

Citation:

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4. As regards the thermomagnetic examination of polymorphous transformations, a discontinuous diminution of 15% of the specific susceptibility was found at the transition-point of α -thallium and β -thallium at 234°. But the most remarkable properties are shewn by tin: If diamagnetic grey tin is slowly heated, at 32° the specific susceptibility ($-0,29$) changes almost suddenly (like the density) and at 35° passes through zero. Possibly this change would wholly take place at the point of transformation (18°) but then at a much slower rate. Further heating continuously increased the susceptibility so that at about 50° the value ($+0,03$) for paramagnetic tetragonal tin was reached, which afterwards remained practically constant; according to DEGENS the point of transformation tetragonal \rightleftharpoons rhombic tin lies at 161° at which temperature nothing particular was noticed; at the melting point (233°) a discontinuity from $\chi = +0,03$ to $\chi = -0,04$ once more appeared; the diamagnetic liquid metal remained nearly unchanged.

An extension of these thermomagnetic investigations towards low temperatures is in preparation

From the above, especially from the conclusions arrived at under 1 to 4, it seems to follow that CURIE's four corresponding rules are certainly devoid of the general meaning, which has rather rashly been ascribed to them. At the same time the experimental starting-points of LANGEVIN's theory are evidently undermined; more solid and broad foundations for future theories can only be laid with the aid of more extensive research.

Chemistry. — "*Studies on Tellurium: 1. The mutual behaviour of the elements sulphur and tellurium*". By Prof. F. M. JAEGER. (Communicated by Prof. VAN ROMBURGH).

(Communicated in the meeting of January 29, 1910)

§ 1. Whilst we are in the main thoroughly informed as to the relation of selenium and sulphur, the views as to the mutual behaviour of the elements tellurium and sulphur still differ somewhat. KLAPROTH¹⁾ has already investigated this subject. He states that on melting together tellurium and sulphur leaden coloured masses are formed crystallising in rays, which, on heating, give off sulphur and yield a porous metallic looking mass, which he takes to be telluriumsulphide. BERZELIUS²⁾, thirty years later again broached the subject; he found that no compounds were formed on melting, but thought that the

¹⁾ KLAPROTH, Crelle's Ann. (1798). 191.

²⁾ BERZELIUS, Gilb.-Pogg. Ann. 8. (1826). 413.

compounds TeS_2 and TeS_3 are present in the brownish-black precipitates, formed when passing H_2S through solutions of tellurites and tellurates. He arrived at that conclusion on account of the solubility of these precipitates in aqueous potassium or sodium hydroxide, which is also the case with TeO_2 and TeO_3 .

BECKER¹⁾ was the first to analyze these precipitates and he finally arrived at the conclusion that their composition actually corresponds with TeS_2 and TeS_3 . He proved however, that nearly all the sulphur may be removed from these substances by treatment with carbon disulphide: TeS_3 yielded a residue containing 6.14% of sulphur instead of 42.85%, TeS_2 a residue containing 3.69% instead of 33.4%. He concludes that the black precipitates are only mixtures whose composition agrees nearly with those of the supposed compounds. According to him they are formed primarily as ephemeral compounds, which are at once decomposed by the solvent. BERZELIUS²⁾ and OPPENHEIM³⁾ obtained double sulphides to which they assigned the formulae $3\text{K}_2\text{S} + \text{TeS}_3$, etc. In more recent times, BRAUNER⁴⁾ and GUTBIER⁵⁾ again inclined to the opinion that we are dealing here with mixtures of the elements.

§ 2. Since DUMAS placed tellurium in the sulphurgroup, as the first homologue of selenium, and thus the well-known difficulty as to the position of tellurium, in regard to iodine, in the periodic system introduced later, was created, — the question as to the relation of tellurium on the one side and sulphur and selenium on the other has again become of actual importance. For now it is undoubtedly certain that the atomic weight of tellurium is 127.6 and therefore *greater* than that of iodine. On the other hand the differences between tellurium and the other two elements are so strongly pronounced that RETGERS on account of the isomorphism between tellurates and osmiates, thought it would be better to include tellurium in the group of the platinum metals. Tellurates to wit, are not isomorphous with sulphates, selenates, manganates, ferrates etc. On the contrary, PELLINI showed an isodimorphism in the case of $(\text{C}_6\text{H}_5)_2\text{SeBr}_2$ and $(\text{C}_6\text{H}_5)_2\text{TeBr}_2$, whilst NORRIS and MOMMERS noticed a direct isomorphism between the selenium- and tellurium double chlorides and bromides of dimethyl-

1) BECKER, Lieb. Ann. d. Chem. 180. (1876). 257.

2) BERZELIUS, Traité de Chimie. (1830).

3) OPPENHEIM, Journ. f. prakt. Chem. 71. (1857). 270

4) BRAUNER, Journ. Chem. Soc. 67. (1895). 527.

