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than P_B, a part from BA The curve remains, therefore, within the triangle as well on increase as on decrease of P.

c) Both the binary P, T-curves proceed from the point B towards higher pressures; consequently two points of maximumpressure occur [$W_x < 0$, $\Delta W_y < 0$; case sub c; fig. 4—6]. A boilingpointcurve situated in the vicinity of B cuts off from the side BC a smaller part than from the side BA. The curve comes, on increase of P, within the triangle.

In each of the cases, mentioned sub a, b, c, the temperature along a boilingpointcurve situated in the vicinity of B, increases in that direction in which this curve comes nearer to B (figs. 3—6).

(*To be continued*).

Chemistry. — "*Studies in the Field of Silicate-Chemistry*: I. *On Compounds of Lithiumoxide and Silica*. By Prof. Dr. F. M. JAEGER and Dr. H. S. VAN KLOOSTER. (Communicated by Prof. P. VAN ROMBURGH)

§ 1. In connection with a series of investigations going on in this laboratory, on natural and synthetical lithiumaluminiumsilicates, it seemed to us of importance once more to take up the study of the binary system: lithiumoxide-silica, by means of the equipment and methods, which are now at our disposal; only in this way it seemed to us possible, to obtain thermical data, which are reliable and reducible to the nitrogen gasthermometer. At the same time we hoped to get information on the origin of in some respects rather strongly deviating results of earlier investigators, who have occupied themselves also with the study of these lithiumsilicates.

The two-componentsystem · Li_2O—SiO_2 has already several times been an object of research; thus some time ago by one of us[1]), using the method, already so often successfully employed upon metalalloys, of the crystallizationphenomena on cooling, which will show themselves in such binary mixtures of varying composition. Later it was studied in the same way by ENDELL and RIEKE [2]), who of course in general also came to the same results, but who were not able finally to answer the question, if a third compound, the lithiumbisilicate, could separate from molten mixtures, like the ortho-, or meta-silicate.

· [1] H. S. VAN KLOOSTER, Dissertatie Groningen (1910); Zeits. f. anorg. Chemie **69**, 136 (1910).

[2] K ENDELL und R. RIEKE, Sprechsaal, **44**. No 46 (1910); **45**. No 6 (1911).

Again another problem originated from a publication of G. FRIEDE who gave the description of a second modification of the metasilica this new modification was never obtained either by WALLACE [2], by ENDELL and RIEKE, or by ourselves from a molten mass. the occasion of a renewed meltingpointdetermination, made by the fi of us [3] in 1910 at the Geophysical Laboratory in *Washington*, a ne indication of an eventually appearing inversion was not found; at t same time it was once more demonstrated by this study, that ev in this relatively favorable case, where the liquid was highly moval and the crystallization-velocity of the silicate could be considered exceptionally great, the "coolingmethod" was by no means adopt to give reliable and reproducible results. Other factors in the earl determinations, e.g. the use of crucibles and tubes of porous carbc and the insufficient control of the variations in chemical compositi of the studied mixtures, caused by the volatility of the lithium-oxic and finally the impossibility to reduce, the existing thermical de to the scale of the nitrogengasthermometer, — seemed to us a ser of reasons, to take up a new study of this binary system by mea of the gradually developed exact methods [4].

§ **2.** The necessary binary mixtures were prepared from t purest lithiumcarbonate and from pure, ground quartz of Americ origin. The lithiumcarbonate was dried at $100°$ C.; there was a lc of weight of only $0,05°/_0$. Only sodium could be detected spectr copically; the quantity was however so small, that it could not determined by weight, using the amylalcohol-method. A trace iron was found also, but scarcely sufficient to give a reaction wi potassiumsulfocyanide as a pale pink colouring of the solution. T lithium was weighed as lithiumsulphate; determined: $18,72°/_0$ *1* calculated: $18,79°/_0$ *Li*.

The quartz lost on heating on the blast no more than $0,01°/$ a small trace of iron, less than $0,03°/_0$, appeared to be the sing impurity. On evaporating with hydrofluoric acid in a platinum-dis no residue was left; the used quartz therefore can be considered : pure SiO_2. [5]

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[1] G. FRIEDEL, Bull. de la Soc. Minér. **24**, 141 (1901); HAUTEFEUILLE et MA GOTTET, Compt. Rend. **93**, 686 (1881).

[2] R. C. WALLACE, Zeits. f. anorg. Chemie, **63**, 1 (1909).

[3] F. M. JAEGER, Journ of the Wash. Acad. of Sciences, **1**, 49 (1911).

[4] F. M. JAEGER, Eine Anleitung zur Ausführung exakter physiko-chemiscl Messungen bei höheren Temperaturen. Groningen, 1913.

[5] Those preparations were supplied by BAKER and ADAMSON; the used mater is the same as at the Geophysical Laboratory in *Washington*, and employed standardizing purposes.

According to this high degree of purity of the components, all the binary mixtures, employed in this research, were absolutely white. They were obtained by heating weighed quantities of both oxides in a finely divided state in platinum or nickel crucibles; this manipulation was done in small resistance-furnaces, at temperatures ranging from 900° to 1000° C., and every contact with a reducing atmosphere was carefully avoided. After grinding down the masses and sifting, they were treated in just the same way, etc., till the whole preparation was shown to have a homogeneous composition. Mixtures between ortho-, and meta-silicate were prepared from both these compounds in quire the same way. The preparations were analysed after HILLEBRAND's indications[1]), and always in duplo.

Every admixture of formed nickel-oxide was carefully avoided; mixtures rich in lithiumoxide however, needed to be heated in platinum crucibles, because they would dissolve otherwise finely divided nickel, which coloured the preparation with a beautiful violet hue. For instance the orthosilicate could be obtained in this way, as a splendid, intensively coloured, violet product. The study of mixtures, richer in lithiumoxide, corresponding with the composition cf the ortho-silicate was not possible in the usual way, both because of the volatility of the oxide at the prevailing temperatures, and by the fact, that the lithiumperoxide Li_2O_2, generated at higher temperatures, will very quickly attack the platinum and the wires of the thermoelements; the platinum is superficially coated with a dull olive-green or greenish-yellow layer, and every accurate temperature-measurement thus gets practically impossible. Experiments, made in hermetically closed platinum-vessels however, have given many good results, as will be described further on, in § 12 of this paper.

