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Enthalpy of Formation of Chlorine Pentafluoride

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The enthalpy of formation of liquid chlorine pentafluoride was determined by two independent sets of experiments. In one, the compound reacted with hydrogen and in the other with ammonia. From the measured enthalpies of reaction and the known enthalpies of formation of products and reactants, corrected to their standard states, the standard enthalpy of formation of ClF_5 was derived. The enthalpy of formation calculated on the basis of the hydrogen reaction was $\Delta H_f^\circ(ClF_5) = -66.4 \pm 6.9$ kcal. per mole. Calculated on the basis of the ammonia reaction, $\Delta H_f^\circ(ClF_5) = -59.9 \pm 3.9$ kcal. per mole. Assuming that one questionable hydrogen run was invalid, the enthalpy of formation calculated with the data from both sets of experiments was $\Delta H_f^\circ(ClF_5) = -60.9 \pm 4.5$ kcal. per mole.

AS PART OF A PROGRAM to characterize the interhalogen, chlorine pentafluoride, its enthalpy of formation was determined by two independent sets of experiments. In one set, the compound reacted with hydrogen, and in the other set with ammonia.

EXPERIMENTAL

Materials. The chlorine pentafluoride used in both the hydrogen and ammonia reactions was prepared at Rocketdyne. Gas chromatographic analysis of the sample showed the following impurities (weight per cent): F_2, 0.1; Cl_2, 0.5; ClF, 0.2; and ClO_2, 0.1. The assay of ClF_5 was 99.1%; the F/Cl molar ratio was 4.89 to 1.

The hydrogen was a prepurified grade of 99.9% minimum purity (Matheson Co.).

The ammonia was a commercial grade which, by mass spectrometer analysis, contained considerable nitrogen. Therefore, the ammonia was vacuum-distilled over metallic sodium into a stainless steel container. After the transfer, the condensed ammonia was placed under vacuum to remove any volatile contaminants. This produced ammonia of a minimum purity of 99.9%.

The impurities (F_2, Cl_2, ClO_2, and ClF) in the starting materials, which are reactive under the conditions of these experiments, were accounted for in the calculations.

Chlorine pentafluoride is a very toxic chemical, and inhalation of even dilute concentrations should be avoided. Until more systematic and definitive studies have been conducted, the toxicity level now utilized for ClF_5 is that previously established for ClF_3 by the American Conference of Governmental Industrial Hygienists. This level is expressed as a threshold limit value (TLV) of 0.1 p.p.m., by volume, or 0.4 mg. per cu. meter. (The TLV represents the average concentration to which the average human can be safely exposed on a daily basis without adverse effects.) The odor of ClF_5 has been used as a warning of potential danger. ClF_5 vapors have been inhaled for short periods without any adverse effects. Any contact of this corrosive compound with living tissue will result in severe chemical burns that are difficult to heal.

Notwithstanding the toxicity of ClF_5, the greatest hazards associated with this strong oxidizer lie in its extreme reactivity with most inorganic and organic materials. These chemical reactions are often followed by fire and/or explosion, although ClF_5 itself is nonflammable in air and insensitive to mechanical shock.

Calibration. The energy equivalent of the calorimeter was determined in the standard manner by combustion of National Bureau of Standards Sample 39h benzoic acid. The combustions were carried out with the sample ampoule in place and pressurized with He to prevent collapse of the diaphragm.

The standard calorimeter system for these series of experiments was specified as the Bureau of Standards calorimeter containing the Parr fluorine combustion bomb plus sample ampoule. The standard bomb was defined as the Parr fluorine combustion bomb plus sample ampoule without

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the benzoic acid pellet, the Hastelloy cup for containing the pellet, the oxygen, and the helium for pressurizing the ampoule.

The energy equivalent of the calorimeter system (Monel reaction bomb) used in the ClF_5–H_2 experiments was 48,533.4 ± 6.5 cal. per ohm. The energy equivalent of the system (nickel reaction bomb) used in the ClF_5–NH_3 experiments was 48,310.0 ± 30.0 cal. per ohm.

