considered to be functions of a characteristic quantity, the molecular "vibration frequency."[1]

Expressions containing this quantity have been derived by means of which the actually observed variation with temperature of certain of the above properties can be reproduced with remarkable accuracy. Now the flow pressure φ at the temperature t is determined by a complicated expression, the value of which depends upon t, T_1 (the ordinary melting point), L (the heat of melting at T_1), V (the specific volume at T_1) and upon the variation of L and V with pressure and temperature; that is, for any particular substance, φ depends upon the above constant quantities and upon the specific heats and coefficients of thermal expansion and of compressibility; each of these quantities is some function of the "vibration frequency," consequently the flow pressure φ is also a function of this same characteristic parameter.

In view of the state of our knowledge (at the best, very approximate only at the present time) of the experimental data and of certain of the relations involved, it seems premature to endeavor to deduce a definit mathematical relation between φ and the frequency, or even to determin the exact form of the function. The existence of such a relationship accounts simply for the parallelism between the calculated φ values (of Table I) and the mechanical properties of metals brought together in Table II; for all of these quantities are functions of the vibration frequency, a fact which indicates that all the mechanical properties of metals will be found to be periodic functions of their atomic weights, since the vibration frequency itself is doubtless such a periodic function.

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SULFIDE OF TELLURIUM.

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When hydrogen sulfide gas is passed into a slightly acid solution of tellurous acid or the solution of a tellurous salt, a dark colored precipitate is formed and continues to separate as long as any tellurium remains in the solution. At the moment of formation this precipitate is dark reddish brown in color, but after a short time it becomes still darker, until it is quite black. When dried and heated the substance softens, and on cooling forms a gray, somewhat lustrous mass. On being heated still higher it gives off sulfur.

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[1] For a discussion of the exact significance of this quantity, the reader may be referred, in addition to the papers cited above, to recent papers by Einstein in *Ann. Physik.*

These facts were known to Berzelius[1] as early as 1826, and as he found by analysis that the precipitate formed in the manner described contained sulfur and tellurium in the ratio required for the compound TeS_2, he announced the discovery of that compound, and described its physical properties and the method of its formation, and considered the reaction between hydrogen sulfide and tellurous acid to have the form expressed by the equation

$$2H_2S + H_2TeO_3 = TeS_2 + 3H_2O.$$

For fifty years after the publication of Berzelius' work no further attention seems to have been given to the reaction between tellurium and sulfur, and it was not until 1876 that the results of any further studies were published. In that year Becker[2] announced some experiments which showed that the precipitate supposed by Berzelius to be TeS_2 was in reality only a mixture of tellurium and sulfur in those proportions, carbon disulfide dissolving out the sulfur from the material, and thus proving that no chemical union existed. Becker also analyzed the precipitate formed, and confirmed Berzelius' results in regard to its constituents being present in the ratio required for the formula TeS_2, but instead of the reaction taking place as supposed by Berzelius, Becker assumed that the reduction of the tellurous acid took place in the manner expressed in the reaction

$$2H_2S + H_2TeO_3 = Te + S_2 + 3H_2O,$$

which will be seen to equally well explain the ratio of sulfur to tellurium found to exist in the precipitate.

Becker stated his conclusions as follows: "In any case we can draw the conclusion from these observations that the precipitate with hydrogen sulfide cannot be a compound, but must be a mixture of tellurium and sulfur in constant relations." He also states, however, that he thinks it likely that at the moment of decomposition of the tellurous acid by hydrogen sulfide a sulfurous compound of the tellurium forms, only to decompose quickly.

Since the publication of Becker's results, several workers have contributed to the subject, notably Brauner[3] and Gutbier.[4] No proof has been given, however, to show that a compound of tellurium with sulfur can exist, and the results of these later studies confirm Becker's conclusion in regard to the dissolving out of the sulfur, and of the mass being but a mixture of free sulfur and tellurium in constant proportions.

The first experiments of the writer, in the attempt to find whether or not a true compound of sulfur with tellurium could exist, were made by

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[1] *Ann. chim. phys.*, 8, 411.

[2] *Ann.*, 180, 257.

[3] *J. Chem. Soc.*, 67, 545.

[4] "Studien über das Tellur," p. 51.

varying very widely the conditions under which the precipitation of the tellurous solution took place, in the hope of thus finding some set of conditions which would be favorable to the permanency of the TeS_2, if such compound was truly at first formed. These experiments, wholly without result as far as finding such conditions was concerned, will be briefly described, as they throw light on the more successful quantitative experiments which were later taken up.

