so-called Weiss molecular field and its dependence on crystalline field and exchange interaction. In general the theory is supported although discrepancies are noted. Preparation and properties are given for anhydrous neodymium perchlorate.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CHICAGO]

The Behavior of Dichlorodifluoromethane and of Chlorotrifluoromethane in the Electric Discharge

BY NANNIE V. THORNTON[1] AND ANTON B. BURG WITH H. I. SCHLESINGER

Dichlorodifluoromethane under ordinary conditions is a very stable, relatively inert gas. Midgley and Henne[2] report that it reacts slowly with metals and with water at 175°; in each case they describe some attack upon the chlorine–carbon bond, but the fluorine remained attached to carbon. Our experiments with pure metals at higher temperatures confirm this result. It was difficult to obtain any extensive reaction under controlled conditions, and the side reactions of intermediate products with the glass walls of the containing tubes made it difficult to determine the course of the main reaction.

In a high-tension electric discharge, however, this rather inert substance is easily broken up to form products of higher and lower volatility. Chief among these are chlorine, chlorotrifluoromethane and carbon tetrafluoride. Considerable quantities of dichlorotetrafluoroethane and less volatile substances, including slightly volatile solids not soluble in any ordinary solvent, also are obtained. And there is good evidence that tetrafluoroethylene is produced in small quantities. These result are satisfactorily explained by supposing that the molecular fragments CF_2, F and Cl are present in the discharge; it is supposed that they combine in random fashion outside the region of activation. After this first combination, secondary reactions may occur: any free fluorine would displace chlorine, and any double bonds would soon be saturated by the chlorine. It is probable that most of the dichlorotetrafluoroethane is formed in this way. Fragments containing less than two fluorine atoms may account for some of the heavier products.

Chlorotrifluoromethane, a substance which seems to be about as inert as dichlorodifluoromethane, may be decomposed in like manner, to produce chlorine, very good yields of carbon tetrafluoride, and small quantities of dichlorodifluoromethane. In this case, no light substances less volatile

than dichlorodifluoromethane were found, but there were some small quantities of the unidentified solids mentioned above.

Experimental Part

Source of Material.—The dichlorodifluoromethane for this study was obtained through the courtesy of E. I. du Pont de Nemours and Company. Measurements of the vapor tension and vapor density of successive fractions showed the sample to be uniform. Four measurements of the vapor tension at widely different temperatures agreed within 0.5° with the equation $\log_{10} p = 7.385 - (1105/T)$, according to which the normal boiling point is $-27.8°$, the molal heat of vaporization 5056 cal., and the Trouton constant 20.6 cal./deg.

Reactions with Metals.—None of the metals tried reacted appreciably at the lower temperatures. The reaction with magnesium, which starts only at relatively high temperature, proceeds with the evolution of sufficient heat to melt Pyrex glass; considerable reduction to carbon occurs. Aluminum reacts in the same way, but more slowly, while chromium, iron, zinc and copper appear to form protecting films. Tin reacts at a temperature slightly above its melting point. Among the reaction products are silicon tetrafluoride, carbon dioxide and carbon monoxide, all of which result from the action on the glass container. This reaction with the glass seems to be due to the formation of intermediate radicals or other unstable substances, for neither dichlorodifluoromethane nor any of its stable decomposition products reacts with Pyrex glass at the temperature employed. Even with "molecular" silver,[3] whose reaction with dichlorodifluoromethane is far less energetic, the same by-products of reaction with the glass were obtained. In this case the experiment was continued for a week at 500° in a quartz tube. About five grams of the original fifty-gram sample reacted to form silver chloride, without producing a detectable trace of silver fluoride.

Dichlorodifluoromethane in the Electric Discharge.—The apparatus used for studies of decomposition in the electric discharge is represented in Fig. 1. It is attached at I to a high-vacuum apparatus for fractional distillation.[4] The discharge tube D was made from tubing 10 mm. wide; the constriction is 2 cm. long and 7 mm. wide. The electrodes, which were made of 6-mm. copper tubing, are fixed in place by the use of Picein. They are set 3–4 cm. apart. The discharge is maintained by a 1/4 KVA transformer giving a maximum potential of 13,500 volts. Both the discharge tube and the electrodes are water cooled.

The sample evaporates from the roughly graduated tube A and passes through the capillary tube C. The rate of flow is controlled by adjusting the pressure; this is done by adjusting the rate of heat flow into the tube A, by raising or lowering a Dewar tube containing a small quantity of liquid ammonia. The capillary tube used in all of the experiments was of such size that dichlorodifluoromethane under a pressure of 560 mm. passed through at the rate of 35 cc. (referred to standard conditions) per minute. The pressure in the discharge tube is maintained constant by the mercury in the bubbler B. The products of the reaction are condensed completely in the tube R.

