[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

# The Thermodynamics of Hexafluoroethane from Calorimetric and Spectroscopic Data

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The existence of barriers hindering the mutual internal rotation of methyl groups in a wide variety of compounds has been demonstrated from thermal, spectroscopic and other sources. An empirical method of calculation has been proposed, based on the assumption that the value of the potential barrier hindering the rotation of the groups depends exclusively on repulsive forces between hydrogen atoms.[2] The discovery of barriers in 1,1,1-trifluoroethane[3] and 1,1,1-trichloroethane[4] of the order of 3000 calories per mole raises the question of whether the restricted rotation is uniquely a function of the repulsion of hydrogen atoms. It was the purpose of the present work with hexafluoroethane, the fluorine analog of ethane, to furnish more information to help answer this question.

**The Calorimetric Sample.**—The calorimetric sample was prepared and purified at the Fluorine Laboratory of The Pennsylvania State College under the direction of Dr. J. H. Simons.

The sample was freed of air and introduced into the calorimeter in the customary manner. The heat capacity, the heat of transition and the heat of fusion were determined with this sample. The remaining measurements were made with the portion of the original sample remaining after the first 1.5 cc. of product withdrawn from the low-temperature column had been discarded. This fractionation was found necessary when a preliminary set of vapor pressures indicated the presence of a small amount of highly volatile impurity. The operation removed about 75% of the volatile impurity and made it possible to obtain a satisfactory set of vapor pressures.

**The Heat Capacity Measurements.**—The apparatus and method used in the determination of the heat capacities has been previously described.[5a,b] The temperature indications of thermocouple S-7 were used as a standard with thermocouple S-4 as a check. Correction was made for the change in the calibration of these thermocouples based on a recent comparison with oxygen and normal hydrogen vapor pressures. At the oxygen boiling point the indication of thermocouple S-7 was 0.02° and thermocouple S-4 was 0.04° lower than the last comparison. At the hydrogen triple and boiling point S-7 was 0.08° and S-4 0.2° lower than the last comparison. One calorie is taken equal to 4.1833 international joules. The temperatures are reported on the basis of 273.16° K. as the ice-point temperature.

The heat capacities as measured are listed in Table I. The values at rounded temperatures are summarized in Table II. Because the slope of the heat capacity curve in the premelting region showed no abrupt change it was not possible to estimate the temperature at which premelting of the sample began or to extrapolate the curve of heat capacities with no premelting. Therefore no correction was made for premelting in the heat capacities below the melting point.

TABLE I

THE MOLAL HEAT CAPACITY OF HEXAFLUOROETHANE

Mol. wt. 138.02; 0.44183 mole, 99.84 mole per cent. pure; 0.0°C. = 273.16°K.; 1 cal. = 4.1833 int. joules.

| Temp., °K. | $C_p$, cal./deg./mole |
|---|---|
| Crystal I | |
| Series III | |
| 11.51 | 1.885 |
| 12.57 | 2.269 |
| 14.26 | 3.020 |
| 16.40 | 3.913 |
| 18.59 | 4.994 |
| 21.15 | 6.056 |
| 24.06 | 7.081 |
| 27.51 | 8.117 |
| 31.64 | 9.148 |
| 36.10 | 10.196 |
| 40.81 | 11.158 |
| 45.86 | 12.014 |
| 51.20 | 12.713 |
| 56.54 | 13.33 |
| 61.84 | 13.96 |
| 67.12 | 14.65 |
| Series IV | |
| 73.27 | 15.36 |
| 81.44 | 16.30 |
| 89.45 | 17.23 |
| 97.14 | 18.31 |
| Series I | |
| 59.11 | 13.64 |
| 66.24 | 14.52 |
| 72.85 | 15.31 |
| 77.78 | 15.89 |
| Series II | |
| 87.60 | 16.98 |
| 93.10 | 17.76 |
| 98.75 | 18.61 |
| Crystal II | |
| Series V | |
| 110.92 | 21.01 |
| 117.24 | 21.30 |
| 123.81 | 21.68 |
| 130.37 | 22.08 |
| 137.77 | 22.70 |
| 145.32 | 23.39 |
| 152.00 | 24.26 |
| 158.53 | 25.25 |
| Series VI | |
| 110.96 | 21.03 |
| 118.93 | 21.40 |
| 126.91 | 21.91 |
| 133.95 | 22.44 |
| 141.17 | 23.04 |
| 148.61 | 23.86 |
| 156.25 | 24.87 |
| 163.64 | 26.15 |
| Liquid | |
| Series VII | |
| 174.88 | 29.62 |
| 177.71 | 29.79 |
| 180.97 | 29.96 |
| 184.28 | 30.22 |
| 187.51 | 30.49 |
| 190.67 | 30.86 |
| Series VIII | |
| 176.77 | 29.67 |
| 180.94 | 29.89 |
| 185.26 | 30.26 |
| 190.40 | 30.84 |