Apparatus and Procedure. The thermochemical measurements were made using a Parr fluorine combustion bomb and a Bureau of Standards isothermal calorimeter No. 63090 (Precision Scientific Co.). A Monel ampoule, fully described by Bisbee and coworkers (*2*), was fitted into the top of the bomb to retain the ClF_5 sample. The ampoule screws into the bomb head in the position normally occupied by the outlet tube. This prevents the use of the outlet valve. Additional support is provided by a Monel clip that fits around the cylinder body of the ampoule and is attached to the inlet tube. The ampoule is sealed with a rupture disk and fitted with a plunger that is held under spring tension by nickel alloy fuse wire. The internal volume of the ampoule is 8.7 ± 0.2 cc. The volume of the bomb with the closed ampoule in place is 315 ± 1 cc.

To solve the problem of loading and weighing a sample in the ampoule, one side exit was designed to accommodate a small 90° angle valve. The weight of the ClF_5 sample was determined by weighing the empty ampoule, which had been previously evacuated, and then weighing the filled ampoule.

The ClF_5 sample was condensed from a vacuum line into the ampoule, which was weighed on an analytical balance and then attached to the bomb head. Buoyancy corrections were applied to the weight of the ClF_5 sample. Using this technique, the ClF_5 was weighed to ±0.015%. The reaction bomb was assembled and then pressurized with the other reactant and sealed. To start the reaction, the sample was released into the bomb by electrically fusing the nickel-chromium alloy wire. This released the piston that ruptured the diaphragm and allowed the reactant gases to mix. Reaction occurred rapidly and completely; the temperature rise of the calorimeter was measured by means of a platinum resistance thermometer constructed and calibrated by the Leeds and Northrup Co. The thermometer, a four-lead cable type, was used in conjunction with a Leeds and Northrup G-2 Mueller bridge and a high sensitivity galvanometer. The resistance was measured to ±0.00001 ohm.

Dickinson's method was employed to obtain the corrected resistance change (*4*). This method involves the use of the equation $R_x = R_i + 0.63\ (\Delta R_{\text{obsd}})$ where R_i is the initial resistance before the reaction and R_x is the resistance at t_x, the time on a resistance-time plot at which a vertical line will subtend equal areas to the left and to the right of the resistance-time curve. ΔR_c was obtained to a precision of 0.00003 ohm.

Some corrosion of the Monel bomb was observed during the ClF_5–H_2 runs. However, cation analyses of the reaction products, along with emission spectrophotographic examinations, indicated that corrosion was not extensive. A nickel bomb (of the same volume) was used for the study of the reactions of ammonia with chlorine pentafluoride, because previous work had demonstrated that nickel was more passive under the conditions of these experiments.

To eliminate corrections for heats of solution of the products in liquid ammonia, the amount of ammonia was controlled so that no liquid ammonia remained after the reaction was completed. In addition, there was no evidence of the formation of ammonium bifluoride in the reported experiments . An additional problem occurred in the set of ammonium experiments because the pressure differential across the rupture disk was not large enough to prevent elasticity in the disk. The addition of helium eliminated the problem and resulted in successful mechanical rupturing of the disk.

The amount of ammonia decomposed during the reaction was determined from the difference of ammonia initially introduced and the expected excess recovered after reaction.

After the volatiles were removed, the solid reaction products were quantitatively washed from the bomb, and the fluoride, chloride, and ammonium ions quantitatively determined. The fluoride to chloride molar ratios were 4.88 to 1, 4.89 to 1, and 4.97 to 1 from the three reactions reported in Table II. The chloride recovery was 99.5% of theoretical and fluoride, 97.7%. The difficulty encountered in washing the internal parts of the bomb and the failure to remove all of the ammonium salts from the valves, etc. probably contributed to the low chloride and fluoride analyses.