The reaction produces considerable quantities of chlorine. In the earlier experiments it was removed by repeated distillation back and forth through the mercury bubbler. The finely divided scum of mercurous chloride which otherwise is carried to

(3) Prepared by the method of Gomberg, *Ber.*. **39**, 3287 (1906).

(4) This apparatus consists essentially of a central tube, attached through stopcocks to a mercury vapor pump, and a number of adjuncts attached through stopcocks. It is so arranged that three U-tubes may be placed in series for fractional condensations. It includes also a micro-fractionator, a simple reflux fractionating tube, and several large bulbs for storing gas samples. Details of the technique of low temperature, low pressure fractionation, as developed in this Laboratory, are to be published in a separate paper.

all parts of the apparatus is largely removed in the baffles P_1 and P.   In later work it was found that finely divided copper, placed in a tube (5 cm. diameter and 40 cm. long) between D and P_1, and maintained at 200°, served to remove all of the chlorine during the operation of the discharge process.   This method of removing chlorine seems to be advantageous in preventing secondary reaction of the chlorine with some of the other products of the decomposition, notably tetrafluoroethylene.

After removal of the chlorine from the other products of the reaction, the mixture is separated into three fractions: dichlorodifluoromethane, less volatile substances, and more volatile substances.   The dichlorodifluoromethane, amounting to as much as 75% of the original sample, is returned to A and treated again in the same manner.
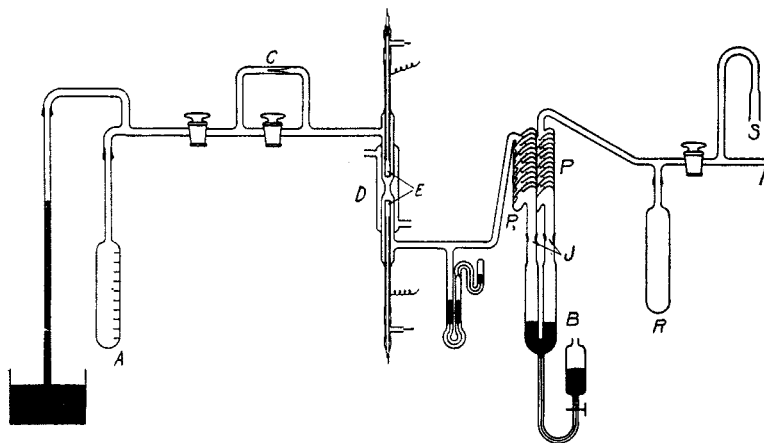

Fig. 1.

This process was repeated until more than 80% of the sample of dichlorodifluoromethane (originally 3500 cc.) had been used up.   The united top fractions were freed from dichlorodifluoromethane by distilling through a bath at −140°, and then subjected to fractionation with a simple reflux tube.[4]   A slow distillation, with the reflux block at −170°, and later at −160°, yielded a fraction (48 cc.)[5] not condensable at −112°, a second fraction containing at least two substances (148 cc.), and a residue consisting entirely of chlorotrifluoromethane (1300 cc.).   The other products of the experiment were 5–6 cc. (liquid) of substances less volatile than dichlorodifluoromethane (further treatment described below), and an unmeasured quantity of chlorine.

At the time of these experiments chlorotrifluoromethane had not been described in the literature.[6]   It was identified by vapor density measurements leading to the molecular weight values 104.5 and 104.2 (theoretical, 104.45), and by analysis.   The latter was carried out by a method similar to that used by Ruff and Keim[7] for carbon tetrafluoride, except that chlorine also was determined, and that the temperature of the reaction vessel had to be kept below 300° to avoid etching of the glass (Pyrex).   The results are in excellent agreement with the theoretical values.

Sample volumes: 56.37 cc., 41.72 cc., 41.37 cc., 41.69 cc. (standard conditions); AgCl, 0.3590, 0.2665, 0.2646, 0.2670 g.; CaF_2, 0.2930, 0.2172, 0.2150, 0.2166 g.   Calcd.

(5) Larger quantities of this substance were obtained by subjecting chlorotrifluoromethane to the discharge, as described below.

(6) Since that time Ruff and Keim. Z. anorg. allgem. Chem., 201, 254 (1931), have reported its preparation and some of its physical constants.