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[1] Phillips Petroleum Fellow, 1944–1946.

[2] Aston, Isserow, Szasz and Kennedy, *J. Chem. Phys.*, **12**, 336 (1944).

[3] Russell, Golding and Yost, THIS JOURNAL, **66**, 16 (1944).

[4] Rubin, Levedahl and Yost, *ibid.*, **66**, 279 (1944).

[5] (a) Aston and Messerly, *ibid.*, **58**, 2354 (1936); (b) Messerly and Aston, *ibid.*, **62**, 886 (1940).

TABLE II

THE MOLAL HEAT CAPACITY OF HEXAFLUOROETHANE AT ROUNDED TEMPERATURES

Mol. wt. 138.02, 0°C. = 273.16°K.; 1 cal. = 4.1833 int. joules.

| Temp., °K. | $C_p$, cal./deg./mole | Temp., °K. | $C_p$, cal./deg./mole |
|---|---|---|---|
| Crystal I | | Crystal II | |
| 12 | 2.070 | 105 | 20.75 |
| 15 | 3.285 | 110 | 20.97 |
| 20 | 5.590 | 120 | 21.46 |
| 25 | 7.330 | 130 | 22.09 |
| 30 | 8.740 | 140 | 22.89 |
| 35 | 9.945 | 150 | 23.98 |
| 40 | 11.000 | 160 | 25.50 |
| 50 | 12.55 | 170 | 27.42 |
| 60 | 13.75 | Liquid | |
| 70 | 14.98 | 175 | 29.62 |
| 80 | 16.15 | 180 | 29.88 |
| 90 | 17.31 | 185 | 30.25 |
| 100 | 18.79 | 190 | 30.77 |
| | | 195 | 31.38 |

Allowance was made for vaporization and sublimation of the sample into the filling by making use of the density of the liquid and solid[6] and the measured vapor pressures and heats of vaporization. In the worst case this correction amounted to 3% in the energy and 0.7% in the number of moles of sample.

The accuracy of the calorimeter is normally 0.3% in the temperature range between 30 and 200° K. However, at the higher temperatures because of the uncertainty introduced by the presence of appreciable amounts of the sample in the filling line the accuracy may fall to 0.5%. Below 30° K. the error may rise to 1% at 20° K. and 5% at 12° K. due to uncertainty in the derivative of the resistance thermometer and the insensitivity of the standard thermocouples. Actually, the heat capacities below 20° K. deviate from a smooth curve by less than 1%. Runs made in duplicate over the entire temperature range above 55° K. reproduced the heat capacity curve with a precision well within the value stated above.

**The Solid–Liquid–Vapor Triple Point.**—The triple point was determined by observing the equilibrium temperature of the solid, liquid and vapor as increasing fractions of the sample were melted by the addition of measured quantities of energy. From these data and the heat of fusion, the amount of liquid soluble, solid insoluble impurity was found to be 0.16 mole per cent. for the first sample introduced into the calorimeter. After removal of this sample from the calorimeter and fractionation through the laboratory low-temperature column, the amount of liquid soluble, solid insoluble impurity was reduced to 0.08 mole per cent.

The solid–liquid–vapor triple point calculated for the pure compound was 173.09 ± 0.05° K. for the first sample and 173.11 ± 0.05° K. for the second. The average value was 173.10 ± 0.05° K. Values reported in the literature are 172.7° K. (−100.5° C.)[6] and 176.9° K. (−106.3° C.)[7].