The chloride was determined gravimetrically as silver chloride. A modification of the conventional method was necessary, as a slight dissolution of the sintered glass crucible during filtration was caused by the presence of hydrofluoric acid at approximately $0.01M$ concentration. The modification consisted of using as the tare weight of the crucible the final weight after dissolving the silver chloride with concentrated ammonia, and the small amount of silver possibly present with a few drops of nitric acid. The method was checked for accuracy by analyzing a standard solution of chloride containing ammonium fluoride. The results were within 0.08% of theoretical.

The fluoride was determined gravimetrically as lead chlorofluoride. The accuracy of the method was checked by analyzing a standard fluoride solution containing ammonium fluoride. The experimental results deviated from theoretical by 0.28%.

The ammonium ion was determined by distillation of the ammonia from an alkaline solution of the salts into boric acid and then titrating with acid standardized against sodium carbonate. The efficiency of the ammonia recovery was determined by distillation of a standard ammonium solution. A 100% recovery was obtained.

A complete analysis of the volatiles, consisting of nitrogen, hydrogen, excess unreacted ammonia, and helium was performed for one combustion. The number of millimoles of nitrogen, corrected for the ammonia decomposition, was 101.8% of the number of millimoles of chlorine pentafluoride put into the combustion bomb.

RESULTS AND CALCULATIONS

The reaction was run at 28° C., which is effectively the standard temperature of 25° C., for the reported heat of formation. The energy unit used is the calorie, defined to be equal to 4.1840 absolute joules.

In the first series of experiments, the reaction, as it takes place in the bomb, is represented by the equation:

$$ClF_5(l) + 3H_2(g) \rightarrow HCl(g) + a(HF)_x(g) + bHF(l) \qquad (1)$$

where x = apparent degree of polymerization, a = number of moles in gas phase with composition $(HF)_x$, and b = number of moles of HF in liquid phase.

Corrections are applied to convert to the heat of reaction for the equation:

$$ClF_5(l) + 3H_2(g) \rightarrow HCl(g) + 5HF(g) \qquad (2)$$

where the species are in the standard state.

To obtain the heat of reaction 2, the following corrections were applied to the measured heat of reaction 1:

1. q_1, heat liberated or absorbed by the reaction of impurities with hydrogen according to the equations:

$H_2(g) + Cl_2(g) \rightarrow 2HCl(g) \qquad \Delta H_f^\circ(HCl) = -22.06$ kcal. per mole (*8*)

$H_2(g) + F_2(g) \rightarrow 2HF(g)$ $\Delta H_f^\circ(HF) = -64.8$ kcal. per mole (*7*)

$H_2(g) + ClF(g) \rightarrow HCl(g) + HF(g)$

$\Delta H_f^\circ(ClF) = -12.1$ kcal. per mole (*9*)

$\frac{5}{2}H_2(g) + ClO_2(g) \rightarrow HCl(g) + 2H_2O(g)$

$\Delta H_f^\circ(ClO_2) = 25.00$ kcal. per mole (*6*)

2. q_2, liquefication of ClF_5 present in the vapor phase. At the conditions of reaction, ClF_5 has a vapor pressure of 4.17 atm. (*11*). Thus, assuming the ideal gas law, the vapor density at 28° is 0.02201 gram per cc. The assumption of the ideal gas law is justified, since a nonideality correction would be a small correction on a small correction. Thus

$$q_2 = \Delta H_v \cdot n_{ClF_5(g)} = \Delta H_v \cdot V_g \cdot \rho_v / M_{ClF_5}$$

where ΔH_v = heat of vaporization of ClF_5 = 4.9 kcal. per mole at 28° (*11*), V_g = volume of vapor, ρ_v = vapor density = 0.02201 gram per cc., and M_{ClF_5} = molecular weight of $ClF_5 = 130.466$.