§ 3. The temperatures of equilibrium were determined in the way always used in this laboratory. A WOLFF-potentiometer (resistance : 83 Ohm) with three decades, and with a constant resistance of the galvanometer-circuit (WHITE—DIESSELHORST), was employed, in connection with a sensitive AYRTON-MATHER-movingcoilgalvanometer, with high resistance, and short period, to compensate the momentaneous electromotive force of the thermoelement; the galvanometer was calibrated and adjusted in such a way, that one microvolt corresponded with a millimeter on the scale. The observations, made with our thermoelements I and II (platinum and platinumrhodium (10°/₀)-alloy) could be compared immediately with the nitrogengas-thermometer, by means of calibration with a standardelement, cali-

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[1]) W. F. HILLEBRAND. Analysis of Silicate and Carbonate Rocks, 2nd. Edit. 1910.

brated in *Washington*, and by determination of the meltingpoints of Na_2SO_4 (884° C.), Li_2SiO_3 (1201° C.), synthetical diopside (1391° C.), and synthetical anorthite (1552° C.), with each of the three mentioned thermoelements successively. The potentiometer-current was kept constant at 0,002 Ampères; two Weston-cells, connected in series, and a Wolff auxiliary-rheostate, served as standard-electromotive force; the Weston-cells were constructed and controlled several times at the Physical Laboratory of the University. The furnaces used were platinum-resistance-furnaces with the heating-coil inside; they had the usual type, and their regulation was executed by means of a decade-rheostate of manganin-wire. The heating-current was direct current of 110 Volts and 20 or 30 Ampères.

§ 4. *The components.*

With respect to the components themselves, the following data may be given. The relation between the three modifications of the silicumdioxide: SiO_2, can be esteemed established in general lines after the recent, most accurate research of C. N. Fenner (Amer. Journal of Science, **36**. 331 (1913)).

The inversiontemperature for β-quartz $\rightleftarrows$ tridymite lies at 870° ± 10° C.; in the same way that for tridymite $\rightleftarrows$ cristobalite is determined at 1470° ± 10° C. The three modifications are enantiotropic forms, but the transformation-velocity is very small, and retardation-phenomena, even in an enormously high degree, are almost always present. This is the reason, why in nature some modifications of SiO_2 often occur within the stability-field of other forms.

Then there is at 575° C. an inversiontemperature for a- → β-quartz; at 117° C. one for a- → β-tridymite, at 163° C. one for β- → γ-tridymite; these inversions occur relatively fast. Probably the a-, and β-forms of cristobalite are in less or more stable equilibrium with each other at temperatures, situated between 198° and 274° C. The relations of those modifications to each other are very complicated, but of no direct interest for the present study.

The meltingpoint of cristobalite is very close to 1625° C.; the liquid is a very viscous mass, which by rapid cooling changes into the wellknown "glass".

Quartz is optically easy to discriminate from both the other forms, by the great differences of the refractive indices; the discrimination between tridymite and cristobalite however is rather difficult.

The refractive indices of quartz are: $n_e = 1.553$ and $n_o = 1.544$; those for tridymite are: $n_a = 1.469$, $n_\gamma = 1.473$, while the true

angle of the optical axes $2V =$ about $35^1/_2^\circ$. For cristobalite these values are: $n_x = 1,484$, and $n_\gamma = 1,487$.

The *lithiumoxide*: Li_2O is only sparely known up to this date. A description of it is to be found in an instructive paper of L. TROOST [1]), whose data we in general could confirm. He obtained the oxide from lithiumcarbonate, by heating it at a high temperature in the presence of coal in a platinum-crucible, and also by heating the nitrate of lithium in silver crucibles at a red heat. The burning of lithium in oxygen gave only partial results, as the protoxide: Li_2O_2 was formed. The presence of this peroxide causes the yellow colour of the product. TROOST describes the Li_2O as a white compound, with cristalline rupture. We prepared the pure oxide after the method of DE FORCRAND [2]), by heating lithiumcarbonate in a platinum vessel at $830^\circ—900^\circ$ C., while a current of dry hydrogen is run over it continuously. We obtained in this way an absolutely white, cristalline product, which makes the impression of having been melted. This however is not the case, as the aspect is caused by the melting of the carbonate itself before its decomposition. For, as we found, the oxide does *not* melt under these circumstances, but can sublime already under 1000° C.

We were able to confirm TROOST's observation, that *pure* Li_2O does *not* attack the platinum, even at very high temperatures, but that the metal is attacked however, as soon as the oxide is heated with it in an oxidizing atmosphere. The cause of this phenomenon is the resulting peroxide, which attacks the platinum most intensily, and gave to it the yellow or olive-green colour, which we have also observed, whenever the lithiumorthosilicate was heated with the metal. The view of the French author, that in absence of oxygen, the Li_2O can be heated to a very high temperature, *without melting*, is also quite right. We have made some experiments, to determine its meltingpoint by means of the use of the "hollow thermoelement", — a method to be described further on, in the study of the orthosilicate and the mixtures, rich in Li_2O. It was found then, that a heating to 1570° C. (about 16400 M.V.) caused only a baking together of the powder to a very hard mass, which was coloured slightly yellowish by a trace of Li_2O_2, formed from Li_2O and the small quantity of air, present in the platinum-bulb; however even now the mass was probably not yet molten, nor at 1625° C., as we found afterwards. Because the platinum is very soft at these tempe-

[1]) L. TROOST. Ann. de Chim. et de Phys. (3). **51**. 144, (1857).

[2]) DE FORCRAND. Compt. rend. **144**. 1402, (1907).

ratures, the platinumbulb was inflated to a balloon, however without bursting.

Further we were able to determine the refractive indices and the specific gravity of the pure oxide. Under the microscope the compound appears as cristalline, irregularly shaped scales, with very weak birefringence. Often they seem to be wholly isotropous, as if they were glass. It may be, that the-substance is finally yet of regular symmetry, for the weak birefringence often makes the impression of being only localised by tensions in the mass, more than of a ·real crystallographical anisotropy, and we found neither in any case an interference-image in convergent polarised light, able to prove that the compound belongs to one of the uniaxial classes. Once some trigonally shaped plates were observed, which looked like flat tetrahedrons or trigondodecahedrons; but it was impossible to prove this view more exactly. The refractive index was found by immersion: $n_D = 1,644 \pm 0,002$; so the refraction is relatively high, this giving some evidence of the fact, why a great many lithiumaluminosilicates, which are rich in Li_2O, show higher refractive indices, if they are richer.in the oxide.

The specific gravity was determined by means of a pycnometer, with ortho-chlorotoluene as a liquid, before it was found, that the oxide does not attack this liquid in any appreciable way. As the most probable value (from three determinations), we found: $d_{4^o} = 2,013 \pm 0,015$, at $25°,1$ C.

The oxide dissolves slowly into water, without giving a great heat-effect. The solution shows very strong alkaline reaction; it tastes lixivial and at the same time somewhat bitter. With acids no development of CO_2 was observed; so the product may be declared free from carbonate.

§ 5. We have now given in the following table the obtained results with mixtures of different composition; the numbers in the 7th, 8th, 9th and 10th columns are reduced on the gasthermometerscale of Day and Sosman [1]), this being at the moment the most accurate one. The composition of each mixture was determined *after* each experiment by direct analysis, according to Hillebrand's [2]) indications for the determination of the silicic acid. The thermoelements used, were I in the furnace, II in the mass; they were read alternately every half minute. Even with masses of hardly 1,5 gram, the heat-

[1]) A. L. Day and R. B. Sosman, Carnegie-Publication No. 157 (1912).

