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§ 5. The compound  $TeJ_4$  was once more recrystallised by us from strong  $HJ$  with addition of some  $NH_3$ . Instead of the ammonium-compound, we obtained crystals with a metallic lustre, which on analysis contained 1% more of  $J$  than corresponded with  $TeJ_4$ . A little too much iodine was also found in the hydrate obtained from telluric acid.

An investigation by one of us as to the phenomena occurring in solutions of  $TeJ_4$  in strong  $HJ$  with excess of iodine, is already in progress.

December 1911.

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**Chemistry.** — “*The question as to the miscibility in the solid condition between aromatic Nitro- and Nitroso-compounds*”. III. By Prof. F. M. JAEGER and Dr. J. R. N. VAN KREGTEN. (Communicated by Prof. P. VAN ROMBURGH).

(Communicated in the meeting of December 30, 1911).

§ 1. In consequence of the formation of solid solutions between *o-Nitroso-benzoic acid* and *o-Nitro-benzaldehyde*, also owing to a treatise of BRUNI and CALLEGARI<sup>1)</sup> on the formation of solid solutions between aromatic *nitroso-* and *nitro-*derivates, as a general phenomenon, investigations have been carried out by one of us (J.) to get a better knowledge of the mutual relation of both classes of nitrogen-derivatives<sup>2)</sup>. This investigation which comprises many *nitro-*, and *nitroso-*derivates of analogous structure could only lead to the conclusion, that, certainly, in some cases, there was a question of a morphotropous relation and resulting miscibility, but that in most cases such a relation did not exist and could not, in homologous series, even be called a generally occurring phenomenon.

In the following some more data regarding these questions have been collected, which enable us to supplement the previous statements in some respects.

§ 2. *Nitrobenzene and Nitrosobenzene.*

The simplest representatives of the compounds to be discussed are *nitro-* and *nitroso-benzene*.

<sup>1)</sup> BRUNI and CALLEGARI. *Gazz. Chim. Ital.* **34**. II. 243. (1904).

<sup>2)</sup> F. M. JAEGER, *Proc.* 1905. 658, 1908. 436; *Zeits. f. Min. und Kryst.* **42**. 236. (1906). Comparisons have been made between: *p-Nitro-*, and *p-Nitroso-diethylaniline*; *Nitro-*, and *Nitrosobenzene*; *p-Nitro-*, and *p-Nitroso-phenol*; *o-Dinitro-*, and *o-Nitro-nitrosobenzene*; *o-Nitro-*, and *o-Nitroso-aceto-anilide*.

The *nitro-benzene* was purified by three times freezing and subsequent distillation. The fraction boiling at  $211^{\circ},6$  under  $76,7$  m.m. pressure was used for the investigation. The thermometer was compared with a normal thermometer; at  $0^{\circ}$  it appeared to indicate  $0^{\circ},2$ , and at  $100^{\circ}$ ,  $0^{\circ},1$  too low.

The solidifying-point, with different outer-bath-temperatures, appeared to be always  $+4^{\circ},9$ ; the same temperature was also found for the melting-point. In these last experiments the solid substance was heated slowly in an oil-bath. Pure *nitrosobenzene*<sup>1)</sup> therefore solidifies and melts at  $+4^{\circ},9$ .

BINARY MELTING-POINT-LINE OF NITRO-BENZENE + NITROSO-BENZENE.				
Composition in mol. %		Solidifying point	Eutectic temp.	Time in seconds
% $NO_2$ -Com- pound	% $NO$ -Com- pound			
100.0	0.0	$4^{\circ},9$	—	—
97.5	2.5	3.6	—	—
95.7	4.3	3.1	$0^{\circ},8$	—
94.1	5.9	2.1	$-0.7$	240
92.3	7.7	1.2	0	480
88.9	11.1	—	0	560
86.0	14.0	—	0	1080
82.8	17.2	1.8	0.1	990
78.3	21.7	5.2	0.2	960
67.0	33.0	18.6	0.5	780
56.5	43.5	27.5	0.2	630
45.3	54.7	36	0.2	480
26.4	73.6	46	$-2.1$	240
15.0	85.0	54.8	$-4.0$	—
7.3	92.7	61	$-10.0$	—
4.0	96.0	60	—	—
2.1	97.9	60.2	—	—
0.0	100.0	68	—	—

<sup>1)</sup> In the literature are given for this temperature-values varying from  $+3^{\circ}$  and  $+5^{\circ}$ ; for the boiling-point is found  $208^{\circ}$  under  $760$  m.m. pressure. We, however, find both values a little higher.