5) GUTBIER, Berl. Ber. 34. 2114. (1901).

amine. But on the other hand many objections have been raised to the position assigned to tellurium: for instance, the different constitution of telluric acid which, probably, must be looked upon as H_6TeO_6 , and the totally different hydration of tellurates in comparison with sulphates and selenates. However this may be, it is highly desirable to obtain more *data* as to the position of tellurium among the other elements and for this reason, the relation to sulphur had to be ascertained in the first place.

§ 3. The tellurium was obtained from $1\frac{1}{2}$ kilo of crude tellurium probably derived from American ore. It appeared to contain the following elements: tellurium, selenium, sulphur, lead, copper, bismuth, iron, silicon and traces of antimony, zinc and a few other metals.

The first purification was carried out by oxidation with *aqua regia*, evaporation of the filtrate to dryness, and repeated extraction of the residue with strong hydrochloric acid. The boiling filtrate was then precipitated by sulphur-dioxide; the first portions of the precipitate being rich in selenium were each time rejected. This operation was repeated three times. The amorphous tellurium was divided into two parts; one portion was converted, by the process given by NORRIS, FAY and EDGERLEY¹⁾, into basic tellurium nitrate $Te_2O_5(OH)(NO_3)$ and by repeating the process five times, which operation lasted many weeks, it was finally obtained quite pure in the form of the said salt: from this, pure TeO_2 was then obtained by gentle ignition and this, dissolved in pure hydrochloric acid was precipitated by SO_2 . The other portion was converted into telluric acid by means of CrO_3 , according to STAUDENMAYER'S process as modified by GUTBIER²⁾; this was purified by precipitating twelve times with nitric acid and then crystallising from water. It is necessary to reduce the adhering CrO_3 with alcohol, otherwise the telluric acid crystals retain a yellow colour which is caused by occluded solid CrO_3 ; this matter I hope to refer to shortly.

The pure telluric acid was then reduced completely by hydrazine hydrate.

The crystalline form of the basic nitrate has not been described up to the present. The following *data* have been obtained from the substance crystallised from nitric acid.

¹⁾ NORRIS, FAY and EDGERLEY, *Americ. Chem. Journ.* **23**. 105.

²⁾ GUTBIER, *Z. f. anorg. Chem.* **29**. 22. (1901); **32**. 96. (1902).

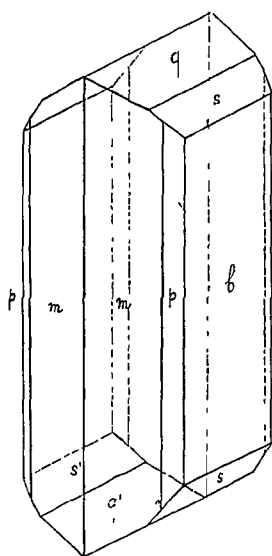


Fig. 1.
Crystalline form of basic
tellurium nitrate.

Colourless, very lustrous needles up to 5 m.m. in length and usually flattened along $\{010\}$. They exhibit many vicinal planes particularly in the vertical zone, and greater angular differences occur also in different individual crystals. The measurements must, therefore, be regarded only as approximations.

Rhombic-bipyramidal.

$$a : b : c = 0.590 : 1 : 0.607.$$

Forms: $m = \{110\}$, $b = \{010\}$ and $p = \{120\}$, very lustrous; particularly b , which is also a cleavage plane and possesses a high lustre. On the other hand $q = \{011\}$ and $s = \{021\}$ are dull, the form $\{021\}$ is mostly absent. The crystals exhibit a pronounced inclination to tetragonal symmetry.

Angular values:	Measured:	Calculated:
$m : m = (110) : (\bar{1}\bar{1}0) =^* 61^\circ 5'$		—
$b : q = (010) : (011) =^* 58 44\frac{1}{2}$		—
$m : p = (110) : (120) = 19 25$		$19^\circ 18\frac{1}{2}'$
$p : b = (120) : (010) = 39 59$		$40 2\frac{1}{2}$
$q : q = (011) : (0\bar{1}\bar{1}) = 62 50$		$62 31$
$m : q = (110) : (011) = 74 54$		$74 43$
$m : b = (110) : (010) = 59 27\frac{1}{2}$		$59 27\frac{1}{2}$
$b : s = (010) : (021) = 39 46$		$39 29$
$s : q = (021) : (011) = 19 0$		$19 16$

Completely cleavable towards $\{010\}$.

The optical axial plane is $\{001\}$ with the a -axis as first diagonal. Strong rhombic dispersion with $\rho < \nu$; the apparent axial angle in cedar oil (1.51) was about 63° .

It may be observed here that the tellurium precipitated from telluric acid by hydrazinehydrate is distinguished from that precipitated from a hydrochloric acid solution by sulphurdioxide which is also amorphous, by a perceptible darker colour. It is, as yet, undecided whether this is merely due to another degree of division or to a real allotropism of the amorphous modification.

