REVIEW OF AMERICAN CHEMICAL RESEARCH.

ARTHUR A. NOYES, Editor.
REVIEWERS: Analytical Chemistry, H. P. Talbot and W. H. Walker; Biological Chemistry, A. G. Woodman; Carbohydrates, G. W. Rolfe; General Chemistry, A. A. Noyes; Geological and Mineralogical Chemistry, W. O. Crosby and M. L. Fuller; Inorganic Chemistry, Henry Fay; Metallurgical Chemistry and Assaying, H. O. Hofman; Organic Chemistry, J. F. Norris; Physical Chemistry, H. M. Goodwin; Sanitary Chemistry, E. H. Richards; Industrial Chemistry, A. H. Gill and F. H. Thorp.

INORGANIC CHEMISTRY.

HENRY FAY, REVIEWER.

Some Double Halides of Cadmium with the Methylamines and Tetramethylammonium. By C. D. RAGLAND. *Am. Chem. J.*, **22**, 417–434.—These double salts were prepared by bringing together concentrated solutions of the separate salts. The volumes of the solutions were so taken as to vary the molecular proportions, making a series in which the salts varied from a 1 : 4 to a 4 : 1 mixture. When solutions of methylamine hydrochloride and cadmium chloride were mixed in varying proportions, only one salt could be obtained, that of the 2 : 1 type. With cadmium chloride in large excess there was some evidence of another salt, but it could not be obtained in pure condition. Methylamine hydrobromide and cadmium bromide form two salts representing the 1 : 1 and the 2 : 1 types. It was impossible to prepare the double iodides. Dimethylamine hydrochloride and cadmium chloride form three salts in which the proportions of the former to the latter are 1 : 1, 1 : 2, and 3 : 2. The double bromides likewise form three salts, but of the types 1 : 1, 2 : 1, and 1 : 4. Dimethylamine iodide and cadmium iodide form one salt in which the ratio is 1 : 1. Trimethylamine hydrochloride and the hydrobromide with the corresponding cadmium salts each give two double salts of the same types, 1 : 1 and 3 : 2. Trimethylamine iodide and cadmium iodide form the 1 : 1 and 2 : 1 salts. Tetramethylammonium chloride forms with cadmium chloride the one salt in which the proportions are 1 : 1. The 1 : 1 and 2 : 1 salts are formed with tetramethylammonium bro-

mide and cadmium bromide and with tetramethylammonium iodide and cadmium iodide. The $3:2$, $1:2$, and $1:4$ salts have no analogues among the double halides of the alkali metals and ammonium with cadmium.

Some Double Halides of Tin with the Aliphatic Amines and with Tetramethylammonium. BY C. G. COOK. *Am. Chem. J.*, **22**, 435–446.—These salts show a marked regularity throughout the series. With the single exception of the triethylamine chlorstannate, which is a $3:1$ salt of the composition $[(C_2H_5)_3 NH]_2SnCl_6$, all of the series are $1:1$ or $2:1$ salts. The double salts formed by bringing together the chlorides of methyl, dimethyl, trimethyl, ethyl, triethyl, and tetramethylammonium with stannous chloride are all of the $1:1$ type. Stannous bromide forms the $1:1$ type with the bromides of methyl-, dimethyl-, and ethylamine. All of the above amine salts give with the corresponding halogen salt of stannic tin, the $2:1$ type of salt. In addition, trimethylamine and triethylamine bromstannate are described. Both are $2:1$ salts. When stannous chloride was mixed with triethylamine hydrochloride oxidation always took place, so that from such solutions it was possible to isolate only the chlorstannate.

Notes on the Double Halides of Tin with the Organic Bases. BY GEORGE M. RICHARDSON AND MAXWELL ADAMS. *Am. Chem. J.*, **22**, 446–449.—The authors describe a few additional salts of this series which were not found by Slagle (*this Rev.*, **5**, 29). Tetraniline chlorstannate was obtained by concentration of solutions of aniline hydrochloride and stannous chloride, after the first crop of crystals, dianiline chlorstannite, had been removed. Dimethylaniline chlorstannite, $C_6H_5NH(CH_3)_2.SnCl_3.\frac{1}{2}H_2O$, was prepared in the same way, and is entirely analogous to the corresponding toluidine compounds described by Slagle. Aniline bromstannite, $C_6H_5NH_3SnBr_3$, dianiline bromstannate, $(C_6H_5NH_3)_2SnBr_6$, and tetraniline bromstannate,

$$(C_6H_5NH_3)_4SnBr_8,$$
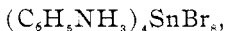
were prepared and described.

