water, dulute stigma-liquid, and kinds of sugar, in the same way as the pollen of *Mussaenda*, i. e. do not germinate in water, but only in dilute stigma-liquid and in liquids containing levulose.

Now it is certainly striking that levulose acts quite differently on the pollen of the *Pavettas*. Of some of these, namely of *P*. *macrothyrsa* and *P*. *Reginae*, the pollen germinates already in destilled water; that of *P*. *javanica*, *P*. *fulgens*, *P*. *longipes*, *P*. *pauciflora*, *P*. grandiflora, and others, only in presence of a stigma.

For all these *Pavetta*-species however, the presence of levulose is an obstacle to the development of the pollen-tube. Of not a single species I have been able to make the pollen germinate in levulose, and what in particular deserves attention, is that of most *Pavettas* the germination is not only prevented, but that the pollen bursts and allows its contents to stream out when brought into contact with a liquid containing levulose.

What has just now been communicated about the relation of the pollen of *Begonia gorgocensis* to water, holds also good for that of *Pavetta macrothyrsa*.

Now it forms beautiful tubes in this liquid, then again no trace of germination is to be detected. In the latter case the process of germination is not to be called forth by saccharose or dextrose, whilst, if it does germinate in water, addition of these sugars does (271)

impede the process. If now to the liquid a trace of levulose is added, whether this liquid consists in destilled water or in a solution of sugar, the coats burst and the contents spread in the liquid.

I have not succeeded in finding a chemical compound able to call forth germination in *Pavetta*. What has been told above about the different behaviour of this pollen towards the stigma-liquid of the plant itself and towards that of other species, makes it appear probable that in distinct species there are also distinct substances present in the stigma-liquid. Which substances however these are, I have not as yet been able to detect.

The pollen of Murraya exotica (belonging to the Rutaceae) corresponds in its relation to levulose completely with that of many Pavettas. Put in water, the pollen-grains show a commencement of germination. As a rule the tubes attain no greater length than of 1-2 times the diameter of the pollen-grains. In dilute stigmaliquid or in a solution of saccharose, mannite or dextrose, the growth of the tubes is not furthered. In this solution the pollen behaves as in water.

On addition of levulose, however, whether to the water, or to the sugar solutions, the grains burst and there is no question of formation of tubes.

What has been said here about the prejudicial action of levulose on the pollen of *Murraya exotica*, has induced me to examine whether this pollen might be caused to germinate in the dilute stigma-liquid of *Mussaenda*. If the pollen of *Murraya* would burst in a liquid wherein a stigma of *Mussaenda* is laid, then the supposition that the chemical compound which in the stigma-liquid of *Mussaenda* causes germination, is levulose, would have acquired a high degree of probability.

It has now become evident to me that this is not the case; the pollen of *Murraya* does not die in the dilute stigma-liquid of *Mussaenda rufinervis*; it germinates in it in the same way as in water.

The possibility is not excluded that still we have to do here with levulose, but that this compound, diffunding from the stigmaliquid produces a too weak solution to act prejudicially on the pollen of *Murraya*; but how this may be, the said experiment shows that the substance able to cause germination in the stigma-liquid of *Mussaenda*, cannot, as yet, be identified with levulose.

The fact that the pollen of some *Pavettas* is greatly prejudiced by levulose, while that of other *Pavettas* and of *Murraya exotica* is even destroyed by the presence of that substance in the germin-

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ation liquid, has induced me, also for a few other plants, to examine how their pollen behaves towards levulose, of which research the results follow here:

The pollen of *Ipomoea imperialis*, Calonyction speciosum (Ipomoea bona nox), and of some other cultivated species of Canna, belong to those species of pollen which are not proof against water.

The grains burst immediately after they have come into contact with water and the same takes place in dilute solutions of saccharose. Only at a concentration of 20 pCt. no rupture of the pollencoats occurs; it remains intact, but does not pass into germination.

If now, however, to such a solution a trace of levulose is added, the grains burst just as in water.

