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Chemistry. — “*Studies on Tellurium II. On compounds of Tellurium and Iodine*”. By Prof. F. M. JAEGER and J. B. MENKE. (Communicated by Prof. P. VAN ROMBURGH).

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

§ 1. The object of this investigation was to ascertain what compounds of tellurium and iodine can form from the binary fusions of the two elements and such in connection with the experience gained thus far in the study of the mutual behaviour of iodine and one of the other elements of the oxygen-group.

When we provisionally, disregard the oxygen itself, because in any case well defined compounds with iodine such as O_3J_2 , are positively known, the chance of forming iodides of these elements is, evidently, not particularly great.

Of iodides of *sulphur* a great many were supposed to exist, such as S_3J_2 ¹⁾, S_2J_3 ²⁾, SJ^3 , SJ_6 ⁴⁾, SJ_2 ⁵⁾.

After a long controversy it now seems well understood that these are merely *mixtures*, and the recent work of SMITH and CARSON ⁶⁾ and a little later that of EPHRAÏM ⁷⁾ have proved conclusively that from binary fusions of *S* and *J* *no* compounds are deposited. Iodine can take up 7 to 8 % of S in solid solutions; but further there is only a eutecticum at 65,° and 81,3 mol. % of sulphur. The melting-point 66° attributed by GROSOURDY to the so-called S_3J_2 is, therefore, evidently the eutectic temperature. Sulphur in the liquid state has here probably the formula S_8 and the previously accepted double compounds of sulphur-iodides with As_2S_3 and SnJ_4 have also proved to be only mixtures.

In an analogous manner we find described iodides of selenium SeJ_2 and SeJ_4 ⁷⁾. TROMMSDORFF, however, states that these products obtained by melting together the components, allow all their iodine

¹⁾ GROSOURDY, Journ. de Chim. Médic. 9 429; LAMERS, Journ. f. prakt. Chem. 84. 349. (1861); EMERSON, MAC IVOR, Chem. News 86. 5. (1902).

²⁾ LINEBARGER, Amer. Chem. Journ 17. 33. (1895); BOULOUCH, Compt. rend. 136 577. (1903); PRUNIER, Journ. Pharm. Chem. (6). 9. 421. (1899).

³⁾ GAY-LUSSAC, Ann. de Chim. et Phys. 88. 319. (1813); GUTHRIE, Journ. Chem. Soc. 14. 57, (1862); MENKE, Chem. News 39. 19; (1879); MAC LEOD, Chem. News. 66. 111. (1892).

⁴⁾ Besides the mentioned investigators, also: RATH, Pogg. Ann, 110. (116. 1860); HENRY, Journ. Pharm. Chem. 13. 403. (1848).

⁵⁾ SMITH and CARSON, Zeits. f. phys. Chem. 61. 200. (1908).

⁶⁾ EPHRAÏM, Zeits. f. anorg. Chem. 58. 333. (1908).

⁷⁾ TROMMSDORFF, N. Journ. Pharm. (2). 12. 45. (1826); SCHNEIDER, Pogg. Ann. 129. 627. (1866); GUYOT, Compt. rend. 72. 685. (1871).

to be extracted by alcohol and GUYOT observed that on heating, the iodine volatilises. The SeJ_4 of SCHNEIDER was prepared in different ways; from $C_2H_5J + SeBr_4$; from $SeO_2 + HJ$; by melting Se with J . In all cases the character was doubtful and the little stability of these so-called compounds created suspicion. It is very probable that, as in the case of the sulphur, there is here also only a question of mixtures with a eutecticum, which is situated in the vicinity of 70° . A short time ago this has been finally confirmed by PELLINI and PEDRINA¹⁾, who demonstrated that from binary fusions only mixed crystals are deposited.

§ 2. The analogous problem in the case of the element *tellurium* is of importance from more than one point of view. On a previous occasion one of us²⁾ was able to conclude, from the behaviour of Te to S , to the complete analogy in this respect, between S, Se and Te . The behaviour of Te and J might therefore be expected to be also analogous to that of the elements S and Se .

Such a behaviour would then be in conflict with the statements as to the tellurium-oxides which are found in literature. On the other hand if we could meet with some compound which is permanent and, therefore, but little dissociated in the melt and which possesses a sharp melting-point, it might be possible to decide whether the atomic weight of tellurium is greater or smaller than that of iodine.

