A blank should be run using all the reagents, and any acidity found must be deducted from the final results.

The following results were obtained with borax and boric acid : One gram borax gave 36.57 per cent. boric acid, the theoretical per cent. being 36.65 per cent. ; one gram boric acid gave 99.9 per cent. boric acid.

A distillation of crystallized boracic acid, without the addition of phosphoric or other acid, was found to yield all the boric acid present. A similar distillation of borax was found to yield 19.50 per cent. boric acid out of a total of 36.65 per cent. present, or slightly more than fifty per cent. of the whole amount. This behavior may be useful in some analyses.

A gentle suction, by means of aspiration bottle, upon flask C, is desirable to avoid loss by possible leakage.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 29.]

ACTION OF SULPHUR MONOCHLORIDE UPON MINERALS.

BY EDGAR F. SMITH.

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SULPHUR monochloride has frequently been applied in organic chemistry in the synthesis of various bodies, and the results obtained by the employment of this reagent have invariably had great attraction and interest for the investigator. There are, however, other directions in which the same reagent may be followed with equal interest ; *e. g.*, in the action upon the natural products furnished by the mineral world. To illustrate, mention may be made of the behavior of such substances as arsenopyrite, chalcopyrite, pyrite, and marcasite with the reagent in question. Finely divided arsenopyrite and sulphur monochloride were brought together in a glass tube. After slight agitation, action set in, accompanied by the evolution of much heat, and the almost complete decomposition of the mineral. The tube was then freed from air by the introduction of carbon dioxide. It was sealed and heated to about the boiling-point of the sulphur monochloride (139°) for a period of nine hours. On cooling, beautiful olive-green colored plates or scales separated. After their removal from the tube and separation from the adherent liquid they proved to be deliquescent and readily soluble in water. Their aqueous solution tested with potassium ferrocyanide and silver nitrate showed the presence of iron in the ferric condition, and also of chlorine. In subsequent decompositions the crystals were filtered out, and washed with petroleum ether; then they were dissolved in water and the iron content determined quantitatively by means of stannous chloride. In this manner it was proved that 32.6 per cent. of iron was present in the ferric condition in arsenopyrite. This is certainly a confirmation of the work previously carried out in this direction on arsenopyrite by Starke, Shock, and Smith.[1]

The petroleum ether solution from the ferric chloride crystals was distilled, the product diluted with water, and tested with hydrogen sulphide, when the arsenic was precipitated. Its quantity was not estimated.

Chalcopyrite treated in a similar manner with sulphur monochloride, was completely decomposed, with the production of ferric and cupric chlorides. Marcasite and pyrite also gave beautiful crystallizations of iron chloride. The decompositions were in both instances complete and the total iron content determined. On the addition of sulphur monochloride to marcasite and pyrite no action was observed in the cold. With chalcopyrite and arsenopyrite the evolution of heat, as already mentioned, was very great, so that the vessel containing them could not be held in the hand. This difference in behavior evidently indicates a marked difference in the union of the elements concerned. In pyrite and marcasite we deal with iron and sulphur alone and with them there is an absence of marked reactivity, whereas in arsenopyrite and chalcopyrite we have substitution products in which there is perhaps a less intimate union of the sulphur than exists in the pyrite and marcasite. It may be observed here that Brown,[2] while working with marcasite, found that it contained its total iron in the ferrous condition, but when this same mineral was dissolved in sulphur monochloride it gave a mass of iron chloride crystals showing the presence of about forty-one per cent. of iron in the ferric state. This would mean that this reagent undoubtedly acts as an oxidant; that its power is in a large measure due to its chlorine content,

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[1] This Journal, 19, 948.

[2] *Proc. Am. Phil. Soc.*, 33, 1894.

so that we may say of sulphur monochloride, it is "chlorine in disguise." This view of its action is corroborated by other decompositions which will be presented later. The experiments upon which the preceding statements are based werecarried out by Mr. F. W. Moore.

The mineral stibnite dissolved immediately and completely in sulphur monochloride with a violent ebullition and the generation of much heat. When the solution cooled crystals separated. These were collected and heated with water, with the formation of antimony oxychloride. Much heat was also evolved when cinnabarite and sulphur monochloride were mixed. To effect complete decomposition the mixture was heated in a sealed tube. On cooling long needles were observed throughout the liquid. These proved to be mercuric chloride. Chalcocite was also completely decomposed, with the production of a crystalline powder, which on examination was found to. be cupric chloride. This is additional evidence of the oxidizing character of the solvent employed, and explains the reason for the obtainment of so much ferric chloride when using marcasite, which contains its iron in the ferrous condition. Tetrahedrite, although of a complex nature, yields in the cold to the influence of the sulphur monochloride, and crystals of ferric chloride appeared in a very short time, although to effect the complete decomposition of the mineral it was necessary to heat it with the reagent to 140° C. Sphalerite was not attacked in the cold, and at 150° its decomposition was very slight, but at 250° C. complete solution occurred. On cooling, a mass of anhydrous zinc chloride separated. This was quickly collected and treated with water when it dissolved with a hissing noise. The zinc in solution equaled 67.5 per cent.

