

JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

(Registered in U. S. Patent Office) (© Copyright, 1959, by the American Chemical Society)

VOLUME 81

MARCH 13, 1959

NUMBER 5

PHYSICAL AND INORGANIC CHEMISTRY

[CONTRIBUTION NO. 77 FROM THE THERMODYNAMICS LABORATORY, PETROLEUM EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

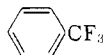
Benzotrifluoride: Chemical Thermodynamic Properties and Internal Rotation¹

By D. W. SCOTT, D. R. DOUSLIN, J. F. MESSERLY, S. S. TODD, I. A. HOSSENLOPP, T. C. KINCHELOE AND J. P. McCULLOUGH

RECEIVED OCTOBER 2, 1958

Thermodynamic and spectroscopic information was used to show that internal rotation in benzotrifluoride is nearly free. The chemical thermodynamic properties in the vapor state (0 to 1500°K.) were calculated by methods of statistical mechanics. Experimental studies provided the following information. Values of heat capacity for the solid (12°K. to the triple point), the liquid (triple point to 370°K.) and the vapor (363 to 500°K.); the triple point temperature; the heat of fusion; thermodynamic functions for the solid and liquid (0 to 370°K.); heat of vaporization (334 to 375°K.); second virial coefficient (334 to 500°K.); and vapor pressure (328 to 412°K.).

Systematic investigations of the thermodynamic properties and molecular structure of representative organic fluorine compounds are in progress in this Laboratory. Detailed thermodynamic studies of fluorobenzene were described in a previous publication.² This paper reports results of a similar investigation of benzotrifluoride (α, α, α -trifluorotoluene)



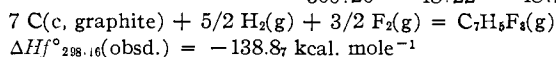
One of the reasons for studying benzotrifluoride was to compare the barrier hindering internal rotation of the CF₃ group with that of the CH₃ group. The height of the methyl barrier is known to be low if the barrier has sixfold symmetry. For toluene and *m*- and *p*-xylene,^{3,4} the values determined by thermodynamic methods have an upper limit of about 1000 cal. mole⁻¹ and are probably much lower. For nitromethane⁵ and CH₃BF₂,⁶ the barrier heights determined by the

more sensitive methods of microwave spectroscopy are only 6.00 and 13.77 cal. mole⁻¹, respectively. In contrast, for methyl rotations with only threefold symmetry, the barrier heights are in the kilocalorie mole⁻¹ range. Therefore, it was of interest to see if the sixfold barrier of the CF₃ group in benzotrifluoride also is low.

The experimental work consisted of low temperature calorimetry, vapor flow calorimetry and comparative ebulliometry. The detailed results are given later in the Experimental section. The results that are needed for discussing the barrier height and thermodynamic properties are collected in Table I.

TABLE I
OBSERVED AND CALCULATED THERMODYNAMIC PROPERTIES
OF BENZOTRIFLUORIDE

T, °K.	Entropy, S°, cal. deg. ⁻¹ mole ⁻¹		T, °K.	Heat capacity, C _p °, cal. deg. ⁻¹ mole ⁻¹	
	Obsd.	Calcd.		Obsd.	Calcd.
334.22	92.84	92.81	363.20	37.42	37.37
353.31	94.78	94.78	388.20	39.60	39.59
375.21	97.01	97.03	423.20	42.45	42.51
			458.20	45.22	45.23
			500.20	48.22	48.22



Barrier to Internal Rotation

Determining the barrier height required accounting for all degrees of freedom of the molecule. The external degrees of freedom (translation and rotation) could be handled in a straightforward way. It

(1) This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under contract No. CSO-680-37-4. Reproduction in whole or in part is permitted for any purpose of the United States Government.

(2) D. W. Scott, J. P. McCullough, W. D. Good, J. F. Messerly, R. E. Pennington, T. C. Kincheloe, I. A. Hossenlopp, D. R. Douslin and G. Waddington, *THIS JOURNAL*, **78**, 5457 (1956).

(3) K. S. Pitzer and D. W. Scott, *ibid.*, **65**, 803 (1943).

(4) W. J. Taylor, D. D. Wagman, M. G. Williams, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **37**, 95 (1946).