[2]) W. F. Hillebrand, loco citato.

effects could be fixed on the temperature-time-curves very accurately, and if the furnace. was run at a higher speed, again these temperatures were reproducible within ca. $1°C$; they therefore can be considered as temperatures of true equilibrium.

Meltingpointdiagram of the Binary System· $Li_2O—SiO_2$.
(Thermoelement II placed in the mass).

Number of Experiment:	SiO_2 in Proc. of Weight:	SiO_2 in Proc. of mol.	Observed Temperatures in Int. Microvolts:		Observed Temperatures in $°$ C.		Corr.Temp. in intern. Microvolts		Corr. Temp. in $°$ C.	
			1st Effect	2d Effect	1st Effect	2d Effect	1st Effect	2d Effect	1st Effect	2d Effect
0	91.8	84.7	9902	—	1029	—	9866	--	1025.5	—
1	89.0	80.0	9919	—	1030	—	9883	—	1027	—
3	85.3	74.2	9922	—	1030.5	—	9886	—	1027	—
4	82.1	69 4	9920	—	1030.5	—	9884	—	1027	—
5	79.6	65.9	9972	—	1035·	—	9936	·—	1032	—
6	75.7	60.7	9982	10958	1036	1118	9946	10918	1032.5	1115
7	71.1	54.9	9912	11624	1029.5	1174.5	9876	11580	1026	1170 5
8	66.67	49.7	—	11992	—	1205	—	11944	—	1201
9	63.9	46.7	9800	11908	1020	1198	9764	11860	1017	1194
10	62.4	45.1	9854	11622	1025	1174	9818	11578	1021.5	1170.5
11	57.4	40.0	9872	10680	1026.5	1094	9836	10640	1023	1092
12	52.8	35.6	9870	10732	1026.5	1096.5	9834	10692	1023	1097
13	50.7	33.7	9850	11600	1024.5	1172	9814	11556	1021	1169.5
*14	49.9	33.0	9736	12154	1014.5	1218	9700	12106	1011	1215
15	49.8	32.9	9812	12448	1021	1243	9776	12402	1018	1239
*16	49.2	32.4	—	12634	—	1258.5	—	12590	—	1255
17	49.7	32.8	9826	12440	1022	1238	9790	12394	1019	1238.5

* The marked preparations must accidentally have been changed before analysis; we had however afterwards no means to ascertain this.

It may be remarked, that a preparation, having exactly the composition of the orthosilicate, always gave a slight heat-effect, corresponding with a eutectic temperature. We were able to show, that the cause of this phenomenon is the high volatility of the Li_2O: after one single meltingpointdetermination, already a loss of Li_2O
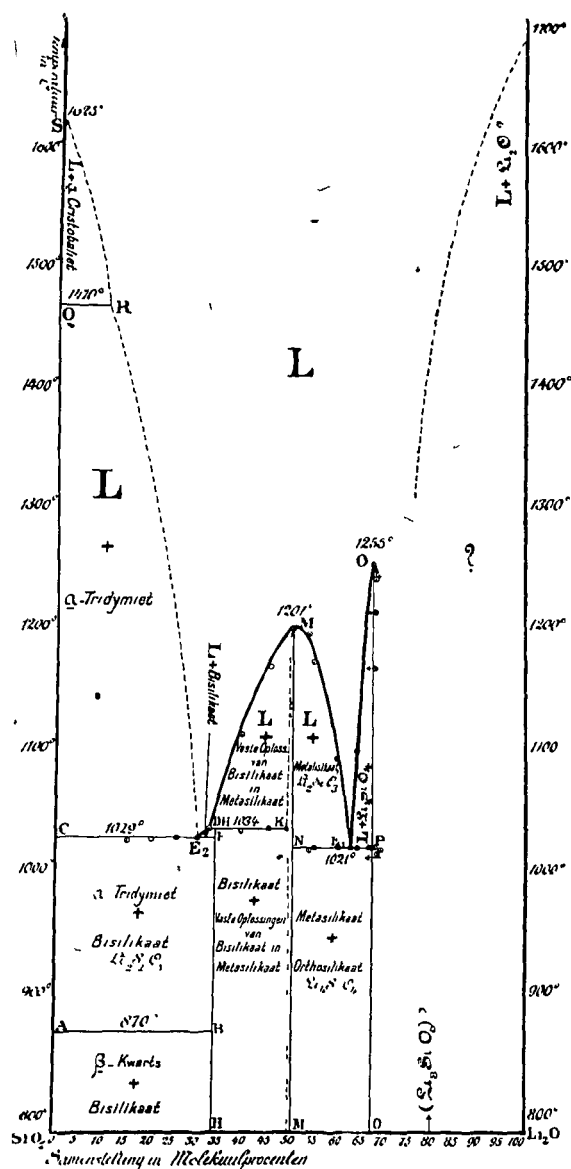
Fig. 1.

Temperatuur = Temperature. Cristobaliet = Cristobalite. Tridymiet = Tridymite.
Bisilikaat = Bisilicate. Vaste oplossing van Bisilikaat in Metasilikaat = Solid solutions
of Bisilicate in Metasilicate β-Kwarts = β-Quartz. Samenstelling in Molekuul-
procenten = Composition in Molecule-procents. Orthosilikaat = Orthosilicate.

of 0.4°/₀ could be stated. We finally obtained a temperature-time-
curve, in which the eutectic effect had disappeared, starting with
a mixture, which showed a small excess of the lithiumoxide; the
meltingpoint was now at 12598 M.V. (corr.) corresponding with
1255°,5 C. This temperature we must consider as being the true
meltingpoint of the orthosilicate, with an uncertainty of about

$\pm$ 3° C, caused by the variability in chemical composition as a result of the extraordinary volatility of the lithiumoxide, which will sublime already at temperatures, much lower than this melting-temperature. Further below we will give the determinations of the meltingpoint of the orthosilicate by means of a closed crucible and a new method of observation; we shall see, that the true melting-point does not differ appreciably from the here given value.

In fig. 1, we have composed these numbers graphically in the usual way. At the same time also the results, of our experiments, concerning the determination of the field, in which the bisilicate can exist in contact with the liquid, are indicated in this figure. The last mentioned determinations have given us much trouble, because great difficulties were connected with the limitation of this very narrow field of stability of the compound. We have only succeeded by numerous quenching-experiments: preparations, heated during a long time on known and constant temperatures, were momentaneously chilled, and investigated in all details by means of the microscope. Only in this way the place of the bisilicate in the series could be fixed with sufficient accuracy; the experiments on this subject are described afterwards.

