sures are corrected for aqueous tension and the relative humidity (Line 4) as directed by Evans.[1]

Since the substances under investigation do not follow the perfect gas law in the vapor state, the use of this law can not lead to correct molecular weights from vapor-density measurements. Usually, however, the deviations are of no practical significance. In the present case it is interesting to find out whether these deviations are those to be expected from the substances used or are due to experimental error. For this purpose an equation of state more accurate than the perfect gas law is necessary. Berthelot's equation is useful for this purpose as it expresses the behavior of most substances closely and the data to substitute into it are readily available. Rearranged to give the molecular weight, it may be stated as follows:

$$M = \frac{mRT'}{PV'}\left[1 - \frac{9\,PT_c}{128\,P_cT}\left(1 - 6\,\frac{T_c^2}{T^2}\right)\right]$$

In this equation M is the true molecular weight, $m$ the mass of the substance; R is the gas constant; P and $P_c$ are the (corr.) barometric pressure and the critical pressure, respectively. T, T′ and $T_c$ are, in turn, the temperature at which the substance is vaporized, the temperature at which the volume of air is measured, and the critical temperature. V′ is the volume of the displaced air. V′ and T′ can be substituted for T and V of the original equation if the volume of the displaced air is proportional to the absolute temperature. This is almost exactly true in the range involved, as can be seen by substituting the appropriate constants for oxygen and nitrogen into Berthelot's equation. Referring to the table it will be seen that the molecular weight calculated by using the perfect gas law (Line 6) is one or two units higher than the accepted molecular weight (Line 8) while the molecular weight from Berthelot's equation (Line 7) varies by only a few tenths of a unit.

URBANA, ILL.

# A NEW OXYCHLORIDE OF TIN.

BY HARRY F. KELLER.

Received September 5, 1917.

While engaged upon the chemical examination of certain objects brought from the Indian mounds of Florida by Mr. Clarence B. Moore, of this city, the writer's curiosity was aroused by minute brilliant crystals which he observed in a cavity inside of a metallic mass found in an aboriginal cemetery on Hogtown Bayou, Santa Rosa County, Florida.

This mass was of lenticular form, as if the metal had been melted in a shallow vessel, rather more than 5 cm. in diameter, and about 4 mm. in

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[1] THIS JOURNAL, 35, 958 (1913).

thickness near the center. On the surface it was earthy and of a pinkish gray color, but when a piece was broken off it was found to consist of a white metal inside, and of a sharply defined gray crust, about 1 mm. in thickness on the outside. Within the metal were several fairly large cavities lined with the shining little crystals above mentioned. The metal was easily recognized as tin; while the crust was found to be a mixture of the metal (probably gray tin) and oxide of tin.

Some of the crystals were readily detached from the metal, while others were disseminated through it. They were mostly in the form of thin plates, though a few were distinctly acicular. They are easily crushed to a chalk-white powder which on heating in the closed tube melts, turning dark and giving off acrid fumes which form a sublimate without a trace of moisture. The powder dissolves in dilute acids without effervescence. The hydrochloric acid solution gives a brown precipitate of stannous sulfide when treated with hydrogen sulfide. The nitric acid solution, upon addition of silver nitrate, gives a white precipitate at first, but this rapidly turns reddish brown owing to the reducing action of the stannous salt. After dissolving the precipitate in ammonia and filtering the solution, a white curdy precipitate is thrown down by adding an excess of nitric acid.

The qualitative tests thus indicated that tin in the stannous state and chlorine are the principal constituents of the compound. To obtain an amount of material sufficient for quantitative determination it was necessary to practically destroy the specimen, and Mr. Moore very generously allowed this to be done. From the several cavities that were found over 0.3 g. of somewhat impure material was recovered. A preliminary quantitative analysis yielded 67% tin and 13.6% chlorine, as well as a small insoluble residue which gave reactions for alumina and iron (clay?). As the dilute nitric acid solution could not be precipitated with silver nitrate without bringing down also considerable amounts of tin, the chlorine was separated from the tin by boiling the powdered substance either with a solution of sodium carbonate, or with sodium sulfide and sulfur, the tin being precipitated from the latter solution by the addition of dilute sulfuric acid.

Nearly 0.2 g. of pure material having been obtained by laborious picking with the aid of a lens, the powder was decomposed by boiling with sodium carbonate. The tin was then determined as tin dioxide and the chlorine as silver chloride. The analysis gave:

| | | |
|---|---|---|
| Sn | 70.92% | 73.06 |
| Cl | 21.68 | 21.98 |
| Impurities | 0.26 | .... |

Calculated as stannous chloride the chlorine requires 36.03% Sn, and the difference between this amount and 70.92%, or 34.89 Sn, is undoubtedly present in the form of SnO, requiring 4.73% O. Considering the small amount of substance which was available for these determinations, and also the difficulties involved in the separation of the constituents, the results obtained agree quite well with the calculated percentages. These correspond to the formula $SnCl_2.SnO$.

The writer is inclined to believe that his determination of the tin was a little too low, rather than assuming that some of this tin was present in the stannic form. In spite of diligent search no reference to the existence of an anhydrous stanno-oxychloride could be found in the literature of the subject.

The occurrence of tin in the burial places of the aborigines will doubtless by discussed by Mr. Moore when he publishes his investigation of the Florida mounds. It is difficult to account for the formation of the chloride inside of a mass of metallic tin, unless we assume that some chloride solution had access to the hollow interior through an opening at the surface.

PHILADELPHIA, PA.

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[CONTRIBUTION FROM THE IOWA AGRICULTURAL EXPERIMENT STATION.]

# THE USE OF SODIUM PARATUNGSTATE IN THE DETERMINATION OF METALLIC OXIDES FROM CYANIDES.

BY S. B. KUZIRIAN.

Received June 25, 1917.

The use of sodium paratungstate as a flux capable of completely expelling certain volatile acid radicals in a remarkably short time and conserving the residual oxides in definite and stable form for weighing under ordinary atmospheric conditions has been proposed by Gooch and Kuzirian.[1] Kuzirian[2] has further demonstrated the use of this flux in analysis of halogen and oxy-halogen salts. The present work has to do with the extension of the use of the same flux to include cyanides. The commercial sodium cyanide, labelled C. P., when treated with hydrochloric acid and evaporated to dryness in a good draft hood, left a dirty reddish residue, indicating the presence of iron and other impurities. It was therefore discarded. When, however, potassium cyanide that had been packed in a tin can and labelled 99% pure was likewise treated, it left a white residue. This sample was therefore taken for the analytical experiments with sodium paratungstate. This commercial product when analyzed gravimetrically yielded an average of 0.9460 g. of silver cyanide per half gram sample. When titrated with 0.1 $N$ silver nitrate, using Liebig's method, an exact check of the gravimetric method was obtained,

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[1] *Am. J. Sci.*, 31, 497 (1911).

[2] *Ibid.*, 36, 301 (1913).