[Contribution from the Chemical Laboratory of the University of Illinois]

HEAT OF FORMATION OF NITROGEN TRICHLORIDE[1]

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Deville and Hautefeuille[2] determined the heat of formation of nitrogen trichloride by two methods; by the action of chlorine on ammonium chloride and by the action of hypochlorous acid on ammonium chloride. The results of their experiments gave the heat of formation as —37,777 calories by the first method and —38,477 by the second. The second value is given in another paper by Troost and is quoted by both Ostwald and Abegg with the statement that no method is described and no experimental data are given. Thomsen[3] pointed out very serious errors in the calculation of the results of the first method and his recalculation gives the heat of formation as —52,008. The value that he calculates from the second series of experiments is —39,522. The supposed agreement of the results of the two series is, therefore, illusory. Dr. Bichowsky,[4] using the values of the "International Critical Tables," has recently calculated the value —58,400 from the first series and —48,600 from the second, and had selected a weighted average of —55,000, before seeing this paper—as he remarks, "a very good guess."

One of us has found[5] that when hydrogen chloride is passed into a solution of nitrogen trichloride in carbon tetrachloride, solid ammonium chloride and chlorine are formed quantitatively in accordance with the equation: $NCl_3 + 4HCl = NH_4Cl + 3Cl_2$. Considerable heat is evolved in this reaction and we have made this the basis for a new determination of the heat of formation of the trichloride. The new determinations required were: (1) the heat of the reaction given above; (2) the heat of solution of chlorine in carbon tetrachloride; (3) the heat of solution of hydrochloric acid in carbon tetrachloride; (4) the heat of solution of nitrogen trichloride in carbon tetrachloride.

The determination of the last of these quantities involves such difficulties that it has not been attempted. There seems to be good reason for believing that the heat of solution for two compounds so closely alike in composition as nitrogen trichloride and carbon tetrachloride is negligible in comparison with the other factors.

Materials.—The carbon tetrachloride was purified by allowing it to stand for

[1] Abstract of a thesis presented by William Feagan Tuley to the Graduate Faculty of the University of Illinois in partial fulfilment of the requirement for the degree of Master of Science.

[2] Deville and Hautefeuille, *Compt. rend.*, **69**, 152 (1869).

[3] Thomsen, *Ber.*, **4**, 922 (1871).

[4] Bichowsky, private communication through the kindness of Professor Washburn.

[5] Noyes, This Journal, **42**, 2167 (1920).

several days with powdered potassium hydroxide to remove carbon disulfide. It was then washed with water, dried with concd. sulfuric acid and distilled.

The solution of nitrogen trichloride was prepared by passing chlorine into carbon tetrachloride in contact with an equal volume of a 10% aqueous solution of ammonium sulfate, the two being mixed with a mechanical stirrer.[6] The bright yellow solution was washed with two more portions of the ammonium sulfate solution for half an hour each, then with distilled water and was dried with concd. sulfuric acid, which has no effect on the trichloride.[7]

The nitrogen in the solution was determined by converting it into ammonium chloride by means of concd. hydrochloric acid.[8] The chlorine was determined in a separate portion by reducing it with sodium sulfite, oxidizing the excess exactly with potassium permanganate and titrating the chloride by Volhard's method. The samples were weighed in a 25cc., glass-stoppered flask, and great care was taken to avoid loss. Determinations made with different samples gave values approximating closely to the atomic ratios of one to three for nitrogen and chlorine. Preparations in which the mixing with the fresh solution of ammonium sulfate was continued for a shorter time contained an excess of chlorine. With the exception of Expts. 2 and 5 of the first series, the calorimetric determinations were made with freshly prepared solutions.

The weights used in the quantitative determinations were calibrated and 50cc. burets checked by the Bureau of Standards were used in the titrations.

