value, 33.0° C., is 1.6° higher than ours. The authors of this report note one possible error in his work. As a check on the accuracy of his temperature measurements he calibrated his apparatus against the melting point of pure chloroform, assuming this to be 63.1°. Recent measurements by Henning, place it at 63.7°.[1]

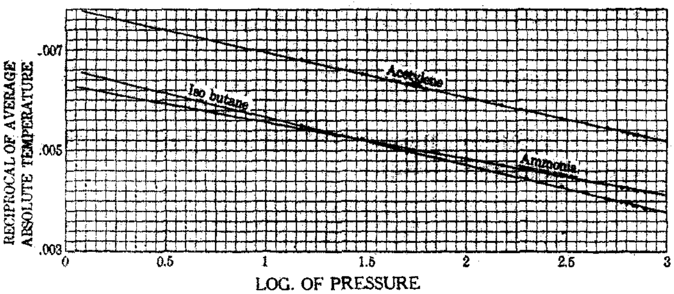

Fig. 2.—Log. of pressure plotted against reciprocal of absolute temperature.

Brill's work on ammonia is the only work on vapor pressures of gases at low temperatures that covers an extensive range for a gas that the authors also have worked on. We extended the observations 20° lower than Brill.

Pittsburgh, Pa.

[From the Department of Chemistry of Rutgers College.]

THE ACTION OF THIONYL CHLORIDE ON SULFIDES.

By H. B. North and C. B. Conover.

Received September 1, 1915.

Investigation of the action of thionyl chloride on inorganic substances has been confined almost entirely to its deportment toward metals, metalloids and oxides. The action of the reagent on these has been quite exhaustively studied by North and Hageman and described in This Journal.[2] Letting M represent a divalent metal of metalloid, reaction follows the general equation

$$3M + 4SOCl_2 = 3MCl_2 + 2SO_2 + S_2Cl_2.$$

With oxides, reaction takes place according to the following:

$$MO + SOCl_2 = MCl_2 + SO_2$$

In the case of metals or metalloids having more than one compound with chlorine, the lower chloride is usually, but not always, produced if the metal is in excess. Likewise the higher chloride is formed when the metal is treated with a large excess of the reagent.

The chief difference in the two reactions given above is that with metals

---

[1] *Ann. Physik,* **43,** 294 (1913).

[2] This Journal, **34,** 890 (1912); **35,** 352 (1913); **35,** 543 (1913).

or metalloids sulfur monochloride is always one of the products. Sulfur monochloride is not produced in reactions with oxides. In the case of higher oxides or peroxides, reaction does not follow the general equation given above but always results in the formation of a mixture of chloride, sulfate and sulfuryl chloride, if an excess of the oxide is used, or chloride, sulfur dioxide and sulfuryl chloride when an excess of thionyl chloride is employed.

So far as the authors have been able to ascertain, only three reactions of thionyl chloride on sulfides have heretofore been studied. The action on phosphorus pentasulfide was studied in 1858 by Carius,[1] who undoubtedly was the first to prepare thionyl chloride in a pure condition. Carius thought the reaction proceeded according to the equation

$$P_2S_5 + 5SOCl_2 = P_2O_5 + 5S_2Cl_2,$$

but in 1884 Prinz[2] found this to be incorrect. According to Prinz the reaction takes place as follows:

$$2P_2S_5 + 6SOCl_2 = 4PSCl_3 + 3SO_2 + 9S$$

Prinz also tried the action of thionyl chloride on antimony trisulfide, finding that reaction takes place as follows:

$$6SOCl_2 + 2Sb_2S_3 = 4SbCl_3 + 9S + 3SO_2$$

Both of these reactions must have been carried out at a temperature lower than 150°, for above this point thionyl chloride and sulfur react according to the equation:

$$2SOCl_2 + 3S = SO_2 + 2S_2Cl_2$$

No further reaction with a sulfide was studied until 1896, when Besson[3] investigated the reaction of this reagent on hydrogen sulfide. He found the reaction to proceed according to the following equation:

$$2SOCl_2 + 2H_2S = 4HCl + SO_2 + 3S$$

The reactions described in this paper were brought about in sealed glass tubes at a temperature of 150–180°. With the exception of ferrous sulfide, the sulfides employed were made by precipitation. They were thoroughly dried at 110° and were preserved in tightly stoppered tubes. In every case sulfur dioxide and sulfur monochloride were formed.