On the Effect of Various Solvents on the Allotropic Change of Mercuric Iodide. BY J. H. KASTLE AND MARY E. CLARK. *Am. Chem. J.*, **22**, 473–484.—Kastle had previously observed that the yellow modification of mercuric iodide could be obtained by dissolving the red modification in boiling amyl alcohol and allowing the solution to cool. The authors have now studied the solutions of mercuric iodide in a large number of organic solvents of different boiling-points. With the exception of the solutions in the alkyl halides, which were colored pink due to a

small amount of double decomposition, all solvents tried were colored yellow. From these solutions the yellow modification crystallized, but on standing it gradually passes back into the red form. When an excess of red mercuric iodide is used in a solvent some of the solid is changed to the yellow. The yellow crystals which come out of solution are soon converted into red on coming in contact with the red variety. Low-boiling liquids apparently produce the conversion as well as high-boiling liquids. Mercuric iodide, like phosphorus, appears capable of existing in solution and in the form of vapor only in the condition of the yellow compound, and this is either identical with or a polymer of the solid yellow mercuric iodide.

The Preparation of Pure Tellurium. BY JAMES F. NORRIS, HENRY FAY, AND D. W. EDGERLY. *Am. Chem. J.*, **23**, 105–119.—This paper is a preliminary study of methods for the preparation of a pure material which might be used for a determination of the atomic weight of tellurium. The tellurium was obtained from a residue produced in the electrolytic refining of copper. The residue was extracted with strong hydrochloric acid, and from this solution the tellurium was precipitated with acid sodium sulphite. Much of the selenium which is invariably present may be removed by filtering off the first precipitate produced by acid sodium sulphite. Further addition of sulphite throws out the tellurium with traces of other elements which may be present. To purify the crude metal it was added to warm, dilute nitric acid (sp. gr. 1.25), and the resulting solution evaporated to dryness, in order to insure complete removal of silica. The basic nitrate of tellurium was converted into oxide, extracted with hydrochloric acid, and from this solution it was again precipitated as a metal, dissolved in dilute nitric acid, and the basic nitrate, $Te_2O_3(OH)NO_3$, obtained by crystallization. Two crystallizations rendered it perfectly pure. It was shown to be free from selenium dioxide by a delicate reaction based on the fact that selenium dioxide liberates iodine while the tellurium is converted into tetraiodide. Other impurities were tested for but not found present. The basic nitrate of tellurium crystallizes from strong nitric acid solution in well-developed orthorhombic prisms, which are entirely stable in the air. Dilute nitric acid decomposes the basic nitrate of tellurium with formation of the dioxide. The basic nitrate does not begin to decompose until heated to 170°. At 190° the oxides of nitrogen begin to be evolved. When heated slowly to a higher temperature, decomposition continues until it is converted into the oxide. By rapid fusion of the oxide, after previous slow heating, very accurate determinations could be made. To test the homogeneity of tellurium a fractionation, involving 215 crystalliza-

tions, of the double bromide of tellurium and potassium was carried out. This salt was prepared from carefully purified materials. There were no indications, during the fractionation, of any change in the salt, so that it was necessary to make an analysis of the end fractions. To this end the basic nitrate, made from the double tellurium bromide, was decomposed in a platinum crucible arranged with several disks over which the escaping gases were forced to pass in order to avoid mechanical loss. The decomposition was accomplished slowly by heating at various periods to a gradually increasing temperature. The oxide was finally fused quickly in the oxidizing flame of a Bunsen burner. The analysis of the nitrate prepared from the tellurium from the fraction which would contain the most soluble portion, gave 83.45 and 83.44 per cent. of TeO_2; from the least soluble portion, 83.48 and 83.49 per cent. TeO_2. The fractionation, therefore, did not effect any decomposition of the tellurium which could be detected by a method capable of giving results accurate to 0.4 of a unit in the atomic weight.