§ 4. Both masses of tellurium mixed with 5—6 times the amount of powdered, freshly prepared potassium cyanide were fused for some hours in large ROSE crucibles in an atmosphere of coal gas, with the aid of a large PÉROT-furnace. In the course of a few months, about 5 kilos of these melts were obtained. When carefully powdered, the dark coloured masses dissolve in recently boiled, hot water to beautiful purple coloured solutions, which on cold oxidation by purified air deposit from the K_2Te all the tellurium in brilliant needles. On melting the masses, the poisonous influence of the hydrogen telluride, which is formed in small quantities, was experienced only too plainly, also the disagreeable consequences of breathing the very small quantities of $TeCl_2$ formed during the treatment with *aqua regia*. For weeks afterwards the breath has a powerful odour of $(CH_3)_2Te$, which resembles phosphine and is exceedingly sensitive to the olfactory nerve of bystanders. 1)

The crystalline and already very pure tellurium thus obtained is free from selenium as proved by the exceedingly delicate NORRIS' potassiumiodide-reaction and by the non-reduction of the TeO_2 by hydroxylamine in strong hydrochloric acid solution. All the selenium has been removed as $KCNSe$, whilst the tellurium has passed into K_2Te and then has again been liberated by the action of air free from H_2S .

The purified element was now distilled in vacuo at about 600--700° in long tubes made of hard glass and containing plugs of asbestos; a TECTU furnace was used. This operation was repeated about seven times, each time about 10 grams were used. The pure tellurium thus obtained was silvery white and coarsely crystalline, much resembling crystallised antimony.

The determinations carried out have been made with the product obtained from telluric acid. The sulphur was recrystallised twice from boiling toluene and heated in a drying oven at 90° for some hours.

1) The opinions as to the physiological actions of tellurium are still very much divided. Although selenium is an element hardly less poisonous than arsenic, tellurium is considered by CZAPEK and WEILL (Chem N (1893), 1098 2) to be comparatively harmless, owing to the much more rapid reduction of the tellurium compounds and the consequent localisation in the organism. The experience gained in my laboratory proves this view to be incorrect.

Tellurium is undoubtedly poisonous, but the individual sensitiveness to small traces varies widely with different persons. TeH_2 , in particular, is a poison causing severe headache and vomiting; other tellurium compounds such as $TeCl_2$, for instance are supposed to cause much inconvenience only, owing to their conversion into malodorous substances, but still there can be no doubt whatever as to their poisonous nature.

§ 5. The construction of the melting apparatus will be readily seen from fig. 2. The hard glass tubes always filled with 10 grams of the weighed and well mixed complex of the two elements were placed in iron cylinders filled with fine sand. Tube and cylinder were covered with asbestos; the requisite atmosphere of nitrogen was supplied by way of a hard glass gas-inlet-tube. The nitrogen was prepared from NH_4Cl and KNO_3 , freed from oxygen by means of alkaline pyrogallol and sodiumhydrosulphite and dried by sulphuric acid. The furnace was constructed of chamotte stone furnished

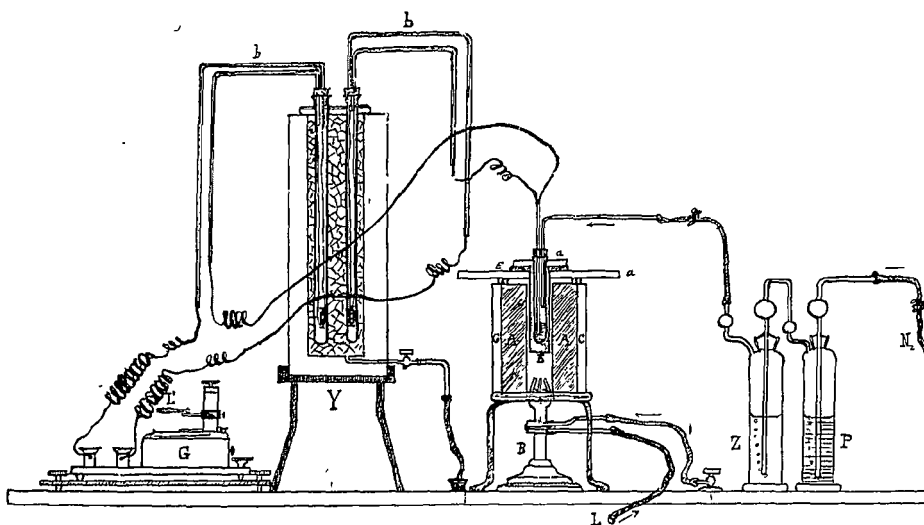


Fig 2.

with an asbestos filling and a central cylinder of unglazed earthenware; it was covered with an asbestos board resting on three little chamotte blocks, which were either removable or not so, for the regulation of the velocity of cooling. The icekettle for the cold solderplace of the platinum-platinumrhodium thermolement (3 mm.) is double walled and allows of working for some six hours with the single supply of ice; all the conducting wires were isolated by glass tubes.