(5) E. Tannenbaum, R. D. Johnson, R. J. Myers and W. D. Gwinn, *J. Chem. Phys.*, **22**, 949 (1954).

(6) R. E. Naylor, Jr., and E. B. Wilson, Jr., *ibid.*, **26**, 1057 (1957).

was then necessary to account for the internal degrees of freedom (vibration and internal rotation) by evaluating the fundamental vibrational frequencies and the barrier height from spectroscopic and calorimetric data. Of the 38 vibrational fundamentals, 37 were evaluated from spectroscopic data alone. The remaining vibrational fundamental and the barrier height then were selected to give agreement between calculated and calorimetric values of entropy and heat capacity at the lower temperatures at which the effects of vibrational anharmonicity are small. (The values of heat capacity at the higher temperatures were available to evaluate two parameters of an empirical anharmonicity function.)

Translation and Rotation.—The contributions of translation and rotation to the entropy and heat capacity were computed by the standard formulas of statistical mechanics. As the structure of the benzotrifluoride molecule has not been determined experimentally, the moments of inertia were calculated for an assumed structure with bond distances and angles selected by analogy with related molecules. These parameters were: C—C 1.397₃ Å., C—H 1.084 Å., and all angles 120° for the phenyl group, as in benzene⁷; and C—F 1.335 Å., C—C 1.530 Å., and C—C—F angle 111° 02' for the C—CF₃ group, as in CH₃CF₃.⁸ For this assumed structure, the product of the three principal moments of inertia is 2.750×10^{-112} g.³ cm.⁶, and the reduced moment of inertia for internal rotation is 73.65×10^{-49} g. cm.².

Vibrational Fundamentals.—Before discussing the interpretation of the molecular spectra, it is well to anticipate the result of the next section, namely, that the internal rotation is nearly free. Therefore, the potential energy is nearly independent of the angle of internal rotation, and the normal vibrations effectively divide more than would be expected from the ordinary point group of the whole molecule, even for the most favorable orientation; that is, the effective molecular symmetry is C_{2v}, and the 38 genuine vibrations divide into 13a₁ + 13b₁ + 3a₂ + 9b₂.

The Raman and infrared spectra of benzotrifluoride have been studied carefully by Narasimham, Nielsen and Theimer.⁹ The assignment based on their spectroscopic data is listed in Table II. The one frequency inferred from calorimetric data, as discussed in the next section, is included for completeness. Narasimham, *et al.*, have treated in detail the interpretation of the molecular spectra in terms of the selection rules. Therefore, the discussion here will be limited to a few matters not treated in their paper.

In benzotrifluoride, the vibrations of the phenyl group are approximately those of a hypothetical molecule C₆H₅X with X a point mass equal to that of the CF₃ group (69 at. wt. units). Similarly, the vibrations of the CF₃ group are approximately those of a hypothetical molecule CF₃Y with Y a point mass equal to that of a phenyl group (77 at.

TABLE II
VIBRATIONAL FUNDAMENTALS OF BENZOTRIFLUORIDE AND COMPARISON WITH THOSE OF BROMOBENZENE AND TRIFLUOROBROMOMETHANE

Designation	C ₆ H ₅ CF ₃	C ₆ H ₅ Br	CF ₃ Br
6a	336	314	350
12	657	671	
1	1004	1001	
18a	1028	1020	
7a	1072	1070	
9a	1187	1176	
a ₁ 19a	1459	1472	
8a	1593	1578	
13	3022	3029	
2	3076	ca. 3050	
20a	3096	3067	
CF ₃ bend	770		761
C—F stretch	1328		1085
16a	(398) ^a	409	
a ₂ 10a	844	832	
17a	[970] ^b	[970] ^b	
18b	[169] ^c	254	
6b	618	614	
15	(1072)	ca. 1068	
9b	1161	1158	
3	1253	1264	
14	(1328)	1321	
b ₁ 19b	(1459)	1443	
8b	1614	1578	
7b	(3076)	3056	
20b	(3096)	3067	
CF ₃ rock	398		305
CF ₃ bend	(657)		550
C—F stretch	1179		1206
11	139	181	
16b	485	459	
4	695	681	
10b	(770)	736	
b ₂ 17b	923	904	
5	990	989	
CF ₃ rock	317		305
CF ₃ bend	596		550
C—F stretch	1152		1206

^a Parentheses denote frequencies used a second time.

