907. *The Heat of Formation of Sulphur Chloride Pentafluoride.*

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The heat of hydrolysis of sulphur chloride pentafluoride in 2N-sodium hydroxide has been measured, and the result used to deduce a value of 245 kcal. mole^{-1} for its heat of formation.

SULPHUR CHLORIDE PENTAFLUORIDE is quantitatively hydrolysed by aqueous sodium hydroxide to sodium sulphate, fluoride, and chloride.[1] This reaction has been carried out in an isothermal calorimeter and the heat of hydrolysis so measured has been used to calculate the heat of formation of sulphur chloride pentafluoride.

EXPERIMENTAL

Sulphur chloride pentafluoride was prepared and purified by the method described by Roberts and Ray.[1]

The heat measurements were made in a Bunsen-type isothermal calorimeter, diphenyl ether being used as the working substance. The design of the calorimeter was similar to that of Giguère, Morissette, and Olmos.[2] The diphenyl ether was distilled twice under reduced pressure and fractionally crystallised from the melt until the m. p. was constant at 26·87°. The thermostat in which the calorimeter was immersed was kept at 26·85° ± 0·01°. At equilibrium, the mercury in the indicator capillary receded into the calorimeter at a rate of ∼1 mm. per min. as the diphenyl ether slowly solidified. A return to contraction at this rate at the end of an experiment gave a good indication of completion of the reaction. A correction for this constant heat loss must be made and in the experiments subsequently described was of the order of 5% of the total heat measured.

The calibration constant of the calorimeter can be defined as the number of calories evolved in the calorimeter per gram of mercury expelled. This was determined by dropping synthetic sapphire, whose specific heat is accurately known,[3] from a steam thermostat mounted directly above the calorimeter well into dibutyl phthalate, which acts as a heat-transfer medium, in the calorimeter. The values obtained in five experiments were 19·17, 19·14, 18·82, 19·03, 18·97 cal. per g., giving a mean value of 19·03 ± 0·13 cal. per g. This value is in good agreement with the value of 19·01 ± 0·02 cal. per g. obtained by Giguère, Morissette, and Olmos.[2]

Sulphur chloride pentafluoride (b. p. −21°) is a gas at the working temperature of the calorimeter. The experimental procedure adopted was to seal a sample of about 0·2 g. of liquid sulphur chloride pentafluoride into a capillary tube, the fine tip of which could be broken by an external plunger below the surface of the 20 ml. of 2N-sodium hydroxide solution contained in the calorimeter well. In this way the liquid at the working temperature of the calorimeter slowly evaporates, giving a stream of fine bubbles of gas which react rapidly with the sodium hydroxide solution. The weight of sulphur chloride pentafluoride which reacts was estimated by analysis of the solution at the end of the experiment for sulphate and chloride. The satisfactory agreement between these two values indicated that the reaction had followed the expected course:

$$SF_5Cl + 8NaOH \longrightarrow Na_2SO_4 + 5NaF + NaCl + 4H_2O$$
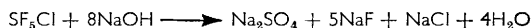
As the gravimetric determination of sulphate as barium sulphate was thought to be more accurate than the estimation of chloride by a volumetric method, the former result was used in the subsequent calculations. The heat of hydrolysis so obtained was combined with the known heats of formation [4] of sodium hydroxide, sodium sulphate, sodium fluoride, and sodium chloride in the appropriate quantity of water, and the heat of formation [4] of water, to give a value for the heat of formation of liquid sulphur chloride pentafluoride. The value of 4560

[1] Roberts and Ray, *J.*, 1960, 665.
[2] Giguere, Morissette, and Olmos, *Canad. J. Chem.*, 1955, **4**, 657.
[3] Ginnings and Farakawa, *J. Amer. Chem. Soc.*, 1953, **75**, 522.
[4] Nat. Bur. Stand. Tables, Circular No. 500.

cal. mole^{-1} being used for the latent heat of vaporisation,[1] this can be converted into the heat of formation of gaseous sulphur chloride pentafluoride at 1 atm. The results obtained are shown in the Table.

Wt. (g.) of SF$_5$Cl used		Heat of reaction (cal. mole^{-1}) with 20 ml. of 2N-NaOH	Molar heat of hydrolysis (kcal. mole^{-1})	Molar heat of formation (kcal. mole^{-1}) of SF$_5$Cl	
(a) by SO$_4{}^2$ analysis	(b) by Cl$^-$ analysis			(a) liquid	(b) gas
0·258	0·254	374·4	235·8	247·8	243·2
0·267	0·270	379·0	230·4	253·1	248·5
0·158	0·157	226·8	232·8	250·9	246·3
0·242	0·242	351·0	235·2	248·4	243·8

Mean value of heat of formation of SF$_5$Cl gas = 245 ± 2 kcal. mole^{-1}.

As a check on the experimental procedure, a similar set of experiments with sulphur dioxide was carried out. The values of the heat of formation of liquid sulphur dioxide obtained were 74·37, 74·44, 74·37, 74·60, 74·96, 75·04, 74·56 kcal. mole^{-1}. These values may be compared with values of 74·6 kcal. mole^{-1} obtained by Frost [5] and 76·96 kcal. mole^{-1} obtained by Eckmann and Rossini [6] by direct combustion of sulphur in oxygen.

Discussion.—The heat of formation of sulphur hexafluoride has been determined by the direct combustion of sulphur in fluorine, giving a value [7] of 289·8 kcal. mole^{-1}. By taking the heat of atomisation of sulphur as 57 kcal. per g.-atom and the heat of dissociation of the F$_2$ molecule [8] as 37 kcal. mole^{-1}, a value of 76 kcal. mole^{-1} is obtained for the bond energy of the S–F bond in SF$_6$. This value can be used in conjunction with the heat of formation of SF$_5$Cl and the known dissociation energy of the Cl$_2$ molecule [8] to make an estimate of the S–Cl bond energy if it is assumed that the S–F bond energy is the same in each case. The value so obtained, 45 kcal. mole^{-1}, is considerably lower than the value of 61 obtained from S$_2$Cl$_2$. A study of the infrared spectrum of sulphur chloride pentafluoride [9] indicates, however, that the S–Cl bond length in SF$_5$Cl is similar to that in S$_2$Cl$_2$. Further, the fact that SF$_5$Cl is stable above 250° suggests that the S–Cl bond in SF$_5$Cl is quite strong.

In discussing the conditions under which a sulphur atom can form six covalent bonds, Craig and Magnusson [9] predict that the greatest bond energies can be expected when all six bonded atoms are fluorine. They further state that, if one fluorine atom is replaced by a larger less-electronegative chlorine atom, not only will the S–Cl bond be weaker than the S–F bond but also the five remaining S–F bonds will be weaker than in SF$_6$. Such a picture is entirely consistent with the chemical and thermodynamic data on SF$_6$ and SF$_5$Cl, as a value of the S–Cl bond energy which is higher than 45 kcal. mole^{-1} can only be permitted if the S–F bond energy is lower than the value of 76 found in SF$_6$. A similar picture emerges from the S–F bond force constants, a lower value being obtained for SF$_5$Cl than SF$_6$.[10]

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[5] Frost, Diss., University of California, 1926.

[6] Eckmann and Rossini, *J. Res. Nat. Bur. Stand.*, 1929, **3**, 597.

[7] Hayaman, Gross, and Levi, International Symposium on Fluorine Chemistry, Birmingham, July, 1959.

[8] Cottrell, " The Strengths of Chemical Bonds," Butterworths Scientific Press, London, 1958.

[9] Craig and Magnusson, *J.*, 1956, 4895.

[10] L. A. Woodward, personal communication.