The Reduction of Selenium Dioxide by Sodium Thiosulphate.
BY JAMES F. NORRIS AND HENRY FAY. *Am. Chem. J.*, 23, 119–125.—In a previous paper (*this Rev.*, 4, 31) a volumetric method for the determination of selenium dioxide was described. It was based on the reaction between selenium dioxide and sodium thiosulphate, four molecules of the latter reacting with one of the former. It was not known at the time what was the nature of the reaction, but the reaction is now shown to proceed according to the equation :

$$SeO_2 + 4Na_2S_2O_3 + 4HCl =$$
$$Na_2S_4SeO_6 + Na_2S_4O_6 + 4NaCl + 2H_2O.$$
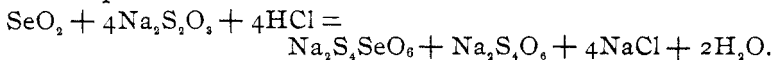
The formation of sodium selenopentathionate, similar to potassium pentathionate, seemed probable since no selenium was precipitated in the reduction. A solution prepared by mixing the constituents in the proportions represented in the equation, gave all the characteristic reactions of the pentathionates with the exception that selenium was precipitated instead of sulphur. Attempts to isolate the sodium selenopentathionate were not successful. Tellurium seems to form an analogous compound. In reply to a criticism by Mr. Norton (*this Rev.*, 5, 89) the authors have again studied the conditions under which the volumetric method can be most accurately carried out. It was found that Mr. Norton had confused *excess* of acid with *amount*. The amount, however, which was recommended by the authors is more than is absolutely necessary, although it does not interfere with the accuracy of the method. It is shown that low temperature and the presence of acid have great influence on the delicacy of the starch reaction.

The Double Halides of Antimony with Aniline and the Tolui-dines. BY HOWARD H. HIGBEE. *Am. Chem. J.*, 23, 150–173. —Mixtures of the halide of the base were brought together with the antimony halide, each constituent having been previously dissolved in the corresponding halogen acid. From the various mixtures of aniline hydrochloride and antimony trichloride, tri-aniline chlorantimonite, $(C_6H_5.NH_2.HCl)_3.SbCl_3.H_2O$, crystal-lized from most of the mixtures; from the mixture in which the proportion of base to antimony was 1 : 2, monaniline chloranti-monite, $C_6H_5.NH_2.HCl.SbCl_3.H_2O$, was obtained. From *o*-tolui-dine hydrochloride and antimony trichloride only one salt was isolated, di-*o*-toluidine chlorantimonite, $(C_6H_4.CH_3.NH_2.HCl)_2.$ $SbCl_3$; *m*-toluidine hydrochloride gave two salts, tri-*m*-toluidine chlorantimonite, $(C_6H_4.CH_3.NH_2.HCl)_3.SbCl_3$, and di-*m*-tolui-dine chlorantimonite, $(C_6H_4.CH_3.NH_2.HCl)_2.SbCl_3.H_2O$; *p*-tol-uidine hydrochloride likewise gave two salts, di-*p*-toluidine chlorantimonite, $(C_6H_4.CH_3NH_2.HCl)_2.SbCl_3.\frac{1}{2}H_2O$, and tri-*p*-toluidine chlorantimonite, $(C_6H_4.CH_3.NH_2.HCl)_3.SbCl_3.H_2O$. Aniline hydrobromide and antimony tribromide yielded the two salts $(C_6H_4.CH_3.NH_2.HBr)_2.SbBr_3$ and $(C_6H_4.CH_3.NH_2.HBr)_4.$ $SbBr_3.H_2O$. One salt, tri-*o*-toluidine bromantimonite $(C_6H_4.$ $CH_3.NH_2.HBr)_3.SbBr_3$ was obtained from *o*-toluidine hydrobro-mide and antimony tribromide; *m*-toluidine hydrobromide also gave but one salt in which the ratio of base to antimony was 2 : 1; *p*-toluidine hydrobromide gave three salts in which the ratios of base to antimony were respectively 2 : 1, 3 : 1, and 4 : 1. In dry air all three compounds are canary-yellow, but lose their color on contact with moisture. Aniline hydriodide gave with antimony triiodide three salts in which the ratios of base to anti-mony were 1 : 1, 3 : 2, and 4 : 1. From *o*-toluidine hydriodide and antimony triiodide the 1 : 1 and 3 : 2 salts were obtained; from *m*-toluidine hydriodide the 3 : 2 salt; from *p*-toluidine hy-driodide the 1 : 1 salt.