The *nitroso-benzene* was first repeatedly recrystallised from hot alcóhol and then from benzene. The melting-point was always found too low. Afterwards the substance was recrystallised from a mixture of alcohol and ether in an atmosphere of carbon-dioxide to prevent oxidation. After rapid suction it was dried in vacuo over sulphuric acid. The melting-point was then found to be at  $+68^{\circ}$ . This compound, however, is decomposed a little above its melting-point (at about  $7^{\circ}$ ) suddenly and with great evolution of heat, with formation of a brown liquid.

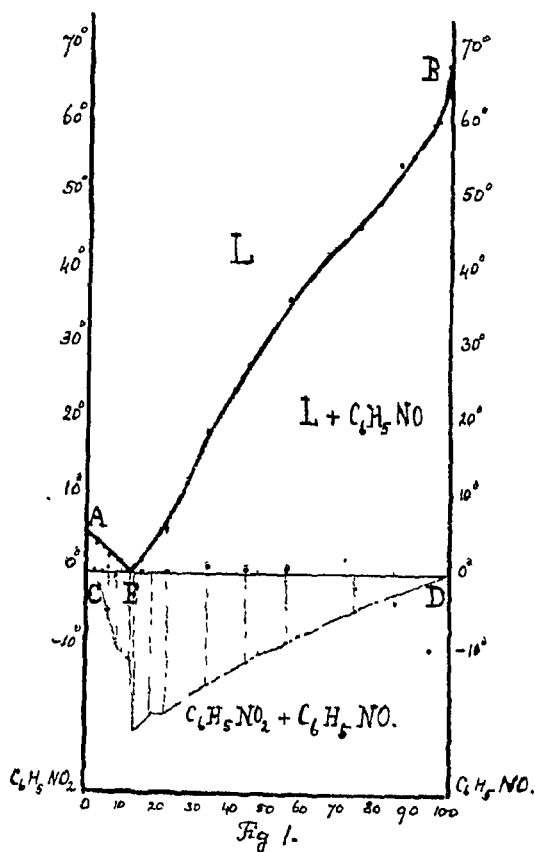
If the decomposition, caused by careless heating, is only partial, the solidifying-point will be found later to be somewhat lower.

*Solidifying*-points only could be recorded with sufficient sharpness.

The data given in the table on p. 730 have been recorded by us.

These data are represented in fig. 1 in the usual graphical way.

§ 3. From this it appears that *nitro*- and *nitroso-benzene* — perhaps



with exception of concentrations situated in the immediate vicinity of the axes — do not, or hardly at all, form mixed crystals.

A miscibility at exceedingly small concentrations of both components occurs, however, more or less distinctly in all systems formed from carbon-compounds.

Otherwise, the differences in crystal-form are not readily noticed, because the *nitro-benzene* is liquid and can only be obtained from fusions at a low temperature in a crystallisable form. It is, probably, rhombic and analogous to the crystal-form of benzene, at least in one of the two parameter-relations.

*Nitroso-benzene* is rhombic-bipyramidal<sup>1)</sup> with  $a : b : c = 1,4770 : 1 : 0,7006$  and the forms: {100}, {110}; {111}; {340}; {221}; {001}.

*Benzene* is rhombic, with  $a : b : c = 0,891 : 1 : 0,799$ ; these parameters are in no case analogous to those of the *nitroso*-derivative and probably also not to those of the *nitro*-compound.

All this seems to indicate that there can be no question either of

BINARY MELTING-POINT-LINE OF p-NITRO-ANILINE + p-NITROSOANILINE			
Composition in mol. %		Solidifying temperature	2nd Heat effect
% $NO_2$ -anil.	% $NO$ -anil.		
100.0	0.0	147°	—
91.4	8.6	144	141
82.9	17.1	137.7	—
74.7	25.3	133	—
66.7	33.3	125.3	—
58.6	41.4	120.5	119
50.8	49.2	119	120
43.2	56.8	—	120
35.6	64.4	—	115
21.0	79.0	—	124
13.8	86.2	decomp.	124
6.9	93.1	decomp.	124
3.4	96.6	decomp.	122
0.0	100.0	169°	—

<sup>1)</sup> F. M. JAEGER, Zeits. f. Min. u. Kryst. 42. 246. (1907).

a pronounced form-analogy, or of a perceptible formation of solid solutions between *nitroso-* and *nitro-benzene*.