V_g was computed as follows:

$$V_g = V_{total} - V_l$$

where V_{total} = 8.7 cc. and V_l = volume occupied by liquid ClF_5.

$$V_l = \left[\frac{m_{ClF_5}}{\rho_l} - V_{total} \frac{\rho_v}{\rho_l}\right] / \left(1 - \frac{\rho_v}{\rho_l}\right)$$

where ρ_l = 1.76 grams per cc. and m_{ClF_5} = mass ClF_5.

3. q_3, vaporization of liquid HF. In making the corrections for HF, first the liquid HF was corrected to the equilibrium vapor and then all the vapor corrected to unit fugacity of the monomer. To find the amount of liquid, the distribution of HF was found, assuming that the vapor consists of monomer and hexamer (*10, 13*). Then the equation of state can be written $PV = nRT/x$ where x = apparent degree of polymerization and n = number of formula moles of HF present (*13*). The extent of polymerization was taken from Jarry and Davis (*10*) to give $x = 3.49$. Thus

$$n_{(HF)_x} = \frac{PV}{RT} = n/x = 0.01729$$

where V = 324 ml. (volume of bomb), P = 1.318 atm. (vapor pressure of HF), and $T = 301°$ K.

The correction for the heat of vaporization of liquid HF to the gaseous hydrogen fluoride, based on one mole of ClF_5, is equal to $b \cdot \Delta H_v$; using Equation 1, b is found to be

$$b = 5 - \frac{n_{(HF)_x}}{n_{ClF_5}}(3.49)$$

Expressing this correction in terms of experimental quantities of ClF_5, and introducing ΔH_v = 1.742 kcal. per mole (*10*),

$$q_3 = [5 - (3.49) \cdot (n_{(HF)_x}/n_{ClF_5})] \cdot 1.742 \cdot n_{ClF_5} = (8.710\, n_{ClF_5} - 0.1045)\text{kcal.}$$

4. q_4, polymerization of HF vapor. The correction of the heat of depolymerization of hexamer to monomer was determined from the heat of polymerization (6.8 kcal. per formula weight HF as hexamer) (*13*). The distribution between monomer and hexamer is found from the equation:

$$(HF)_x = y\,HF + z\,(HF)_6 \qquad (3)$$

where y = mole fraction of HF and z = mole fraction of $(HF)_6$.

y and z were found as follows: $y + 6z = x$; $y + z = 1$; $x = 3.49$. Thus $y = 0.502$ and $z = 0.498$. Thus, according to Equation 3, the heat of depolymerization per mole of $(HF)_x$ is:

$$\Delta H_p = 6z \cdot 6800 = 40{,}800z \text{ (calories)}$$

For this case, ΔH_p = 20.32 kcal. per mole $(HF)_x$. The correction for the polymerization of HF becomes:

$$q_4 = (20.32) \cdot (5 \cdot n_{ClF_5}/3.49) = 29.11\, n_{ClF_5} \text{ kcal.}$$

5. q_5, conversion of ΔE, heat of reaction at constant volume, to ΔH, heat of reaction at constant pressure.

$$\Delta H = \Delta E + \Delta nRT = \Delta E + 3RT$$

$$q_5 = 3RT \cdot n_{ClF_5}$$

The results of the ClF_5-H_2 experiments are given in Table I. In the second series of experiments, the heat of reaction of the following system was measured:

$$ClF_5(l) + 8NH_3(g) \rightarrow NH_4Cl(s) + 5NH_4F(s) + N_2(g) \qquad (4)$$

The corrections that were applied to the measured heat of this reaction are:

1. q_1, heat liberated or absorbed by the reaction of impurities with ammonia according to the equations:

$8NH_3(g) + 3Cl_2(g) \rightarrow 6NH_4Cl(s) + N_2(g)$

$\Delta H_f^\circ(NH_3) = -10.97$ kcal. per mole (*9*)

$8NH_3(g) + 3F_2(g) \rightarrow 6NH_4F(s) + N_2(g)$

$\Delta H_f^\circ(NH_4F) = -111.8$ kcal. per mole (*5*)

