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SELENIUM AND TELLURIUM.

TWO "RARE ELEMENTS" WITH POSSIBILITIES.

BY VICTOR LENHER,

Professor of Chemistry in University of Wisconsin, and Member of the National Research Council's Committee, on the "Uses of Selenium and Tellurium."

THE two "rare elements," selenium and tellurium, which are in many respects similar

rare as is generally supposed. Indeed the term "rare element" is in general a rather vague and indefinite expression. For example, titanium is commonly regarded as a rare element, although F. W. Clarke has shown it to be more plentiful than carbon, sulphur and phosphorus combined. Titanium is, therefore, very plentiful, but the number of its chemical compounds is very limited.

A recent estimate of the amount of selenium and tellurium that can be produced at present in the United States, without making any material additions to the present plants, has shown that this country can furnish annually more than 300,000 pounds of selenium and about 125,000 pounds of tellurium. The elements are marketed commonly in elementary form although some of the refineries have produced small quantities of derivatives, such as sodium selenite and tellurium dioxide.

The general chemical characteristics of these two elements closely follow those of sulphur, indeed the types of selenium and tellurium compounds are in general those of sulphur, but due to their higher atomic weights they are more metallic. Tellurium in elementary form looks much like antimony. It is white, strongly crystalline, so strongly crystalline that it is quite brittle and can be easily powdered. Toward the acids it is as refractory as antimony. Toward alkaline solutions it is strongly resistant while in water or in moist air, it does not rust or corrode appreciably. It is known that antimony can be electroplated and gives a durable plating. It would be interesting to study tellurium in this direction. A systematic study of the available electrolytes that can hold tellurium in solution could be carried out advantageously. Antimony has been successfully used for many years in antifriction alloys and is an essential constituent of stereotype metal. No recorded study is known of an attempt to utilize tellurium in these alloys. The whole field of the metallic alloys of tellurium needs to be studied carefully, and, unquestionably, an element whose general characteristics are so close to antimony will almost certainly be found to be a useful metal instead of as at present having no practical applications.

Another metallurgical line which has not been studied in any detail is the action of these two elements in the iron and steel industry. The effects of sulphur and phosphorus on iron and steel have been very carefully studied. The objectionable phosphorus has been most scrupulously removed by the basic open-hearth process as a result of years of study and observation, yet today we are actually adding iron phosphide to open-hearth steel, which is to be used for certain purposes, to bring up its phosphorous content. It is interesting to contemplate what careful experimentation would develop on the influence of selenium and tellurium on the various grades of steel.

Selenium in the so-called metallic form has long been char-

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acterized by its unique action toward light. Its conductivity of the current varies so greatly when brought from the dark into the light that this peculiar property of its conductivity, varying as it does, directly proportional to the intensity of the light, has caused the development of the selenium cell. This cell, or, in reality, a resistance apparatus, has found numerous uses at various times, such as automatically controlling gas lights at daylight. It has been used in lighting and extinguishing the lights in light buoys, in army signalling of various kinds based on the heliograph principle, as a control in chemical processes such as sulphuric acid manufacture, and in the wireless telephone.

It has been known for a long time that selenium gives to glass a red color. This principle during the wartime was made use of in the decolorization of glass owing to the shortage of manganese which had been hith-

erto used largely for this purpose. Selenium is introduced into the glass either in the elementary form or as a salt of selenium. The rose color which selenium imparts to the glass is not exactly the complement of the green of the ferrous iron hence it is common practice to add a small amount of cobalt oxide along with the selenium. Since both selenium and its compounds are very readily volatile at such temperatures as are used in glass making, a large amount of the selenium decolorizer is volatilized. The loss of selenium is therefore high, and as a consequence selenium can only be used to decolorize glass when the glass manufacturers are willing to pay the higher cost price. During the war when the supply of manganese was limited selenium was used extensively in glass decolorizing, but as soon as shipping was resumed and manganese again became available, the use of selenium in the glass business fell to almost nothing.

There are a number of possible uses that suggest themselves for these elements, none of which has received the attention that it deserves. Lithophone, the intimate mixture of barium sulphate and zinc sulphide made by bringing together barium sulphide and zinc sulphate, is full of suggestions. Various colored lithophones can be produced by using an antimony sulphate liquor with barium sulphide when the white barium sulphate produced is colored by the orange sulphide of antimony. Similarly cadmium or arsenic liquors give a corresponding yellow lithophone. The substitution of selenium and tellurium in lithophone is very suggestive inasmuch as it should be possible to replace the sulphur of either the sulphate or that of the sulphide by either of these elements. The selenate and tellurate of barium are white and insoluble like the sulphate, while the selenides and tellurides like many of the metallic sulphides are variously colored.

The uses of the various compounds of selenium in medicine have received some attention, but the derivatives have had almost no systematic study. Professor W. J. Gies, of Columbia University, in a very careful study has shown that tellurium compounds have a physiological action quite similar to that of arsenic, but that the toxicity is much less than that of arsenic. The selenides and tellurides as well as the oxidized salts have been experimented with in cancer, tumors, and syphilis, but their efficacy is more or less questionable. These few compounds, which are of the simplest chemical character,

are almost the only ones of which any experimental results are recorded. When one considers the vast field of important and valuable sulphur-containing organic compounds ranging from saccharin to sulphur and in the arsenicals from Fowler's solution to salvarsan, it would seem that there exists an almost virgin field for research by the physiological chemist. When one thinks of the physiological action of the derivatives of tellurium as medicinals, the offensive garlic odor of the "tellurium breath" is brought to mind. This will unquestionably act as a deterrent in the minds of some, but should certain physiological actions be found, they might be so valuable as to overcome the objections due to the characteristic methyl telluride odor.

