the coking industry and does not alone have to pay interest on the investment. This is borne also by the coke (the main product), gas, tar, and benzol, the last two of rapidly increasing importance due to the stimulated demand for domestic coal-tar products and the enhanced price of gasoline. So the capital requirement really does not enter into the present discussion so long as there is some product to pay the interest demanded. The rapid installation of the by-product oven is proof enough that the interest on investment is forthcoming. By-product ammonia, therefore, fortified by the other products produced simultaneously, is in a position to withstand the rigors of market. It yet remains to be demonstrated that ammonia from any other artificial source can be made to pay interest on investment under American conditions.

By-product ammonia may lack the further characteristic, elasticity, desirable in a source of fixed nitrogen for emergency purposes, may not be susceptible of an immediate, enormously increased production. But this quality is lacking to any proposal which does not involve the erection of industrial plants to lie idle during those periods when there is no emergency; or if not lying idle, to operate under artificial conditions, affording no profit and therefore requiring public subsidy. That it is susceptible of enormous increase, should the people demand such an increase, becomes evident when it is recalled that there are enormous quantities of low-grade coal produced as a by-product in coal mining, other quantities available for mining, and immense beds of lignites and peat, practically untouched, all of which, on distillation, yield ammonia and other by-products; the residual carbon, valuable for fuel or gas production, and large volumes of gas for fuel or power production, is available for the manufacture of additional great sources of ammonia by fixation methods. In this connection it should be added that by-product gas as a source of power for the electrical fixation of nitrogen has the advantage over water power that by-product ovens can be erected and put into operation in a much shorter time than can the usual stream be dammed and its water power developed.

Likewise, coal as a power producer is much more efficiently used when it is first converted into gas and the gas used in gas engines, effecting a great saving over the steam engine—a practice which, if instituted, would make available the ammonia and other by-products of the coal now used for power production. Finally, as an extreme though visionary measure, at the same time one of enormous value to the public and one that should be looked forward

to by the public as an end to be striven for, the unrestricted use of bituminous coal as a fuel could be prohibited by public enactment and the universal use of coke or gas encouraged, thus conserving to the public the enormous aggregate wastage now existing in present methods of using coal. Such an enactment, it is reported, has been in effect in Germany since 1914. It is needless to compute the quantity of ammonia which thus would be made available for all uses or to speculate on the effect on American agriculture which such a supply of cheap and valuable fertilizer would have.

As preparedness measures let us advocate those things which will work for the good of the people as a whole. The salient feature of the foregoing is that it is a conservation measure affording profits under normal conditions and therefore not requiring a public subsidy to guarantee profits. Difficulties which appear in connection with it should not be permitted to prevail against the considerations which commend it. There is no conflict between true preparedness and true conservation since there can be no true preparedness with which conservation does not go hand in hand; and both are only applied common sense. That nation is best prepared for any emergency whose people are united and are working together to obtain the best possible returns from their common natural resources and labors. Any preparedness measure which does not have first consideration for conservation, for the welfare of the people as a whole, should be regarded with suspicion.

It is apparent from the above that we have at hand a source of fixed nitrogen adequate for normal times and capable of immense expansion in case of emergency. Let us then not hurry into the adoption of measures which later may come to be a source of humiliation. Let us rather with diligence and with the welfare of the nation in mind, investigate in the scientific way, in our laboratories and mills, these questions about which there is doubt and which demand no instantaneous decision. The atmosphere doubtless must be looked to ultimately to supply combined nitrogen for human needs. Progress to the present in that field, marked as it is, should only inspire investigation, and not acceptance of the position that the problem of combining nitrogen is solved. It is not solved. From our point of view it can be regarded as solved only when the fixation of atmospheric nitrogen becomes commercially feasible under the conditions that normally exist in this country.

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ORIGINAL PAPERS

THE OCCURRENCE OF GERMANIUM IN ZINC MATERIALS

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In a recent issue of *THIS JOURNAL*,¹ W. F. Hillebrand and J. A. Scherrer contribute a short article

¹ *THIS JOURNAL*, 8 (1916), 225.

on "The Recovery of Gallium from Spelter in the United States." In addition to the observations on gallium, mention is made of the fact that Dr. K. Burns, of the Bureau of Standards, has examined spectroscopically several samples of zinc ore from various sources, and has identified in several of them,

notably in a Missouri sulfide, the very rare element germanium. These observations concerning germanium are of particular interest to us since in recent work we also have encountered this element in a by-product derived from Wisconsin blende. The exact nature of this by-product it is not possible to disclose at present.