**The Vapor Pressure.**—The vapor pressure of the liquid and solid hexafluoroethane was measured in the usual manner.[5a,b] The values listed are for international millimeters of mercury.

The data were fitted by equations derived by the method of least squares. The equation for the liquid is

$$\log_{10}P_{\text{mm.}} = -\frac{1125.329}{T} - 2.33917\log_{10}T - 0.001098587T + 14.22568 \quad (1)$$

and for the solid

$$\log_{10}P_{\text{mm.}} = -\frac{2227.0}{T} - 0.0915\log_{10}T - 0.05161T + 24.307 \quad (2)$$

Vapor pressure determinations made after one third of the sample had been distilled from the calorimeter indicated the presence of a volatile impurity which affected the pressures by an amount corresponding to 0.05° near the normal boiling point.

The observed vapor pressures differed, on the average, from those calculated from the formulas by ±1.4 mm. for the solid and ±0.02 mm. for the liquid. The vapor pressures observed by Ruff and Bretschneider[6] were 6 to 10 mm. higher for the solid and 5 mm. higher to 10 mm. lower for the liquid.

Because of the presence of a small amount of volatile impurity in the sample satisfactory equilibrium was not obtained in the vapor pressure of the solid even though the sample was allowed to stand for several hours before each measurement was made. However, the impurity did not noticeably disturb the equilibrium in the case of the liquid vapor pressures.

The triple point pressure was determined from observation of the equilibrium pressure simultaneously with the equilibrium temperature during the determination of the triple point and purity of the sample.

The equilibrium triple point pressure was calculated by adding to the pressure (extrapolated) at the 100% melted point the pressure rise for the sample from the 50% melted to the 100% melted point. The equilibrium triple point temperature was determined in an analogous manner.

The normal boiling point of hexafluoroethane calculated from the vapor pressure equation (1) is 194.87° K. (−78.29° C.). Values previously reported in the literature are −78.1° C. (195.1° K.; 0.0° C. = 273.16° K.)[6] and −79° to −78.6° C. (194.2 to 194.6° K.)[7]

**The Heat of Transition and Transition Temperature.**—The method used in measuring these properties in a similar case has been previously described.[5a] The data are summarized in Tables III and IV.

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[6] Ruff and Bretschneider, *Z. anorg. allgem. Chem.*, **210**, 173 (1933).

[7] Swarts, *Bull. soc. chim. Belg.*, **42**, 114 (1933).

TABLE III

THE HEAT OF TRANSITION OF HEXAFLUOROETHANE

Mol. wt. 138.02; 0.44183 mole; 0°C. = 273.16°K.; 1 cal. = 4.1833 int. joules.

| Temp. interval, °K. | Total cor. heat input cal./mole | $\int C_p dT$ cal./mole | $\Delta H$ transition cal./mole |
|---|---|---|---|
| 100.223–109.172 | 1179.9 | −287.8 | 892.1 |
| 99.946–107.543 | 1134.6 | −241.5 | 893.1 |
| 100.537–107.454 | 1114.6 | −221.2 | 893.4 |
| | | Average | 892.9 ± 1.7 |

TABLE IV

EQUILIBRIUM TEMPERATURES OF THE TRANSITION OF HEXAFLUOROETHANE

| % Transformed | T, °K. S-7 |
|---|---|
| 14.8 | 103.86 |
| 46.3 | 104.00 |
| 78.0 | 104.05 |
| (100.0) (extrapolated) | 104.10 |
| Average | 103.98 |

**The Heat of Fusion.**—The data for the heat of fusion are summarized in Table V. Because the heat capacity curve below the triple point did not have the usual change in shape resulting from the effect of premelting the heat capacity values were used with no premelting correction in applying the $\int C_p dT$ correction. The weight of the sample was corrected for vaporization into the filling line of the calorimeter.