The pollen of a species of *Acanthacea*: Justicia (Tyloglossa) cultivated at Batavia and Buitenzorg, is perfectly proof against water and sugar solutions. It can remain in it for a long time without any change being observed and without passing into germination.

A slight quantity of levulose, however added to the destilled water, or to the saccharose solution, causes the pollen to burst.

Of Antirrhinum spec. [Maurandia antirrhinifolia Hort. Bog.] the pollen germinates in water; a solution of saccharose does not impede the germination, so long as the degree of concentration does not exceed 5 pCt. Addition of levulose prevents the germination, the pollen-grains, however, do not burst.

The pollen of *Pentas carnea*, of which the germination in water is doubtful (like that of *Begonia gorgocensis* and *Pavetta macrothyrsa*) germinates, on the contrary, with very fine tubes in presence of levulose, whilst, lastly, the pollen of *Impatiens Sultani* and *Impatiens latifolia*, which germinate in water, are as little prejudiced by levulose as by saccharose and dextrose.

It will be remembered that STRASBURGER<sup>1</sup>) has come to another conclusion.

From his observations, that pollen could often come to germination on stigmas of plants having no systematic affinity to the specimen which produced the pollen, and that the pollen-tubes of foreign pollen, could often penetrate through the canal of the style, a little way into the ovary, STRASBURGER thought himself justified in inferring that no preventives occurred on the stigma against the germination of foreign pollen.

He was therefore of opinion, that when a foreign pollen species does not germinate on a stigma this should not be considered as a favorable adaptation, but much more as an accidental phenomenon

) STRASBURGER. Ueber fremdartige Bestäubung, PRINGSHEIM's Jahrb. Bd. XVII, 1886.

caused by this pollen being exposed on that stigma to prejudicial influences, or by its not finding there the conditions of nutrition required for the development of the pollen-tube.

That foreign pollen-tubes get only rarely into the ovary and still more rarely between the ovules, would further be related to the circumstance that the noxious influences to which they are exposed in the extraordinary surrounding accumulate more and more, and so the conditions become still more unfavorable.

Protecting contrivances against foreign pollen would in consequence not exist, and it was STRASBURGER's opinion that they were superfluous because the investigation had taught him, that the normal development of the plant's own pollen was not prevented by the presence of foreign pollen.

The tubes of the own pollen grew unhindered among the foreign tubes and arrived to normal function.

It seems to me that STRASBURGER's observations are not sufficient to prove that no protecting contrivances are found against foreign pollen.

Opposite to the fact that pollen of the most distinct botanic origin can come into germination on a determined stigma, is the fact that still a great many other species of pollen cannot be stimulated into the formation of pollen-tubes on it at all, and this holds good even for pollen of plants which stand in close, even in the very closest affinity to the stigma-bearing specimen.

This latter fact, as it will appear to me, points as clearly to the existence of protective means, as the reverse points to the opposite.

Besides, when the tube of foreign pollen together with the own pollen, penetrates a little way into the style-canal, but then ceases growing, while that of the plant's own pollen goes on and reaches the ovule, this is not necessarily the consequence of an accumulation of unfavorable influences.

It is not impossible, and even not improbable, that the further growth of the pollen-tube and the penetrating into the micropyle is bound to special exigencies satisfied only for the plant's own, or for allied pollen. Those special exigencies for further growth may be obtained by adaptation.

I think that from STRASBURGER's research no more must be deduced, than that not always preventive means are found on the stigma against fertilisation with foreign pollen. Doubtful it is, moreover, whether it is really relations of nutrition, which govern the germination on the stigma and the penetrating of the tubes into the style-canal.

The fact that many species of pollen require a determined degree

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of concentration in a sugar solution in order to germinate, and cannot be brought to the formation of the tube above and below that degree, points, as it seems to me, to quite other relations than those of nutrition, while the fact that number of pollen species form beautiful and long tubes in destilled water, proves that in any case not all species of pollen must find on the stigma a nutriment specially fit for their growth.