(7) Ruff and Keim, ibid., 192, 251 (1930).

for CF₃Cl: Cl, 33.94; F, 54.46. Found: Cl, 33.75, 33.88, 33.91, 33.92; F, 54.26, 54.37, 54.25, 54.24.

The vapor tensions of chlorotrifluoromethane are shown in Table I. The temperatures were established in a vigorously-stirred ether bath, and measured by means of a carbon dioxide vapor tension thermometer.[8] Most of the values given represent averages of a number of measurements.

<div align="center">TABLE I</div>

t, °C.	−111.9	−106.5	−101.0	−97.0	−93.8
p, mm.	104	166.6	232.4	303	371
t, °C.	− 90.4	− 85.1	− 83.5	−81.1	
p, mm.	456	615	673	757	

These values deviate less than 0.5° from the equation $\log_{10} p = 7.347 - (857.3/T)$. According to this the normal boiling point of chlorotrifluoromethane is −81.1°, the molal heat of vaporization 3922 cal., and the Trouton constant, 20.4 cal./deg. Our data are not in complete agreement with those of Ruff and Keim. Inasmuch as the values of Table I check the Clapeyron equation very closely, giving a practically normal value for the Trouton constant, we believe the difference to be due to impurities in the sample used by Ruff and Keim.

Dichlorotetrafluoroethane.—The 5–6 cc. sample of liquid mentioned above was separated into two nearly equal fractions. The more volatile fraction was freed from dichlorodifluoromethane,[9] and then the bulk of the most volatile remaining material was separated by fractional condensation. This sample was purified by means of a micro-fractionator,[4] in which a mixture of solid carbon dioxide and ether was used to control the temperature of the reflux. The vapor escaped from the fractionator through a 6-mm. column of mercury. The vapor density of the tensiometrically uniform sample thus obtained corresponded to a molecular weight of 170.3; that of dichlorotetrafluoro-methane is 171.0. The vapor pressure–temperature data are presented in Table II. These values deviate less than 0.5° from the equation $\log_{10} p = 7.568 - (1300/T)$, from which we calculate the normal boiling point to be 4.1°, the molal heat of vaporization 5948 cal., and the Trouton constant, 21.4 cal./deg. The close agreement with the integrated Clapeyron equation and the normal value of the Trouton constant show that the sample was a single pure substance. Dichlorotetrafluoroethane is the only compound of carbon, fluorine and chlorine whose molecular weight approximates that observed.[10]

Chlorotrifluoromethane in the Electric Discharge.—Larger quantities of the most volatile material were obtained by subjecting chlorotrifluoromethane to the effect of the electric discharge. In this case the rate of flow was regulated by the use of a carbon dioxide–ether bath, instead of liquid ammonia. The product was fractionated by means

(8) Stock, *Z. Elektrochem.*, **29**, 354 (1923).

(9) This dichlorodifluoromethane may have contained some chloropentafluoroethane, which may be almost equally volatile.

(10) There is some evidence that traces of tetrafluoroethylene, a substance recently described by Ruff and Bretschneider [*Z. anorg. allgem. Chem.*, **210**, 173 (1933)], are among the more volatile reaction products. A sample from which the chlorine had been removed quickly by hot copper was very carefully freed from dichlorodifluoromethane and treated with chlorine. A fair quantity of dichlorodifluoromethane was obtained, evidently by a reaction in which the carbon to carbon linkage, already rendered unstable by loading with the highly electronegative fluorine, was broken by the action of chlorine. We are at present engaged in experimental work to decide whether dichlorotetrafluoroethane is an intermediate. It is quite possible that this substance was produced mainly by the reaction of chlorine with tetrafluoroethylene; the low temperature at which these two were together would have prevented the bond-breaking reaction to a large extent. We hope to publish more on this subject in the near future.

Table II

Vapor Tensions of Dichlorotetrafluoroethane in Mm. of Mercury

Temp., °C.	Press., mm.	Temp., °C.	Press., mm.	Temp., °C.	Press., mm.
−67.0	19.0	−35.0	125.0	−12.5	384
−62.0	25.5	−32.0	146.0	−11.0	412
−60.0	29.0	−30.0	164.0	− 8.5	456
−55.0	41.0	−27.0	191.0	− 5.4	512
−50.0	56.0	−24.0	221.0	− 3.8	544
−46.0	70.0	−20.0	270.0	0.1	647
−40.0	97.0	−17.0	311.0	4.0	750

of a reflux distilling column, with the reflux block at −170°. The most volatile fraction (556 cc., nearly pure) was redistilled with the block at −180°; the distillation was repeated until a tensiometrically uniform sample (185 cc.) was obtained. The values of the molecular weight (87.5; theoretical 88.0) and the boiling point showed the substance to be carbon tetrafluoride. At the time of these experiments there was some doubt concerning this boiling point: Ruff and Keim gave −130°[11] and Lebeau and Damiens gave −126°.[12] Our intention to use carbon tetrafluoride for vapor tension thermometry led us to make an especially trustworthy set of measurements of its vapor tensions at different temperatures. These measurements led to the value −127.8° for the normal boiling point. This agrees very closely with the value recently published by Menzel and Mohry.[13] Our results for the vapor tension at other temperatures also agree extremely well with those published by these workers.