As a general result, we can thus say, that there are *three* compounds : $Li_2 Si O_3, Li_4 Si O_4$ and $Li_2 Si_2 O_5$; the compound $Li_8 Si O_6$, proposed by Niggli on a very weak argumentation in no case exists in contact with a molten mass, while the compound $Li_2 Si_2 O_5$ has evidently no real meltingpoint, but only a transformationtemperature at 1032° C., at which it decomposes with deposition of some metasilicate, or of a solid solution of a little of the bisilicate in an excess of metasilicate [1]). We think we are right in this last view, because the refractive indices of the needles of $Li_2 Si O_3$, which are deposited at this temperature, have evidently somewhat lower values (1.57 instead of 1.585 etc.), than the pure metasilicate.

The composition of both the eutectic mixtures E_1 and E_2, can be indicated by :

E_1 .... (1022° C.) : 55 Proc. of Weight SiO_2 = 37.7 Mol. Proc. of $Si O_2$.

E_2 .... (1027° C.) : 82,1 Proc. of Weight SiO_2 = 69.4 Mol. Proc. of $Si O_2$.

§ 6. The *lithiummetasilicate* crystallizes from the thin molten mass very rapidly ; for this reason we succeeded in obtaining a "glass"

[1]) P. Niggli, Journ. of Amer. Chem. Soc. (1913) ; Zeits. f. anorg. Chem. 84, 263. (1913). In fig. 1 is wrongly written 1034° C, instead of 1032° C

of this substance only by cooling very small quantities of the compound. The cristallized liquid consists of long, opaque, porcelain-like looking needles, which show a principal and very complete cleavage in the direction of their elongation; heavier individuals therefore will decay very easily in a number of thin, felty needles, showing normally orientated extinction. In the zone of the longer axis we could measure some angles between 59° and 61°; this form of the silicate seems to be the same as that, described by HAUTEFEUILLE and MARGOTTET as rhombic, with pseudo-hexagonal symmetry. Doubtless the silicate is biaxial, and probably monoclinic, the plane of the optical axes parallel to the elongation of the needles, and perhaps almost perpendicular to the formes {100} or {001}.

Fig. 2.

Lithiummetasilicate (Enlargement 50 ×)
(immersed in a liquid).

The silicate used was the same, as formerly described by one of us [1]. Its analysis gave the following values:

SiO_2	66.60%
Li_2O	32.80%
Na_2O	0.51%
Fe_2O_3	0.02%
CaO	0.03%
	$99\ 96\%$

There is thus about 0.3% Li_2O too little. The metasilicate is decomposed by water, however much more slowly than the ortho-silicate. Finally however the water shows some alkaline reaction. The meltingpoint was determined with SOSMAN's element C at 11954 M.V., corresponding with 1201°.8 C.; DAY and SOSMAN determined 1200°.6 C. Another preparation, (CRENSHAW), whose analysis gave the following numbers:

SiO_2	65.89%
LiO_2	32.83%
FeO	0.05%
H_2O	$1.2\ \%$
	99.97%

had a meltingpoint of 11930 M. V., or 1199,°8 C.; with the thermoelements G and H of SOSMAN and DAY. The meltingpoint of pure

[1] F. M. JAEGER, Journ. of Wash. Acad of Sciences 1, 49, (1911).

Li_2SiO_3, can be indicated thus at 11944 $\pm$ 12 M. V. or 1201° C. $\pm$ 1°. The meltingpoint can be localised so sharply on the heating-curves, that the compound can be used with success for calibration purposes ; the temperature of equilibrium is here really *in*dependent of the speed of heating, in very wide limits.

By means of the method of immersion, the refractive indices for sodiumlight were determined on :

$n_D = 1{,}609 \pm 0{,}004$, for vibrations parallel to the direction or elongation of the needles,

$n_D = 1{,}584 \pm 0{,}002$, for vibrations, orientated perpendicularly to the first direction.

The birefringence is strong and of positive character, being about 0,025. The specific gravity at 25° C. was: $d_4 = 2{,}520$. In fig. 2 a microphotograph of the crystallized meta-silicate between crossed nicols is given while this is immersed in a liquid of about the same refractive index.

With the aid of the method of quenching, used in this laboratory with substances, heated at a constant temperature during a long . time, we were able to get some *glass* of the metasilicate. As the compound crystallizes extraordinarily rapidly, it was only possible to succeed by using very small quantities of the silicate, about 0,05 to 0,1 gram, wrapped in platinum-folium, and suddenly chilling them by means of cold mercury. The refractive index of this glass was found to be: $n_D = 1{,}548 \pm 0{,}002$ at 25° C, thus it appears to be appreciably less than the smallest index of the crystallised substance. The specific gravity of the glass was determined at : $d_4 = 2{,}330$, thus being at 25° C. also much lower than for the crystallized substance.

§ 7. We found no indication whatever of an inversion temperature in heating and cooling our preparation; also in the microscopical work we were not able to find any other modification of the meta-silicate than the one just described.

However G. FRIEDEL [1]) described in 1901 another form of lithiummetasilicate, which he claimed to be trigonal and, strangely enough, to be homeomorphous with phenakite. He obtained this form of Li_2SiO_3 by heating the product, obtained by the reaction between Li_2O, SiO_2, and muscovite in solution at 540° C. under pressure. His results do not agree with those of MARGOTTET and HAUTEFEUILLE [2]), who used $LiSi$ as a flux, and obtained needles, to which they attribute rhombic symmetry, with pseudo-hexagonal character.

[1]) G. FRIEDEL, Bull. de la Soc. Miner. de France. **24**, 147 (1901).

[2]) HAUTEFEUILLE and MARGOTTET, ibid. **4**, 241 (1881); Compt. rend., loco cit,

Just because neither we, nor our predecessors, ever found any indication of another form of the metasilicate, than the mentioned biaxial one, we wrote to Mr. Friedel, asking him to send us a sample of his modification. We wish to offer this mineralogist our best thanks once more, for his aid and the trouble he has given himself, to help to elucidate the complicated problem of those form-deviations.

The preparation sent to us, soon appeared to be an aggregation of flat needles, often radially ordered, *which were however doubless_-biaxial.* As was indicated on the label, they were obtained from molten $LiCl$, showed a pale pink tinge, and an extinction, directed perpendicularly and parallel to their elongation ; the refractive index for vibrations parallel to their direction of elongation, was: $n_D = 1,585 \pm 0,003$, (being thus identical with that of our needles, perpendicularly to their elongation), while the refractive index for vibrations orientated perpendicularly to the above, was: $n_D = 1,563 \pm 0,002$, from which there results a birefringence of about : 0,022, being thus only slightly less than for pure metasilicate. The flat needles showed at their top-, and base-end, two small faces, making with the longer edge of the crystals angles of respectively: 114°, 126°, and 120°.

In an experiment, where finely crushed Li_2SiO_3 was heated during eight hours with molten $LiCl$ at 900° C. no other crystals were obtained than the ordinary, biaxial needle-shaped form, which we described already.