$8NH_3(g) + 3ClO_2(g) \rightarrow 3NH_4Cl(s) + 6H_2O(g) + 5/2N_2(g)$

$8NH_3(g) + 3CLf(l) \rightarrow 3NH_4Cl(s) + 3NH_4F(s) + N_2(g)$

$\Delta H_f^\circ(NH_4Cl) = -75.18$ kcal. per mole (*9*)

The $\Delta H_f^\circ(NH_4F)$ value taken from Higgens (*5*) was corrected for the more recent value of $\Delta H_f^\circ(HF)$ as reported in JANAF (*7*).

2. q_2, heat absorbed to vaporize the liquid ammonia. From the equation of state $n_{NH_3} = PV/zRT$ [where z = 0.909 (*3*), P = 10.49 atm. (v.p. NH_3) (*3*), V = 315 ml. (volume of bomb), and $T = 301°$ K], the number of moles of gaseous NH_3 was determined (using the correction for liquid volume given above for volume of ClF_5 gas). The difference between this value and the total number of moles of NH_3 added to the bomb was multiplied by $\Delta H_v(NH_3)$ = 4.716 kcal. per mole (*3*).

3. q_3, heat of decomposition of excess ammonia. The amount of ammonia decomposed was determined from the difference between the ammonia initially introduced and the excess recovered, taking into account the amount that reacted, based on the quantity of ClF_5 used. ΔH_{decomp} = 10.97 kcal. per mole.

4. q_4, conversion of ΔE, heat of reaction at constant volume, to ΔH, heat of reaction at constant pressure. $\Delta H = \Delta E + \Delta nRT$. The initial moles of gas were taken to be the number of moles of NH_3. The final moles of gas were taken as the unreacted ammonia according to Equation 4 plus the resulting nitrogen.

5. q_5, liquefication of ClF_5 present in the vapor phase. This calculation was described in detail as q_2 for the ClF_5-H_2 experiments.

6. q_6, a negligible correction for the energy liberated during the expansion of helium from the ampoule into the bomb:

$$q_6 = \mu \cdot C_p \cdot \Delta P \cdot n_{He}$$

where $\mu = (\partial T/\partial P)$ = Joule-Thompson coefficient = −0.062° C. per atm. (*1*), C_p = 4.968 cal./deg.-mole (He) (*12*), ΔP = change in pressure of He before and after expansion = $nRT/\Delta V$, and n_{He} = number of moles of He added to ampoule = 0.0072.

7. q_7, a correction for the nonideality of NH_3. The non-

Table I. ClF_5-H_2 Experiments[a]

Run No.	n_{ClF_5}, Mole	ΔR_c, Ohm	ΔE_b, Kcal.	q_1, Kcal.	q_2, Kcal.	q_3, Kcal.	q_4, Kcal.	q_5, Kcal.	ΔH°, Kcal.	ΔH°_{25}, Kcal./mole
1	0.015796	0.10445	-5.0693	+0.0257	+0.0064	+0.0331	+0.4598	+0.0284	-4.5159	-285.9
2	0.014135	0.08923	-4.3306	+0.0230	+0.0064	+0.0186	+0.4115	+0.0254	-3.8457	-272.1
3	0.012116	0.07847	-3.8084	+0.0197	+0.0066	+0.0010	+0.3527	+0.0217	-3.4067	-281.2
						Mean			-279.7	
						Standard deviation of mean			±4.2	

[a] n_{ClF_5}, number of moles of ClF_5 based on 99.1% purity of weighed sample. ΔR_c, corrected temperature rise. ΔE_b, heat of reaction as obtained in the bomb process. q_1, heat contributed by reaction of known impurities. q_2, heat of condensing gaseous sample to liquid state. q_3, heat of vaporization of liquid HF. q_4, heat of polymerization of HF gas. q_5, a term ΔnRT equal to $\Delta H^\circ - \Delta E^\circ$. ΔH°, standard heat of reaction per sample. ΔH°_{25}, standard heat of reaction per mole of ClF_5.

