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NOTES ON SELENIUM AND TELLURIUM.

BY EDWARD KELLER.

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IT is not very frequently that the technical chemist and the assayer, or the metallurgist, meet with the two elements, selenium and tellurium, although the assayer's work in gold assaying and treatment of the ores is often rendered more difficult by their presence. No analysis of any of the western, crude copper, however, is now complete without the joint, or separate, determination of selenium and tellurium.

It is not the object of this paper to fully describe any of the methods in use for their separation from other elements. A few new features, merely, will be pointed out.

It has long been known that many acid-forming elements are precipitated by ferric hydroxide as insoluble salts, from ammoniacal solution.

To have introduced this principle into copper analysis is entirely the merit of present and former chemists of the Baltimore Copper Smelting and Rolling Co.—the Messrs. Lehmann, Mager, and Johns.¹

The elements of this group which occur, or may occur, in copper are phosphorus, arsenic, antimony, tin, selenium, and tellurium.² With all these elements this method may be most successfully employed when they are present in small quantity and the precipitation of the copper becomes impracticable.

¹ Lehmann and Mager: *Am. Chem. J.*, July, 1885.

² Cabell Whitehead: *This Journal*, 17, 280.

When the proper conditions are observed it is most efficient, rapid, and simple. From five to many hundred grams of copper, with a comparatively very small amount of iron, are dissolved in nitric acid, enough ammonia added to hold all copper in solution, boiled, and the ferric hydroxide filtered and washed.

From this precipitate the enumerated elements can easily be separated by known methods.

The following is illustrative of the behavior of selenium and tellurium in relation to this ferric hydroxide separation method. Of each element one gram was taken, and by oxidation with dilute nitric acid a solution of selenous and one of tellurous acid obtained. One gram of ferrous sulphate was dissolved and oxidized, and that amount of iron added to each solution, as well as to each succeeding filtrate (previously acidified) after the ferric hydroxide, precipitated by ammonia, was collected on a filter and washed. The ferric hydroxide precipitates were each dissolved in hydrochloric acid of the proper strength, and the selenium precipitated with ferrous sulphate, the tellurium with sulphur dioxide, and determined on tared filters.

The quantitative results were as follows:

| Element. | Quantity taken. | No. of precipitations. | | | | | | | | | | Quantity found. |
|----------|-----------------|------------------------|--------|--------|--------|--------|--------|--------|--------|--------|------|-----------------|
| | | 1. | 2. | 3. | 4. | 5. | 6. | 7. | 8. | 9. | 10. | |
| Se.. | 1 | 0.0892 | 0.0973 | 0.1546 | 0.1297 | 0.2219 | 0.1416 | 0.1236 | 0.0513 | 0.0121 | 0 | 1.0213 |
| Te.. | 1 | 0.9548 | 0.0448 | 0 | | | | | | | | 0.9996 |

It is clear that the reaction is quantitative only when a certain excess of iron is present, which for selenium must be many times greater than for tellurium.

The method universally recommended for the separation of selenium and tellurium is the potassium cyanide method, selenium being readily soluble in a solution of that compound. Tellurium is also dissolved in small quantities, which must be again separated, and for that reason the method is unsatisfactory.

The best precipitant for both elements is declared to be sulphur dioxide.

To obtain the metallic precipitates by any reducing agents the two elements must be in solution as selenous and tellurous acids. The same is true if the sulphides are desired by precipi-

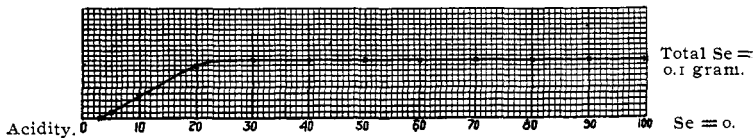
tation with hydrogen sulphide. Selenic and telluric acids are only reduced to the lower form by strong boiling hydrochloric acid. In describing the experiments made, the solutions spoken of are always those of the former acids.

