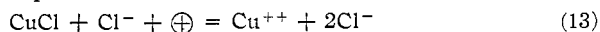


the calorimetric data were obtained it seems probable that our value is nearer the truth.

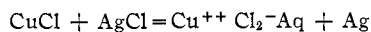
By combination of Equations 8 and 11 we obtain for the reaction



$\Delta F = 12984$  cal., corresponding to a value of  $-0.5627 v$ . for the molal electrode potential for this reaction.

### Summary

1. The equilibrium of the reaction



has been measured at  $25^\circ$  and at  $40^\circ$  in the presence of varying quantities of hydrochloric acid.

2. The equilibrium constants have been calculated, making use of the principle of "ionic strength."

3. The increases in free energy and heat content of the system have been calculated and compared with the values obtained by previous investigators.

4. On the whole, the data support the methods employed by Lewis and Randall in calculating the activities of mixed electrolytes.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY]

## ABSORPTION OF CARBON DISULFIDE VAPOR BY AQUEOUS SOLUTIONS OF SODIUM TRINITRIDE<sup>1</sup>

BY A. J. CURRIER WITH A. W. BROWNE

Received September 1, 1922

Macagno<sup>2</sup> has proposed a method for the determination of carbon disulfide which consists in the precipitation of a copper xanthate from the solution obtained by absorption of the disulfide in alcoholic potassium hydroxide. Subsequent measurement of the unused excess of the standard solution of copper sulfate by titration with potassium ferrocyanide yields data from which the amount of carbon disulfide may be computed.

Schmitz-Dumont<sup>3</sup> considered this method unreliable because under certain conditions the initial reaction between the disulfide and the alkali was not found to be quantitative. He suggested treatment of the alcoholic solution with lead acetate dissolved in 90% alcohol, resulting in quantitative precipitation of the sulfur as lead sulfide, which is finally oxidized by

<sup>1</sup> This article is based upon a part of the thesis submitted by A. J. Currier to the Faculty of the Graduate School of Cornell University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

<sup>2</sup> Macagno, *Chem. News*, **43**, 138 (1881).

<sup>3</sup> Schmitz-Dumont, *Chem.-Ztg.*, **21**, 487, 510 (1897), through *Chem. Zentr.*, **1897**, **II**, 265.

nitric acid and bromine, and weighed as barium sulfate. A different method for use in the determination of carbon disulfide in certain liquids and gases involves the use of an alcoholic silver solution with aniline.

Goldberg<sup>4</sup> has devised a method based upon the reaction between carbon disulfide and ammonia, which yields ammonium thiocarbamate. After treatment with a standard ammoniacal zinc solution of which the excess is determined by titration with a solution of sodium sulfide, the amount of carbon disulfide may be calculated.

It is stated by Russell<sup>5</sup> that "the only useful absorbent for the vapor of this substance is alcoholic potash, and the application of this reagent in gas analysis, for reasons already stated, is very limited." The explosion method used by Pedler<sup>6</sup> has been modified by Russell, who suggested the use of lead dioxide instead of manganese dioxide for absorption of the sulfur dioxide formed.

Harding and Doran<sup>7</sup> have applied the method of Macagno to the determination of carbon disulfide in illuminating gas.

Stock and Seelig<sup>8</sup> have described a method for the analysis of gas mixtures containing carbon disulfide, carbon oxysulfide, carbon monoxide, and carbon dioxide, based upon the selective absorption of the various constituents by sodium or potassium hydroxide of suitable concentration. An alternative method used by these investigators depends upon measurement of the increase in vapor pressure resulting from the addition of a few drops of liquid carbon disulfide.

Sommer<sup>9</sup> has shown that liquid carbon disulfide reacts at 40–50° with aqueous solutions of sodium trinitride, forming sodium azido-dithiocarbonate,  $\text{NaSCSN}_3$ .