^b Assumed same as in benzene. ^c Estimated from thermodynamic data.

wt. units). The masses of X and Y are not grossly different from the mass of a bromine atom (80 at. wt. units). Therefore the vibrational fundamentals of benzotrifluoride should be similar to those of bromobenzene¹⁰ and trifluorobromomethane.¹¹ The comparison in Table II shows the expected similarity.

Two weak Raman lines not assigned to fundamentals are observed at 235 and 583 cm.⁻¹. If these are the difference and sum combinations of 18b and 16a, then the frequencies are calculated to be 174 and 409 cm.⁻¹. The former is in good agreement with the frequency 169 cm.⁻¹ estimated from thermodynamic data for 18b. The latter is reasonable for vibration 16a, which appears with low intensity in the Raman spectra of monosubstituted benzenes at 406 ± 10 cm.⁻¹ if it is not ob-

(7) B. P. Stoicheff, *Can. J. Phys.*, **32**, 339 (1954).

(8) W. F. Edgell, G. B. Miller and J. W. Amy, *THIS JOURNAL*, **79**, 2391 (1957).

(9) N. A. Narasimham, J. Rud Nielsen and R. Theimer, *J. Chem. Phys.*, **27**, 740 (1957). This paper gives references to earlier work.

(10) D. H. Whiffen, *J. Chem. Soc.*, 1350 (1956).

(11) W. F. Edgell and C. E. May, *J. Chem. Phys.*, **22**, 1808 (1954).

TABLE III

THE MOLAL THERMODYNAMIC PROPERTIES OF BENZOTRIFLUORIDE ^a								
T, °K.	(F° - H° ₀)/T, cal. deg. ⁻¹	(H° - H° ₀)/T, cal. deg. ⁻¹	H° - H° ₀ , kcal.	S°, cal. deg. ⁻¹	C _p °, cal. deg. ⁻¹	ΔHf° ^b , kcal.	ΔFf° ^b , kcal.	log Kf ^b
0	0	0	0	0	0	-134.20	-134.20	Infinite
273.16	-69.71	16.72	4.569	86.43	28.68	-138.57	-119.42	95.54
298.16	-71.22	17.83	5.317	89.05	31.17	-138.87	-117.65	86.24
300	-71.33	17.92	5.374	89.24	31.35	-138.89	-117.52	85.61
400	-77.10	22.46	8.983	99.56	40.59	-139.91	-110.23	60.23
500	-82.59	26.88	13.44	109.47	48.20	-140.63	-102.72	44.90
600	-87.86	30.95	18.57	118.81	54.20	-141.14	-95.09	34.64
700	-92.91	34.62	24.24	127.53	58.94	-141.46	-87.39	27.28
800	-97.75	37.91	30.33	135.66	62.75	-141.65	-79.65	21.76
900	-102.39	40.85	36.76	143.24	65.86	-141.72	-71.90	17.46
1000	-106.84	43.48	43.48	150.32	68.45	-141.65	-64.14	14.02
1100	-111.09	45.85	50.44	156.95	70.63	-141.48	-56.41	11.21
1200	-115.18	48.00	57.60	163.17	72.48	-141.25	-48.69	8.87
1300	-119.10	49.94	64.92	169.04	74.06	-140.97	-40.99	6.89
1400	-122.86	51.72	72.40	174.58	75.44	-140.67	-33.30	5.20
1500	-126.49	53.34	80.01	179.82	76.63	-140.34	-25.64	3.74

^a To retain internal consistency, some values in this table are given to one more decimal place than is justified by the absolute accuracy. ^b The standard heat, standard free energy and common logarithm of the equilibrium constant for the formation of benzotrifluoride by the reaction: $7 \text{ C(c, graphite)} + 5/2 \text{ H}_2(\text{g}) + 3/2 \text{ F}_2(\text{g}) = \text{C}_7\text{H}_5\text{F}_3(\text{g})$.

scured by neighboring strong lines.¹² In the Raman spectrum of benzotrifluoride, this vibration is obscured by the ν_1 CF₃ rocking frequency. For vibration 3, the choice between the observed frequencies of 1238 and 1253 cm.⁻¹ was arbitrary, but the difference is unimportant thermodynamically. The assignment in Table II leads to satisfactory interpretations, as combinations or overtones, of the weak Raman lines and infrared bands observed by Narasimham, *et al.*, and not assigned as fundamental frequencies.