Zinc Sulfide.—When zinc sulfide was treated with thionyl chloride, reaction commenced in the cold but soon stopped. The sealed tubes containing the material were heated at 150–200° for several days without any change in appearance, due to the fact that both the chloride and sulfide are white. When the tubes were opened they were found to contain, in addition to the white solid, considerable sulfur dioxide and sulfur

---

[1] *Ann.*, **106**, 303 (1858).

[2] *Ibid.*, **223**, 355 (1884).

[3] *Compt. rend.*, **122**, 467 (1896).

monochloride. The white solid was analyzed and found to be zinc chloride. Reaction proceeds, therefore, according to the equation:

$$ZnS + 2SOCl_2 = ZnCl_2 + SO_2 + S_2Cl_2$$

Cadmium Sulfide.—Reaction did not commence in the cold when cadmium sulfide and thionyl chloride were brought together. When the tube was heated at about 200° reaction appeared to take place slowly, as indicated by the very gradual change in color from yellow to white. After being heated for about 15 days, the solid contents of the tube appeared entirely white. Analysis showed this compound to be cadmium chloride, hence reaction proceeds as follows:

$$CdS + 2SOCl_2 = CdCl_2 + SO_2 + S_2Cl_2$$

The tube also contained much sulfur dioxide and sulfur monochloride.

Silver Sulfide.—Thionyl chloride did not react with silver sulfide in the cold. After heating for several days the sulfide was found to have changed into silver chloride, as was shown by subsequent analysis. The action of thionyl chloride on silver sulfide proceeds according to the equation

$$Ag_2S + 2SOCl_2 = 2AgCl + SO_2 + S_2Cl_2.$$

Arsenic Sulfide.—Arsenic sulfide was found to react readily with thionyl chloride at 150°, going completely into solution. Inasmuch as thionyl chloride and arsenic chloride are both liquids and miscible, it was supposed that reaction had taken place with the formation of the latter compound according to the equation

$$As_2S_3 + 6SOCl_2 = 2AsCl_3 + 3SO_2 + 3S_2Cl_2.$$

The liquid in the tube was therefore a mixture of arsenic trichloride, sulfur monochloride and the excess of the thionyl chloride. This liquid was fractionated in an attempt to bring about a separation, but on account of the small amount of material, a complete separation was impossible. A small amount of distillate was obtained at a temperature above 126°. This had a very pronounced odor of sulfur monochloride, and when decomposed in water gave a precipitate of sulfur. The solution gave a strong test for arsenic, hence the authors are of the opinion that reaction took place according to the equation given and that the distillate obtained above 126° was a mixture of arsenic trichloride and sulfur monochloride.

Antimony Sulfide.—Antimony sulfide reacts readily with thionyl chloride at a temperature of 150–200°, giving the trichloride, sulfur dioxide and sulfur monochloride according to the equation

$$Sb_2S_3 + 6SOCl_2 = 2SbCl_3 + 3SO_2 + 3S_2Cl_2.$$

This reaction was studied by Prinz in 1884 and was found by him to result in the formation of a mixture of trichloride, sulfur monochloride and sulfur. Prinz must have carried out this experiment below 150° or without excess of thionyl chloride, inasmuch as the latter reacts with sulfur at 150° to give sulfur dioxide and sulfur monochloride.

Ferrous Sulfide.—The sample of ferrous sulfide employed was the crude article such as is used for the preparation of hydrogen sulfide. An analysis of the powdered sample for iron and sulfur showed a slight excess of the latter. This would not interfere with the reaction, however, inasmuch as sulfur itself reacts with thionyl chloride, giving sulfur dioxide and sulfur monochloride.