The galvanometer of SIEMENS and HALLSKE was verified by determining the meltingpoints of tin, lead, bismuth, cadmium, zinc, antimony and silver and by making use of the values found by DAY and HOLBORN and by DAY and CLEMENT, which were compared with the gas thermometer. The reading was taken with the aid of a lens, the counting of the time by means of a clockwork, which gave a signal every 10 seconds.

§ 6. Great difficulties were experienced in the determination; when we dealt with mixtures containing much tellurium every precaution had to be taken to prevent the boiling off of the sulphur, and in the case of complexes containing much sulphur trouble arose from the great viscosity of the fusions and the very slow crystallisation of the masses. If the percentage of sulphur exceeds 80, the deter-

MELTING POINT DIAGRAM OF SULPHUR-TELLURIUM COMPLEXES.				
Mol. % Sulphur	% by Weight Sulphur	Initial solidifying point C°	End solidifying point C°	Period of solidifying in seconds
0	0	452½	—	—
5	1.3	440	437	—
10	2.7	435	430	—
15	4.2	431	423	—
20	5.9	426	—	—
25	7.7	421	—	0
30	9.7	413	103	30
35	11.9	401	102	60
40	14.4	394	106	80
45	17.1	389	104	—
50	20	387	105	100
55	23.5	385	105	—
60	27.4	374	109	—
65	31.7	368	101	145
66.67	33.4	366	105	160
70	36.9	361	105	—
75	43	348	108	180
80	50	339	109	180
85	58.7	—	110	240
90	69.3	288	108	230
95	82.7	—	109	260
98	92.4	—	110	—
100	100	115	—	—

minations often become very uncertain; some of these mixtures only exhibited a sharp end-solidifyingpoint. Still it was generally possible to get concordant results on repeating the experiments.

The subjoined table shows the results of the experiments.

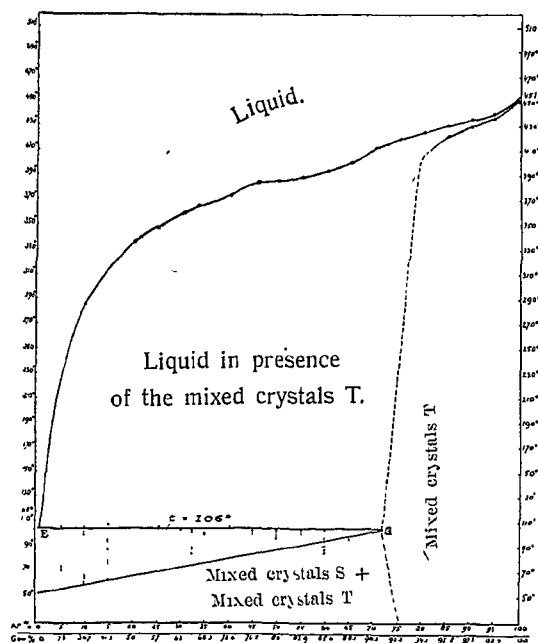


Fig. 3.

§ 7. These *data* represented graphically in Fig. 3 in the usual manner show, therefore, that the elements sulphur and tellurium when melted together yield, when solidifying, two series of mixed crystals of a different crystalline form. The condition diagram is that which has been noticed frequently with isodimorphous substances; there is a very extended hiatus starting from almost pure sulphur to perhaps 27% of sulphur at the side of the trigonal mixed crystals. The temperature of the eutectic point *E* is 106°; the time required for solidification, as far as could be ascertained, increases continuously with the percentage of sulphur until the pure sulphur is reached. The mixed crystals rich in sulphur have a slight ruddy colour; as very small amounts of tellurium impart to sulphur an intensely red colour, their tellurium content must be small indeed. They exhibit the thin needle shaped form of monoclinic sulphur. The transformation at 106° may be seen beautifully with the eye in the various melts on cooling as well as on warming. The monoclinic mixed crystals

rich in sulphur appear to change into the rhombic form at a lower temperature. In these circumstances nothing is noticed as to compounds between tellurium and sulphur; even at lower temperatures no heat effects are observed. The melts of the mixtures rich in tellurium are dark brownish black and in thin layers yellowish brown; unlike the melts rich in sulphur they are thin fluid up to their solidifying points.