TABLE V

THE HEAT OF FUSION OF HEXAFLUOROETHANE

Mol. wt. 138.02; 0.44183 mole; triple point 173.10 ± 0.05°K.; 0°C. = 273.16°K.; 1 cal. = 4.1833 int. joules.

| Temp. interval, °K. | Total cor. heat input, cal./mole | $\int C_p dT$ cal./mole | $\Delta H$, cal./mole |
|---|---|---|---|
| 168.471–174.406 | 894.0 | −252.0 | 642.0 |
| 167.333–174.603 | 948.6 | −307.4 | 641.2 |
| 168.543–173.806 | 863.6 | −221.8 | 641.8 |
| | | Average | 641.7 ± 1.5 |

**The Heat of Vaporization.**—The heat of vaporization was measured in the usual manner.[8] The results are listed in Table VI. The molal heat of vaporization at the normal boiling point calculated from the equation in the table is 3859.7 calories.

**The Vapor Density.**—The vapor density, determined in the usual manner,[8] is summarized in Table VII.

The molecular weight calculated by the method of limiting density is 138.26. The formula weight of the pure compound is 138.02.

The second virial coefficient at 298.16° K. in the last column of Table IX was calculated from the density data. The discrepancies noted in individual values indicate an uncertainty of about ±10%. The experimental coefficients are in good agreement with the value of −0.268 liter/mole calculated from the modified Berthelot equation of state with a value of 292.9° K. for $T_c$ as given by Swarts[7] and 29.9 atm. for $P_c$ as determined from $T_c$ by the empirical method of Meissner and Redding.[9a] Using the three and five constant equations of state, respectively, derived by Gouq Su[9b] we obtain −0.244 and −0.262.

TABLE VI

THE HEAT OF VAPORIZATION OF HEXAFLUOROETHANE

Mol. wt. 138.02; 0°C. = 273.16°K.; 1 cal. = 4.1833 int. joules.

| Moles vaporized | Mean temp. of vaporization, °K. | Total cor. heat input, cal./mole | $\int C_p dT$ cal./mole | $\Delta H$ at mean temp. of vaporization to real gas state cal./mole Obsd. | Calcd.[a] |
|---|---|---|---|---|---|
| 0.09578 | 179.96 | 4062.9 | −20.8 | 4042.1 | 4038.9 |
| .09499 | 180.22 | 4101.9 | −67.0 | 4034.9 | 4035.8 |
| .09496 | 188.30 | 3923.0 | +10.8 | 3933.8 | 3938.7 |
| .09556 | 190.05 | 3878.4 | +30.1 | 3908.5 | 3917.7 |
| .11406 | 194.87 | 3880.0 | −22.6 | 3857.4 | 3859.7 |
| .11436 | 194.90 | 3896.9 | −36.9 | 3860.0 | 3859.4 |
| .11169 | 195.10 | 3871.8 | −10.0 | 3861.8 | 3857.0 |
| .12946 | 195.21 | 3874.9 | −11.5 | 3863.4 | 3855.7 |

[a] Calculated from $\Delta H = 6201.1 - 12.015T$.

TABLE VII

THE VAPOR DENSITY OF HEXAFLUOROETHANE AT 298.16° K.

| Pressure, atm. | Density, g./cc. | $P/d$, obs. | $P/d$, calcd.[a] | $B$,[c] liters/mole |
|---|---|---|---|---|
| 0.99938 | 0.0056995 | 175.347 | 175.415 | −0.224 |
| .99066 | .0056464 | 175.449 | 175.430 | − .212 |
| .78270 | .0044522 | 175.801 | 175.758 | − .208 |
| .69896 | .0039740 | 175.883 | 175.890 | − .216 |
| .68887 | .0039144 | 175.934 | 175.905 | − .199 |
| .63925 | .0036331 | 175.952 | 175.984 | − .222 |
| .47859 | .0027161 | 176.205 | 176.236 | − .223 |
| .00000 | | 176.983[b] | | |

[a] Calculated from $P/d = 176.983 - 275.07d$. [b] Extrapolated. [c] $B = -0.268$ from Berthelot equation, $B = \left(\frac{9PV_gT_c}{128P_cT}\right)\left(1 - 6\frac{T_c^2}{T^2}\right)$ $T_c = 292.9$°K, $P_c = 29.9$ atm.

