(a) $5TeO_2 + 4SbCl_5 = 5TeCl_4 + 2Sb_2O_5$;
(b) $TeCl_4 + SbCl_5 = TeCl_4,SbCl_5$;
or $5TeO_2 + 9SbCl_5 = 5[TeCl_4,SbCl_5] + 2Sb_2O_5$.

The compound $TeCl_4.SbCl_5$ appears in white tabular crystals which are readily decomposed by water.

Phosphorus Oxychloride and Tellurium Dioxide.—When phosphorus oxychloride is brought in contact with tellurium dioxide and the two are allowed to remain together in a warm place, a crystalline mass of large flat monoclinic plates begins to form. The excess of phosphorus oxychloride can be readily removed by means of carbon bisulphide. These crystals are deliquescent and are readily decomposed by water.

Analysis, $TeCl_4.POCl_3$: Calculated, Te, 31.32; P, 7.61; Cl, 61.06.
Found, Te, 30.22; P, 7.90; Cl, 59.13.

While phosphorus oxychloride doubtless first reacts with tellurium dioxide to form tellurium tetrachloride, the tetrachloride, as soon as produced, unites with one molecule of the excess of phosphorus oxychloride forming the addition product. The first reaction could be indicated:

$$3TeO_2 + 4POCl_3 = 3TeCl_4 + 2P_2O_5,$$

and the entire reaction may be expressed:

$$3TeO_2 + 7POCl_3 = 3[TeCl_4.POCl_3] + 2P_2O_5.$$

When the above reaction is carried out with an excess of phosphorus oxychloride, a considerable portion of the reaction product remains in solution in the excess of the reagent.

It thus appears that by the action of the various anhydrous chlorides which have been studied on tellurium or tellurium dioxide, three series of products can form; either tellurium tetrachloride or the dichloride can be produced, or by the use of such compounds as phosphorus oxychloride or antimony pentachloride, double chlorides can be obtained.

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THE HOMOGENEITY OF TELLURIUM.

BY VICTOR LENHER.

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When tellurium or its dioxide reacts with a number of the liquid anhydrous chlorides,[1] crystals of tellurium tetrachloride or of a double chloride are formed along with a mother liquor which contains the excess of the reacting anhydrous chloride. This mother liquor contains such by-products of the reaction as may be soluble in it, and has also been found invariably to contain greater or less quantities of tellurium.

When sulphur monochloride is the reacting liquid, the amount of tel-

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[1] See preceding paper.

lurium appearing in the excess of the reagent is quite small, so small indeed that a fairly good separation of tellurium from selenium can be effected by use of this reagent in the cold, inasmuch as selenium dissolves readily in sulphur monochloride. When, however, the sulphur chloride is warm, its solvent power on tellurium chloride is materially increased.

Other chlorides studied, such as thionyl chloride, sulphuryl chloride, phosphorus oxychloride and antimony pentachloride, when in excess, dissolve considerable quantities of tellurium chloride or of the double chloride as the case may be.

Inasmuch as the question of the complexity of tellurium has been repeatedly raised, especially so after the prediction of Mendeléeff in his London address,[1] when he predicted that tellurium contained another element, whose atomic weight would be 212 and which he called dvi-tellurium; and after the work of Brauner,[2] when he thought from some of his experiments that the so-called element was actually a composite, it has been deemed important to examine these mother liquors, arising from the reactions above indicated, to ascertain whether any of the reagents studied would possibly allow of a splitting apart of tellurium.

Norris, Fay and Edgerley[3] studied the elementary character of tellurium by carrying out an elaborate fractional crystallization of the double bromide of tellurium and potassium. Later Norris[4] made fractional distillations of tellurium oxide, following the distillations by determinations of the atomic weight. The conclusions drawn by Norris are that his results have furnished positive evidence in favor of the elementary character of tellurium.

Baker and Bennet[5] have recently published an account of their investigations on the atomic weight and elementary character of tellurium. Their work was carried on for a period of thirteen years. They studied the fractional crystallization of telluric acid, the progressive solubility of barium tellurate, the fractional distillation of the metal, chloride and dioxide, the fractional decomposition of the hydride, the fractional electrolysis of the bromide and chloride and the fractional precipitation of the chloride by water. They have been unable to distinguish any difference in the atomic weight and consider 127.6 to be the true atomic weight.