The conditions which were varied in the course of these first experiments were (*a*) light, (*b*) heat, (*c*) pressure, (*d*) presence of acids in the solution precipitated, (*e*) presence of salts in the solution precipitated, (*f*) presence of water. The manner of carrying out some of these experiments, and the results achieved, were as follows:

The darkening of the precipitate formed by hydrogen sulfide a few moments after its formation suggested a possible analogy to the darkening of silver chloride, and it accordingly seemed desirable to see if in the case of the tellurium compound light had anything to do with the change. Three experiments were tried, in each case the solutions being prepared, the precipitation being effected, and the drying of the solid taking place, in the complete absence of light. The dry precipitates were found to be black, and the sulfur was found to be readily extracted by carbon disulfide, showing that even in the absence of light no permanent compound of tellurium with sulfur was formed.

A considerable number of experiments differing widely in their details were tried in the attempt to prepare a stable combination of sulfur with tellurium by keeping the temperature as low as possible. In one experiment, the hydrogen sulfide gas, after being cooled to —10° by being passed through tubes immersed in a freezing mixture of ice and salt, was caused to bubble through a solution of tellurous acid maintained at 0° by being surrounded by a bath of water containing ice. When the precipitation was complete the liquid was filtered (the filter and funnel having been previously chilled by passing iced water through them) and the precipitate was at once transferred to a desiccator which had stood for several hours previously in a box packed with ice. The desiccator and its contents were then maintained at 0° for eighteen hours, until the precipitate seemed to be dry. It was found to consist of sulfur and tellurium, uncombined. In another experiment, tellurous acid was added to alcohol and cooled to —10°, and hydrogen sulfide at —20° was passed into the alcohol mixture. A precipitate resulted as in the previous cases but, after careful drying, it too was found to consist of sulfur and tellurium, in the state of simple mixture. In yet another experiment, advantage was taken of the direct vaporization of ice to free the solid of its admixed water, the filtered precipitate from a solution of tellurous acid being at once frozen, and exposed for several hours to a current of air brought to the temperature of —10° by passing through an ice-salt freezing mixture.

In none of these cases was it possible to obtain a substance which would not allow sulfur to be readily removed from it by carbon disulfide. One fact, however, was noted which proved to be of great assistance in later work, and this was, that the changing color of the precipitate from brown to black took place much more readily at high temperatures than at low. When the solutions were kept at 0°, several hours might elapse before the precipitate became black, while at higher temperatures several minutes sufficed to bring about the change. The final solution of the problem in regard to the existence of a chemical compound of sulfur and tellurium was directly connected with this observation, as will be brought out when further experiments, carried out quantitatively, are described in a later part of this paper.

Experiments made under decreased pressure, and other tests made in absence of acids or dissolved salts, and where only traces of water vapor were present, were alike without results in obtaining a compound of tellurium and sulfur. Many other experiments were tried along the same general lines as those which have been already noted, and the physical conditions surrounding the solution of tellurous acid at the time of precipitation, and the conditions under which the precipitate was filtered off and dried, were varied through the widest limits, and particular care was given to every detail that might bring about increasing stability in the substance formed. Since all these experiments gave negative results, not offering in any case even the slightest evidence of a combination between the sulfur and tellurium, the conclusion reached by earlier workers seemed inevitable, and the hope of proving that a combination between the two elements could truly exist seemed unwarranted. One line of study, however, still presented itself, and further experiments seeking to explain the phenomena which had been noted in regard to the slow change of color of the precipitate in solutions which had been kept at 0° were taken up. Tests were first made to determin the relative lengths of time which elapsed before the precipitates would turn black, in solutions at known temperatures. This matter was tested for every five degrees between 0° and 100°, and it was found that the change in color from brown to black which took place almost instantly at 100°, required increasingly longer time as the temperature became lower, until about four hours was required when the solution was kept at 0°. The change in color from brown to black being a progressive one, consisting of a slow darkening without any accompanying phenomena which could be used as points of reference, it was naturally very difficult to say when it was complete, and the results of these experiments were therefore not very concordant except as showing the marked difference between the rapidity of the change at high temperature and the slowness with which it took place at temperatures near 0°.