Calorimetric Determinations.—All measurements were made in a 1-liter Dewar flask placed in a can and packed in ice. The flask was protected by placing cork rings above and below the bulb and wrapping with sheet copper. The neck of the flask was wrapped with sheet rubber and the stopper held in place by a section of Gooch crucible tubing. Changes in the temperature of the contents of the flask were measured by a Beckmann thermometer. A tube was passed through the stopper to the bottom of the flask for introducing the chlorine or hydrogen chloride and a small outlet tube closed by a rubber tube and screw clamp was provided. The contents of the flask were mixed by rocking the whole apparatus on an edge of the tin can container. This method was found to be sufficient to mix the contents thoroughly. The chlorine or hydrogen chloride was cooled before entering the calorimeter by passage through a loop of glass tubing extending around the outside of the calorimeter in the ice-bath. The heat capacity of the Dewar flask was determined by heating about 600 g. of carbon tetrachloride with an electric coil in a bulb containing toluene, immersed in the liquid.

To avoid gain or loss of heat to the ice-bath during the determination, the carbon tetrachloride or its solution was cooled to —8° before putting it in the flask. Six hundred g. of the material at this temperature when placed in the flask had a temperature of —1.5° to —2°. As the rise in temperature was only 2° or 3° and the loss or gain of heat through the walls

[6] Noyes, This Journal, **42**, 2176 (1920). Coleman and Noyes, *ibid.*, **43**, 2214 (1921).

[7] Seliwanow, *Ber.*, **27**, 1018 (1894).

[8] Noyes, This Journal, **42**, 2178 (1920).

of a Dewar flask takes place very slowly, we may assume that the correction for radiation is negligible.

The heat capacity of the bulb and heating coil was determined by heating the bulb to 100° and transferring it immediately to about 700 g. of water contained in the Dewar flask. Three determinations gave, respectively, a heat capacity of 14.2, 15.4 and 14.9; mean, 14.8 calories per degree. The bulb contained about 16 g. of toluene. Correcting for the lessened heat capacity of toluene at 0°, the heat capacity of the bulb was 14.2 calories.

The resistance of the coil was 2.603 ohms and the current used, 1.55 amperes. This gives, by the formula ($rI^2t/4.18$), 269.3 calories in three, or 359.06 in four minutes. Six hundred and thirty-six g. of carbon tetrachloride gave a rise in temperature of 1.83° in three minutes; 577 g. a rise of 2.675° in four minutes and 645 g. a rise of 2.405° in four minutes. Correcting to 600 g., these values give 140.5, 138.5 and 140.8, mean, 139.9, for the heat capacity in calories per degree for the system consisting of the toluene heating-bulb, the Beckmann thermometer, Dewar flask and 600 g. of carbon tetrachloride. Subtracting from the average the heat capacity of the toluene coil (14.2) and of the 600 g. of carbon tetrachloride (0.1854[9] $\times$ 600 = 111.2) the heat capacity of the Dewar flask and thermometer is found to be 14.5 calories per degree. In the calculations that follow, the heat capacity of the system consisting of the Dewar flask, the Beckmann thermometer and 600 g. of carbon tetrachloride was taken as 125.7 calories per degree.

The Heat of Solution of Chlorine in Carbon Tetrachloride was found to be in five determinations, 6986, 4646, 4534, 4532, 4550; mean, rejecting the first, which is evidently in error for some unknown reason, 4565 calories for one mole of chlorine.

The Heat of Solution of Hydrochloric Acid in Carbon Tetrachloride was found to be 3740, 3617 and 3684; mean, 3680 calories per mole. It is worthy of note that this value corresponds closely with the heat of vaporization of hydrochloric acid, found by Estreicher and Schnerr[10] to be 3600 calories at —84.3°, and by Elliott and McIntosh[11] as 3560 at —83°.

The Heat of the Reaction between Nitrogen Trichloride and Hydrochloric Acid. First Series.—Six hundred g. of a dilute solution of nitrogen trichloride, prepared as has been described, was cooled to about —8° and placed in the Dewar flask surrounded with ice water. Hydrogen chloride was passed in, the contents of the flask were gently agitated and the reading of the thermometer was noted. While the reaction was in progress the temperature rose rather rapidly. After 15 to 20 minutes the rise became slow. This was taken as indicating the end of the reaction.

[9] Williams and Daniels, THIS JOURNAL, **46,** 912 (1924).