Study of the Products of the Reaction of Various Anhydrous Chlorides on Tellurium and Its Oxide.—The mother liquor arising from each of the reactions studied was decomposed by water, and the tellurium pre-

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[1] *J. Chem. Soc.*, **55**, 649.

[2] *Ibid.*, **55**, 411.

[3] *Am. Chem. J.*, **23**, 105.

[4] THIS JOURNAL, **28**, 1675.

[5] *J. Chem. Soc.*, **91**, 1849.

cipitated from hydrochloric acid solution by sulphur dioxide, after which it was carefully purified from such materials as might be introduced by the reagents used.

In each case the tellurium obtained was found to answer to all of the tests to which the original material responded and behaved in all respects similarly to what we commonly know to be tellurium.

The method of approaching this problem can be illustrated by the experiments in which the action of phosphorus oxychloride on tellurium dioxide was studied. In this case a crystalline compound is found which careful analysis has shown to have the composition $TeCl_4.POCl_3$. The excess of phosphorus oxychloride used was observed to carry considerable quantities of tellurium in solution. This mother liquor was carefully decanted from the crystallized salt and treated with water. By this procedure, the phosphorus oxychloride is converted into phosphoric and hydrochloric acids and the tellurium tetrachloride decomposed into hydrated dioxide.

After addition of sufficient hydrochloric acid to completely dissolve the tellurium dioxide, treatment with sulphur dioxide yielded elementary tellurium. It has been observed in working with this particular liquid that when an attempt is made to precipitate tellurium out of a solution containing a large quantity of phosphoric acid the reaction is very much retarded and the tellurium precipitates very slowly. This can be overcome, in a large measure, by the addition of hydrochloric acid and considerable dilution with water. The retardation of precipitation of tellurium in presence of phosphoric acid is doubtless due to lack of dissociation and the precipitation can better be effected after addition of considerable quantities of hydrochloric acid.

The tellurium, after having been converted into chloride by means of aqua regia, was again precipitated by sulphur dioxide, converted into the basic nitrate and crystallized from nitric acid solution, as has been suggested by Norris, Fay and Edgerley[1] for the purification of tellurium. The basic nitrate, when ignited, gave the dioxide.

Determination of the amount of tellurium in the dioxide by precipitation as element gave the ratio

0.85635 TeO_2	0.6845 Te	127.52 at. wt. Te.

The tellurium thus obtained from the excess of phosphorus oxychloride showed by the ratio of tellurium dioxide to element that no apparent change in atomic weight had taken place, and that no splitting apart of the element had occurred was evidenced by the fact that the salt $TeCl_4.POCl_3$ which did not dissolve in the excess of phosphorus oxychloride, and which contained all of the tellurium not appearing in the

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[1] *Am. Chem. J.*, 23, 105.

mother liquor, showed by analysis a rational formula with tellurium taken at the commonly accepted atomic weight.

The mother liquors appearing in all the reactions of the anhydrous chlorides which were brought in contact with tellurium or the dioxide were examined in a manner similar to that with phosphorus oxychloride and the same character of results were obtained. A rational formula for the insoluble crystalline product always appeared when a careful analysis was made, while the tellurium appearing in the mother liquor, after decomposing the excess of reagent and purifying the element from such products of the reaction as might contaminate it, always showed the ratio of tellurium dioxide to element corresponding to the atomic weight of 127.5 for tellurium.

Tellurium and Ferric Chloride.—By heating together in the dry condition tellurium and anhydrous ferric chloride, reaction ensues with the production of ferrous chloride, and tellurium tetrachloride. This reaction can also be accomplished and much more conveniently so by the continued action of a hot solution of ferric chloride on tellurium,

$$4FeCl_3 + Te = TeCl_4 + 4FeCl_2.$$

Pethybridge[1] has studied the action of a solution of ferric chloride having a density of 1.18 on telluride gold ores and claims to be able to extract the tellurium as tetrachloride with the simultaneous formation of ferrous chloride, leaving behind gold and silver as follows:

$$8FeCl_3 + (AuAg)Te_2 = 2TeCl_4 + 8FeCl_2 + (AuAg).$$

This is in line with the results previously obtained by the author,[2] which indicate that the tellurium in the natural tellurides of gold is not strongly united to the gold.