As regards the first fact we find indeed a description of several tellurim-iodides: TeJ_2 , TeJ_4 , TeJ_6 , by BERZELIUS and other investigators³⁾; the latter compound, however, has never been isolated and was only suspected by BERZELIUS to exist in the brown liquid obtained from telluric acid and HJ . TeJ_2 is said to be a substance readily fusible at about 80° and prepared by subliming 1 at. of Te with a little over 1 at. of J ; it readily loses iodine and finally leaves iodine-containing tellurium.

TeJ_4 ¹⁾ can be obtained as a hydrate $TeJ_4 \cdot HJ \cdot 8H_2O$ from TeO_2 and strong HJ -solution; the hydrate melts according to METZNER at 55° , and solidifies on cooling — at least in a closed tube, — again unchanged.

¹⁾ PELLINI and PEDRINA, Atti dei Lincei (5). 17. II. 78; Chem. Centr. Bl. (1908). II. 1010.

²⁾ F. M. JAEGER, Proc. (1910).

³⁾ BERZELIUS, Ann. de Chim. et Phys. 58. 113. 150, 225, 282, (1835); METZNER, ibid. (7). 15. 208. (1898). WHEELER, Z. f. anorg. Chem. 3. 428. (1893); GUTBIER and FLURY, Z. f. anorg. Chem. 32. 31, 108. (1902); HAMPE, J. Chem. Soc. 54. 887. (1888).

Further, there are double salts of TeJ_4 with NH_4J , KJ etc. described by WHEELER. GUTBIER and FLURY prepared the compound from a very concentrated solution of telluric acid with strong HJ ; it is totally resolved by H_2O with formation of TeO_2 ; alcohol also decomposes the compound. According to their opinion however, the substance TeJ_2 cannot be considered as a compound and no trace of this was observed neither in the case of TeJ_4 . It is, therefore, evidently of importance to obtain a better insight in the matter.

§ 3. For our purpose we have made use of the tellurium obtained and purified ¹⁾ by one of us (J.) in the manner described previously. The investigation on tellurium was quietly continued notwithstanding the alarming statements of BROWNING and FLINT²⁾ on the complicated nature of tellurium, because their method employed — after experiences gained in the hydrolysis of tellurium-chloride — appeared to us very much open to criticism. A short time ago the incorrectness of their conclusions was proved elsewhere³⁾, and after the exact determinations of MARCKWALD and FOIZIK, BAKER and BENNETT, LENHER and HARCOURT and BAKER⁴⁾, the elementary nature of tellurium may be accepted as being undisputable. As atomic weight has been accepted here the most probable value of **127.6** and **126.9** for iodine. The latter was purified and distilled in the usual manner.

In order to prevent any loss of iodine, the binary fusions were prepared in sealed tubes; with mixtures containing 80% of Te or more, this is unavoidable. Weighted quantities of the two elements were thus melted together at 500°. After solidifying, the mass was powdered and the cooling curve repeatedly recorded in another tube made of hard glass which possessed an egg-like form and to which was sealed a hard-glass screening tube for the thermo-element. With mixtures containing 0—10% of Te the heating-curves were determined in an oil-bath; for higher temperatures a small gas-furnace as previously described in the case of the tellurium-sulphur-mixtures was always employed. After the behaviour of the melt was thus sufficiently known, an analysis was made there-of by placing about 0.15 gram in a distilling flask and adding 20 cc. of sulphuric acid

¹⁾ Loco citato.

²⁾ BROWNING and FLINT, Amer. Jour. of Science (4). 28 347. (1909); (4). 30. 209. (1910).

³⁾ HARCOURT and BAKER Trans. Chem. Soc. 99. (1911); Chem News 104. 260. (1911).

⁴⁾ MARCKWALD and FOIZIK, Ber. d. chem. Ges. 43. 1710. (1910); BAKER and BENNETT, Trans. Chem. Soc. 91. 1849. (1897); LENHER, Jour. Amer. Chem. Soc. 31. 1. (1899); HARCOURT and BAKER, loco cit.

(1,4). After passing a slow current of CO_2 through the ground-joint apparatus, the liquid was carefully distilled into a receiver filled with Na_2SO_3 -solution, while through the funnel-tube a solution of sodium-nitrite ran continuously into the reaction-mixture. In this manner all the iodine could be carried over. To the distillate was now added an excess of $AgNO_3$ and Na_2SO_3 , then nitric acid (D.1.4) and the liquid boiled for some time. The AgJ was then determined by weighing.