For another preparation of Mr. Friedel, (with the number IV), also obtained from molten $LiCl$, which preparation contained some metallic copper [1]), and some $LiCl$, we found : $n_D = 1.584 \pm 0.002$, and $n_D = 1.574 \pm 0.002$, the directions of the vibrations corresponding with those, given earlier. The birefringence is . thus now : 0.010 or 0.012 ; evidently the refractive index for vibrations in the elongation-direction of the needles, seems to be *variable.* We think it not improbable, that a slight admixture in solid solution, of the bisilicate: $Li_2Si_2O_5$ with its lower refractive index : ca 1.54, must be supposed, to be the cause of this variability.

§ 8. After having received the account of these experiments, Mr. Friedel was so kind as to repeat his experiments of 1901. Further he succeeded in finding again a preparation of the year 1898 (C; exp. I, 1898), prepared by heating a solution of 2,5 grams of dried SiO_2 and 0.65 gram of Li_2O, with 6 grams of muscovite at 540° C.

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[1]) From the lining of the steelbomb, used in this and other experiments.

during 27 hours in a steelbomb lined with platinum. Of this preparation, looking also like radial bundles of needles with trigonal symmetry, we obtained some sections, normal to the axis of the needles. In convergent polarized light it was in reality possible to observe an interference-image, closely similar to that of an optically uniaxial crystal of positive character; however, on moving the section and rotating the table of the microscope, the image did not remain unaltered, but the black cro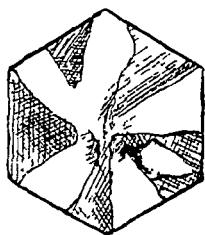ss opened its branches somewhat, and it was immediately evident, that a *biaxial* crystal, however with a very small axial angle, was present. Of yet higher importance however seemed the fact, that the crystalplate showed itself in parallel polarized light, to be composed of a number of sectors (fig. 3); in every sector the black cross between crossed nicols seems to open itself somewhat. It is hardly to be doubted, that a pseudo-symmetric aggregation is present here, with noticeable optical anomalies.

Fig. 3.

The repeated experiments of Mr. FRIEDEL gave, as he wrote us, no other crystals whatever, than *biaxial* ones, with very small axial angles, amounting occasionally to about 27°. The experiments were made in these cases, by heating 2,68 grams of dry SiO_2 and 0.885 grams of Li_2O (as hydroxyde) in solution, with a known quantity of finely divided muscovite, at 545° or 550° C. during 30 hours. Also without addition of mica, and at lower as well as at higher temperatures, the same results were obtained. (*A* and *B*, experiment XI, 1913). Although all conditions of the earlier experiment I, 1898) were as much as possible fulfilled, the obtained needles appeared however, *always to be biaxial*: a form of *complete* trigonal symmetry was never produced in any of these cases.

The birefringence of the pseudo-trigonal needles of preparation (I, 1898) was about: 0.021; that of the crystals from molten $LiCl$ was: 0,023 values do not differ noticeably from that, obtained by us formerly with the biaxial silicate.

The preparations *A* and *B*, and XI, 1913, were investigated in convergent and in parallel polarized light. Some sections, perpendicular to the axis of the needles, are reproduced in fig. 4. Doubtless it must result from this, that very complicated individuals and polysynthetic twins of lamellae, crossing under 60°, are present; the pseudo-trigonal habitus is caused thus by polysynthetic twinning.

The composing lamellae are all biaxial, the axial angle is very small, and rarely exceeds, as said already, 27°. By means of the immersion-method we were able to determine with some of

these needles the following values for the refractive indices:

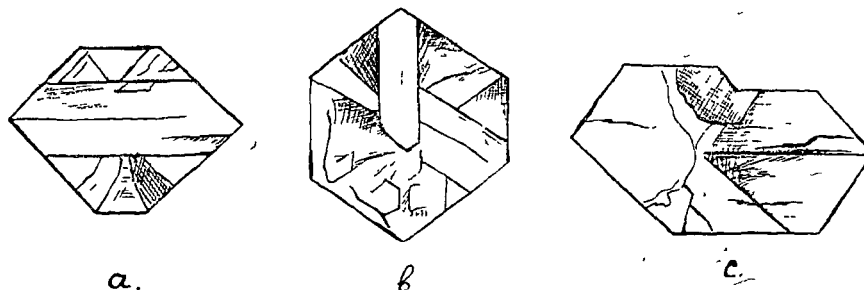$n_D = 1.600 \pm 0.003$ for vibrations parallel to the longer axis of

a. ß c.

Fig. 4.

the needles, and: $n_D = 1.584 \pm 0.002$ for vibrations, perpendicular to the first named.

The question, whether the composing lamellae must be considered, in agreement with HAUTEFEUILLE and MARGOTTET, as rhombic, is in our mind, very doubtful. As already the French author himself suggested, it is more probable to suppose *monoclinic* symmetry, and a pseudo-trigonal aggregation of these monoclinic individuals. Indeed, by such a polysynthethic twinformation, no pseudo-*trigonal*, but a pseudo-*hexagonal* aggregation woult result, because the original axes of binary period would involve a symmetry-axis of the whole struc-ture, having a period of $60°$.

The specific gravity of the modification (I, 1898) being: $(d_{15°} =$ $= 2,529$, is in complete agreement with that of our biaxial metasi-licate, which had: $(d_{4°}^{25°} = 2.520$ at $25°$ C.

Summarizing all these data, we must conclude from our experience in this matter, that the so-called pseudo-trigonal modification of the metasilicate can be *no new* modification of Li_2SiO_3, but only a polysynthetic twinformation of the original biaxial form, imitating very closely a true trigonal individual.

This form with its apparent symmetry, must in questions of ther-modynamical equilibria be considered as *the same phase* of the compound, which is deposited from the molten mass ordinarily as long, truly biaxial needles. In accordance with experience, brought up to this date by the study of such mimetic crystals, it is just quite clear, that no appreciable thermic effect, indicating some noticeable, sudden difference in the total energy of the system, could be detected in our experiments.

§ 9. *The lithiumbisilicate:* $Li_2Si_2O_5$ crystallizes from molten binary

mixtures of the same chemical composition, in the form of the great, flat crystals, which are characterised by their tabular shape and their peculiar aspect. O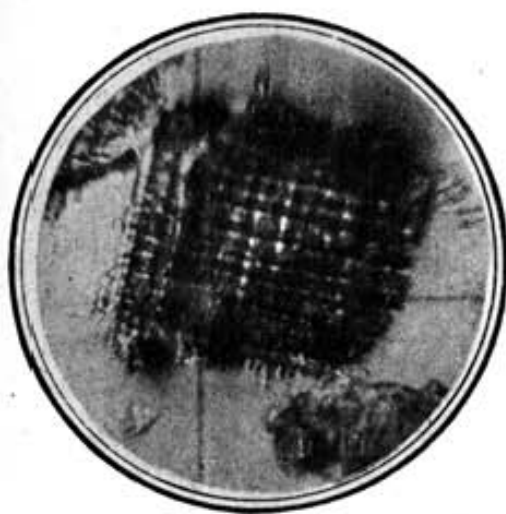ften they are recognisable (Fig. 5) by a system of cleavage-directions, crossing each other almost normally in three directions of space; the plates, as if covered with a fine network, are thus often bordered by right angles. The symmetry seems to be rhombic, or probably monoclinic; the crystals are biaxial, with positive character of their birefringence, which is about 0,020, — being slightly less than for the metasilicate. The apparent axial angle is probably rather great; more or less complicated twins are present. The figures 6 and 7 may

Fig. 5. Lithiumbisilicate; cleavage-directions (enlargement 500 ×).

give some representation of the habitus of this compound, as it looks between crossed nicols. The refractive indices are about: 1.545 and 1.525; it is very difficult to determine them accurately, because the crystals are intergrown with fine, felty needles of tridymite, or in some preparation with those of the metasilicate. The peculiar cleavage-directions are in every case most typical for this compound.