**The Second Virial Coefficients from Heats of Vaporization and Vapor Pressures.**—The second virial coefficients can be determined as a function of temperature from the heat of vaporization and vapor pressure data. The method has been described previously.[10] The data are summarized in Table VIII. In view of the agreement of the value of $B$ obtained above using the five constant equation of Gouq Su with that from the Berthelot equation, further tests of his equation were not made.

**The Entropy from Calorimetric Data.**—The calculations of the entropy for the liquid at the melting point, for the gas at a temperature of 176.61° K. at which its vapor pressure is $^1/_3$ atm., and for the gas at the normal boiling point are summarized in Tables IXa and IXb.

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[8] Aston, Sagenkahn, Szasz, Moessen and Zuhr, THIS JOURNAL, **66**, 1171 (1944).

[9] (a) Meissner and Redding, *Ind. Eng. Chem.*, **34**, 521 (1942); (b) Gouq Su, *ibid.*, **38**, 803 (1946).

[10] Aston, Fink, Bestul, Pace and Szasz, THIS JOURNAL, **68**, 52 (1946).

TABLE VIII

VOLUMES OF SATURATED VAPOR OF HEXAFLUOROETHANE FROM HEATS OF VAPORIZATION AND VAPOR PRESSURES

| $T$, °K. | $P$, atm. | $dP/dT$, mm./deg. | $\Delta H$, cal./mole | $V_l$, liters/mole | $V_g$, liters/mole | $B$, liters/mole This research | $B$, liters/mole Berthelot[a] |
|---|---|---|---|---|---|---|---|
| 179.96 | 0.41563 | 20.369 | 4042.1 | 0.083 | 34.694 | −0.837 | −0.822 |
| 180.22 | .42265 | 20.644 | 4034.9 | .083 | 34.132 | − .815 | − .819 |
| 188.30 | .69261 | 30.597 | 3933.8 | .084 | 21.515 | − .758 | − .738 |
| 190.05 | .76593 | 33.123 | 3908.5 | .085 | 19.572 | − .766 | − .721 |
| 194.87 | .99979 | 40.804 | 3857.4 | .086 | 15.312 | − .641 | − .678 |
| 194.90 | 1.00141 | 40.856 | 3860.0 | .086 | 15.310 | − .653 | − .678 |
| 195.10 | 1.01220 | 41.198 | 3861.8 | .086 | 15.166 | − .611 | − .676 |
| 195.21 | 1.01820 | 41.388 | 3863.4 | .086 | 15.095 | − .624 | − .675 |

[a] Calculated from Berthelot equation.

TABLE IXa

THE MOLAL ENTROPY OF LIQUID HEXAFLUOROETHANE

Mol. wt. 138.02; 0°C. = 273.16°K.

| | E. u. |
|---|---|
| 0.0–11.35°K., Debye extrapolation ($\theta$ = 87.5, 6 degrees of freedom) | 0.65 |
| 11.35–104.10°K., graphical | 21.65 |
| Transition, 892.9/103.98 | 8.59 |
| 104.10–173.10°K., graphical | 11.70 |
| Fusion, 641.7/173.10 | 3.70 |
| Entropy of liquid at solid–liquid–vapor triple point | 46.29 ± 0.14 |

TABLE IXb

THE MOLAL ENTROPY OF GASEOUS HEXAFLUOROETHANE AT CERTAIN TEMPERATURES

Mol. wt. 138.02; 0°C. = 273.16°K.

| | E. u. 176.61° K. | E. u. 194.87° K. |
|---|---|---|
| Liquid at triple point | 46.29 | 46.29 |
| 173.10-$T$°K., graphical | 0.62 | 3.59 |
| Vaporization at $T$°K. | 23.10 | 19.81 |
| Gas imperfection correction | 0.09 | 0.19 |
| Correction to 1 atm. | −2.18 | 0.00 |
| Entropy, ideal gas at $T$°K., 1 atm. | 67.92 ± 0.20 | 69.88 ± 0.20 |

**The Entropy from Molecular and Spectroscopic Data.**—The molecular data were taken from the available electron diffraction measurements for several fluorinated hydrocarbons including hexafluoroethane.[11] From these data, a C–F bond distance of 1.35 Å. and a C–C distance of 1.45 Å. were assumed. The $CF_3$ group was assumed to be tetrahedral.