There are number of facts which decidedly point out, that for some plants there exist really preventives on the stigma against fecundation with a particular kind of pollen. STRASBURGER calls them exceptions, but still they are so striking as to highly draw the attention.

So it is already known since DARWIN, that the long-styled form of Linum grandiflorum, a heterostyle-dimorph plant, is absolutely sterile when fertilised with the illegitimate pollen of the same species, and this is likewise the case with the illegetimate pollen of both forms of L. perenne. Nobody doubts but the sterility of these both plants when fertilised with illegitimate pollen should be considered as an adaptation.

With *Linum grandiflorum* the pollen-grains donot try at all on the stigma to form tubes.

With Linum perenne they do, but the pollen-tubes do not reach the ovary, or at least are not able to fecundate the ovules. Would it not be allowed to conclude therefrom, that both species have the means to protect them against illegitimate fecundation, that these means for Linum grandiflorum are already found on the stigma and for Linum perenne in the style-canal?

The pollen of Oncidium flexuosum, O. unicorne, O. pubes and of some other Orchideae<sup>1</sup>) is not only unable to fertilise its own flower, but it has even a poisonous effect on the stigma. Here again the preventive against self-fertilisation is found on the stigma. In Corydalis cava, on the other hand, whose own pollen germinates very well on the stigma, but where the tubes do not reach the ovules, it is evidently found in the ovary, etc.

If now in these cases there is nothing else to be thought of but a special contrivance, then it might a priori also be expected that preventives should be found against fecundation with foreign pollen in general, and that they should be sought in the first place on the stigma, and if not found there, in the style canal and the ovary. To this view I think to have given some support in the above communication.

Batavia, May 1900.

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<sup>1</sup>) DABWIN, Variation etc, Chapter XVII.

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## Physics. — Communication N<sup>0</sup>. 59<sup>α</sup> from the Physical Laboratory by Prof. H. KAMERLINGH ONNES: "Contributions to the knowledge of VAN DER WAALS' ψ-surface. I. Graphical treatment of the transverse-plait".

#### (Read June 30, 1900.)

1. According to VAN DER WAALS' theory it is possible by means of a sufficient number of well selected observations with mixtures of two known normal substances, to determine the constants  $(a_{12} \text{ and } b_{12} \text{ of VAN DER WAALS})$ , which allow us to construct the general equation of state for the mixtures of these substances and especially to predict the phenomena of condensation by  $\psi$ -surfaces derived from that equation of state.

KUENEN, who among other things aimed at determining VAN DER WAALS' constants for mixtures of methyl chloride and carbon dioxide, has mentioned already in his thesis for the doctorate that calculations had been made in order to construct the  $\psi$ -surfaces from the observations for mixtures of these substances.

I have carried out and very nearly completed these calculations for the temperature at which KUENEN has made his most important observations, i.e. those on the retrograde condensation.

For each of the values of the molecular proportion of  $CO_2$  in his mixtures x = 0,  $x = \frac{1}{4}$ ,  $x = \frac{1}{2}$ ,  $x = \frac{3}{4}$ , x = 1 KUENEN gives the values of the constants  $R_x$ ,  $b_x$ ,  $\beta_x$ ,  $K_x = Ta_x$  in the equation of state

$$p = \frac{R_x T}{v - b_x} - \frac{K_x}{T (v + \beta_x)^2}$$

(p = the pressure in atmospheres, v = the volume referred to the normal-volume, T = absolute temperature).

By means of this I calculated the free energy for mixtures of the composition x,

$$\psi_x = -\int p \, dv + R T \left\{ x \log x + (1-x) \log (1-x) \right\},$$

(to which <sup>1</sup>) a temperature function linear in x can be added <sup>2</sup>)) for equal

) In the drawings we have used for 
$$\int p \, dv : \int_{\infty}^{v} dv + 9.4383$$
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<sup>2</sup>) VAN DEE WAALS, Théor. Moléc. p. 11.