In the vulcanization of rubber a few experiments are recorded which seem to indicate the similarity of the action of selenium to that of sulphur. Much more remains to be done especially along the lines of the use of the chlorides or bromides of these elements as accelerators. Tellurium and its derivatives have received practically no attention in the rubber industry. Possibly from the nature of the organic materials present, the objectionable methyl telluride again would militate against its use.

A relatively small amount of research has been conducted with selenium in the dye industry while almost nothing has been done along these lines with tellurium. One of the first lines that would naturally occur to one would be the substitution of selenium for sulphur in the so-called sulphur colors. These are among our cheapest colors. There are at present two serious obstacles in the replacement of sulphur by selenium in the sulphur colors. The first is the relative cost of selenium to that of sulphur. The second is the nature of the bath which in the present development of the sulphur color process would make the cost prohibitive. There is, however, the possibility that a brilliant and fast color of considerable intensity could be found which could be manufactured profitably. The field of synthetic dye-stuffs does, however, possess great opportunities for experiment and is almost undeveloped.

The utilization of the less common elements has always been a problem which has interested chemists. Not many years ago elementary silicon was sold at a high price per gram and even then it was almost a curiosity to be found wholly in museums, yet in combined form it comprises one-fourth of the crust of the earth. Today silicon in elementary form is produced in large quantities at a few dollars per ton and is used on a large scale in deoxidizing non-ferrous alloys. Similarly a few years ago, tungsten was known only as a gray metallic powder with no other uses than that of the formation of the self-hardening tungsten wire in the lamp bulb and of the sheet metal in the spark coil to replace the more expensive platinum, makes metallic tungsten a very important commercial product. Along the same line molybdenum, tantalum, and the oxide of zirconium are substances which until recently were only museum specimens but today are very useful products. Only a few years before the war, large money prizes were offered in Europe for methods of utilization of bromine and of boron. We well know how valuable an element bromine was during the war and of its large consumption since the war, particularly in organic synthesis.

All of the elements which nature has furnished to us must find their place as a useful necessity to man. It is indeed incomprehensible to think that in the entire chemistry or physics of one or more elements there cannot be at least a single compound or property that can be utilized by mankind.

Except for the wartime use of selenium in the glass industry, the present uses for selenium and tellurium are very limited. A few hundred pounds of each would supply all demands. The large amounts of these elements which are available today and for which there is no practical use, have caused the National Research Council to create a committee on the Uses of Selenium and Tellurium. This committee, consisting of A. E. Hall, Chairman, with H. G. Greenwood,

Victor Lenher, O. C. Ralston, E. W. Rouse, S. Skowronski and A. W. Smith, has been working in close contact with the producers of selenium and tellurium in the United States, and it has been possible to make arrangements whereby large quantities of these elements can be secured at a very low figure for experimental purposes. The Raritan Copper Works, Perth Amboy, N. J., the U. S. Metals Refining Company of Chrome, N. J., the American Smelting and Refining Company, Omaha, Nebr., and the Baltimore Copper Smelting and Rolling Company, Baltimore, Md., which includes all of the producers of these elements in this country, will furnish workable quantities of these elements for research purposes at cost price.

Mr. E. W. Rouse, of the Baltimore Copper Smelting and Rolling Company, will ship at any time reasonable quantities of selenium to investigators gratis, upon the recommendation of the Committee of the National Research Council on Uses of Selenium and Tellurium, and Mr. Arthur E. Hall of the Omaha Plant of the American Smelting and Refining Company, will forward reasonable quantities of tellurium, gratis, under the same circumstances.

THE SEARCH FOR CEREALS.

By H. E. Howe, Vice-Chairman of the National Research Council's Division of Research Extension.

NOTWITHSTANDING the still unsettled question as to whether heredity or environment exercises the greatest influence upon an individual, it seems certain that both play a very vital rôle in plant life, particularly in the more useful plants, such as wheat, which we have had occasion to study somewhat intensively. Unfortunately, under the circumstances which produce the survival of the fittest, we can hardly secure the varieties necessary to guarantee maximum production in the various wheat areas of so large a country as the United States. Our occasional severe winters lead to the abandonment of large areas, and under these severe conditions the entire acreage in a particular locality is very apt to be wiped out, so that we have no survival which will produce seed to withstand other unusually hard winters. Statistics tell us that during the past five years a total of thirty million acres of winter wheat have been abandoned in this country, which, at the average yield of fifteen bushels, means a loss of four hundred million bushels of wheat, with a corresponding monetary loss—and, more important, a loss of food to the world.

It was to improve conditions of this sort, as well as to introduce new cereals from foreign countries, that some time ago Dr. M. A. Carleton, then of the Bureau of Plant Industry of the U. S. Department of Agriculture, began a systematic collection of cereals from foreign countries for the purpose of introducing new strains and varieties quite different from the species to be found ordinarily in North America. To what extent this work was successful may be indicated by the following:

Wheats used in the production of macaroni and the like must be unusually high in gluten. Previous to 1902, wheat satisfactory for this use was not produced in important quantity in the United States. Some years before that, a new form, now called durum wheat, was obtained from a semi-arid district in East Russia, and introduced in similar districts in our country, where other kinds of wheat do not succeed. Regular grades of this wheat were established at the different boards of trade following the harvesting of the first crop of any importance, which was, as indicated, in 1902. By 1908, our annual exports of this variety had reached twenty-seven million bushels, all of which were sent to Europe, where there is a constant demand for wheat possessing the characteristics of the durum variety.

In April, 1913, No. 1 durum wheat sold at a premium of $8\frac{1}{2}$ c a bushel at Duluth and $6\frac{1}{4}$ c at Minneapolis over our No. 1 northern wheat. At the present time, the average crop of this variety is approximately fifty million bushels a year, and in the last two years its popularity has increased. Our Ca-