It has been found in this Laboratory by Browne and Hoel<sup>10</sup> that carbon disulfide vapor is irreversibly absorbed at room temperature (20–25°) by aqueous solutions of potassium or sodium trinitride, with quantitative formation of the azido salt. It was suggested by these investigators that solutions of the trinitrides might be of use in the field of gas analysis as absorbents for carbon disulfide. The research described in the present article was undertaken in order to test the applicability of this suggestion. In its broader aspect the problem involves a study of the determination of carbon disulfide when present (1) in certain gas mixtures (*a*) in relatively large amounts, and (*b*) in small amounts, or in mere traces; (2) in liquid mixtures. In the first part of the work, with which the current article is solely con-

<sup>4</sup> Goldberg, *Z. angew. Chem.*, **12**, 75 (1899).

<sup>5</sup> Russell, *J. Chem. Soc.*, **77**, 352 (1900).

<sup>6</sup> Pedler, *ibid.*, **57**, 625 (1890).

<sup>7</sup> Harding and Doran, *THIS JOURNAL*, **29**, 1480 (1907).

<sup>8</sup> Stock and Seelig, *Ber.*, **52**, 672 (1919).

<sup>9</sup> Sommer, *ibid.*, **48**, 1833 (1915).

<sup>10</sup> Browne and Hoel, *THIS JOURNAL*, **44**, 2106 (1922).

cerned, the procedure consists in measuring, in a gas buret, the volume of the gas mixture before and after absorption of the carbon disulfide. In the second part, which will be made the subject of further investigation, the procedure involves quantitative absorption of the small amounts of vapor, or of the liquid carbon disulfide, with subsequent determination of the thiocyanate finally formed by decomposition of the azido salt.

**Materials and Apparatus.**—The carbon disulfide was purified<sup>11</sup> by prolonged treatment with anhydrous copper sulfate, solid sodium hydroxide, mercuric sulfate, and metallic mercury. The liquid was finally distilled, over the mercury and mercuric salt, and the middle fraction was preserved for use over anhydrous copper sulfate. The commercial sodium trinitride was recrystallized from water, after the concentrated solution had in certain cases been treated with a small quantity of dil. hydronitric acid, to replace that lost by hydrolysis.<sup>12</sup>

In part of the work an accurately calibrated, water-jacketed gas buret provided with a 2-way stopcock and filled with mercury, was employed. This was fused onto one side to a Hempel gas pipet filled with the solution of sodium trinitride used as absorbent, and containing pieces of glass tubing to increase the surface of contact. On the other side was a gas pipet filled with liquid carbon disulfide. In the remainder of the work the standard Hempel buret and pipet were used.

**Procedure and Results.**—The total absorbing power of an approximately 1% aqueous solution of sodium trinitride was determined by successively passing measured volumes of air containing from 27 to 50%, by volume, of carbon disulfide vapor, into the pipet containing the absorbent. After 27 samples of the mixture had been introduced, corresponding to a total volume of 657.7 cc. (corrected) of carbon disulfide vapor, it was noted that the rate of absorption appreciably decreased. The amount of sodium trinitride, 1.900 g., contained in the 190 cc. of solution used in the pipet, was theoretically capable of absorbing 2.2215 g. of carbon disulfide, as calculated from the equation,  $\text{NaN}_3 + \text{CS}_2 = \text{NaSCSN}_3$ . This corresponds to 654.6 cc. of the vapor, computed from the theoretical density under standard conditions. After the absorption of the full equivalent of carbon disulfide had been effected, it was found that small additional amounts of the vapor were gradually absorbed. This is attributed to a slow, continuous, physical solution of the vapor in the reagent, accompanied by diffusion through the liquid and ultimate escape from its outer surface. This is attested by the distinct odor of carbon disulfide detected at the end of the pipet, after chemical saturation had taken place.

A second series of experiments was performed, under conditions similar to those just described, except that mercury was employed as confining liquid in the pipet, to prevent diffusion of carbon disulfide at the end of the absorption, and that only 49.5 cc. of the reagent, containing 0.500 g.

<sup>11</sup> Nillon, *Jahresber.*, 1868, 928. Sidot, *Compt. rend.*, 69, 1303 (1869). Cloëz, *ibid.*, 69, 1356 (1869). Palmieri, *Z. anal. Chem.*, 21, 254 (1882).