The resulting moments were $I_x = 306.6 \times 10^{-40}$ g. cm.$^2$, $I_y = I_z = 435.6 \times 10^{-40}$ g. cm.$^2$ and $I_{\text{red.}} = I_x/4 = 76.7 \times 10^{-40}$ g. cm.$^2$ A symmetry number of six for the rigid molecule was used in the calculations.

The entropy due to translation and external rotation was calculated from

$$S_{t+r} = 4.575\,(3/2 \log M + 4 \log T + 1/2 \log I_xI_yI_z - \log 6) + 265.289 \quad (5)$$

where $I_xI_yI_z$ is the product of the principal moments of inertia.

The entropy contribution for the degree of freedom corresponding to the free rotation of the $CF_3$ group was obtained from

$$S_f = 4.575\,(1/2 \log T + 1/2 \log I_{\text{red.}}\ 10^{-40} - \log n) - 1.540 \quad (6)$$

in which $n = 3$ is used. Because of the presence of restricted rotation, the contribution $S_f$ was reduced by an amount $(S_f - S)$ as given by Pitzer's tables.[12]

The frequency assignment in Table X[13] is based on the infrared spectrum[14] of the gas obtained by Dr. J. Rud Nielsen of the University of Oklahoma Research Institute along with a value of $\nu_8$ obtained at the Naval Research Laboratory by Dr. Donald Smith, and a Raman spectrum[15] of the liquid obtained in the Spectroscopy Laboratory of The Pennsylvania State College under the direction of Dr. D. H. Rank.

TABLE X

THE FREQUENCY ASSIGNMENT FOR HEXAFLUOROETHANE, POINT GROUP $D_{3d}$

| Designation | Description | Species | Activity | Frequency obsd., cm.$^{-1}$ |
|---|---|---|---|---|
| $\nu_1$ | CF stretching | $A_{1g}$ | R. pol. | 1420 |
| $\nu_2$ | $CF_3$ deformation | $A_{1g}$ | R. pol. | 809 |
| $\nu_3$ | CC stretching | $A_{1g}$ | R. pol. | 349 |
| $\nu_4$ | Torsion | $A_{1u}$ | inactive | |
| $\nu_5$ | CF stretching | $A_{2u}$ | I. | 1116.9 |
| $\nu_6$ | $CF_3$ deformation | $A_{2u}$ | I. | 714.0 |
| $\nu_7$ | CF stretching | $E_u$ | I. | 1250.5 |
| $\nu_8$ | $CF_3$ deformation | $E_u$ | I. | 522.5 |
| $\nu_9$ | Bending | $E_u$ | I. | 216 |
| $\nu_{10}$ | CF stretching | $E_g$ | R. dep. | 1237 |
| $\nu_{11}$ | $CF_3$ deformation | $E_g$ | R. dep. | 620 |
| $\nu_{12}$ | Bending | $E_g$ | R. dep. | 380 |

Calculations of the entropy have been made with the barrier hindering the internal rotation adjusted to obtain the best agreement with experiment. The results at 176.61° K. and 194.87° K. are given in Table XI.

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(11) Brockway, Secrist and Lucht, Abstracts, Buffalo Meeting of American Chemical Society, September, 1942.

(12) Pitzer, *J. Chem. Phys.*, **5**, 469 (1937).

(13) Frequencies labeled according to Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., New York, N. Y., 1945, p. 343.

(14) From the paper by Nielsen, Richards and McMurry presented at the Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, June, 1947.

(15) Rank and Pace, *J. Chem. Phys.*, **15**, 39 (1947).