Barrier to Internal Rotation, Unobserved Frequency and Anharmonicity.—The best fit to the observed values of entropy and heat capacity was obtained with the height of the barrier to internal rotation taken as zero (free rotation). For free rotation, the unobserved frequency, ν_{18b} , was calculated to be about 170 cm.⁻¹. For a finite barrier height, it would be necessary to select a lower frequency to obtain agreement with the observed entropy, but the calculated heat capacity would then be greater than observed. With internal rotation taken to be free, the unobserved frequency, ν_{18b} , and two parameters of an empirical anharmonicity function,¹³ ν and Z , were evaluated by an iterative procedure with the results $\nu_{18b} = 169$ cm.⁻¹, $\nu = 850$ cm.⁻¹ and $Z = 0.68$ cal. deg.⁻¹ mole⁻¹. The contributions of anharmonicity are only 0.01 and 0.04 cal. deg.⁻¹ mole⁻¹ in S° and C_p° at 298.16°K. but increase to 1.02 and 1.61 cal. deg.⁻¹ mole⁻¹ in S° and C_p° at 1500°K.

The upper limit to the barrier height in benzotrifluoride, if allowance is made for possible experimental error in the calorimetric, spectroscopic and molecular-structure data, is at most a few hundred cal. mole⁻¹. A sixfold barrier for a CF₃ group, as for a methyl group, therefore is usually low.

The foregoing conclusion will not be altered if

(12) R. R. Randle and D. H. Whiffen in "Molecular Spectroscopy," Institute of Petroleum, 1955, p. 111.

(13) J. P. McCullough, H. L. Finke, W. N. Hubbard, W. D. Good, R. E. Pennington, J. F. Messerly and G. Waddington, *THIS JOURNAL*, **76**, 2661 (1954).

results of further spectroscopic studies should require reassignment of some frequencies below 500 cm.⁻¹. Any reasonable set of seven nearly classically excited vibrations that gives the same contribution to the entropy as the seven selected would also give nearly the same contribution to the heat capacity.

Thermodynamic Properties

Thermodynamic Functions.—The molecular structure parameters described in the preceding paragraphs were used to compute the values of the thermodynamic functions listed in columns 2–6 of Table III.¹⁴ Calculated values of S° and C_p° are compared with the experimental values in Table I. It is seen that the agreement is within 0.03% of S° and 0.15% of C_p° .

Heat, Free Energy and Equilibrium Constant of Formation.—The values of the thermodynamic functions, the value of $\Delta Hf^\circ_{298.16}$ (Table I) and values of the thermodynamic functions of C(graphite),¹⁵ H₂(g)¹⁵ and F₂(g)¹⁶ were used to compute the values of ΔHf° , ΔFf° and log Kf in columns 7–9 of Table III.

Experimental

The basic experimental techniques used for benzotrifluoride are as described in published descriptions of apparatus and methods for low temperature calorimetry,¹⁷ vapor flow calorimetry¹⁸ and comparative ebulliometry.¹⁹

(14) The vibrational contributions were computed at the Bureau of Mines Computation Laboratory, Pittsburgh, Pa.; the empirical anharmonicity contributions were computed by use of the table of R. E. Pennington and K. A. Kobe, *J. Chem. Phys.*, **22**, 1442 (1954).

(15) D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **34**, 143 (1945).

(16) W. H. Evans, T. R. Munson and D. D. Wagman, *ibid.*, **55**, 147 (1955).

(17) H. M. Huffman, *Chem. Revs.*, **40**, 1 (1947); H. M. Huffman, S. S. Todd and G. D. Oliver, *THIS JOURNAL*, **71**, 584 (1949); D. W. Scott, D. R. Doulin, M. E. Gross, G. D. Oliver and H. M. Huffman, *ibid.*, **74**, 883 (1952).