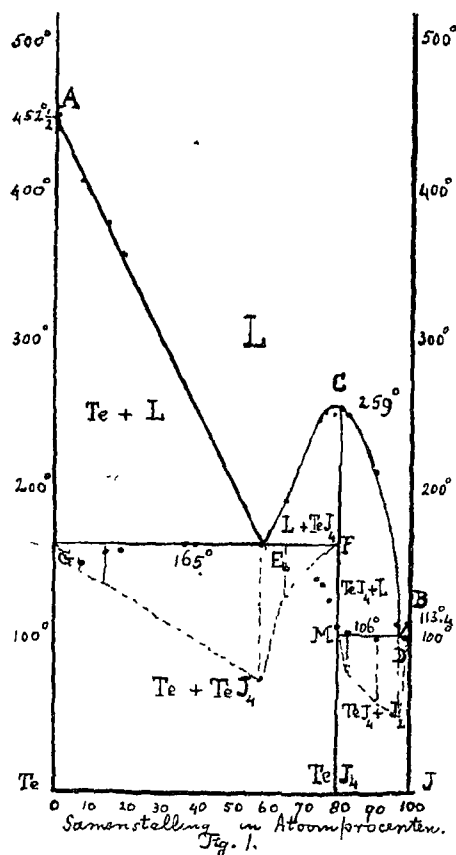
For the measurement of the higher temperatures was used a platinum-platinumrhodium thermoelement, which was standardised on the melting points of *icc*, *tin*, *lead* and *zinc*; for the lower temperatures also an element standardised on *ice* and *lead* and made of silver and constantan. Evidently a stirring of the mass was excluded; consequently, undercooling often took place, which rendered the

<i>Binary Melting point line from tellurium and iodine.</i>								
Composition of the melt				First effect	Undercooling	Second effect	Undercooling	Duration in seconds
in mol. %		in % by weight						
<i>Te</i> :	<i>J</i> :	<i>Te</i> :	<i>J</i> :	—	—	—	—	—
100	0	100	0	452° 5	—	—	—	—
92.2	7.8	92.3	7.7	405	29°	152° (155°)	2° (5°)	120"
84.7	15.3	85.3	14.7	385 (386)	5 (10)	159 (161)	6 (5)	180
80.7	19.3	81.3	18.7	362 (360)	10 (10)	161 (161)	3 (3)	—
71.4	28.6	71.6	28.4	306	—	165	—	—
41.66	58.34	41.8	58.2	169	—	165	10 (12)	840
35.0	65.0	35.2	64.8	196 (195)	0 (0)	151 (152)	10 (10)	330
25.6	74.4	25.7	74.3	250 (250)	0 (0)	141 (140)	0 (0)	—
24.8	75.2	24.9	75.1	253 (253)	0 (2)	139 (137)	1 (2)	—
22.4	77.6	22.5	77.5	259 (258)	2 (2)	130 (129)	—	120
20.5	79.5	20.6	79.4	255	—	109 (109)	—	—
20.4	79.6	20.5	79.5	258 (259)	—	110 (110)	—	—
17.5	82.5	17.5	82.5	256 (256)	3 (5)	106 (107)	0 (0)	540
10.0	90.0	10.0	90.0	217	—	106	0	840
3.0	97.0	3.0	97.0	—	—	106	—	900
0	100	0	100.0	113.4	—	—	—	—

measurement of the *time-intervals*, if not quite illusory, still rather uncertain. These must, therefore, be only taken as approximations.

The data obtained are collected below and represented graphically in Fig. 1 in the usual manner.

In previous determinations the eutecticum was always found at 170° up to 60% of *Te*.



§ 4. From these data and from the diagram of Fig. 1, it may be concluded that from binary fusions a single compound is only formed, namely TeJ_4 , which in the melted condition is fairly strongly dissociated. The formerly accepted TeJ_2 is a product which lies in the neighbourhood of the eutecticum, situated between tellurium and this compound; this eutecticum has a content of about 41% of *Te* and corresponds with a temperature of 165° . The eutecticum at the iodine-side lies in the immediate vicinity of the pure iodine and corresponds with a temperature of about 108° . Solid solutions are evidently not formed to any extent. No trace can be found either of a compound TeJ_6 .

§ 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.

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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).

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§ 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 CALLEGARI¹⁾ 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-derivatives²⁾. 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*.

¹⁾ BRUNI and CALLEGARI. *Gazz. Chim. Ital.* **34**. II. 243. (1904).

²⁾ 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*.