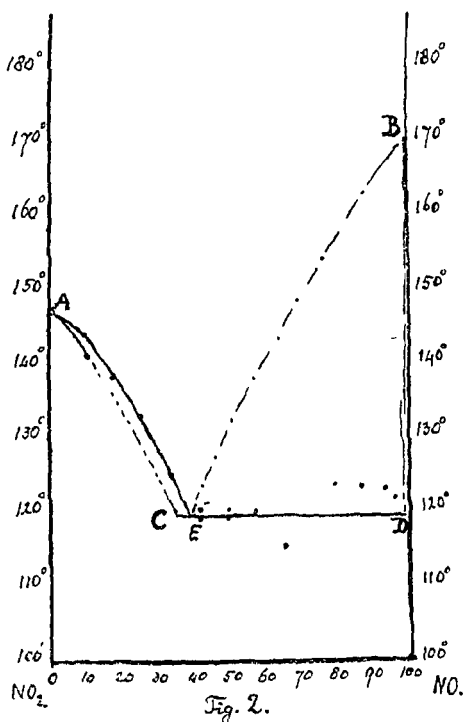
§ 4. *p-Nitro-Aniline* and *p-Nitroso-Aniline*.

Whereas, on account of the presence of *H*-atoms in the amino-group, a tautomeric structure of the *nitroso*-compound is not excluded, this system was sufficiently interesting to deserve further investigation. This investigation, however, was, unfortunately, rather unsatisfactory, owing to the fact that a decomposition of the *p-Nitroso-Aniline* could not be prevented: whereas the melting point is situated at 168°—169°, the temperature of decomposition is about 170°.

The *p-Nitro-Aniline* used was recrystallised from benzene and also from water; at 100° 2,2 grams of the compound dissolve in 100 cc. of water. The melting temperature proved, on repetition, to be 147°.

The *p-Nitroso-Aniline* was recrystallised from benzene and dried in a current of carbon-dioxide to prevent oxidation. Immediately after melting at 163°—169° a sudden decomposition took place with evolution of heat and a violent evolution of gas.

By working carefully, the approximate data contained in the table on p. 732 could still be obtained.



In fig. 2 these results are represented graphically; there can be no question of an exact determination of the diverse points, but only of a first orientation. The whole seems to point to a formation of mixed crystals at the side of the *Nitro*-compound to a considerable concentration (35 to 40 %) with the *Nitroso*-compound, but to only a slight mixing at the side of the latter.

As all the fusions were too dark in colour owing to the decomposition, a microscopical investigation did not much avail. In no case, however, is there any question of a continuous mixing-series.

A few remarkable phenomena, which are communicated here, were, however, noticed microscopically.

From the brownish-red melt of 83%  $NO_2$ - and 17%  $NO$ -aniline, there are deposited on cooling, at first fairly rapidly, elongated, orange-red needles in thick bundles. After waiting for some time, these apparently become covered with an innumerable number of very small yellow needles; if a primary needle has been placed between two crossed nicols in such a position that it gets dark, it suddenly becomes luminous in the process described. There are now present in the preparation two components: the partly unchanged, original brownish-red needles and the subsequent yellow ones; both are feebly dichroic. In convergent polarised light is seen a remarkable, biaxial interference image can be observed, namely four orange-red, equilateral hyperboles and a green cross; apparently, the axial planes for the diverse colours are crossed, and an enormous dispersion is present.

A mixture with 73% of  $NO_2$ -compound also behaves, optically, like the above. The transformation, however, takes place more slowly than in the first case. With the 51%  $NO_2$ -compound brownish-red needles are obtained; of a transformation little more is visible; with the 21%  $NO_2$ -compound there are present dichroic (red-orange yellow) aggregates, spherulitically built. In these two latter cases it is difficult to decide whether we have one or two structural components; the fused masses are also almost opaque by decomposition.

In each case, the mixed crystals at the  $NO_2$ -side, therefore at a lower temperature, seem to pass into another modification, with considerable changes in their symmetry and volume.