The iron sulfide and thionyl chloride were heated together at 150°. Reaction took place readily with the formation of bright green, hexagonal plates which, by transmitted light, were ruby red. Analysis proved these to be ferric chloride, $FeCl_3$. Reaction took place according to the equation

$$6FeS + 16SOCl_2 = 6FeCl_3 + 8SO_2 + 7S_2Cl_2.$$

A small amount of light colored insoluble matter, probably silica, was obtained when the sample was dissolved in water for analysis. This was collected on a Gooch crucible, dried and weighed and the weight deducted from the weight of the sample.

This reaction differs from the others studied, inasmuch as the ferrous sulfide was oxidized to the ferric state. No indication of ferrous chloride was found.

Copper Sulfide.—Upon heating copper sulfide with the reagent at 150°, reaction took place within a few hours with the formation of a dark brown solid substance. This was analyzed and found to be anhydrous copper chloride. Reaction therefore took place according to the equation

$$CuS + 2SOCl_2 = CuCl_2 + SO_2 + S_2Cl_2.$$

Stannic Sulfide.—The material used for this experiment was the ordinary mosaic gold, made in the dry way. After heating for six hours at 150° no apparent change had taken place. The tube was then heated for a number of days at a temperature of from 150 to 200°, after which it was noticed that a considerable portion of the sulfide had dissolved. When the tube was opened sulfur dioxide was evolved. Furthermore, the odor of sulfur monochloride was very prominent. Considering this, together with the fact that the compound used was a compound of tetravalent tin, the authors are of the opinion that reaction proceeds slowly with the formation of tin tetrachloride according to the equation

$$SnS_2 + 2SOCl_2 = SnCl_4 + 2SO_2 + 2S_2Cl_2.$$

The liquid in the tube was probably a mixture of tin tetrachloride, sulfur monochloride and the excess of thionyl chloride. An attempt was made to fractionate this, but it was a failure, due to the small amount of material at hand.

Mercuric Sulfide.—Mercuric sulfide was found to react readily with thionyl chloride at 150° with the formation of long needle crystals of mercuric chloride. Reaction proceeds according to the equation

$$HgS + 2SOCl_2 = CuCl_2 + SO_2 + S_2Cl_2.$$

Summary.

Thionyl chloride reacts with sulfides according to the following equation, in which M represents a divalent metal:

$$MS + 2SOCl_2 = MCl_2 + SO_2 + S_2Cl_2$$

With sulfides as with oxides and metals, thionyl chloride seems to show a selective action, reacting much more readily with some than with others.

NEW BRUNSWICK, N. J.

THE DETERMINATION OF GASES DISSOLVED IN WATERS AND EFFLUENTS.

BY A. A. SWANSON AND G. A. HULETT.

Received September 9, 1915.

The importance of a knowledge of gases dissolved in natural waters and effluents has lead to the development of many methods for their estimation. The results obtained by these different methods are, however, not always concordant or satisfactory. Our attention was directed to this subject by some special difficulties encountered in the determination of the oxygen in mine waters and we were led to examine this whole subject of the determination of gases dissolved in waters and solutions. The method we have devised for our special purpose makes use of a principle which does not appear to have been used in this kind of work heretofore, but it has solved our problem and seems to be generally applicable.

The methods which have been used for the determination of gases dissolved in waters fall into two groups: First, those methods which are based on chemical reaction involving the gas in solution in a reaction which may be followed "titrimetrically." In the second group the gases are first removed from the water and then determined gasometrically. The chemical methods work well in the determination of oxygen and carbon dioxide, while no success has been attained in determining other dissolved gases such as nitrogen, owing to a lack of suitable chemical reactions.

At the present time most attention is given to the determination of oxygen and carbon dioxide in natural waters and effluents. The methods in favor for the determination of dissolved oxygen are the Winkler[1] and Levy[2] methods. A modification of the Winkler method by Hale and Melia[3] has made it possible, however, to determine the dissolved

---

[1] *Ber.*, **21**, 2843 (1888); **22**, 1764 (1889).

[2] *Ann. l'obseratorie Municipal de Montosouris, Paris*, 1884.

[3] *J. Ind. Eng. Chem.*, **5**, 976 (1913).