[10] Estreicher and Schnerr, *Chem. Zentr.*, **1910,** II, 1737.

[11] Elliott and McIntosh, *J. Phys. Chem.*, **15,** 54 (1911).

The agitation of the solution was then continued until the thermometer became stationary and the final temperature was read.

The number of calories liberated was calculated by multiplying the rise in temperature by 125.7, the heat capacity of the system including 600 g. of carbon tetrachloride, the Beckmann thermometer and the Dewar flask (see above). The liberated chlorine was determined in duplicate in each experiment by mixing a weighed sample of the carbon tetrachloride solution with a solution of potassium iodide, then with an excess of a standard solution of sodium thiosulfate and titrating back with a standard iodine solution. The excess of hydrochloric acid was then determined in the same solution by titration with standard sodium hydroxide, a blank being run to determine the alkalinity due to hydrolysis.

To reduce the heat of the reaction to the basis of the heat of formation of nitrogen trichloride in solution in carbon tetrachloride from chlorine gas and nitrogen gas we must first subtract from the calories found the heat of solution of the excess of hydrochloric acid and the heat of solution of the chlorine found in 600 g. of the solution. Since the reaction gives 3 molecules of chlorine for each molecule of nitrogen trichloride, if the corrected calories are multiplied by three and divided by the number of moles of chlorine in 600 g. carbon tetrachloride, we shall have the heat of the reaction between nitrogen trichloride and hydrochloric acid.

The results of seven experiments were as follows.

Table I

Heat of Reaction between Nitrogen Trichloride and Hydrochloric Acid

Expt.	1	2	3	4	5	6	7
Rise in temp., °C.	3.085°	2.770°	2.945°	1.699°	2.833°	2.050°	3.046°
Calories	387.8	348.2	370.2	213.6	356.1	257.7	382.9
Moles excess of HCl in 600 g. of CCl_4	0.0012	0.0373	0.0180	0.00334	0.00699	0.00566	0.0125
Moles of Cl_2 in 600 g. of CCl_4	0.02095	0.01816	0.01626	0.01085	0.02352	0.01275	0.01795
Corr. for HCl	4.5	137.4	66.4	12.3	25.7	20.8	46.0
Corr. for Cl_2	95.7	82.9	74.2	49.6	107.4	58.2	81.9
Corr. calories for 600 g. of CCl_4	287.6	127.9	229.6	151.7	223.0	178.7	255.0
Heat of reaction for 3 moles of Cl_2	41,380	21,130	42,360	41,950	28,440	42,050	42,620

Mean, 42,030 calories

Expt. 2 was made with a solution that had stood for several days in the dark. The result indicates that considerable decomposition takes place, even under those conditions. To verify this, Expt. 5 was made with the same solution used in Expt. 4, after it had stood for three days. These two results were omitted in calculating the mean.

Second Series.—A second series of determinations was made with several changes in the method to insure more reliable results. The important changes were (1) in the calibration of the calorimeter and (2) in the determination of both chlorine and ammonium chloride formed by the decomposition of the nitrogen trichloride with hydrogen chloride.

Calibration of the Calorimeter.—The apparatus was similar to that used in the first series of determinations. It was calibrated by passing a current through a heating coil in direct contact with the carbon tetrachloride in the Dewar flask and measuring the amperage and the potential by means of a standard potentiometer arrangement. The resistance of the heating coil was determined independently as a check on these measurements. The heating coil was constructed by winding a section of Therlo resistance wire about a strip of mica. From the specific heats of mica, the resistance wire and the copper leads, the heat capacity of the unit was calculated to be 0.228 cal. per degree. The heat equivalent of the current was calculated and the heat capacity of the system of the Beckmann thermometer, and calorimeter vessel containing 600 g. of carbon tetrachloride, correcting for the heat capacity of the heating unit. As a mean of three determinations differing by only 0.61 calorie, the value of 142.40 calories was obtained as the heat capacity of the system.

The Heat of Solution of Chlorine in Carbon Tetrachloride.—The heat of solution of chlorine was redetermined, using the calibration factor given above and determining the free chlorine by an iodimetric method. The mean of three determinations differing by only 11 calories was 4539 calories. This value, although 26 calories less than the value previously determined, was considered to be more accurate and was used in the calculations of this series.