#### § 5. *p*-Nitromonoethylaniline and *p*-Nitrosomonoethylaniline.

The *p*-Nitro-Monoethylaniline was recrystallised repeatedly from benzene and afterwards the heating- and also the cooling-curves were several times recorded.

The melting-point was situated at  $94^\circ$ , the solidifying-point at  $93^\circ.9$ . The melting point given in the literature ( $95^\circ-95^\circ.5$ ) is, evidently, a little too high.

The *p*-Nitroso-Monoethylaniline was also recrystallised repeatedly from benzene; it melted, constant,  $75^\circ-76^\circ$  in a capillary tube; when taking the melting-, and solidifying-points in the more delicate manner, these were, however, always situated at  $74^\circ$ , undercooling was always avoided by inoculation.

The following data were obtained:

( 735 )

BINARY MELTING POINT LINE OF p-NITRO- AND p-NITROSOMONOETHYLANILINE			
Composition in mol. %		Solidifying temperature	Eutectic temperature
% NO <sub>2</sub>	% NO		
100	0	94°	—
95	5	92	ca. 40°
90	10	89.2	54
80	20	84	53
70	30	77.5	54
60	40	73	51
50	50	64.7	51.4
40	60	58	54.6
30	70	54	—
20	80	59.6	49
10	90	66.9	46
5	95	70.5	53
0	100	74.1	—

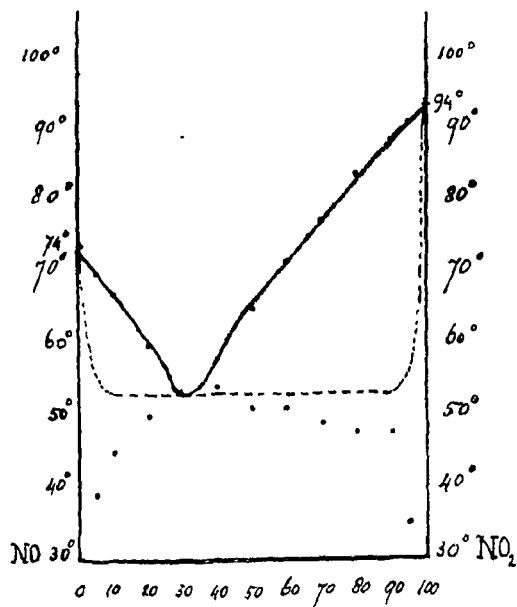


Fig 3.

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As, notwithstanding the inoculation, a great undercooling was sometimes perceptible, the deviations especially from the eutectic temperature are considerable here and there.

§ 6. Although the diagram makes the impression as if no mixing in the solid condition were present here, but that there is only a question of an ordinary binary melting-point-line with a eutecticum, — in each case declining at both sides, — the microscopical investigation still shows that we have no right to look at the matter in this way without further evidence.

The pure *nitroso*-compound presents itself under the microscope in the form of spherulitically-grouped, strongly dichroic platelets; the colours are may-green and grass-green.

The *nitro*-compound forms long, lemon-yellow but faintly dichroic platelets, which between two crossed nicols do not become dark in a single position, but exhibit on turning of the table, a vivid display of colours, green, yellow etc. In convergent light it appears that we have here nearly parallel to the direction of the "normal" of the platelet, the bisectrix of a very remarkable interference image of a biaxial crystal, for we notice a dark horizontal beam which intersects a bright green field in the centre, while in the vertical plane are situated two red fields, which are intersected by dark beams, terminating at some distance from the centre. The green field is limited in four quadrants by a system of bluish-purple equilateral hyperboles.

Evidently we are dealing here with a crystal, whose axial plane for red and green light is the longitudinal direction of the needles, but for blue rays their latitudinal direction: such in connexion with an exceedingly small angle for the diverse colours, while that for the red is larger than that for the green.

If now we investigate the binary, solidified fusions, it is at once visible to the naked eye that they congeal to a homogeneous aggregate of crystals. From solutions in ethyl-acetate are also formed homogeneous green crystals.