In the light of these experiments, the previous results obtained in most of the other determinations performed in the course of this work, and of the published writings of others on this subject, became clear, since it is evident that the drying of the precipitate in a steam oven at 100° would bring about its decomposition even if it existed as a compound when the drying commenced, while in the case of those other experiments where the material was dried at a low temperature in a desiccator the length of time required is so long as to lead to the substance being completely decomposed when examined. The only way in which it seemed to be possible to reach successful results, then, would be to find a way of determining the amount of the precipitate formed, and the extent of the solubility of its sulfur in carbon disulfide, without actually drying and weighing the precipitate. The steps in the method which were tried were as follows: A solution of tellurium was first prepared, and careful determinations were made to show its tellurium content. Then known volumes of this solution were precipitated by hydrogen sulfide, and the precipitates were collected, dried and weighed, thus determining the composition of the precipitate by synthesis, since the amount of tellurium is already known by the amount of the solution taken. After repeated experiments had been made to show the exact weight of the precipitate which a given volume of the solution would give when precipitated by hydrogen sulfide, experiments similar in nature were tried, but the precipitates formed were shaken up with carbon disulfide before being collected and weighed. In this way the solubility of the sulfur in the mixture could be determined. Finally these experiments were repeated at various temperatures, and thus the question as to whether a combination between the sulfur and tellurium existed at low temperatures but not at high was determined.

I will now give the results of some determinations carried out in the manner stated and will show the results achieved:

In the first series of tests the solution of tellurium was prepared by dissolving pure tellurium in hydrochloric acid to which a few drops of nitric acid had been added (tellurium not being soluble in hydrochloric acid alone), and the solution was then heated for several hours on a sand-bath, hydrochloric acid being added from time to time until the nitric acid had been removed. The strong hydrochloric acid solution containing tellurium tetrachloride was then diluted with water and was ready for the determination of its strength. In each determination 3 cc. of the solution were taken, and enough hydrochloric acid was added so that tellurium dioxide would not be precipitated upon dilution with water. The solution was then considerably diluted and a freshly prepared solution of sulfur dioxide was added, the precipitation taking place at a temperature of 80°.

The results of four consecutive determinations of the strength of the solution gave figures as follows: 0.0734, 0.0734, 0.0738 and 0.0736 g. Te.

As it has been pointed out by other workers that in the methods of precipitating tellurium by sulfur dioxide the results are likely to be high owing to the oxidation of the tellurium, the lower value 0.0734 g. was taken as the equivalent in tellurium of 3 cc. of the solution. This quantity of the solution was found very convenient to use, and was the standard amount taken in all the determinations which will be given.

A number of tests were next made to determin the weight of the precipitate which would be formed from 3 cc. of this solution, by passing hydrogen sulfide through it as long as a further precipitate resulted. Precautions were taken to have the results of these experiments strictly comparable, and 8 determinations gave results as follows: Wt. of ppt., 0.1103, 0.1098, 0.1102, 0.1079, 0.1088, 0.1100, 0.1102 and 0.1093 g.

These results will be seen to be fairly concordant when it is considered that the determinations represent a very small weight of the material, and that, from the nature of the precipitate, the weighing has to be made of material dried at 100°. The very close relation which these results bear to the theoretical quantity of the precipitate required, assuming the substance to contain tellurium and sulfur in the ratio of Te to S_2, will be seen by reference to these figures:

Used 0.0734 g. Te, equivalent to 0.1103 g. TeS_2; found 0.1103, 0.1098, 0.1102, 0.1079, 0.1088, 0.1100, 0.1102, 0.1093 g.

These results thus completely confirm Becker's and Gutbier's analyses showing that the precipitate contains its sulfur and tellurium in the ratio required for the formula TeS_2. The next determinations taken up were made to show that carbon disulfide would dissolve out the sulfur from this precipitate if the solution was warmed during or after precipitation. These determinations were necessary only to make the work more complete, and to answer any objection which might be raised in regard to whether carbon disulfide added to the solution and shaken up with it, would really dissolve out the sulfur in the material. The reason for this step will be more clearly seen at a later stage of the work. In these determinations the same amount of tellurium (3 cc.) and water (100 cc.) was used as in all the others that have been described. Precipitated by H_2S, extracted by CS_2, 3 cc. of solution "A," after extraction, gave 0.0776 and 0.0773 g. precipitate.