The occurrence of germanium in blendes has been noted by Urbain.¹ By spectroscopic methods this investigator detected germanium in thirty-eight out of eighty-four blendes from various localities. From five hundred and fifty kilos of one of the richest of these, a Mexican blende, he obtained five grams of pure germanium. The amounts of the element found have always been small, the aid of the spectroscope being usually required to establish the identification. In the material at our disposal, however, germanium was found in sufficient quantity to be readily detected by the ordinary chemical reagents.

The presence of an unusual element had been indicated in the course of analysis and further investigation showed that this was some member of the tin sub-group of the hydrogen sulfide group. The materials were therefore examined for the less common elements of this group. By the experiments briefly outlined in the succeeding paragraphs we convinced ourselves that we were dealing with an altogether unsuspected constituent, the element germanium, and that it was present in considerable amount.

Several one hundred-gram portions of the substance were treated with concentrated hydrochloric acid and the resulting solutions were distilled to about one-half volume, a current of chlorine being passed through the boiling mixture to maintain the arsenic in the pentavalent form. The distillate contained the unknown element.

On dilution of the distillate with a small amount of water and treatment with hydrogen sulfide a white flocculent precipitate was formed. If, however, the distillate was greatly diluted with water such precipitation took place but slowly and incompletely; the addition of strong hydrochloric acid to such solutions caused immediate precipitation. A considerable excess of strong acid was always found necessary for rapid precipitation of the sulfide.

The white sulfide, precipitated from strongly acid solutions, was somewhat soluble in water. It was readily soluble in ammonia and in alkaline sulfide solution. The sulfide yielded on ignition a white residue, soluble in water and in ammonia.

To an aqueous solution of the sulfide a little hydrofluoric acid was added and the solution saturated with solid potassium chloride. A heavy grayish white gelatinous precipitate resulted.

These reactions agree throughout with the properties ascribed to germanium by Winkler. The boiling point of the tetrachloride of germanium is 86°. The sulfide of germanium is white. It is soluble in water and in alkali and is precipitated only from strongly acid solutions. The formation of a double potassium fluoride is particularly characteristic.

¹ *Compt. rend.*, 149, 602; 150, 1758.

From two portions of a solution of germanium sulfide in water the sulfide was precipitated with strong acid and hydrogen sulfide. The sulfide was filtered on a Gooch, dried at 110° and weighed. It was then dissolved in ammonia and the crucibles reweighed. The ammoniacal solutions were evaporated to dryness in platinum and the residues transformed to oxides by the method recommended by Winkler. The results follow.

Determination No.	1	2
Weight of sulfide.....	0.0820	0.0812
Weight of oxide.....	0.0614	0.0604
Ratio oxide/sulfide.....	0.749	0.744

The theoretical ratio $\frac{\text{GeO}_2}{\text{GeS}_2}$ is 0.766, assuming the value 72.5 for the atomic weight of germanium.

A roughly quantitative determination of the amount of germanium present in the material was carried out as follows: After distillation with hydrochloric acid and chlorine the sulfide was precipitated from the distillate with hydrogen sulfide. In some experiments the sulfide was weighed directly; in others it was transformed into oxide with nitric acid and weighed as GeO_2 . The mean of several closely agreeing determinations gave the value $\text{GeO}_2 = 0.25$ per cent.

To show whether or not germanium could be found in other zinc ores, samples of similar by-products from different ores were distilled with hydrochloric acid and chlorine. The distillates, after dilution, were treated with hydrogen sulfide. If no precipitate was obtained the test was considered negative. If a precipitate was obtained (other than the turbidity of sulfur) it was filtered off and transformed to oxide with nitric acid. The final test consisted in the formation from the residue of the double potassium fluoride with hydrofluoric acid and potassium chloride.

From several of the materials very definite confirmatory tests were obtained; others gave satisfactory blanks, while in only a few instances were the results uncertain. In none of the cases where positive results were secured was there found an amount of germanium at all comparable to that found in the material first examined, probably not one-tenth as much. A positive test was secured from Joplin ore and also from some Mexican ores. The Franklin ores gave negative results.

The germanium oxide prepared as described above has been examined spectroscopically by Dr. Burns, of the Bureau of Standards, who reports as follows: "It shows: zinc, *absent*; lead, *weak*; silicon, *present*; tin, *fairly strong*; copper, *present* (possibly the last three were introduced accidentally by us); cadmium, *trace*; germanium, *principal constituent*; gallium, *present*; indium, *trace*."

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SODIUM SULFATE AS A SUBSTITUTE FOR POTASSIUM SULFATE IN THE GUNNING MODIFICATIONS FOR DETERMINING NITROGEN

By W. L. LATSHAW

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Owing to the extremely high price of potassium sulfate, chemists who favor the Gunning modification