While tellurium reduces ferric chloride to ferrous with the simultaneous production of the tetrachloride, ferrous salts will precipitate a part of the tellurium when added in excess to a solution of the tetrachloride in hydrochloric acid.

Crane[3] and Rose[4] have attributed this precipitation of small quantities of tellurium by means of ferrous sulphate to the presence of tellurium dichloride in the tetrachloride. Tellurium dichloride is, however, decomposed by water or aqueous hydrochloric acid into the element and oxide or chloride, and with the knowledge that tellurium dissolves in hydrochloric acid in the presence of the air to tetrachloride directly, it would seem that the precipitation of small quantities of tellurium by means of ferrous salts is largely controlled by mass action. The re-

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[1] U. S. Patent No. 709,037, Sept. 16, 1902.

[2] THIS JOURNAL, **24**, 355.

[3] *Am. Chem. J.*, **23**, 408.

[4] *Pogg. Ann.*, **21**, 443.

actions between ferric chloride and tellurium and ferrous salts and hydrochloric acid solutions of the tetrachloride are indeed reversible.

In view of this partial precipitation of tellurium by ferrous salts, a series of experiments was conducted, in which this partial precipitation was made the basis of a fractionation. To this end a quantity of tellurium originally obtained from the Baltimore Smelting and Rolling Co., was precipitated from a caustic soda solution by means of grape sugar. The carefully washed material was dissolved in aqua regia and was precipitated by sulphur dioxide from a hydrochloric acid solution. The tellurium thus obtained was fused with pure potassium cyanide, the resulting fusion extracted with water and a current of air passed through the solution to precipitate the tellurium out of the solution of the alkaline telluride, leaving sulphur or selenium present in solution as alkaline thiocyanate or selenocyanate. The tellurium purified in this manner was introduced into a porcelain boat which was placed in a porcelain tube. This tube was connected with a supply of hydrogen, which was generated from pure zinc and hydrochloric acid and which was washed with water. The tellurium was distilled from the boat (the tube being heated by a blast lamp) into the cooler portion of the tube where it was condensed. The distilled metal was collected and introduced again into a clean porcelain boat and tube and the distillation repeated.

Twenty-five grams of this metal were dissolved in a mixture of nitric and hydrochloric acids and a hydrochloric acid solution of the tetrachloride formed by boiling off the excess of nitric acid. To this solution was added a solution containing about 25 grams of ferrous sulphate, which contained a small amount of ferric salt, when a precipitate of about 0.1 gram of elementary tellurium appeared. The quantity of precipitate obtained did not appear to be materially increased by the addition of a considerably larger quantity of the ferrous sulphate solution. The solution containing the tellurium and iron salts was treated with acid sodium sulphite and the tellurium precipitated. This tellurium was then reconverted into chloride by means of hydrochloric and nitric acids and ferrous sulphate again added to the hydrochloric acid solution. A second precipitate of about the same size as before, appeared. This operation was repeated twenty-four times, fractions being obtained each time of approximately the same size. These twenty-four precipitates were combined, dissolved in hydrochloric and nitric acids and a hydrochloric acid solution obtained as before. Treatment of this solution with ferrous sulphate again yielded a small precipitate of tellurium, the size of the precipitate being about the same as in the previous series of fractions. A second precipitation was made and was combined with the previous one for an atomic weight determination. The metal was treated with nitric acid in a small Jena flask, and the resulting basic nitrate gradually heated to 440°, when the weight was found to be constant.

0.1694 Te gave 0.2119 TeO_2 and if O = 16, Te = 127.55.

Inasmuch as the original material showed the same atomic weight, it is evident that by this method of fractionation no portion can be found which shows a figure radically different from the commonly accepted figure.