In the reaction of selenous and tellurous acids with sulphur dioxide the two show characteristic differences. When precipitated by that gas no heavy metals must be present, since they are also, at least partially, precipitated.

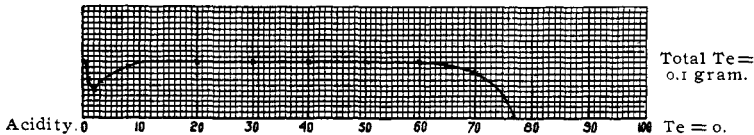
Example.—With one-half gram of copper and 0.1726 gram of selenium in solution, 0.0865 gram of copper was thrown down.

In the following determinations, the acid of which the percentage is given is strong hydrochloric of the specific gravity 1.175. The amount of selenium and tellurium in each case is

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PRECIPITATION OF TELLURIUM BY SULPHUR DIOXIDE.



one-tenth gram. The sulphur dioxide passed through the solution until thorough saturation. Time of standing about twenty hours. The reaction was conducted in the cold.

PRECIPITATION OF SELENIUM AND TELLURIUM BY SULPHUR DIOXIDE.

| | | Percentage of acidity of solution. | | | | | | | |
|------------------|-------|------------------------------------|--------|--------|--------|--------|--------|--------|--|
| | | 1 | 2 | 3 | 5 | 8 | 10 | 20 | |
| Precipitation of | 0.5 | | | | | | | | |
| Selenium ... | | 0 | | trace | 0.0124 | | 0.0349 | 0.0935 | |
| Tellurium ... | total | 0.0761 | 0.0525 | 0.0653 | 0.0745 | 0.0931 | total | total | |

| | | Percentage of acidity of solution. | | | | | | | | | |
|------------------|-------|------------------------------------|-------|-------|-------|--------|--------|--------|-------|-------|-------|
| | | 30 | 40 | 50 | 60 | 65 | 70 | 75 | 80 | 90 | 100 |
| Precipitation of | 30 | | | | | | | | | | |
| Selenium total | total | total | total | total | total | total | total | total | total | total | total |
| Tellurium total | total | total | total | total | total | 0.0965 | 0.0882 | 0.0411 | 0 | 0 | 0 |

The accompanying graphical representation of these figures perhaps conveys a more clear idea of the difference of behavior of the two elements.

From the above facts we learn that even with sulphur dioxide in a hydrochloric acid solution of over eighty per cent. acid a separation is possible. We also see that to obtain a total precipitation of the two elements together in this way, the acidity must be confined to definite limits, safely between thirty and fifty per cent.; otherwise one or the other of the two will remain wholly or partially in solution.

If, after saturation with sulphur dioxide, of a selenous acid solution of insufficient acidity, the necessary amount of hydrochloric acid be added, the precipitation becomes total. The same is the case with tellurium in case of insufficient acidity. In case of too high acidity, diluting to the required strength calls forth total precipitation.

The figures for partial precipitation are not absolutely constant. They show variations under different conditions, such as temperature and time of exposure to the action of the reducing agents.

Both elements are more voluminous when precipitated from weak acid solutions than when precipitated from stronger ones.

Ferrous sulphate does not precipitate tellurium.

A series of determinations of selenium, precipitated from solutions of various acidity by ferrous sulphate, showed that the reaction is rapid and quantitative in strong hydrochloric acid. The degree of rapidity of precipitation diminishes as the acidity is reduced. It is total within twenty-four hours as long as the acid is thirty per cent. or more. In fact the reactions of ferrous sulphate and selenous acid are almost identical with those of that acid and sulphur dioxide.

These facts furnish a simple method to separate selenium from tellurium, or any other of the ordinary elements, for analytical or industrial purposes. Gold and silver only, of the metals usually present, interfere. Gold may previously be precipitated by oxalic acid, which does not affect selenium, and silver is so readily separated as chloride that it is no obstacle. Or gold may be precipitated with the selenium and weighed together and the latter dissolved with nitric acid, leaving the gold in

weighable form. Selenium is then obtained by difference.