The action of the electric discharge on chlorotrifluoromethane also produces chlorine, dichlorodifluoromethane, and some unidentified solids. The question whether hexafluoroethane and tetrafluoroethylene are products of this reaction is still to be decided. These substances have boiling points so near to that of chlorotrifluoromethane that it would be extremely difficult to isolate them. And in any case, we should expect to obtain only traces of them, for there is good reason to believe that they react with chlorine[10]—hexafluoroethane to give chlorotrifluoromethane and tetrafluoroethylene to give dichlorodifluoromethane.

It is consequently impossible to decide by these reactions what molecular fragments are present in the discharge. The production of dichlorodifluoromethane shows that at least one fluorine atom must have been torn away from the original molecule of chlorotrifluoromethane. Since chlorine is comparatively easy to remove, it is reasonable to suppose that the CF_3 radical is an intermediate in this process. These reactions are being studied further.

Summary

The reaction of dichlorodifluoromethane with several metals has been studied qualitatively, showing that, in general, the metal chloride rather than the fluoride is formed.

Dichlorodifluoromethane, exposed to the action of a high-tension electric discharge, decomposes partially, producing chlorine, chlorotrifluoromethane, small yields of carbon tetrafluoride and dichlorotetrafluoroethane, and less volatile substances not yet identified. There is good evidence that tetrafluoroethylene also is among the products of the reaction.

(11) Ref. 7, p. 254.
(12) Lebeau and Damiens, Compt. rend., 191, 940 (1930).
(13) Menzel and Mohry, Z. anorg. allgem. Chem., 210, 259 (1933).

Chlorotrifluoromethane decomposes under similar conditions, producing chiefly carbon tetrafluoride, chlorine and dichlorodifluoromethane. The yields of less volatile substances are very small.

The vapor tensions of a number of the compounds mentioned above have been very carefully measured.

The System Ferrous Sulfate–Manganous Sulfate–Water at 0 and 25°

By A. McLaren White

This study originated in a class problem involving the crystallization of manganese-free ferrous sulfate from steel mill pickle liquor. Data on the solubility of manganous sulfate in the presence of ferrous sulfate were found to be almost completely lacking. Retgers[1] reported that at 10° two series of solid solutions, one heptahydrate and the other pentahydrate, were formed. Raab[2] found at the temperature of melting ice a single heptahydrate solid solution over the entire concentration range. He also reported solubility measurements, but in the presence of an unspecified amount of sulfuric acid. Preston and Gilchrist[3] made a study of this system at 25°, concluding that two series of solid solutions, one heptahydrate and the other pentahydrate, were formed. They likewise reported solubility data over the entire concentration range. The present work is a revision and extension of their study.

Experimental Work

Baker's c. p. ferrous sulfate and manganous sulfate were placed in varying amounts with distilled water in 8-ounce nursing bottles. The samples at 0° were packed in ice and frequently shaken. Those at 25° were kept in a shaking thermostat accurate to within 0.1°. When the bottles were prepared a small amount of sulfur dioxide was injected to reduce any oxidized iron. This was also found sufficient to prevent further oxidation. Samples at 25° were maintained at this temperature for more than one year, and those at 0° a somewhat shorter time.

Samples for analysis were obtained by weight. The analytical procedure of Majdel,[4] involving precipitation of manganese as $MnO(OH)_2$ from a 0.3 N sulfuric acid solution by means of ammonium persulfate, was followed, and the iron subsequently precipitated as ferric hydroxide. The precipitates were ignited and weighed as Mn_3O_4 and Fe_2O_3, respectively. Sulfates were determined as barium sulfate. Results could be duplicated satisfactorily.

(1) Retgers, Z. physik. Chem., 16, 580 (1895).

(2) Raab, Arch. minéral soc. sci. Varsovie, 5, 35 (1929).

(3) Preston and Gilchrist, Jr., unpublished undergraduate thesis, University of North Carolina, 1932.

(4) Majdel, Z. anal. Chem.. 81, 14 (1930).