§ 8. Considering all that is known up to the present as to the behaviour of the elements sulphur, selenium, and tellurium on being melted together, we may say that in this respect, tellurium certainly deserves the place assigned to it by DUMAS. Sulphur and selenium form, according to RINGER¹⁾, a trimorphous series of mixed crystals, selenium and tellurium, according to PELLINI and VIO²⁾ an uninterrupted series of trigonal mixed crystals; but no compounds are formed, as may be expected, looking at the experience gained, apart from the exceptions in such triads of homologous elements, — at any rate in the central groups of the periodic system. With sulphur and selenium the matter is even somewhat still more complicated, as three instead of two heteromorphous kinds of mixed crystals occur in this case. If we accept RETZERS' view according to whom a less stable form, mostly unknown in the free state, of each of the components should correspond to each of these forms, the isotrimorphism in the case of selenium and sulphur is certainly more difficult to explain than the dimorphism of sulphur and tellurium. For of the two monoclinic series in the system: sulphur-selenium one, according to MUTHMANN, is analogous to the form of γ -sulphur, whereas the trigonal series would already possess the form of metallic selenium. But neither of the two known monoclinic modifications of selenium is isomorphous with any monoclinic modification of sulphur³⁾, whilst the trigonal so-called ϵ -form of this element differs from the trigonal form of selenium. Looking from RETZERS' standpoint both these elements should be credited, in addition to their well known allotropic forms, with at least another two unknown, less stable modifications. In the trigonal series of the system: sulphur-tellurium we are dealing obviously with the same less stable trigonal form of sulphur as in RINGER's investigation, whilst the assumption of an unstable monoclinic form of tellurium cannot have anything artificial about it, in view of the fact that this symmetry occurs frequently

¹⁾ RINGER, Z. f. anorg. Chem 32. 183. (1902).

²⁾ PELLINI and VIO, Gazz. Chim. It. (1906). II. 476.

³⁾ GRÖTH, Chemische Krystallographie, Bd. I. (1906). p. 23—35.

both with selenium and sulphur. The research of PELLINI and VIO also does not introduce any further complications; the two elements are united there in all proportions to one trigonal series, so that only the sulphur-containing complexes of selenium and tellurium exhibit the hiatus on mixing in the solid condition.

All this admits of the conclusion that the elements sulphur, selenium and tellurium form indeed a natural triad of perfectly homologous elements which are more adjacent to each other than their group-fellow *oxygen* is to any one of them. There can be only question of true "compounds" when one of the elements combines with oxygen¹⁾.

§ 9. Now there is still the question: what must be thought of the tellurium-sulphur complexes which are formed, at the temperature of the room, by means of H_2S from solutions of tellurites and tellurates, and in what sense must the so-called double sulphides obtained by OPPENHEIM and BERZELIUS be regarded.

First of all, I soon succeeded in showing that the element tellurium and particularly its amorphous modification dissolves, without leaving any residue, when heated with a solution of alkali- or ammonium-sulphide, also that the solubility increases with the concentration of the sulphide; and further that the solubility also increases when potassium hydroxide is added to the sulphide solution, thus retarding the hydrolysis. Clear yellow solutions are so formed turning somewhat ruddy on boiling, and oxidising rapidly in contact with the air with formation of a black precipitate. They are strongly alkaline and give with hydrochloric acid a heavy, black precipitate with evolution of H_2S ; the precipitate appears to contain tellurium as well as sulphur and is soluble in alkali-hydroxyde.

The analysis of these black precipitates did not give constant values; the tellurium content is much dependent on the *modus operandi* and oscillated between 46.9% and 80.9%.

Thereupon, the action of H_2S on different tellurium compounds was investigated: on the basic nitrate, on the finely divided dioxide suspended in absolute alcohol, on dioxide in hydrochloric acid solution, on telluric acid in water and on the tellurite- and tellurate-solutions obtained from TeO_2 or telluric acid. A beautiful, somewhat crystalline looking product was obtained from the alcoholic suspension of TeO_2 ; the analysis of the blue-black substance gave 80.1%—80.9% of tellurium whereas theory requires 79.9% for TeS , 66.6% for TeS_2 .

¹⁾ It is, moreover, also known that O and S, for instance, never give isomorphous substitutions in organic compounds. S, Se and Te, however, behave differently as shown by the research of PELLINI, NORRIS, TUTTON, and others.

and 57% for TeS_2 , so that the composition came very near to that of TeS , but with an *excess* of tellurium.

The telluric acid was not reduced in the cold; the TeO_2 dissolved in hydrochloric acid yielded a black precipitate with 71.2% of tellurium and therefore situated between TeS and TeS_2 .

The basic nitrate is rapidly attacked by H_2S , but only at the surface; on the other hand it dissolved completely in boiling ammoniumsulphide, which solution, after being concentrated in vacuo at 40° , and allowed to crystallise in a vacuum desiccator over CaO , yields hard, pale yellow needles of a compound which may be recrystallised in vacuo without decomposition. The colour of the needles is greenish-yellow: they dissolve in water to a clear, yellow, strongly alkaline solution, which rapidly oxidises when exposed to the air; the crystals also soon turn black on exposure. The analysis gave a varying tellurium-content according to the method of preparation; in one instance were found 20.1% (NH_4) , 42% Te and 37.9% S , which leads to the formula $(\text{NH}_4)_6\text{Te}_2\text{S}_7$ ¹⁾.