The manner in which the extraction of the sulfur by carbon disulfide was effected in these experiments, and in all those to follow, will now be described. In every case the quantity of the diluted tellurous acid solution used (3 cc. sol., 100 cc. water) was put in an Erlenmeyer flask of 250 cc. capacity, and then completely precipitated by hydrogen sulfide gas, the pressure of the gas being noted, and all precautions being taken to have conditions the same in all the experiments. When the precipitation was to take place at 0°, the flask with its contents was brought to 0° by standing for at least an hour in a bath containing ice, and hydrogen sulfide was then passed while the flask remained surrounded by the water and the ice. A bottle containing carbon disulfide was also kept at 0° by a similar bath of ice and water, and the graduate used to measure the volume of carbon disulfide used was kept cool in the same manner. After the precipitation was complete, the hydrogen sulfide was still passed for several minutes, twenty minutes in all being the usual period. Then 20 cc. of carbon disulfide were added to the flask and the whole well shaken. Under these conditions it was found that all of the precipitate was collected in the carbon disulfide, which settled to the bottom, and the precipitate and its solvent were then in intimate contact, and the flask was allowed to stand thus for fifteen minutes, all of that time being kept, of course, in a bath at 0°. The liquid was then filtered, and it was found by experiment that the presence of the two immiscible liquids together did not cause any difficulty in filtration, the operation taking place in about the normal way, but usually somewhat slower than when a simple aqueous solution was filtered. In some of the earlier experiments a small drop of water was first placed on the filter, it being then wet with carbon disulfide, the idea being to have part of its surface for the filtration of the aqueous solution and the remainder to let the carbon disulfide pass through, thus avoiding their mutually repellant action. This method was not found necessary, however, in practice.

The determinations so far mentioned prepared the way for the important ones which will now be described, and which were intended to show whether or not a compound of tellurium and sulfur really exists. If, for example, it can be shown that immediately after precipitation from a solution at 0° by hydrogen sulfide the precipitate formed does not lose any of its sulfur when treated with carbon disulfide, while it does lose its sulfur if it has been warmed or allowed to stand for some time, then the existence of an early decomposed sulfide would be indicated, and the rate at which it decomposed at any given temperature could be determined by finding the relation which the total amount of the sulfur in the compound bore to the amount which could be dissolved out by the solvent after the expiration of regular intervals.

Three experiments were first made to determin the amount of sulfur that could be extracted by carbon disulfide from the precipitate immediately after its formation, and the following interesting results were obtained:

Precipitated by H_2S and extracted by CS_2. 3 cc. of solution "A" gave 0.0908, 0.0940 and 0.0941 g. precipitate.

It is seen from this that almost exactly half of the sulfur is found under these circumstances to be dissolved from the mixture, as will be brought out more clearly from this tabulation:

Te present in 3 cc. of the solution, 0.0734 g.

Required for TeS_2. Gram.	Required for TeS. Gram.	Wt. ppt. found. Gram.
0.1103	0.0918	0.0908
0.1103	0.0918	0.0940
0.1103	0.0918	0.0941

It will be noted that in the first analysis given the result is much lower than in the other two determinations, and this was due to that solution having stood for a few minutes after precipitation, before the carbon disulfide was added, thus giving the unstable sulfide time to partly decompose. In every case the carbon disulfide was in contact with the precipitate for exactly the same length of time, and this time was sufficient to allow all of the sulfur to be dissolved when the compound had been decomposed by heat, thus showing that the difference in the weights of precipitates collected could not be due to any partial or incomplete dissolving of free sulfur. To still further test the matter of the decomposition of the precipitate by simple standing, a series of tests were made in which the precipitates were formed and allowed to stand (always kept at 0°) for fixed periods of time before adding the carbon disulfide. In every case it was found that the longer the precipitate stood before adding the carbon disulfide, the greater was the amount of sulfur which was removed from the mixture, and that this solubility bore a definite and regular ratio to the time of standing. The following table will give the results obtained in this manner:

Precipitated by H_2S, and extracted by CS_2, immediately. 3 cc. of solution "A" gave 0.0941 g. precipitate.

Precipitated by H_2S, and extracted by CS_2, after 1 hour. 3 cc. of solution "A" gave 0.0916 g. precipitate.

Precipitated by H_2S, and extracted by CS_2, after 2 hours. 3 cc. solution "A" gave 0.0863 g. precipitate.

Precipitated by H_2S, and extracted by CS_2, after 3 hours. 3 cc. solution "A" gave 0.0812 g. precipitate.

In all these experiments the time the precipitate was in contact with the carbon disulfide was the same, fifteen minutes, and no other condition in the making up of the solution or the bringing about of the precipitation, varied in any way. The increased solubility of sulfur was a factor simply of the time which had elapsed since the precipitation of the material.