Action of Hydrochloric Acid on Tellurium in Presence of Air.—Although tellurium is ordinarily considered as insoluble in hydrochloric acid, yet it is actually attacked slightly by the acid when exposed to the air, if sufficient time is allowed for contact. This action can be demonstrated by bubbling a current of air, for several weeks, through concentrated hydrochloric acid in which is suspended metallic tellurium. In a comparatively short time the acid becomes yellow, indicating the presence of tetrachloride.

This action of hydrochloric acid on tellurium in the presence of air has been made the basis of an experiment in which it would be possible to have differential solution take place should tellurium contain a higher member of the series of elements in which it is commonly placed.

One hundred grams of carefully purified tellurium was precipitated from hydrochloric acid solution by means of sulphur dioxide and the precipitate washed until the wash water would not react for chloride with silver nitrate. This freshly precipitated and finely divided metal was introduced with pure concentrated hydrochloric acid into a filtering flask and a current of air which had been previously washed with water and then passed through pure hydrochloric acid, was drawn through the solution for three months. At the end of this time a considerable part of the metal had dissolved. The solution was filtered and on treatment of the solution with acid sodium sulphite, tellurium was precipitated. Two portions of tellurium were here obtained, one of which was a smaller portion of a few grams obtained from a tellurium solution that had been formed by the slow action of hydrochloric acid and air on tellurium, and this solution had remained in contact with the main part of the finely divided metal for three months. The portion which dissolved and that still remaining undissolved were found to be identical in chemical character, obeyed the same reactions, and when converted into oxide, and this oxide analyzed, gave an atomic weight of 127.5.

In the hands of the author, tellurium has shown no signs of breaking apart in any of the reactions which had for their object a study of the elementary character of the metal, nor in the various reactions or derivatives which have been studied in our laboratory has the element shown any indications of other than simple character.

The statements of Mendeléeff as to the possibility of tellurium containing another element and his views as to its incorrect atomic weight have led to an extended series of critical studies on this subject. Brauner studied the atomic weight for six years, Norris for nine, Baker and Bennet for thirteen, and the author for ten. We see, therefore, thirty-eight years of experimental work directed to the study of the atomic weight of an element which to-day remains as an element whose elementary character is well established, and which stands with a higher atomic weight than the next element in the horizontal series. While it still remains an exception to the periodic arrangement of Mendeléeff, and so far as its comparison with iodine is concerned, is abnormal, yet in the main points of its chemical behavior and those of its compounds, it properly belongs associated with sulphur and selenium in the sixth group.

The element tellurium still remains, however, an exception to the periodic arrangement of Mendeléeff, its atomic weight being higher than that of iodine. We must hence conclude that either tellurium is abnormal in a direction which has not yet received careful study, or that we do not yet appreciate all of the principles of the periodicity of the elements.

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A STUDY OF THE SOLUBILITY OF POTASSIUM CHLOROPLATINATE.

BY E. H. ARCHIBALD, W. G. WILCOX AND B. G. BUCKLEY.

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The importance of knowing accurately the solubility of a precipitate, in the liquor from which it has been thrown down, if the precipitate is to be used for a quantitative estimation, is apparent to every one. This is the case, in particular, with such substances as potassium chloroplatinate, when this salt is to be used for the determination of the amount of potassium occurring in feldspars and such igneous minerals, where the amount of chloroplatinate which is to be weighed is, generally speaking, comparatively small. The difficulty here encountered is, in a measure, overcome by the methods worked out by Hillebrand[1] and his pupils, who evaporate the solution containing the salt in question, together with the corresponding sodium salt, to dryness and then dissolve out the sodium salt with absolute or eighty per cent. alcohol. The trouble, however, although lessened, is still of the same nature as before, and even under the best conditions some of the potassium salt must be carried into solution, giving a high value to the sodium. With these features of the case in mind, it was thought that it would be of some interest to study the solubility of the potassium chloroplatinate somewhat more carefully than had

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[1] Hillebrand, "Analysis of Silicate and Carbonate Rocks," *Bull.* 305, *U. S. Geol. Survey.* Washington: Analysis of Rocks.