In attempting to make electrolytic copper determinations in copper residues (from electrolytic tanks), these were treated with strong nitric acid, the silver precipitated as chloride, and filtered. The filtrate, now being freed from gold, silver, and much antimony, was then evaporated to dryness and the residue boiled with hydrochloric acid until the nitrates were fully decomposed. The excess of acid was next neutralized with ammonia, and into the slightly acid solution was conducted hydrogen sulphide. The precipitate, after filtering and washing, was digested with a sodium sulphide solution, and after again filtering and washing, redissolved in nitric acid, made ammoniacal and, for the purpose of precipitating lead and bismuth, ammonium carbonate and phosphate added, and boiled. After cooling and filtering, the ammoniacal copper solution was acidified with sulphuric acid and subjected to electrolysis. It was thought to have been freed of all deleterious elements. The precipitate of copper, however, failed to come down bright and thoroughly adhesive, and on solution with somewhat diluted nitric acid a reddish residue would be visible on the cathode. This proved to be selenium.

The selenium in the same residues was then separated and it was found, by a number of quantitative determinations, that by precipitation with hydrogen sulphide, and subsequent treatment with sodium sulphide, from two-thirds to seven-eighths of the selenium was retained by the insoluble sulphides of copper, bismuth, and lead, the remainder being in the sodium sulphide solution, the latter always containing all of the tellurium.

Looking over many text-books and considerable original literature, I found only one allusion to this fact. William Crookes in his *Select Methods in Chemical Analysis*, p. 426, 1894, says: "Selenium cannot be separated from metals with which it is combined when the sulphides of these metals are insoluble in ammonium sulphide, by making use of the solubility of selenium in this reagent. The insoluble metallic sulphide is almost always mixed with selenide."

Here it should be remembered that the precipitation of selenium, as selenium sulphide, SeS_2 , from a solution of selenous

acid with hydrogen sulphide, should be conducted in the cold. The precipitate has then a lemon-yellow color and is very readily dissolved by the alkaline sulphide solutions. On heating, this yellow precipitate darkens to an orange color and becomes insoluble. This is said to be due to decomposition and the insolubility of selenium.

Ditte¹ tells us that when selenium and sulphur combine, in the above-mentioned manner, heat is absorbed, or the heat of formation is negative. This sulphide, like hydrogen iodide, belongs, therefore, to a class of compounds which readily decompose.

After a number of qualitative tests, demonstrating that copper, bismuth, and lead, separately retain selenium, to a greater or less extent, according to conditions, the following quantitative determinations were made :

The quantity of selenium in each case was about two grams. This and the varying quantities of copper were in hydrochloric acid solution, with just enough free acid to prevent any precipitation of copper selenite. The precipitation with hydrogen sulphide was conducted under cooling and the resulting precipitate washed with cold water, digested with a strong solution of sodium sulphide, then washed with water containing a few drops of the same reagent, then with water to which a little ammonium sulphide was added, and finally with strong alcohol. Sulphur, selenium, and copper were then determined in the precipitate. The results are given in the table below :

| | I. | II. | III. | IV. |
|----------------|--------|--------|--------|--------|
| | Gram. | Gram. | Gram. | Gram. |
| Sulphur | 0.3787 | 0.1649 | 0.1730 | 0.0416 |
| Selenium | 0.2828 | 0.1726 | 0.1565 | 0.0239 |
| Copper..... | 0.9880 | 0.4880 | 0.4909 | 0.0979 |

Figuring the theoretical amount of copper, as combined with the sulphur and selenium found, we obtain :

| | I. | II. | III. | IV. |
|-------------------------|--------|--------|--------|--------|
| | Gram. | Gram. | Gram. | Gram. |
| Cu combined with S..... | 0.7503 | 0.3267 | 0.3428 | 0.0824 |
| Cu " " Se..... | 0.2263 | 0.1385 | 0.1256 | 0.0192 |
| Total..... | 0.9766 | 0.4652 | 0.4684 | 0.1016 |

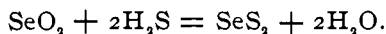
¹ *Ann. Chem. Pharm.*, 163, 187.