Further experiments were made to show the effect upon the solution of the sulfide, by standing four, five, and six hours, but it will be noted that nearly all of the sulfur was extracted at the end of three hours, showing that the compound had almost entirely decomposed at the end of that time, and the removal of the remaining sulfur was quite irregular and concordant results were not obtained.

To show that the regularity shown in the series of analyses was the result of some underlying law, and not of any factor due to the manner of procedure, check determinations were run. The results were entirely concordant, when the differences are considered which the variation of even the smallest fraction of a degree in temperature would cause in the course of three hours.

Precipitated by H_2S, and extracted by CS_2, after 3 hours. 3 cc. of solution "A" gave 0.0812 g. and 0.0827 g. ppt.

The examination of the results which I have already given will bring out the following facts:

(*a*) That when a solution of tellurium is precipitated by hydrogen sulfide, whether the precipitation takes place in a warm solution or one at 0°, and irrespective of whether the solution is allowed to stand several hours or not, the weight of the precipitate formed will bear the constant ratio to the amount of tellurium in the solution, of 191.6 to 127.6 (1.5017 to 1.0000), showing that the precipitate consists of tellurium and sulfur in the proportion of one atom of tellurium to two atoms of sulfur.

(*b*) That the sulfur in the precipitate can be dissolved out of the mixture by carbon disulfide, provided the solution containing the precipitate has been warmed after precipitation, or allowed to stand for several hours.

(*c*) That at the moment of precipitation half of the sulfur in the precipitate is soluble in carbon disulfide, and a residue is left containing sulfur and tellurium in the ratio expressed in the formula TeS, and the sulfur in this residue is not soluble in carbon disulfide, thus indicating that it does not exist in the free state, but is held in chemical combination with the tellurium.

(*d*) That the sulfide of tellurium (TeS) present in the precipitate is very unstable, and decomposes entirely at 0° in about four hours, or instantly if heated.

Although all of the foregoing conclusions seem to me to be justifiable from the evidence which I have just stated, yet it seemed to be at least desirable to check up all these results by confirmatory experiments, and thus have the experimental data so complete that it could not be in any way questioned. I accordingly prepared a new solution differing considerably in strength from solution "A" and confirmed by additional experiments all of the evidence which I have already presented.

These experiments were found in every way to be completely confirmatory of the first series of experiments, the results of which have been already stated.

Until some other explanation can be found to show why this relation should hold, it seems necessary to conclude that a sulfide of tellurium, having the formula TeS, exists; that it is formed by passing hydrogen sulfide gas into a solution of tellurous acid, according to the reaction

$$2H_2S + H_2TeO_3 = TeS + S + 3H_2O,$$

and that this compound decomposes very readily at any temperature higher than 0°, and that it is unstable even at 0°, decomposing in about four hours to tellurium and sulfur.

PRECIPITATION OF THE COPPER-ARSENIC GROUP AND THE SEPARATION OF ITS DIVISIONS.

By J. I. D. Hinds.

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The analysis of solutions containing quinquevalent arsenic and bivalent tin is simplified and expedited by the method here outlined. The facts upon which the method is based are mostly well known, though I have added some definit information, especially as to the loss of arsenous chloride on boiling its acid solution and the solubility of copper sulfide in colorless ammonium sulfide. These facts have been confirmed by careful experiments and are as follows:

1. For the ready precipitation of quinquevalent arsenic by hydrogen sulfide a hydrochloric acid concentration above $2\ N$ is required; for the complete precipitation of other members of the group, notably cadmium, antimony and tin, the acid concentration must be below $0.5\ N$; to hold in solution the metals of succeeding groups the concentration must be above $0.125\ N$. These different concentrations are secured first by evaporation and then by proper dilution.

2. The quantity of arsenous ion lost on long boiling with dilute hydrochloric acid is a *function of the quantity present,* and when a solution normal in HCl is boiled half way, the loss is *less than one thousandth of the quantity present.* I have established this fact by many determinations, an account of which will be given in a subsequent paper. The investigation covered solutions varying in concentration from $0.01\ N$ to normal in arsenous ion. The solutions were distilled half way and the quantity of arsenic in the distillate determined.

3. The sulfides of arsenic, antimony and stannic tin are easily soluble in colorless ammonium sulfide. Stannous sulfide is not thus soluble and its presence is avoided.

4. Copper sulfide is only slightly soluble in colorless ammonium sulfide and in this method the quantity dissolved is inconsiderable, though a