A Preliminary Study of the Cobalticyanides. BY E. H. MILLER AND J. A. MATHEWS. *J. Am. Chem. Soc.*, 22, 62–69.— The cobalticyanides of silver, mercury, copper, bismuth, cad-mium, iron, manganese, zinc, cobalt, and nickel were made by bringing together half-normal solutions of potassium cobalticya-nide with half-normal solutions of the metals. The composition of the precipitates and their solubilities in various reagents were studied qualitatively only.

The Carbide of Gold. BY J. A. MATHEWS AND L. L. WAT-TERS. *J. Am. Chem. Soc.*, 22, 108–111.—By passing acetylene into a strongly ammoniacal solution of sodium aurous thiosul-phate there is formed, after some time, a yellow, flocculent pre-cipitate which, after having been dried over sulphuric acid,

gives on analysis figures which correspond to the formula Au_2C_2. Carbide of gold is highly explosive. Water decomposes it into its elements ; hydrochloric acid liberates acetylene.

On the Decomposition of Nickel Carbonyl in Solution. By VICTOR LENHER AND HERMANN A. LOOS. *J. Am. Chem. Soc.*, **22**, 114–116.—The authors have confirmed the experiments of Berthelot, Mond, and others, that nickel carbonyl is decomposed by moisture. When dissolved in acetone, chloroform, benzene, toluene, or methyl alcohol, there is produced a green precipitate, the composition of which seems to be variable.

GEOLOGICAL AND MINERALOGICAL CHEMISTRY.

M. L. FULLER, REVIEWER.

Some New Minerals from the Zinc Mines at Franklin, N. J., and Note Concerning the Chemical Composition of Ganomalite. BY S. L. PENFIELD AND C. H. WARREN. *Am. J. Sci.*, **158**, 339–353.—The new minerals hancockite, nasonite, glaucochroite, and leucophoenicite were taken mostly from the 1000-foot level of the Parker Shaft on North Mine Hill, where they are associated with native lead and copper, clinohedrite, roeblingite, axinite, willemite, vesuvianite, datolite, barite, garnet, phlogopite, and franklinite. Careful analyses were made of each of the new minerals, and their formulæ computed. 1. Hancockite. This is a brownish-red mineral crystallizing in very minute, lath-shaped crystals, resembling those of epidote, of hardness 6.5–7, and specific gravity 4.030. The analysis gives the empirical formula $H_2R''_2(R'''.OH)R'''_2(SiO_4)_3$ or $R''_2(R'''.OH)R'''_2(SiO_4)_3$. The general formula is that of epidote, differing principally in having the bivalent metals lead (18.53 per cent.) and strontium (3.89 per cent.) isomorphous with calcium. It should be placed, therefore, in the epidote group next to piedmontite. It is named after E. P. Hancock, of Burlington, N. J. 2. Glaucochroite. Glaucochroite occurs in small orthorhombic prisms or columnar aggregates, and is sometimes twinned. It has a hardness of about 6, a specific gravity of 3.407, and in color is a delicate bluish-green. The analysis, disregarding 1.74 per cent. of lead, gives the formula $CaMnSiO_4$, which places it next to monticellite in the chrysolite group. The name is from the Greek, meaning *blue-green color.* 3. Nasonite. This is a white, massive mineral with greasy to adamantine luster, hardness about 4, specific gravity 5.425, and usually shows numerous inclusions of axinite, garnet, and glaucochroite. Its crystallization is probably tetragonal, though this could not be proved. The analyses show the general formula to be $R_{10}Cl_2Si_6O_{21}$, in which R is mostly lead and calcium. Allowing for a few particles of clinohedrite that were