In another experiment selenium and copper were subjected to the action of hydrogen sulphide in ammoniacal solution, and the precipitate treated as those previously described. The results obtained were :

| | |
|-----------------------------|---------------|
| | Gram. |
| Sulphur..... | 0.0098 |
| Selenium..... | 0.0138 |
| Copper..... | 0.0231 |
| Copper (theoretical) | Gram. |
| Combined with sulphur | 0.0163 |
| " " selenium..... | 0.0111 |
| Total..... | <u>0.0274</u> |

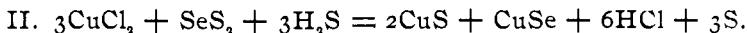
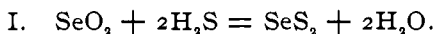
The initial amount of copper in this last case was 0.05 gram, and, as was expected, a large portion remained in the ammonium sulphide solution.

While the results do not appear very satisfactory from the standpoint of analytical accuracy, it should be stated that the purpose of the determinations was to find the existence or non-existence of a definite reaction, and the molecular proportions of the sulphide and selenide formed. At first sight the results might be considered of a negative character. On closer observation, however, two out of the first four determinations show a maximum of selenide, or a minimum of sulphide formation, in which the atomic ratio of selenium and sulphur is approximately 1 : 2, or the same as in selenium sulphide, as formed by the reaction of selenous acid and hydrogen sulphide.



By the precipitation in ammoniacal solution the contents of selenium in the precipitate are higher. It is quite likely, however, that in this case more of the copper sulphide than of the selenide was held in solution by the ammonium sulphide, and it is clear that in acid, as well as in alkaline, solution only a certain maximum quantity of copper selenide is formed which never equals the amount (molecularly) of copper sulphide.

According to the above it may plausibly be supposed that the reaction takes place in two stages :



For this theory there is no positive proof ; but it is plain that the hydrogen sulphide must reduce both copper chloride and selenous acid, that copper and selenium may combine in their nascent state, and that sulphur is precipitated, or that copper may combine with previously formed selenium sulphide, and that this also must be accompanied by sulphur precipitation.

The reaction appears one of the most interesting in inorganic chemistry and deserves further investigation.

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COMPOSITION AND FORMATION OF TANK RESIDUES IN ELECTROLYTIC COPPER REFINERIES.

BY EDWARD KELLER.

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THE production of electrolytic copper and its separation of other metals by means of the electric current, was first established on a commercial scale by James B. Elkington, of England. In two patents, No. 2,838, Nov. 3, 1865, and No. 3,120, Oct. 27, 1869, he laid down all the essential points of the processes which guide the operations at the present day.

The original object of the process was mainly the separation of the precious metals from the copper. The production of a pure copper from the crude metal is, however, now equally important. The process may be described briefly as follows: The crude copper is cast into anodes of generally six to eight square feet by one to one and one-half inches in thickness. These are suspended in tanks, alternating with thin sheets of pure copper, as cathodes, one to two inches apart. Of the cathodes there is one more in number than of the anodes. In the tanks the electrolyte, in which anodes and cathodes are submerged, is forced to circulate in order to maintain uniform density. This electrolyte is said to be generally a solution of three per cent. copper (as sulphate) with six per cent. of free sulphuric acid.

Each anode is connected with the conductor from the positive pole of the dynamo, each cathode with the negative. If the number of anodes in one tank be n , we have n branches of the electric current from the positive pole, and $n + 1$ from the negative. Anodes and cathodes being otherwise insulated, the current must pass from anode through the electrolyte to cathode,