In an analogous way the potassium compounds were prepared from the tellurite and tellurate with H_2S , by solution of the precipitate in the solution saturated with H_2S , or by solution in KOH , and by conduction of H_2S through it; the solutions were evaporated in vacuo, and were then left to crystallize over calcium oxide. Apparently the same yellow compounds are formed in all these cases, which crystallize in rosette-shaped aggregates of hard, fine needles, which in a humid condition smell strongly of H_2S , and yield clear, readily oxidisable solutions. Also the solid salts themselves oxidise rapidly, in which they become greenish yellow, and finally perfectly black. On close investigation the colour appears to assume different shades, even if to all appearances the same mode of preparation is used. Attempts to find a constant composition for these salts, have been unsuccessful; successively it was found to be: 35.4% Te (calculated

¹⁾ The analysis of these complexes is a very tedious operation. If tellurium only has to be estimated and no sulphur, the reduction process with SO_2 or NaHSO_3 is still to be preferred. In our case, the tellurium had to be precipitated from a boiling, strongly ammoniacal solution with hydrazine hydrate, which reduction proceeds very slowly and also incompletely, and had often to be repeated half a dozen times. The last traces of still dissolved tellurium betray themselves on heating by the fine steel blue colour of the colloidal tellurium present; this is generally completely precipitated on rendering the liquid acid, and by way of control the solution may then be heated once more with ammonia and hydrazine hydrate. The tellurium was collected on a weighed filter dried at 100° and weighed as such. The SO_3 was weighed as BaSO_4 , the K as KCl or KClO_4 , the NH_3 as NH_4Cl . For obvious reasons the analysis of the barium salt is a very tedious affair.

for $K_6Te_2S_7$, 35.7%; 33.5% Te, 33.4% S and 33.1% K, which answers to a formula $K_{10}Te_3S_{12}$; another time (for a product prepared from K_2TeO_4): 44.7% Te, 31.47% S, and 23.7% K, which would correspond to $K_{12}S_{20}Te_7$; again another time at somewhat higher temperature: 37.5% Te, 31.3% S and 28.1% K, which leads to a formula $K_{12}Te_6S_{10}$.

The behaviour is practically analogous to that found in the polysulphides of the alkalis towards sulphur, where, according to KÜSTER's researches¹⁾, very complicated equilibria between different polysulphides and their dissociation products occur in the solution; and to that of selenium towards sulphides where, according to MESSINGER²⁾, a portion of the sulphur of the complex sulphohydrogen sulphides may be replaced by selenium, forming such compounds as $Na_3S_2Se_3$, which, therefore, belong to the type of a trisulphide. The behaviour of amorphous tellurium towards sulphide solutions as described previously also agrees with the notion that we are dealing here with salts of complex tellurohydrogen sulphides which in such solutions are in dissociation-equilibria with each other and are moreover split hydrolytically.

The type of the trisulphides becomes then of particular importance next to that of the disulphides: $K_{10}S_{12}Te_3$ may be derived from K_2S_3 by isomorphous substitution of $\frac{1}{6}$ of the S by Te; $K_4Te_2S_7$ and $(NH_4)_6Te_2S_7$ similarly from K_2S_3 , or $(NH_4)_2S_3$; on the other hand $K_{12}Te_6S_{10}$ has again the character of the type K_2S_4 etc.

§ 10. Although these compounds do not as a rule occur in measurable forms (the K-salt was obtained a few times as beautiful rhombic parallelpipeds with faint double refraction and without perceptible dichroism) I finally succeeded in obtaining very large, yellow crystals, with many planes, of a barium salt prepared by dissolving the black precipitate formed by the action of H_2S on potassium tellurite in BaS -solution. The analysis indeed, did not always yield precisely the same results, but still the composition agreed closely with the formula $Ba_3S_7Te_2$; in one instance the normal composition; 45.8% Ba; 25% S and 29.1% Te was actually found. These crystals were accurately investigated and proved to be so well constructed that, in their habit, they did not remind us of mixed crystals but, on the contrary, made a vivid impression of belonging to a true chemical compound. The following data were found:

Large yellow transparent crystals fairly stable in the air but, after some time, assuming a greyish colour. They are well constructed,

¹⁾ KÜSTER, Z. f. anorg. Chem. 44. 431.

²⁾ MESSINGER, Berl. Ber. 30 805 (1897).

yield constant angular values and have, crystallonomically, quite the appearance of a well defined compound of constant composition.