The specific gravity of the bisilicate was pycnometrically determined on: $d_4o = 2,454$ at $25°.1$ C.

It was a difficult thing to fix the borders of the stability-field of this compound, in contact with a binary liquid. We succeeded, by heating preparations of different composition, inclosed in thin platinum-folium, at a constant temperature during a time ranging from 20 to 60 minutes, in a quenching-furnace, and chilling the preparations then suddenly in cold mercury; in this way the momentary state of the mixture is fixed, and can be studied by accurate microscopical investigation.

The results of those experiments were the following:

Preparation N°. 3. Analysis: Weight Proc. of SiO_2 (= 74.2 Mol. Proc.). *Temperature*
in M.V.:

8890 Wholly crystalline; much bisilicate, very little tridymite.

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Fig. 6. Lithiumbisilicate. (cleavage-directions; Fig. 7. Lithiumbisilicate. (Enlarg. 50 times). enlargement: 50 times).

Temperature
  in M.V.

9920   Little bisilicate; mostly feebly birefringent aggregates of tridymite.

9930   Idem.

10370   Much glass, in which imbedded extremely feebly birefringent needles.

10970   Idem.

11570   Idem.

11770   Idem.

Preparation N°. 4.   Analysis: 82.1°/. SiO_2 (= 69.4 Mol. Proc.).

Temperature
  in M.V.:

9910   Crystalline, principally bisilicate, no tridymite in any appreciable quantity.

9930   Very little bisilicate, many feebly birefringent aggregates; a little glass.

9970   All glass.

Preparation N°. 5. Analysis: 79.9 °/. SiO_2 (= 66.6 Mol. Proc.).

Temperature
  in M.V.

9930   Bisilicate in typical form, often undulatory extinction, and finely intergrown with needles of impure metasilicate $n_D = 1.56$ or 1.57.).

Temperature

in M. V.

9950   Idem.

9962   About 10 % glass; further as mentioned above.

9985   About 50 % glass; imbedded bisilicate and needles.

9990   About 70—80% glass; needles of apparently impure metasilicate $n_D = 1.57$.

10005   About 90 % glass; needles with $n_D = 1.56$ or 1.57.

10040   Almost all glass ($n = 1.536$); locally a few needles.

Preparation N°. 6. Analysis: 75.7 % SiO_2 (= 60.7 Mol. Proc.).

Temperature

in M. V.:

9930   Felty aggregations of metasilicate, intergrown with much bisilicate.

9990   About 5 % glass; metasilicate with $n_D = 1.57$.

10030   About 80 % glass; felty birefringent needles.

We are of opinion, that in accordance with these results, the field, in which the bisilicate can exist in contact with a binary liquid, can be indicated as done in fig. 1; the compound must melt at 1032° C. under dissociation into metasilicate, and give a binary liquid of slightly varied composition. However, it seems, that no pure metasilicate is deposited, but a very-dilute solid solution of the bisilicate in it; this we may conclude from the fact, that the refractive indices of the needles are always somewhat less than those of the pure compound.

§ 10. The third possible compound, existing in contact with its binary liquid, the *orthosilicate*: Li_4SiO_4, was prepared in quite the same way by heating of the finely divided, thoroughly mixed components. Although the mixture, in composition identical with the compound, could also in this case be melted with a blast, if in small quantity; it was necessary to keep the molten mass at 1500° C for some time, to be sure, that practically all carbondioxide is expelled. But then some Li_2O volatilizes, and thus the chemical composition must be corrected again and again, till the required composition is reached. If, as is the case in the *Fletcher*-furnace, there is some watervapour present, the mass obtains afterwards a very disagreeable odour of silicohydrogens. It seems, that the flame-gases

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generate platinum-silicides, which afterwards are decomposed by watervapour under generation of silico-hydrogencompounds. The platinumcrucibles are strongly attacked by the Li_2O_2, which forms from the orthosilicate, when melted in the air; the platinum is coloured greenish or yellow, while the mass itself often looks pale-pink.

The fact of the attacking of the platinum by the lithiumperoxide, made it impossible to obtain reliable measurements with mixtures, richer in Li_2O than the orthosilicate, because the thermoelements are spoiled in the same way as the crucibles, and are thus losing their calibration. This fact must be kept in mind also, when meltingpoint determinations of the orthosilicate are made.

The orthosilicate, if brought into cold water, is momentaneously hydrolised by it; the solution shows a strong alkaline reaction. Analogous decomposition finds place by the carbon dioxide and the humidity of the atmosphere.

The heating of the orthosilicate in nickel crucibles, as already mentioned, causes an intensive lilac colouring of the mass, probably by diffusion of metallic nickel from the walls into the central part of the substance. The colour is the same, as many nickel compounds with complex ions show; it is not improbable, that the nickel is present in these products in the colloidal form, as observed e.g. by LORENZ [1]), in the electrolysis of some molten salts.

Microscopical investigation taught us, that the lilac product shows the same polygonal or almost round, very thin scales as the pure orthosilicate; however, they were now tinged homogeneously violet, and also often locally darker than in other places. These coloured crystals are noticeable *dichroitic*, as is often observed in crystals, which take some dyes in solid solution.

The refractive indices of this lilac substance did *not* differ appreciably from those of the pure compound. By means of the immersion-method, we found: $n = 1,595 \pm 0,005$ and $n_2 = 1,610 \pm 0,005$; the birefringence is fairly strong, and about: 0,015 to 0,020. Often a twinning is present, which reminds of that of albite. The specific gravity was determine dpycnometrically, in toluene, to be: $d_{4^o} = 2,392$ at 25,°1 C.; the coloured product showed a value slightly higher: $d_{4^o} = 2,415$ at 25°,1 C. Figure 8 may give a representation of the compound between crossed nicols; some twins are also shown in it.