TABLE XI

THE ENTROPY OF HEXAFLUOROETHANE IN THE IDEAL GAS STATE AT CERTAIN TEMPERATURES FROM MOLECULAR AND SPECTROSCOPIC DATA

| | | |
|---|---|---|
| $T$, °K. | 176.61 | 194.87 |
| $V$, cal. per mole | 4350 | 4350 |
| $S_{t,r}$ | 60.79 | 61.58 |
| $S_f$, one degree of freedom | 5.73 | 5.83 |
| $S_v$ | 3.97 | 4.82 |
| $-(S_f - S)$ | −2.52 | −2.41 |
| Total | 67.97 | 69.82 |
| Calorimetric | 67.92 | 69.88 |

A potential barrier of 4350 calories per mole restricting the free rotation of the $CF_3$ group in hexafluoroethane gives the best fit between the theoretical and experimental entropy of the gas.

That a barrier exists is indicated by the appearance of only seven lines in the Raman spectrum. If rotation were free, the activity of the fundamental frequencies of species $E_u$, when added to that of $A_{1g}$ and $E_g$ which are already active in the Raman spectrum, should result in more lines in the Raman spectrum.

Heat capacity data on the gas would be helpful in confirming the value for the height of the barrier. Its present value indicates that potential barriers are not due to peculiar properties of hydrogen atoms.

**Acknowledgments.**—We wish to thank Dr. J. H. Simons of the Fluorine Laboratory for the calorimetric sample of high purity. We are indebted to Dr. D. H. Rank of the Spectroscopy Laboratory for the Raman Spectrum and to Dr. J. Rud Nielsen of the University of Oklahoma Research Institute for the infrared spectrum and the aid in its interpretation. The work was made possible by the financial aid provided by the Phillips Petroleum Fellowship.

## Summary

1. The heat capacity of hexafluoroethane has been measured from 11.2 to 195.0° K. as well as the density of the gas at 298.16° K.

2. The molal heat of transition of hexafluoroethane has been measured and the average transition temperature determined.

3. The molal heat of fusion together with the solid–liquid–vapor equilibrium temperature of the pure compound has been determined.

4. The vapor pressures of the solid and the liquid to the normal boiling point have been measured.

5. The molal heat of vaporization of hexafluoroethane has been determined for the liquid as a function of the temperature as well as the volumes of the saturated vapor.

6. From the experimental data, the entropy of the gas has been computed at the normal boiling point and at a temperature at which the vapor pressure of the liquid is one-third of an atmosphere.

7. The entropy of the gas has been calculated from a frequency assignment based on the infrared spectrum of the gas and a Raman spectrum of the liquid. A potential barrier of 4350 calories per mole hindering the mutual rotation of the $CF_3$ groups gives the best agreement between the calculated and the calorimetric entropy.

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[CONTRIBUTION FROM WESTERN REGIONAL RESEARCH LABORATORY[1]]

# Equilibrium Moisture and X-Ray Diffraction Investigations of Pectinic and Pectic Acids

BY K. J. PALMER, R. C. MERRILL AND M. BALLANTYNE

In order to obtain some insight into the influence of polar groups on the sorption[2] of water by hydrophilic polymers, the equilibrium moisture contents have been determined for a series of pectinic and pectic acids[3] which have methyl ester contents between 0.2 and 10.9%. This range in methyl ester content corresponds to a variation in free carboxyl groups in the polygalacturonic acid part of the sample of about 23 to 99% when the nonuronide content is taken into account. This series of samples, therefore, offers the opportunity of determining the influence of free and esterified carboxyl groups on the equilibrium moisture content at various relative humidities. There was also the possibility that the data could be used to deduce the amount of water associated with the free and esterified carboxyl groups. Unfortunately, this latter possibility is not realized because, as it turned out, the equilibrium moisture content was essentially independent of the degree of esterification.

It is now quite evident that in addition to the polar groups, the packing of the chains in the crystalline regions plays an important role in determining the equilibrium moisture content of many hydrophilic polymers. For this reason, X-ray diffraction photographs of powders of each sample

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[1] Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Not copyrighted.

[2] The term sorption is used in this paper to indicate the uptake of water; desorption the reverse of this process.

[3] The terms pectinic and pectic acid are used in this paper in accordance with the recommendation of the Committee for Revision of the Nomenclature of Pectic Substances, *Chem. Eng. News*, April 25, 609 (1944).