Determination of Chlorine and Ammonium Chloride.—The chlorine was determined as in the first series of experiments. The ammonium chloride formed by the reaction partly precipitates on the inner walls of the calorimeter vessel and partly remains suspended as loose particles in the carbon tetrachloride. The suspended particles were separated by filtration and the remainder was removed from the calorimeter by washing with a small amount of water after removal of the chlorine by drawing dry air through the vessel. One drop of concd. hydrochloric acid was added

TABLE II

HEAT OF REACTION BETWEEN NITROGEN TRICHLORIDE AND HYDROGEN CHLORIDE

Expt.	1	2	3	4	5
Rise in temp., °C.	3.429	3.005	2.935	3.531	3.341
Calories	488.3	427.9	418.0	502.81	475.77
Moles excess of HCl in 600 g. of CCl_4	0.01148	0.02841	0.01926	0.015025	0.025945
Moles of Cl_2 in 600 g. of CCl_4	0.02467	0.01743	0.01872	0.024576	0.020586
Moles of NCl_3	0.008223	0.005809	0.006241	0.008192	0.006862
Corr. for HCl	42.3	104.5	70.6	55.29	95.48
Corr. for Cl_2	112.0	79.1	84.97	111.55	93.44
Corr. calories for 600 g. of CCl_4	334.0	244.3	262.4	335.97	286.85
Heat of reaction for 1 mole of NCl_3	40,620	42,055	42,045	41,010	41,804
	Mean,	41,507			

to the washings in which the portion of ammonium chloride removed by filtration had also been dissolved. This solution was evaporated to dryness and the ammonium chloride weighed. This method was shown to be accurate within 0.05%.

The approximate mean of this determination and the previous value of 42,030 is 41,800 calories, and this is taken as the best value for the heat of the reaction of one mole of nitrogen trichloride and four moles of hydrogen chloride.

Heat of Formation of Nitrogen Trichloride.—This may be calculated as follows.

$$\begin{aligned}
4HCl &= 2H_2 + 2Cl_2 - 4 \times 2203^{12} = -88{,}012 \text{ calories} \\
\tfrac{1}{2}N_2 + 2H_2(\text{gas}) + \tfrac{1}{2}Cl_2(\text{gas}) &= NH_4Cl\ (\text{solid})^{12} + 75{,}070 \text{ calories} \\
NH_4Cl + 3Cl_2\ (\text{gas}) &= NCl_3\ (\text{solution in } CCl_4) + 4HCl\ (\text{gas}) - 41{,}800 \text{ calories} \\
\hline
\tfrac{1}{2}N_2(\text{gas}) + \tfrac{3}{2}Cl_2(\text{gas}) &= NCl_3\ (\text{solution in } CCl_4) - 54{,}700 \text{ calories}
\end{aligned}$$

The heat of formation is negative and quite large, being of the same order of magnitude as that of acetylene. This is, of course, in accord with the explosive character of the compound. Just as a solution of acetylene in acetone is harmless, a solution of nitrogen trichloride in carbon tetrachloride does not explode.

Summary

The following determinations have been made.

1. The heat of solution of one mole of gaseous chlorine in carbon tetrachloride is 4539 calories.

2. The heat of solution of one mole of gaseous hydrogen chloride in carbon tetrachloride is 3680 calories.

3. The heat of the interaction of one mole of nitrogen trichloride in solution with three moles of gaseous hydrogen chloride giving solid ammonium chloride and three moles of gaseous chlorine is 41,800 calories.

4. A combination of the last value with the known values for the heats of formation of hydrochloric acid and ammonium chloride gives the heat of formation of nitrogen trichloride in solution in carbon tetrachloride from gaseous nitrogen and gaseous chlorine as —54,700 calories.

URBANA, ILLINOIS

NOTE

The Use of Long Mercury Manometers.—In view of the frequent use made of long mercury manometers in research work, it is believed that the following note will prove of help to those involved in making pressure measurements on gaseous systems.

[12] From International Critical Tables by private communication.