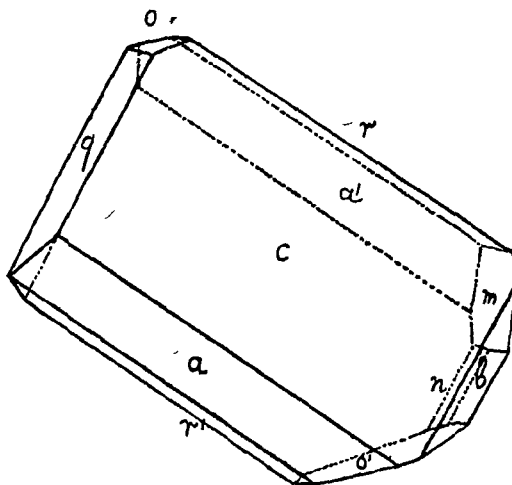


Fig. 4.

The compound has, in moist air, a strong odour of hydrogen-sulphide and is decomposed by water with separation of a black substance which contains tellurium and sulphur.

Triclinic-pinacoidal.

$$a : b : c = 1.6835 : 1 : 1.5515$$

$$A = 109^\circ 43' \quad \alpha = 113^\circ 7\frac{1}{2}'$$

$$B = 122^\circ 10\frac{1}{2}' \quad \beta = 124^\circ 13'$$

$$C = 90^\circ 32' \quad \gamma = 77^\circ 39'$$

Forms observed: $c = \{001\}$, strongly predominating; $a = \{100\}$ and $b = \{010\}$ equally well developed and lustrous; $q = \{0\bar{1}1\}$ and $r = \{\bar{1}01\}$ quite as much developed as a and b , and yielding sharp reflexes; $o = \{11\bar{2}\}$, lustrous and fairly large; $n = \{01\bar{2}\}$ small but lustrous; $w = \{\bar{1}11\}$, small and subordinate, generally with but one plane; $m = \{\bar{1}10\}$, well developed and lustrous, also without the parallel opposite plane.

The habit is flattened towards $\{001\}$ with slight stretching in the direction of the b -axis. A complete or distinct plane of cleavage is not found.

The following angular values were measured:

	Measured :	Calculated :
$a : b = (100) : (010) =$	$*89^{\circ} 281$	—
$b : c = (010) : (001) =$	$*70 \quad 17$	—
$c : a = (001) : (100) =$	$*57 \quad 49\frac{1}{2}$	—
$c : r = (001) : (\bar{1}01) =$	$*53 \quad 46\frac{1}{2}$	—
$c : q = (001) : (0\bar{1}1) =$	$*65 \quad 45$	—
$o : b = (11\bar{2}) : (010) =$	$67 \quad 32$	$67^{\circ} \quad 36'$
$r : b = (\bar{1}01) : (010) =$	$68 \quad 47$	$68 \quad 47\frac{1}{2}$
$a : q = (100) : (0\bar{1}1) =$	$67 \quad 29$	$67 \quad 26$
$c : o = (001) : (\bar{1}\bar{1}\bar{2}) =$	$50 \quad 5$	$49 \quad 49$
$a : r = (\bar{1}00) : (\bar{1}01) =$	$68 \quad 24$	$68 \quad 24$
$c : n = (00\bar{1}) : (01\bar{2}) =$	$38 \quad 17$	$38 \quad 27$
$n : q = (01\bar{2}) : (0\bar{1}1) =$	$27 \quad 24$	$27 \quad 18$
$q : b = (01\bar{1}) : (010) =$	$43 \quad 56$	$43 \quad 58$
$r : o = (10\bar{1}) : (11\bar{2}) =$	$52 \quad 35$	$52 \quad 47$
$o : q = (11\bar{2}) : (0\bar{1}1) =$	$32 \quad 21$	$32 \quad 19$
$m : b = (\bar{1}\bar{1}0) : (010) =$	$33 \quad 51$	$33 \quad 37$
$m : a = (\bar{1}\bar{1}0) : (\bar{1}00) =$	$56 \quad 41$	$56 \quad 55$
$m : r = (\bar{1}\bar{1}0) : (\bar{1}01) =$	$59 \quad 37$	$59 \quad 32\frac{1}{2}$
$m : q = (\bar{1}\bar{1}0) : (0\bar{1}1) =$	$35 \quad 10$	$35 \quad 21\frac{1}{2}$
$\omega : b = (1\bar{1}\bar{1}) : (010) =$	$40 \quad 55$	$40 \quad 47$
$\omega : c = (11\bar{1}) : (00\bar{1}) =$	$85 \quad 46\frac{1}{2}$	$85 \quad 48\frac{1}{3}$
$\omega : a = (11\bar{1}) : (100) =$	$74 \quad 28$	$74 \quad 30\frac{1}{2}$
$\omega : q = (11\bar{1}) : (0\bar{1}1) =$	$38 \quad 5$	$38 \quad 3\frac{1}{2}$

The agreement between the observation and the calculation is an excellent one.