With 5%  $NO_2$ -compound were found green fern-like mixed crystals; with an increasing content of the  $NO_2$ -substance their colour turns more and more yellowish-green, but the solidified melt remains existent as a single crystal-form. Only at a 40%  $NO_2$ -compound the remarkable axial image of the pure *nitro*-compound plainly returns; at 70% the crystals are nearly monaxial for red; at 90% and 95% of the  $NO_2$ -compound, the mixed crystals obtained from a solution in ethyl-acetate are beautifully greenish-yellow, very faintly dichroic and exhibit the characteristic axial image in a remarkably plain

manner. These experiments quite confirm the suspicion that a *continuous series of mixed crystals* is formed here. If so, there is no other possibility but to assume that the binary melting-point-line is also a continuous curve with a minimum temperature at  $54^{\circ}$  and a content of about 30% of the *nitroso*-compound; and that owing to the occurring undercooling, and to the evidently incomplete setting in of the equilibria, the solid line has declined to such an extent that it nearly assumes the form of a eutectic horizontal line. Such has been already observed previously in systems without a minimum in the liquidus-line; compare for instance the case of *Sb + Bi* investigated by HÜTTNER and TAMMANN<sup>1)</sup>.

True in this particular case the said authors-attribute the cause of the deviations to the fact that the mixed crystals which have deposited at first, get coated and that it then becomes impossible for them to get into equilibrium with the melt at any moment; but they still point out that a similar behaviour may be expected each time when the said setting in of the equilibrium takes place with insufficient velocity, and that might be the case here also. The formation of an uninterrupted series of mixed crystals both from solutions and binary fusions, and this without subsequent transformations or dissociations agrees with this view.

#### § 7. *p*-Nitro-Monopropyl-Aniline and *p*-Nitroso-Monopropyl-Aniline.

Finally, we have investigated the system of the above compound in the same way.

The *p*-Nitro-derivate was first recrystallised from hot benzene from which splendid, large crystals are deposited. Their melting-point appeared to be  $53^{\circ}$ — $54^{\circ}$ ; moreover they were found to turn soon turbid owing to loss of benzene. The compound was, therefore, powdered, dried and repeatedly recrystallised from absolute alcohol. From this are also sometimes deposited splendid crystals which melt constant, at  $64^{\circ}$ — $65^{\circ}$ . They mostly have curved planes and consequently can only be measured with difficulty.

The *p*-Nitrosomonopropylaniline was also purified by recrystallisation from benzene; it then also contains benzene of crystallisation and melts at  $45^{\circ}$ — $50^{\circ}$ .

After expelling the benzene in vacuo and repeatedly recrystallising from a mixture of absolute alcohol and ligroin, the melting point, in a capillary tube, was found to be  $58^{\circ}$ , which value is also given in the literature.

<sup>1)</sup> HÜTTNER and TAMMANN, Zeits. f. anorg. Chem. 44, 131. (1905).

BINARY MELTING-POINT-LINE <i>p</i> -NITRO- AND <i>p</i> -NITROSOPROPYLANILINE			
Composition in mol. %		Initial solidi- fying point	End solidi- fying point
% $NO_2$	% $NO$		
100	0	62.9	—
95	5	61.2	— (weak effect at 58°)
90	10	59.3	— effect at 49°)
80	20	56.5	54.5
70	30	52.9	51
60	40	49.3	47.5
50	50	47.0	44.5
40	60	44.5	43
30	70	42.8	42
20	80	40.5	40.5
10	90	48	—
0	100	56.5	—

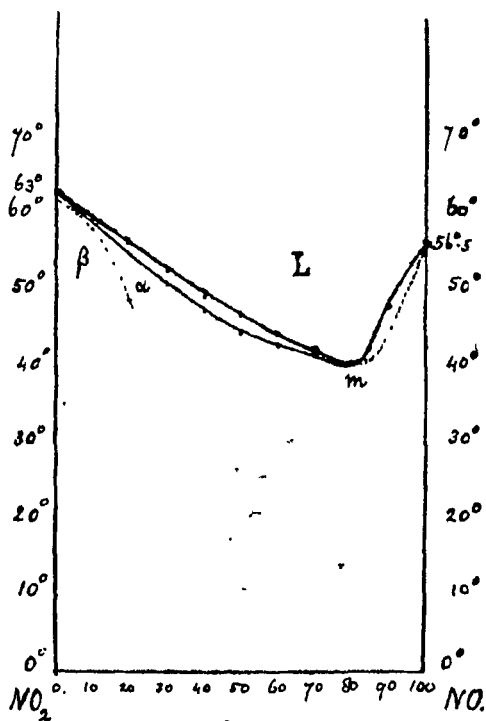


Fig. 4.