Galenite, furthermore, was not affected in the cold, but at 250° C. was changed completely to lead chloride. Finely divided molybdenite was not attacked in the cold, nor was it entirely broken up after heating to 300° C. Many of these experiments show that, where the sulphur estimation of a sulphide is not desired, this method of decomposing such minerals may be of use in analysis. This is particularly true in the case of tetrahedrite. Mr. C. S. Reeve was kind enough to conduct these experiments for me.

At my suggestion, Mr. E. W. Pierce brought pure, artificial arsenic trisulphide in contact with sulphur monochloride. A violent reaction set in, and much heat was liberated. On repeating the experiment at a temperature of 0°, the reaction took place slowly with the gradual solution of the metallic sulphide and the appearance of a slight residue of sulphur, which disappeared on the addition of more sulphur monochloride. Nothing separated when the liquid was further chilled. Arsenic sulphide was precipitated from the diluted solution on the addition of hydrogen sulphide. The minerals linnæite $(Co,Ni)_3S_4$, millerite (NiS), gersdorffite (NiAsS), and rammelsbergite $(NiAs)_2$, were also fully decomposed by the monochloride on heating the mixture in sealed tubes to 170° C. Metallic chlorides were formed in all instances and separated from the cold solutions. Cobaltite (CoAs), smaltite $(Co(FeNi)As_2)$, and ullmannite (NiSbS), in a finely divided condition, were dissolved by the sulphur monochloride when heated to 180° C. in a sealed tube. These observations were made by Mr. Jos. Cauffman, who also found that rutile in powdered form was decomposed almost completely by the same reagent, with the production of titanium tetrachloride. This behavior suggested heating the oxides of molybdenum, tungsten, tantalum, and columbium, as well as the minerals wolframite, scheelite, and columbite with the same reagent, when all were dissolved, and from the cold solutions beautiful crystalline bodies separated. Some of these have been analyzed, while others are yet under examination and will be discussed in a later communication. The indications are that the action of the sulphur monochloride in these substances is both oxidizing and substituting. Combinations of the metallic haloids with sulphur monochloride are not produced. In the case of the sulphides and sulpho salts which were investigated, quantitative determinations of the products were only made in a few instances, for there was no question as to the completeness of the decompositions, and the character of the resulting bodies. Upon considering the facts which are here presented, we recognize that with the sulphides of non-metals, for example stibnite, the action is violent, and the decomposition complete. This is also true of arsenopyrite where arsenic probably facilitates the transposition, whereas with marcasite, pyrite, sphalerite, galenite, etc., the reaction is more sluggish. From an examination of the excess of sulphur monochloride in these different experiments it would seem that the original sulphur of the mineral is merely dissolved out, for upon evaporation it separates in large quantities.

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THE DETERMINATION OF SMALL QUANTITIES OF ALCOHOL.

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THE methods for the determination of alcohol ordinarily in use are for the most part physical. By means of the pycnometer, vaporimeter, and ebullioscope, we are able to determine with reasonable accuracy the amount of alcohol present in alcoholic beverages and solutions, which seldom contain under one per cent. of ethyl alcohol. When, however, the exact estimation of smaller quantities is desired, these methods are unsatisfactory.

The numerous chemical methods for the determination of alcohol depend for the most part on the oxidizing action of potassium bichromate, chromic acid, or potassium permanganate. Only a small portion of the research on the oxidizing action of these compounds, has been done with reference to their oxidation of alcohol. This is partly explained by the previous existence of the physical methods of analysis above referred to and by the fact that while many organic compounds are completely and readily oxidized to carbon dioxide and water, alcohol is oxidized with great difficulty, the oxidation ceasing usually with the formation of acetic acid. The iodoform reaction and the blue coloration produced with a sulphuric acid solution of molybdic acid, furnish tests of the greatest delicacy, and for the most part investigators have been satisfied with a qualitative demonstration of the presence of alcohol when occurring in such small quantities as to preclude the use of the ordinary quantitative methods.

Bodländer[1], pursuing an investigation similar to that for which the methods here reported were devised, *i. e.*, the estimation of

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[1] *Pflüger's Archiv*, 32, 398.