<sup>12</sup> Dennis and Benedict, *THIS JOURNAL*, 20, 225 (1898).

of sodium trinitride, was used. After 7 successive samples of the mixture of air and carbon disulfide had been introduced, a total absorption of 172.9 cc. (corrected) of the vapor was effected, which closely corresponds with the theoretical value, 172.3 cc. An additional absorption of 36 cc. of the vapor took place at a much slower rate, during 5 additional treatments, as a result of the physical solubility of the vapor in the aqueous reagent.<sup>13</sup> Thereafter, no further absorption took place.

The foregoing determinations of the total absorbing power of 1% sodium trinitride solutions were conducted with the aid of the special apparatus described above, which was constructed entirely of glass. In the experiments still to be described the procedure was such as would ordinarily be followed for careful analytical work. Mercury was used as a rule, however, as confining liquid both in the buret and in pipets. It was apparent from the earlier work that the length of time required for complete absorption of the vapor by the 1% trinitride solutions was greater than might be desired under actual working conditions. From a study of the rate of absorption of the disulfide vapor by 3, 5, and 10%, and by saturated aqueous solutions of sodium trinitride, the conclusion was reached that the concentration should be at least as great as 5%. Solutions of this concentration absorb the vapor more rapidly than does the 3%, though not quite as rapidly as do more concentrated solutions, the use of which may be somewhat less desirable, however, for other reasons.

It was found that variation in the mode of bringing reagent and vapor into contact was an important factor in determining the speed of absorption. Experiments showed that successive 1-minute contacts, with thorough shaking, gave better results than prolonged contact without occasional withdrawal of the samples from the pipet. This may indicate that under certain conditions, especially when mixtures containing large percentages of the disulfide are used, the vapor tends to condense upon the walls of the buret, necessitating repeated transfer of the sample from buret to pipet and the reverse.

In addition to the numerous experiments with mixtures of carbon disulfide vapor and air, series of tests were conducted with mixtures containing the vapor with varying proportions of oxygen, nitrogen, hydrogen, methane, and carbon monoxide, respectively. Typical data are summarized in the accompanying table, the last column of which records the number of successive 1-minute periods of contact required for complete absorption.

These data indicate that sodium trinitride in aqueous solution may prove useful as an absorbent for carbon disulfide vapor in mixtures of gases containing a relatively large amount of this constituent. The results obtained in preliminary experiments with certain gases absorbable

<sup>13</sup> Rex, *Z. physik. Chem.*, **55**, 365 (1906).

in potassium hydroxide lead to the belief that the trinitride solution might in some cases be of unique utility in effecting a sharp separation between the disulfide and certain of the more soluble gases.

TABLE I  
ANALYSIS OF GASEOUS MIXTURES CONTAINING CARBON DISULFIDE

NaN <sub>3</sub> sol'n.	Gas		CS <sub>2</sub>		No. of con- tacts	NaN <sub>3</sub> sol'n.	Gas		CS <sub>2</sub>		No. of con- tacts
	Formula	Cc.	taken	found			Formula	Cc.	taken	found	
Sat'd	O <sub>2</sub>	35.0	15.0	15.2	6	Sat'd	H <sub>2</sub>	35.0	14.6	14.4	6
...	..	35.0	17.0	17.0	7	...	..	38.0	2.6	2.6	4
...	..	38.0	3.4	3.4	4	...	..	38.0	2.8	2.6	4
...	..	38.0	3.0	3.0	4	5%	CH <sub>4</sub>	49.8	18.8	18.4	8
5%	N <sub>2</sub>	49.4	15.8	15.8	7	Sat'd	..	35.0	15.0	15.0	5
...	..	50.0	16.0	15.6	8	...	..	35.0	15.0	15.4	4
...	..	40.0	31.6	31.6	10	...	..	38.0	2.8	2.8	4
...	..	40.0	30.6	30.2	9	...	..	38.0	4.4	4.4	5
...	..	80.0	2.8	2.4	6	5%	CO	49.4	19.4	19.4	8
...	..	80.0	2.8	2.4	9	...	..	49.8	24.8	24.8	8
Sat'd	..	20.0	10.6	10.6	5	Sat'd	..	35.0	15.0	14.8	7
...	..	20.0	9.8	9.8	6	...	..	35.0	25.0	24.8	6
5%	H <sub>2</sub>	49.6	27.4	27.2	8	...	..	38.0	2.4	2.2	5
...	..	50.0	21.6	21.2	8	...	..	38.0	2.0	1.8	4
Sat'd	..	35.0	15.2	15.0	6	...	..	..	..	..	.