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[1]) Cf. among others LORENZ, Elektrolyse der geschm. Salze II. S. 40. (1905); Gedenkboek VAN BEMMELEN. (1910). p 395.
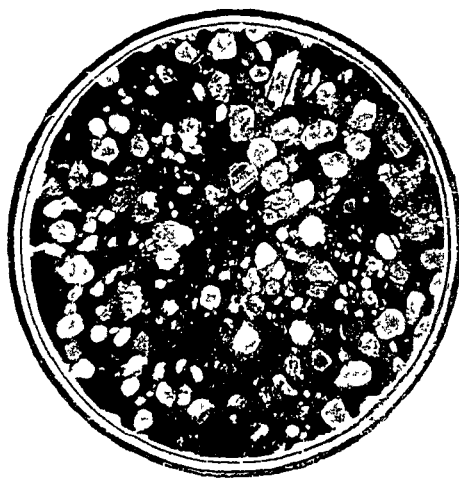
§ 11. The analysis of our product thus obtained, gave $50,8\%$ SiO_2 and $49,2\%$ Li_2O, while one calculates: $50,23\%$ SiO_2 and $49,77\%$ Li_2O. So there was an excess of 0.57% SiO_2, causing the small eutectic heat-effect at $1020°$ C. on the heating-curve. The meltingpoint of this substance, measured four times with the element S_4, was found successively (without correction) to be : 12463 M.V.; 12408 M.V.; 12399 M.V.; 12373 M.V.

The meltingpoint is thus continually lowered, which is caused

Fig. 8. Lithiumorthosilicate (Enlargem. 50 times; in immersion-liquid)

by the fact, that more and more Li_2O evaporates. and some Li_2O_2 is generated at the same time. On cooling, retardation of the crystallization was observed to about 12280 M. V., depending upon the speed of cooling; then, a sudden rise of temperature, caused by the solidification of the mass was observed to 12320 M. V.

To find the true meltingpoint, we started therefore with mixtures, which had a slight excess of Li_2O; the experiment showed, that already after one single determination, a loss of $0,4$ Li_2O could be proved, while a eutectic effect at 9775 M.V. became noticeable. Finally some heatingcurves were obtained, showing no eutectic effect; the crystallized product gave, on analysing, $50,0\%$ LiO_2. With thermoelement II the meltingpoint was now 12590 M.V. (corr.), corresponding with $1255°,5$ C. $\pm$ $3°$.

By means of the method of the "hollow thermoelement" (vid. § 12), we determined the meltingpoint to be : $1256°$ C.; as to the fact, that this temperature could eventually rather correspond to a three-phase-equilibrium, cf. § 12 and § 13 i.

The refractive indices of the scale-shaped crystals were measured by means of the immersion-method, and found to be $n_D = 1,614 \pm 0,003$ and $n_D = 1,594 \pm 0,003$. The birefringence therefore was fairly strong: about $0,020$, perhaps somewhat less than for the metasilicate; the same albite-like twinning as with the lilac crystals was also observed in this colourless product.

The finely divided powder of the orthosilicate, like that of $LiOH$, stimulates intensively to sneezing.

§ 12. We have tried to gain some more data on the thermic behaviour of mixtures, whose composition was lying between that of Li_4SiO_4 and Li_2O, and more particularly, with the aid of a method, which possibly may open an important way in future, to get results in those cases, where one of the components is highly volatile, or changes in contact with the air. Therefore we shall describe it shortly. The method is this, that crucibles are made from the purest stock of platinum, like that used in drawing the wires of the th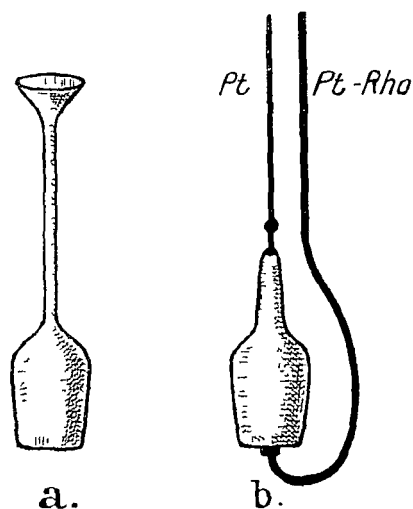ermo-elements, which crucibles have the shape and size, reproduced in fig 9a. A platinumrhodiumwire of a thermo-element, about 0,6 m.m. thick, is soldered to it at the bottom by means of the oxygenflame; then the crucible is filled with the finely powdered material, with the aid of the small funnel and hollow stem; after cleaning it very well, a thick platinumwire of the same diameter as the stem is introduced into it, and the crucible is melted off then at the top. The platinumwire of the used thermoelement, also 0.6 m.m. thick, is soldered then with the oxygenflame at the top of the crucible, and the other wire is bent as shown in the fig. 9b. Both wires are isolated by means of porcelain capillary-tubes, and the whole apparatus then fixed in a MARQUARDT-tube and hung in the furnace. The crucible must be in the region of the furnace, where no appreciable temperature-gradient is present. In the immediate neighbourhood of the crucible a second thermoelement is fixed in position; then the meltingpoint of the substance can be determined in the usual manner, by reading both thermoelements alternately every half minute.

Pt   Pt-Rho

a.   b.

Fig. 9.

Some experiments with $Li_2 Si O_3$ *immediately proved the method to be completely adapted for our purposes*: we found the meltingpoint not only as sharp as formerly, but also the undercooling- and solidification-phenomena gave perfectly analogous results, as in the case, where open crucibles were used. The meltingpoint of $Li_2 Si O_3$, determined in this way, was found at an E.M.F. of 11968 M.V.; as the correction of the thermoelement however was determined to be —26 M.V., thus the temperature i.c. lies at 11942 M.V. or 1201° C.

We now tried first of all, to determine the meltingpoint of pure

Li_2O in this way, if free from peroxide. Although the temperature was increased up to 1625° C. this time, we were not able to find any heat-effect. The crucible was inflated like a balloon, but did *not* crack. After being opened, we found the powder baked together, however *not* molten. An unimportant trace of peroxide only was formed. Therefore we must conclude, that as TROOST already pointed out, the melting-point lies very high, — higher than can be determined by means of our platinumresistance-furnaces and thermoelements. Probably the meltingpoint will be in the neighbourhood of 1700° C.

Thirdly we determined the meltingpoint of the $Li_4Si O_4$ quite in the same way, and found it (without any correction), in several determinations, at an E.M.F. of 12640 M.V., if the thick thermo-element (0,6 m.m.) was used. As the correction of it was —35 M.V. for this temperature, the true meltingpoint is **1256° C.** (G.-Th.), thus not differing appreciably from the formerly obtained value. The heat-effect was not large; but if the thermoelement is fixed in a suitable way at the bottom, which must be bent a little inwardly, the heat-effect is clearly localised on the heating-curves. On cooling, we found a crystallization at 1249° C.

It is of course possible, that this temperature of 1256° C. indeed corresponds to a steep and not very extended maximum in the curve. However we made some more experiments, to find out the form of the curve for mixtures, which are still richer in Li_2O, by means of the described new method. With a mixture, corresponding to 54 weight-procents Li_2O (or 71 Mol. proc. Li_2O), we found a good observable heat-effect at 1405° C.; then the bulb cracked by the enormous vapour-tension. Thus it can be, judging from this, that the temperature of 1256° C. must be considered rather as a temperature of "transformation", at which the orthosilicate melts under dissociation into Li_2O, and into a liquid, whose composition is very close to that of the pure compound.