(18) G. Waddington, S. S. Todd and H. M. Huffman, *ibid.*, **69**, 22 (1947); J. P. McCullough, D. W. Scott, R. E. Pennington, I. A. Hossenlopp and G. Waddington, *ibid.*, **76**, 4791 (1954).

(19) G. Waddington, J. W. Knowlton, D. W. Scott, G. D. Oliver, S. S. Todd, W. N. Hubbard, J. C. Smith and H. M. Huffman, *ibid.*, **71**, 797 (1949).

Some modifications and improvements in the apparatus and methods actually used for benzotrifluoride have not been described in the literature. The reported values are based on a molecular weight of 146.110 (1951 International Atomic Weights)²⁰ and the relations: $0^\circ = 273.16^\circ\text{K.}$ and $1 \text{ cal.} = 4.1840 \text{ abs. j.} = 4.1833 \text{ int. j.}$ The 1951 values of the fundamental physical constants²¹ were used throughout this investigation. Measurements of temperature were made with platinum resistance thermometers calibrated in terms of the International Temperature Scale²² between 90 and 500°K. and the provisional scale²³ of the National Bureau of Standards between 11 and 90°K. All electrical and mass measurements were referred to standard devices calibrated at the National Bureau of Standards. The sample of benzotrifluoride used for this research has been described.²⁴

Heat Capacity in the Solid and Liquid States.—Low temperature calorimetric measurements were made with 63.249 g. of sample in a platinum calorimeter with helium (3 cm. pressure at room temperature) added to promote thermal equilibration. The observed values of heat capacity, $C_{\text{satd.}}$, are listed in Table IV. Above 30°K. , the accuracy uncer-

TABLE IV

THE MOLAL HEAT CAPACITY OF BENZOTRIFLUORIDE IN CAL. DEG.⁻¹

$T, ^\circ\text{K.}^a$	$C_{\text{satd.}}^b$	$T, ^\circ\text{K.}^a$	$C_{\text{satd.}}^b$	$T, ^\circ\text{K.}^a$	$C_{\text{satd.}}^b$
Crystals					
12.45	1.674	54.34	12.285	184.55	29.356
12.45	1.708	58.98	12.973	184.66	29.347
13.74	2.107	64.64	13.773	191.05	30.410
14.04	2.232	70.73	14.553	197.69	31.530
15.20	2.640	77.09	15.330	204.64	32.738 ^c
15.50	2.744	83.32	16.122	211.86	33.993 ^c
16.80	3.211	84.94	16.311	219.34	35.302 ^c
16.92	3.241	89.26	16.829	222.88	35.903 ^c
18.46	3.782	90.34	16.947	226.60	36.527 ^c
18.57	3.812	96.02	17.573	229.08	37.026 ^c
20.34	4.421	101.50	18.187	Liquid	
20.58	4.502	107.23	18.857	252.52	41.45
22.56	5.161	113.21	19.564	261.64	42.15
22.75	5.223	119.00	20.257	271.62	42.92
24.98	5.937	124.53	20.936	281.92	43.75
25.16	6.004	130.36	21.659	292.54	44.56
27.76	6.750	136.53	22.449	293.82	44.66
27.90	6.785	142.52	23.230	301.74	45.34
30.68	7.549	148.83	24.073	312.31	46.22
30.95	7.607	155.21	24.953	323.15	47.13
34.28	8.466	159.30	25.519	333.81	48.03
37.98	9.316	161.19	25.803	344.28	48.93
41.93	10.137	165.16	26.372	354.59	49.82
46.14	10.913	171.44	27.316	364.73	50.72
50.93	11.747	178.09	28.347		

^a T is the mean temperature of each heat capacity measurement. ^b $C_{\text{satd.}}$ is the heat capacity of the condensed phase under its own vapor pressure. ^c Not corrected for the effects of premelting caused by impurities.

tainty is estimated to be no greater than 0.2%. The heat capacity curve for the solid ($C_{\text{satd.}}$ vs. T) has the normal shape. The heat capacity curve for the liquid may be represented within 0.05% between the triple point and 370°K. by the empirical equation

$$C_{\text{satd.}}(\text{liq}) = 27.749 + 2.9306 \times 10^{-2}T + 1.1328 \times 10^{-4}T^2 - 5.7292 \times 10^{-8}T^3 \text{ cal. deg.}^{-1} \text{ mole}^{-1} \quad (1)$$

(20) E. Wichers, *THIS JOURNAL*, **74**, 2447 (1952).