First of all, the solidifying points of both derivatives were accurately determined by recording the cooling lines. In this way was found, with slight undercooling, 62,9° C. for the solidifying point of the *nitro*-compound and 56,3—56,5° C. for the *nitroso*-derivative.

Successively, the following mixtures were investigated (see table previous page).

§ 8. These data graphically represented in fig. 4, prove that there exists here a continuous series of solid solutions between the two components, with a minimum temperature of 40,5° C. and a concentration of about 80 % of the *nitro*-compound.

The microscopical investigation also confirms the existence of such a series of mixed crystals.

The *p-Nitro*-compound crystallises from its yellow melt with great rapidity in lemon-yellow, hexa- or octangular plates, which are *immediately* followed by a darker coloured modification, generally occurring in parallelogram-like plates, joined in all directions. They are strongly dichroic: yellowish-white and dark yellow. Between crossed nicols they are black and on our turning the table slightly to the right or to the left, the colour changes to brown or green. In convergent polarised light one branch of a hyperbola is visible excentrically, and coloured red at the inner side and blue at the outer side. Very strong dispersion.

The *nitroso*-derivative has an extraordinarily small crystallisation-velocity; fern-like aggregates exhibit a splendid steel-blue lustre and are strongly pleochroic: green and brownish-yellow.

Mixed crystals with 5, 10, 40, 60, 90% *NO*-compound have been investigated. A yellowish-green melt with 5% *NO*-derivative solidifies to an aggregate of yellow plates of the *NO*<sub>2</sub>-form, which after about half a minute suddenly burst and pass into another modification of a more yellowish-green colour and a much stronger double refraction; previously dark crystals become luminous etc. The crystallisation-velocity is still very considerable; whereas the first modification, between two crossed nicols, is dark in two positions, the second is not extinguished in any position. After some time the first crystallisation is succeeded by a feather-shaped aggregate of the second one.

With 90 % of the *Nitro*-compound there is hardly anything more to be observed of the polymorphous conversion, notwithstanding the great velocity of crystallisation. With 60% *NO*<sub>2</sub>-derivative we have homogeneous mixed crystals, which are strongly dichroic: green and bright-yellow. With 40 % *idem*; the crystals are: dark-brown and yellow. With 10% *NO*<sub>2</sub>-compound the velocity of crystallisation is

already extraordinarily small; mostly spherulitic aggregates which are strongly dichroic: bright yellow and green.

§ 9. The above proves that the *nitro*-compound is here also dimorphous; with the 90% mixed-crystal, the strongly decreased temperature of conversion of the pure  $NO_2$ -substance -- which lies just below the melting point, -- is still determinable by the corresponding heat-effect.

With a larger content of *NO*-compound, that determination is, however already impossible owing to the enormous retardation of the polymorphous conversion through the admixture of the slowly crystallising *nitroso*-derivative.

§ 10. From the investigation it has appeared anew, that mixed crystal formation can occur in binary fusions of corresponding aromatic *Nitro*- and *Nitroso*-derivatives, but that this miscibility must *not* be looked upon as a general property of these compounds in regard to each other. Moreover, the mutual behaviour of these two kinds of substances becomes often more complicated by the appearance of polymorphous modifications and by the difference in crystallisation-velocity in the two components. The most simple representatives of this class of substances *nitrobenzene* and *nitrosobenzene* do *not*, or only in an insignificant degree, form solid solutions with each other.

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**Chemistry.** — “*Photo-electric phenomena with Antimony sulphide (Antimonite)*”. By Drs. J. OLJE JR. and H. R. KRUYT. (Communicated by Prof. v. ROMBURGH. (Preliminary communication).

(Communicated in the meeting of December 30, 1911).

JÄGGER<sup>1)</sup> discovered some years ago a very remarkable property of native antimonite which, however, seemed to belong exclusively to the large crystals of this mineral found only in Shikoku (Japan). The mineral exhibited, as regards sensitiveness of the electric conductivity power to irradiation, a very great analogy with selenium. Illumination strongly lessened the resistance of the material. The fatigue so troublesome with selenium for the practical application of this property was here but insignificant. Immediately after stopping the irradiation, the resistance regains about its original value called, briefly, “the darkness resistance”.

<sup>1)</sup> Proc. Kon. Acad. v. Wet, Amsterdam 1907, p. 809—814.