suggested: $\log_{10} Kp_1 = (374/T) - 5.431$ and $\log_{10} Kp_2 = (4600/T) - 6.470$. The significance of these results in the practical synthesis of formaldehyde is discussed.

NEW HAVEN, CONNECTICUT RECEIVED JULY 13, 1933
PUBLISHED DECEMBER 14, 1933

[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

Thermodynamic Properties of Trifluorotrichloroethane and Difluorotetrachloroethane

BY FRANK HOVORKA AND FRANCIS E. GEIGER

In the study of the fluorination of hexachloroethane at high temperatures and pressures, Booth, Mong and Burchfield[1] obtained, among others, two liquid compounds, $C_2F_2Cl_4$ and $C_2F_3Cl_3$. A few of the more common physical constants were determined by them, but these only at one temperature. In view of the possible industrial importance of these liquids, it was considered quite desirable to determine accurately their physical constants over a wide range of temperature.

Purification of Materials.—The materials were furnished through the kindness of Dr. Booth of this Laboratory. The $C_2F_2Cl_4$ was refluxed over barium oxide to remove any water which might be present. Then it was fractionally distilled, using a special high fractionating column until a boiling point constant to 0.05° was obtained. Crystallization of this liquid did not affect the boiling point of the liquid. The $C_2F_3Cl_3$ on account of its low boiling point was distilled directly from barium oxide and condensed with carbon dioxide snow to avoid any excessive loss by evaporation. It was then fractionally distilled until a boiling point constant to 0.04° was obtained.

Apparatus and Procedure.—The various physical constants were determined by practically the same method as that described by Hovorka, Lankelma and Naujoks.[2]

Discussion of Results.—In the case of each liquid the boiling point was obtained by extrapolation of the vapor pressure–temperature curve. The heat of vaporization was calculated from the slope of a line obtained by plotting the logarithm of the vapor pressure against the reciprocal of the absolute temperature. Sugden's parachor and the critical temperature were obtained by the usual methods. All of these are summarized in Table I.

The freezing point of $C_2F_2Cl_4$ was found to be 28.1°. Its Eötvös constant was 2.34. All the other properties as shown in the Table exhibited the usual variation of a normal liquid.

---

[1] Booth, Mong and Burchfield, *Ind. Eng. Chem.*, **24**, 328 (1932).

[2] Hovorka, Lankelma and Naujoks, THIS JOURNAL, **55**, 4820 (1933).

TABLE I

PHYSICAL PROPERTIES OF COMPOUNDS

DIFLUOROTETRACHLOROETHANE

Molal heat of vaporiz., 8350 cal.; crit. temp., 278.0°C.; Sugden's parachor, 271.9

T, °C.	Abs. density	Visc. × 10^3	Surf. tens.	Index of refr.	V. p., mm.
28.1	1.6396[a]	12.47[a]	22.98[a]	1.4119[a]	65.8
30.0	1.6358	12.08	22.73	1.4109	72.2
40.0	1.6157	10.36	21.56	1.4069	108.6
50.0	1.5959	9.08	20.44	1.4015	164.3
60.0	1.5754	7.96	19.38	1.3960	243.6
70.0	1.5552	7.13	18.36	1.3900	357.1
80.0	1.5356	6.29	16.93	1.3840	509.3
90.0	1.5146	5.66			

T, °C......	10.0	20.0	85.0	91.0	91.50 ± 0.05
V. p., mm..	28.9	45.8	604.9	744.3	760.0[a]

TRIFLUOROTRICHLOROETHANE

Molal heat of vaporiz., 7010 cal.; crit. temp., 187.6°C.; Sugden's parachor, 244.2

0.0	1.6195	9.25	19.85	1.3697	109.3
10.0	1.5971	8.05	18.96	1.3642	177.3
20.0	1.5760	7.11	17.75	1.3590	272.5
30.0	1.5531	6.27	16.56	1.3539	406.4
40.0	1.5278	5.59	15.30	1.3480	588.2
46.0					727.4
47.25 ± 0.04					760.0[a]

[a] Value obtained by extrapolation.