(21) F. D. Rossini, F. T. Gucker, Jr., H. L. Johnston, L. Pauling and G. W. Vinal, *ibid.*, **74**, 2699 (1952).

(22) H. F. Stimson, *J. Research Natl. Bur. Standards*, **42**, 209 (1949).

(23) H. J. Hoge and F. G. Brickwedde, *ibid.*, **22**, 351 (1939).

(24) W. D. Good, D. W. Scott and G. Waddington, *J. Phys. Chem.*, **60**, 1080 (1956).

Heat of Fusion, Triple Point Temperature, Cryoscopic Constants and Purity of Sample.—Values of the heat of fusion, ΔH_m , from three determinations were 3293.1, 3293.2 and 3295.2 cal. mole⁻¹. The average with the uncertainty taken as the maximum deviation, both rounded to the nearest integer, is $3294 \pm 1 \text{ cal. mole}^{-1}$. The only literature value is that estimated by Sears and Hopke²⁵ from vapor pressure data, 2520 cal. mole⁻¹, which is seen to be grossly in error. The results of a study of the melting temperature, $T_{\text{obsd.}}$, as a function of fraction of total sample melted, F , are listed in Table V. Also listed in Table V are the values obtained for the triple point temperature, $T_{\text{T.P.}}$, the mole fraction of impurity in the sample, N_2^* , and the cryoscopic constants,²⁶ $A = \Delta H_m/RT_{\text{T.P.}}$ and $B = 1/T_{\text{T.P.}} - \Delta C_m/2\Delta H_m$, calculated from the observed values of $T_{\text{T.P.}}$, ΔH_m and ΔC_m (the heat capacity of the liquid less that of the solid, 1.25 cal. deg.⁻¹ mole⁻¹). The purity of the sample, 99.9987 mole %, is noteworthy. It is higher than ever observed previously in this Laboratory in melting point studies of more than 125 samples of organic compounds.

TABLE V

BENZOTRIFLUORIDE: MELTING POINT SUMMARY

Triple point temperature, $T_{\text{T.P.}} = 244.14 \pm 0.05^\circ\text{K.}$; mole fraction of impurity = $N_2^* = \Delta F(T_{\text{T.P.}} - T_{\text{obsd.}}) = 0.000013$; cryoscopic constants, $A = 0.02781 \text{ deg.}^{-1}$ and $B = 0.00391 \text{ deg.}^{-1}$.

Melted, %	$1/F$	$T_{\text{obsd.}}, ^\circ\text{K.}$	$T_{\text{graph}}, ^\circ\text{K.}^a$
11.21	8.921	244.1398	244.1398
26.14	3.826	244.1423	244.1421
50.98	1.962	244.1429	244.1430
70.86	1.411	244.1432	244.1433
90.75	1.102	244.1434	244.1434
100.00	1.000		244.1434
Pure	0.000		244.1439

^a Temperatures read from a straight line through a plot of $T_{\text{obsd.}}$ vs. $1/F$.

Thermodynamic Properties in the Solid and Liquid States.—Values of thermodynamic properties for the condensed phases were computed from the calorimetric data for selected temperatures between 10 and 370°K. The results are given in Table VI. The values at 10°K. were computed from a Debye function for 5.5 degrees of freedom with $\theta = 95.7^\circ$; these parameters were evaluated from the heat capacity data between 12 and 21°K. Corrections for the effects of premelting have been applied to the "smoothed" data recorded in Table VI.

Vapor Pressure.—Observed values of vapor pressure, determined by comparative ebulliometry with water as the reference substance, are listed in Table VII. The condensation temperature of the sample was 0.001° lower than the boiling temperature at 1 atm. pressure. The Antoine and Cox equations selected to represent the results are

$$\log p = 6.96911 - 1305.509/(t + 217.280) \quad (2)$$

$$\log(p/760) = A(1 - 375.208/T) \quad (3)$$

$$\log A = 0.856286 - 7.2760 \times 10^{-4}T + 6.9747 \times 10^{-7}T^2$$

In these equations, p is in mm., t is in $^\circ\text{C.}$ and T is in $^\circ\text{K.}$ Comparisons of the observed and calculated vapor pressure for both the Antoine and Cox equations are given in Table VII. The normal boiling point, calculated from either equation, is 102.05° (375.21°K.). In the temperature range over which the measurements overlap the earlier ones of Potter and Saylor,²⁷ the vapor pressure calculated by those workers' Antoine equation differs by no more than 0.12% from that observed in this research.