Etching figures were not obtained. It may be, — looking at the acentric habit and plane-development of some of the forms, — that the symmetry is *triclinopiedial*. The situation of the optical axial angle could not be determined. That of the optical main directions was such that the angle of extinction on $\{001\}$ with the side $(001) : (\bar{1}01)$, was about 15° , but on $\{\bar{1}01\}$ with the same side it amounted to about 12° , and that with an inclination which on $\{\bar{1}01\}$ proceeds from the left in front to the right at the back, and on $\{001\}$ from the right above to the left below.

Here we are, consequently, also dealing with a polysulphide of the type BaS_x in which $\frac{2}{3}$ of the sulphur has been replaced by tellurium.

Efforts to obtain this compound, prepared from BaS and S , in a measurable form, and thus to obtain an argument in favour of the said view, in the event of an isomorphism between the two substances, have been found so far unsuccessful.

§ 11. In the electrolysis of a dilute solution of the potassium salt, in which the platinum-dish acted as the cathode and a disc-shaped platinum-electrode as anode, it looked as if tellurium was precipitated at both electrodes. The liberation of the black substance at the anode is nothing else than an oxidationphenomenon.

The tension at the electrodes was 2.6 Volt, the current 0.05 Am-père; the oxygen formed at the anode oxidises the liquid, so sensitive to oxygen, with separation of tellurium-sulphur complexes which partly stick to the anode and partly collect above the same on the liquid; if the current passes for some time the precipitate redissolves and the anode again turns bright. I have ascertained that the adhering precipitate contains tellurium as well as sulphur.

On the other hand, the precipitation of a black substance at the cathode takes place continuously but very slowly; after twelve hours only a small portion of the salt, about one gram and a half in 50 cc of distilled water, had been decomposed by the current. This black precipitate has now proved to be pure tellurium and this observation would, therefore, go against the assumption that tellurium forms a constituent of the anion. This experiment, however, *cannot* be used as evidence against that view, since we know an analogous case in the electrolysis of sodium-sulphantimonate¹⁾, where the antimony also proceeds, apparently, to the cathode, although it acts, in the salt, as a constituent of the anion.

It has also transpired in these experiments that the metal does not wholly take part in the electric conductivity, but that in the electrolysis of the solution, the sodium sulphide is decomposed, and either the sodium liberated at the cathode, or the hydrogen which it causes to be evolved, precipitates the antimony by a secondary reaction. Only when a very little alkalisulphide is present, the anion " SbS_4 ", also moves towards the anode. Obviously, the explanation in our case is the same; the tellurium is formed secondarily at the cathode, whilst at the anode, as in the experiments cited, fairly complicated and somewhat obscure oxidationphenomena occur. In each case, this apparent contradiction does by no means prove the incorrectness of the view, that the said salts may be considered as derivatives of

¹⁾ OST und KLAPPROTH, Zeitschr. f. angew. Chemie (1900). p. 827.

complex tellurohydrogen sulphides. The investigation of this exceedingly complicated subject is being continued in the direction indicated.

§ 12. Summarizing the results of these investigations, I believe I may say:

1. That the elements tellurium and sulphur do not form compounds, but mixed crystals.

2. That the elements tellurium, selenium and sulphur behave in quite an analogous manner towards the sulphides of the alkali and alkali-earth metals, and cause the formation of complex sulpho-, seleno- or tellurohydrogen sulphides of a different type, and that it is quite unnecessary to presuppose the intermediate formation of selenium-sulphur or tellurium-sulphur compounds.

3. That the position, given by DUMAS, to tellurium in the sulphur group as the first homologue of selenium is quite justified so far as the mutual behaviour of these elements is concerned, and that sulphur, selenium, and tellurium form a natural triad of elements, which are more adjacent to each other than any one of them is to oxygen.

Groningen, Inorg. Chem. Lab. of the University.

Physics. — “*Some remarks on Prof. KOHNSTAMM’s reply.*” By Dr. J. J. VAN LAAR. Communicated by Prof. LORENTZ.

In these Proceedings of Jan. 6th 1910 Prof. KOHNSTAMM has inserted a reply to my remarks suggested by a paper by Messrs. TIMMERMANS and KOHNSTAMM. Though I, too, very reluctantly continue the discussion, I feel obliged to briefly revert to this matter for the last time, in order to prevent further misunderstanding.

So I will just point out that Mr. KOHNSTAMM is quite silent about the *cardinal* point of my remarks, given in point *a* second part, point *e* and point *f*; viz. that Messrs. T. and K. in consequence of their disregard of the last five of my seven papers on the subject in question have wrongly asserted that the “abnormal” type III could not occur for *normal* substances, and that this would be due to my restricting supposition $a_{12} = \sqrt{a_1 a_2}$. Only to remove this misunderstanding — as I had asserted the very opposite of this — I wrote my preceding paper.