In view of the explosive character of the azido-dithiocarbonates in solid form, certain tests were conducted upon solutions of the sodium salt obtained after absorption of carbon disulfide by sodium trinitride solutions. A 3cc. sample of a saturated solution of the trinitride that had been used repeatedly as an absorbent for the disulfide was allowed to evaporate to dryness on an iron plate. The residue showed no tendency to explode when rubbed or struck with an iron rod. When brought into contact with a red hot iron rod, it decomposed with a crackling noise. In a second experiment 10 cc. of a 1 % solution of sodium trinitride that had been completely saturated with carbon disulfide and kept in a stoppered bottle for about 4 months, was subjected to similar treatment without giving any indication of explosive character. This loss of explosiveness is explained by the fact that solutions of sodium and potassium azido-dithiocarbonate decompose very slowly on standing, with evolution of nitrogen, liberation of sulfur and formation of thiocyanates.

Two 100cc. samples of approximately 5% sodium trinitride solution were treated with carbon disulfide in such amount as to saturate the first completely, and half saturate the second. The resulting solutions were placed in Lunge nitrometers. During the first 14 days neither solution evolved appreciable quantities of gas. After an additional 16 days the saturated solution yielded 4 cc. and the other 5.8 cc. of nitrogen. From these results it is evident that the rate of evolution of gas is not sufficiently

rapid to endanger the accuracy of analytical work with sodium trinitride as absorbent.

### Summary

1. The total absorbing power of a 1% solution of sodium trinitride for carbon disulfide vapor has been determined. This dilute solution absorbs irreversibly about 3.5 times its volume of the vapor, with quantitative formation of sodium azido-dithiocarbonate,  $\text{NaSCSN}_3$ .

2. Various mixtures of carbon disulfide vapor with air, or with oxygen, nitrogen, hydrogen, methane, and carbon monoxide have been analyzed, using 5% or saturated aqueous solutions of sodium trinitride as absorbent.

3. The solution of azido salt resulting from the interaction of absorbent and vapor has been found to possess no dangerously explosive qualities, but to decompose very slowly after long standing, with formation of nitrogen, sulfur and sodium thiocyanate.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

## GERMANIUM. IV. GERMANIUM TETRA-IODIDE<sup>1</sup>

BY L. M. DENNIS AND F. E. HANCE

Received September 7, 1922

Winkler<sup>2</sup> prepared germanium tetra-iodide by heating pulverulent germanium in vapor of iodine that was carried over the metal by a slow current of carbon dioxide. He found it necessary to sublime the product repeatedly in carbon dioxide to remove free iodine. He describes the substance as highly hygroscopic, of orange color, yellow when powdered, possessing a melting point of 144°, and appearing to boil between 350° and 400°. He gives the results of an analysis of the compound, and adds that L. F. Nilson found that germanium tetra-iodide did not dissociate up to 440°, but showed considerable dissociation at 658°.

The present investigation describes the preparation and further study of this substance.

**Preparation.**—Powdered, crystalline germanium was placed in alundum boats which were then inserted in a tube of Jena glass lying in an electric combustion furnace. A thermometer was laid in the combustion tube beside the boats. The portion of the tube projecting beyond the furnace was drawn down to small diameter at 7 points 10 cm. apart. Each constriction was packed with glass wool. Into the other end of the combustion tube was inserted the neck of a 500cc. glass retort containing purified iodine. The tubulus of the retort was joined to an apparatus that supplied pure, dry carbon dioxide. An asbestos box was built around the retort, and this was heated from the outside to a temperature sufficiently high to keep the retort filled with vapor of iodine.

<sup>1</sup> The investigation upon which this article is based was supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

<sup>2</sup> Winkler, *J. prakt. Chem.*, **142** [N. S. 34], 177 (1886).