Table II. ClF_5-NH_3 Experiments[a]

Run No.	n_{ClF_5}, Mole	n_{NH_3}, Mole	ΔR_c, Ohm	ΔE_b, Kcal.	q_1, Kcal.	q_2, Kcal.	q_3, Kcal.	q_4, Kcal.	q_5, Kcal.	q_6, Kcal.	q_7, Kcal.	ΔH°, Kcal.	ΔH°_{25}, Kcal./Mole
1	0.011276	0.13431	0.10938	-5.2841	+0.0336	0	-0.1827	-0.0471	+0.0074	+0.0004	-0.0316	-5.4941	-487.2
2	0.035952	0.43346	0.31531	-15.233	+0.1069	-1.3683	-0.7778	+0.0598	+0.0057	+0.0004	-0.1176	-17.3239	-481.9
3	0.030253	0.42335	0.27115	-13.099	+0.0899	-1.3199	-0.5170	+0.0638	+0.006	+0.0004	-0.0558	-14.8136	-490.3
										Mean		-486.5	
										Standard deviation of mean		±2.5	

[a] n_{ClF_5}, number of moles of ClF_5 in weighed sample. n_{NH_3}, number of moles of NH_3 added to bomb. ΔR_c, corrected temperature rise. ΔE_b, heat of reaction as obtained in bomb process. q_1, heat contributed by reaction of known impurities. q_2, heat absorbed to vaporize liquid NH_3. q_3, heat of decomposition of excess NH_3. q_4, a term ΔnRT equal to $\Delta H^\circ - \Delta E^\circ$. q_5, heat for condensing gaseous ClF_5 to liquid. q_6, a term for expansion of helium. q_7, a correction to bring gaseous NH_3 to unit fugacity. ΔH°, standard heat of reaction per sample. ΔH°_{25}, standard heat of reaction per mole of ClF_5.

ideality of NH_3 was obtained from Table II and the table "enthalpy" from Davies (*3*). The initial pressure was the vapor pressure of ammonia or was calculated from the equation of state. The final pressure was calculated from the equation of state using the actual remaining ammonia. The tabulated correction is the difference of the final and initial heat required to convert to unit fugacity.

The ClF_5-NH_3 data are reported in Table II.

The heat of formation of $ClF_5(l)$ calculated on the basis of the hydrogen reaction is $\Delta H_f^\circ = -66.4 \pm 6.9$ kcal. per mole. The heat of formation, calculated on the basis of the ammonia reaction, is $\Delta H_f^\circ = -59.9 \pm 3.9$ kcal. per mole where the error is the standard deviation of the mean. Run 2 in the hydrogen set has a significant deviation. Averaging the calculated heats of formation for the remaining runs for both hydrogen and ammonia, calculating a standard deviation, and comparing with the questionable run, the questionable run was not statistically eliminated—it was exactly four times the standard deviation from the average. However, the heat of formation without the questionable run was $\Delta H_f^\circ = -60.9 \pm 4.5$ in very satisfactory agreement with the set of ammonia runs. Thus, while the agreement between the two sets of runs was well within the estimated accuracy, the set of ammonia runs was believed to be closer to actuality.

The uncertainties in the heats of formation were calculated by taking the square root of the sum of the squares of the accuracy error and the precision error. In the hydrogen experiments, the accuracy was estimated to be about ±0.5 kcal. per mole and the precision ±4.2 kcal. per mole. For the ammonia reactions, the errors were about ±3.0 kcal. per mole for the accuracy and ±2.5 kcal. per mole for the precision. The precision errors were taken as the standard deviation from the mean. The accuracy error was determined by estimating the effects of various factors on the reaction, such as errors in existing thermodynamic data used in the calculations and errors from corrosion, which appeared negligible in the set of ammonia runs and greater in the set of hydrogen runs.

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