In the case of $C_2F_3Cl_3$ the physical properties (Table I) showed a fairly uniform variation, with the exception of surface tension. Here the surface energy variation with temperature did not produce a straight line. The value of Eötvös constant for this liquid is 2.59 near its boiling point, while at 0° it is 1.69. This would indicate that the liquid is probably associated. That may not be surprising if one considers the unsymmetrical arrangement of fluorine and chlorine atoms in this compound as compared with $C_2F_2Cl_4$ where we have a well-balanced molecule and apparently no association.

In the case of both of these liquids the calculated value for the parachor is higher than the value calculated from experimental results. It is probable that the theoretical value of the parachor constant of fluorine is too high because the same variation was noticed for all the other fluorine compounds thus far studied.

The vapor pressure variation with temperature of $C_2F_2Cl_4$ may be expressed by the equation

$$\log P = (-764.783/T) + 7.4446 \log T - 14.0934$$

and for $C_2F_3Cl_3$

$$\log P = (-2030.38/T) - 3.69666 \log T + 18.4810$$

where pressure is expressed in millimeters of mercury, and T is absolute temperature.

Summary

The following physical properties for $C_2F_2Cl_4$ and $C_2F_3Cl_3$ have been determined over a wide temperature range: density, index of refraction, surface tension, vapor pressure and viscosity.

Critical temperatures, molal heat of vaporization, parachor and vapor pressure–temperature equation have been calculated for each liquid.

CLEVELAND, OHIO RECEIVED JULY 17, 1933
PUBLISHED DECEMBER 14, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF ROCHESTER]

The Decomposition of Formic Acid by Sulfuric Acid

BY ROBERT E. DERIGHT

Introduction

A study of the decomposition of formic acid by sulfuric acid has been reported by Schierz,[1] who also cites early workers in this field. Schierz, and later Schierz and Ward,[2] determined the velocity of decomposition in sulfuric acid solutions as concentrated as 96.69%. The results obtained can be accounted for on the basis of Taylor's theory of negative catalysis.[3]

Since the decomposition of several organic acids by sulfuric acid, when small amounts are dropped into large amounts of sulfuric acid, follows the unimolecular law it was thought that some light might be cast on the mechanism of the reaction if the conditions were reversed. In this case the concentration of formic acid would not change; hence, the true order of the reaction might be determined.

The effect of water in smaller concentration and the effect of sulfur trioxide were also thought worthy of investigation.

Experimental Part

Preparation and Purification of Materials.—The 85% formic acid was concentrated by the method described by Schierz[1] and the last traces of water removed by the method described by Coolidge.[4] The formic acid thus obtained was run from a glass stoppered storage bottle through an all glass siphoning system to a micro-buret, air being admitted through a drying train.

Four sulfuric acid solutions corresponding to 94.74, 100.16, 100.08 and 106.5% were prepared. The first solution was the ordinary C. P. reagent, the second and third were prepared by mixing C. P. fuming sulfuric acid and the ordinary reagent, and the fourth solution consisted of C. P. 30% fuming sulfuric acid. The 94.74 and the 106.5% acids were analyzed by precipitation as barium sulfate, due precautions being taken to prevent absorption of water and loss of sulfur trioxide. The 100.16 and 100.08% solutions were found by preliminary experiment to be slightly fuming, they melted at 9.99 and 10.25°, respectively, so that their concentration could be determined from the data

---

[1] Schierz, THIS JOURNAL, **45**, 447 (1923).

[2] Schierz and Ward, *ibid.*, **50**, 3240 (1928).

[3] Wiig, *ibid.*, **52**, 4742 (1930).

[4] Coolidge, *ibid.*, **50**, 2166 (1928).