

Citation:

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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).

JÄGGER¹⁾ 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”.

¹⁾ Proc. Kon. Acad. v. Wet, Amsterdam 1907, p. 809—814.

JAEGER, however, found that the remarkably strong sensitiveness to light totally disappeared on remelting; the specific resistance then also became several thousand times smaller. On powdering the mineral, the sensitiveness to light also completely disappeared, but the resistance was only little affected. It was therefore obvious to connect the sensitiveness to light with the macrocrystalline structure of the material, to which JAEGER already called attention¹⁾ without, however, attempting to further explain the phenomenon.

As, however, with none of the other substances which exhibit a similar sensitiveness to light in a greater or lesser degree, such as selenium²⁾ tellurium, sulphur, Ag₂S, Ag₂J etc. (although in most of these substances the causes of the phenomenon are far from being elucidated) anything like a dependence of the photo-electric effect on macrocrystalline structure has up till now been noticed, the antimonite would then constitute a case by itself. This seemed to us somewhat improbable and caused us to investigate whether the explanation of the phenomena observed by JAEGER might not perhaps be found by working in another direction.

Now, according to JAEGER, his Japanese antimonite is very pure and has almost exactly the composition Sb₂S₃; all other specimens (none of which exhibit a light effect) are less pure. We, therefore prepared from pure materials³⁾ an artificial antimonite in order to test this as to its sensitiveness to light. Already at a first experiment we succeeded in obtaining a strongly sensitive preparation⁴⁾ by rapidly heating, in an open tube, antimony powder mixed with a small excess of sulphur. The subsequent orientating experiments gave alternately a positive or negative result, which made us resolve to investigate systematically a series of mixtures of varying quantities of S and Sb in order to ascertain whether small modifications in the composition of the antimony sulphide, which was otherwise quite free from foreign substances, might be the cause of the greater or lesser sensitiveness to light.

As on heating in open tubes in an atmosphere of carbon dioxide a loss of sulphur through volatilisation could not be avoided, we proceeded to operate in sealed evacuated tubes, which could be

¹⁾ Zeitschrift für Krystallographie etc. Vol. XLIV, p. 45—48.

²⁾ By one of us, an explanation of the phenomenon in the case of selenium has been given from a phase-rule point of view H. R. KRUYT, Die dynamische allotropie des Selenes Zeitschr. f. Anorg Chem. 64. p. 305 (1909).

³⁾ Sb from KAHLBAUM. S recrystallised from CS₂.

⁴⁾ The illumination always was done in the same manner with a small Halbertsma arc-lamp at about 30 cm. distance from the preparation.

heated in a specially constructed oven at about 600° and also be regularly shaken to make sure of a complete homogeneous mixing.

As regards the result of this investigation it may be stated provisionally that the pure compound — Sb and S in the exact proportion Sb_2S_3 — appeared to possess the highest photo-electric effect. This sensitiveness to light amounted in some cases to about 400% ¹⁾. This sensitiveness relates to Sb_2S_3 in massive little rods of about 10 mm. in diameter. As the light effect must be a superficial action and as relatively thick massive rods are therefore a less advantageous form to promote this effect, the relative sensitiveness can be very strongly enhanced by choosing a more suitable form of antimonite-cell in which the relation of the surface to be irradiated to the section of the conductor is very much larger. In any case it has appeared that the observed sensitiveness to light in artificial antimonite is of the same order as that found by JÄGER in the native mineral ²⁾ and which we have verified ourselves with Japanese Antimonite procured from KAHLBAUM. We hope, shortly, to refer more in detail to the method employed in the investigation of the dependence of the photoelectric effect on the composition of the substance. In the main it amounted to this, that by means of a very sensitive instrument (galvanometer, system SIEMENS HALSKE *Deprez-d'Arsonval*) we determined the relative conductivity power in darkness of small rods of antimonite of different composition and also the relation of the "conductivity in darkness" to their "conductivity in the light" (namely the conductivity power on illumination).

From the relative conductivity power in darkness and better still from the temperature coefficient thereof we were able to deduce the form of the melting diagram of the system S—Sb in the sphere investigated ³⁾ that is in the vicinity of the compound Sb_2S_3 ; starting from the compound towards the antimony side we first found a very small mixed crystal sphere — about 0.3 at % and further a sphere of partial miscibility. All this is greatly in harmony with the investigations published in these proceedings, by JÄGER ⁴⁾ on the system S—Sb where the melting diagram was constructed by means of a thermic analysis. JÄGER, however, found no mixed crystals. It is, however, just this mixed crystal series, (notwithstanding its small extent

1) That is to say when the conductivity power in the dark is expressed in an arbitrary measure, say 100, this rose to 500 by illumination.

2) Prof. JÄGER kindly obliged us with one of his antimonite-cells for comparison.

3) From 57—62 at. % of sulphur.

4) *Verslag Kon. Akad.* November 1911 p. 497—510.

and the difficulty to determine thermally such a very small sphere with certainty) which could be determined very sharply by the electric process. And this seems to us all the more of importance because a connection seems to exist between the appearance of solid solutions on the one side, photoelectric or photochemical effects and photoelectro- or triboluminosity on the other side.

We further got the impression that certain very small impurities may be of influence on the sensitiveness to light, and think we have observed at any rate an influence exerted by the kind of glass of which the melting tubes were constructed. In a whole series of experiments which took place, accidentally, with tubes constructed of a different kind of glass, we obtained not a single sensitive preparation, but when again using tubes of the old kind of glass the phenomenon reappeared as expected.

In this may be probably found, in our opinion, a partial explanation of the fact that, contrary to JAEGER's experience, we succeeded in remelting the native (Japanese) antimonite *without* this losing its sensitiveness to light. It is, however, necessary to operate, as we did, in sealed evacuated tubes. The compound at the melting point is already somewhat dissociated so that the operation in an open tube could not take place without loss of sulphur and change in the composition of the melt. According to our observations this loss of sulphur need amount to only 0.5 at %, to obtain a totally inert preparation.

The conductivity power in darkness remained, on remelting, also quite of the same order. On the other hand it appeared that on powdering the mineral, which was then again compressed to a very solid pastille, the conductivity power very strongly decreased. The light effect, however, remained unaffected.

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Chemistry. — "*On gas equilibria*". By Dr. F. E. C. SCHEFFER. (Communicated by Prof. J. D. VAN DER WAALS).

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1. It may be accepted as known that the total energy, the free energy, the entropy and the thermodynamic potential are quantities which can only be determined with the exception of an additive constant. In the purely physical processes, i.e. changes of state, in which the molecules of the substances do not change, these constants need not be taken into account, and on the other hand a physical