§ 13. *Microscopical investigations.* All preparations were microscopically investigated, and the results were in every case compared with those of the thermical determinations. It is an agreeable task to us, to express our thanks once more to Dr. F. E. WRIGHT in *Washington* for his kindness and readiness to look over our preparations again, and for the information he has given us in some doubtful cases.

In general we can say, that the results of these investigations by means of the microscopical method agree fairly well in all respects, with the conclusions drawn from our thermical work. The prepara-

tions are ranged in the following, in series of increasing quantities of SiO_2.

_ a. 91:8 Weight Proc. SiO_2 ($= 84.7$ Mol. Proc.).

· This preparation showed two components: firstly a substance of weak birefringence and a refractive index of about 1.480. It is present in irregular felty needles, spread through the other component, or in corns of indefinite boundaries. This substance seems to be no other than a-tridymite.

Another substance of stronger birefringence and of a positive character, with a refractive index of about 1.545 is seen accompanying it. The birefringence is about: 0.020, thus being a little less than for the metasilicate. This component is the bisilicate: $Li_2Si_2O_5$. Solid solutions between this compound and SiO_2, which we were inclined to suppose, seem after Dr. WRIGHT's judgment not to be present.

b. 89% SiO_2 ($= 80$ Mol. Proc.). This preparation is in all respects analogous to the former one.
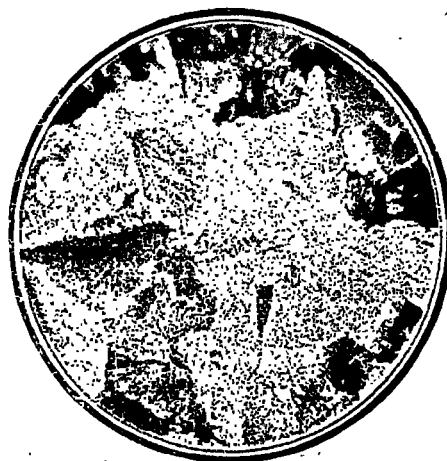

Fig. 10. 89 Weight Proc. SiO_2.
(Enlargement: 50 ✕).

Fig. 11. 85,2% SiO_2. (Enlargement: 50 ✕).

· c. 85.3% SiO_2 ($= 74.2$ Mol. Proc.).

The quantity of tridymite is considerably diminished; it is only present in exceedingly small needles. The bisilicate presents itself in tabular crystals, intergrown with tridymite. In convergent polarised light, the substance is shown to be biaxial; however the axial angle seems to be too large, to observe a complete interference-image. Sometimes the crystals have the aspect as if subjected to torsion.

d. 82.1% SiO_2 ($= 69.4$ Mol. Proc.). This preparation is almost homogeneous, and consists of tabular crystals; the macroscopical aspect

of the preparation gives already immediately the same impression. Most characteristic is the system of cleavage-directions which seem to cover the plates as with a fine net-work of lines in three directions, arranged perpendicularly to each other in space. The boundaries of the tables are often rectangular; they show normal extinction. The refractive indices are: 1.545 parallel to the axis of elongation of the -crystals, and 1.525 perpendicularly to it. The birefringence is of positive character and about: 0.020.

Often twins or very complicated intergrowths occur.

e. 79.6% SiO_2 (= 66.0 Mol. Proc.).

The preparation is again fairly homogeneous. Only some fine needles are found locally on the table-shaped crystals, probably representing the metasilicate. This fact would prove, that the bisilicate will dissociate on melting. The birefringence is positive and about: 0.020; the refractive indices are found to be about: 1.545 and 1.530. Many parallel intergrowths, and polysynthetical twins seem to be present; the fine lines, indicating the system of cleavage-directions, are here most typical. Locally the preparation shows a little quantity of glass.

f. 75.7% SiO_2 (= 60.7 Mol. Proc.).

Fig. 12. 78,8 Weight Proc. SiO_2. (Enlarg. 50×).

This preparation is inhomogeneous; longshaped needles, with $n = 1.585$ and normal extinction are intergrown with the grains and plates of the bisilicate. The refractive indices of the needles are somewhat less than those for pure Li_2SiO_3; we found e.g.: 1.595 and 1.569 in the same individuals.

g). 71.1% SiO_2 (= 54.9 Mol. Proc.).

The quantity of the metasilicate is considerably increased; for the remaining part just as *f.*

h). 66.7% SiO_2 (= 49.7 Mol. Proc.).

Homogeneous. It is the Li_2SiO_3, with all properties, formerly indicated. The axial angle seems to be rather small.

i). 63.9% SiO_2 (=46.7 Mol. Proc.). In general lines this preparation resembles the former; locally small grains of the orthosilicate, with its weaker birefringence, but stronger refraction, are visible.

The following preparations are then analogous to i; the quantity of the metasilicate diminishes gradually, compared with the closely intermixed orthosilicate, which presents itself in round or polygonal corns, often twinned in a particular way. The preparations, which are in gross composition very close to Li_4SiO_4, show the crystals of the orthosilicate often in a highly altered condition; the immersion-liquids also seem to be attacked by the expelled alkali, and measurement is often impeded by it.

The fact, that the crystals of the orthosilicate appear often more or less attacked under the microscope, could make more probable the view, according to which the temperature of 1256° C. were rather a "transformation"-temperature than an ordinary meltingpoint; the compound would be converted thus into a liquid, with partial dissociation.

In the principal outlines we may say, that the binary diagram of SiO_2—Li_2O is known now. It will doubtlessly prove for the present impossible, to investigate the behaviour of the components at concentrations between orthosilicate and lithiumoxide in their complete details, because of the enormous volatility of this oxide at these extreme temperatures.

Laboratory of Inorganic and
Groningen, February 1914. *Physical Chemistry of the University.*

Physics. — *"The volume of molecules and the volume of the component atoms."* By Prof. J. D. VAN DER WAALS.

(Communicated in the meeting of January 31, 1914). -

I think I may assume as known that for normal substances the volume of the molecules expressed in parts of the gas volume at 0° and 1 atmosphere pressure may be calculated in a simple way by means of the critical quantities. When it is not yet taken into account that the quantity b of the equation of state decreases with v we find:

$$\frac{RT_k}{p_k} = 8\,b$$

$$\text{or } \frac{T_k}{p_k} = \frac{8 \times 273}{(1+a)(1-b)}\,b,$$

in which b represents 4 times the volume of the molecules. If we do take into account that this factor 4 diminishes when the volume, as is the case for the critical state, has decreased to almost $2b$, we find by approximation:

$$\frac{T_k}{p_k} = \frac{7 \times 273}{(1+a)(1-b)}\,b,$$