Heat of Vaporization, Vapor Heat Capacity and Effects of Gas Imperfection.—The experimental values of heat of vaporization and vapor heat capacity are given in Tables VIII and IX. The estimated accuracy uncertainty of the values of ΔH_v and C_p° are 0.1 and 0.2%, respectively.

(25) G. W. Sears and E. R. Hopke, *J. Phys. Colloid Chem.*, **52**, 1137 (1948).

(26) A. R. Glasgow, A. J. Streiff and F. D. Rossini, *ibid.*, **35**, 355 (1945).

(27) J. C. Potter and J. H. Saylor, *THIS JOURNAL*, **73**, 90 (1951), who give references to earlier work.

TABLE X

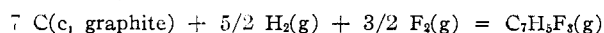
THE MOLAL ENTROPY OF BENZOTRIFLUORIDE IN CAL. DEG. ⁻¹

<i>T</i> , °K.	334.22	353.31	375.21
<i>S</i> _{std} (liq.)	70.21 ^a	72.92 ^a	75.97 ^b
$\Delta H_v/T$	25.27	23.07	20.79
<i>S</i> (ideal) - <i>S</i> (real) ^c	0.11	0.17	0.25
Compression, <i>R</i> ln <i>P</i> ^c	-2.75	-1.38	0.00
<i>S</i> ^o (obsd.)(±0.20)	92.84	94.78	97.01

^a Interpolated from Table VI. ^b Extrapolated by use of eq. 1. ^c Calculated by use of eq. 3 and 5.

The heat of vaporization was calculated to be $\Delta H_{v298.15} = 8.96$ kcal. mole⁻¹ from a thermodynamic network that utilized the thermodynamic functions of Table III. Alternate calculations by extrapolation of eq. 4 and by use of the

Clapeyron equation with eq. 3 and 5 gave results that agreed within 0.02 kcal. mole⁻¹. The standard heat of vaporization was calculated to be $\Delta H_{v298.15} = 8.98$ kcal. mole⁻¹ from eq. 3 and 5 and the relationship $\Delta H_v^o = \Delta H_v - BRT/V + (dB/dT)RT^2/V$. This value was used to obtain the standard heat of formation of the vapor, $\Delta H_f^o_{298.15} = -138.87$ kcal. mole⁻¹ for the reaction



Acknowledgment.—The authors are grateful for the cooperation of R. W. Smith of the Computation Laboratory at the Bureau of Mines Pittsburgh Station in programming and performing calculations of the harmonic oscillator contributions to the thermodynamic functions.

BARTLESVILLE, OKLA.

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF FLORIDA]

The Novel Synthesis of (PNF₂)₃ and (PNF₂)₄ from P₃N₅¹

By T. J. MAO, R. D. DRESDNER AND J. A. YOUNG

RECEIVED OCTOBER 14, 1958

Both (PNF₂)₃ and (PNF₂)₄ can be prepared at 700° by treating P₃N₅ with a source of fluorine, in this case CF₃SF₅ or NF₃. Infrared assignments of these two phosphonitrilic fluorides are presented.

Both the trimer and tetramer of PNF₂ have recently been reported,² having been prepared by treating the corresponding chlorides with KSO₂F. Prior attempts to prepare the fluorides from the chlorides using the so-called more conventional fluorine exchange agents such as PbF₂ were only partially successful in that the trimer chloride gave P₄N₄Cl₂F₆ and (PNCIF)₄.^{3,4} In this work, quantities of (PNF₂)₃ and (PNF₂)₄ were obtained in the same reaction when P₃N₅ reacted with either CF₃SF₅ or NF₃. At temperatures 100 to 150° below 700° the conversions to the phosphonitrilic fluorides are vanishingly small and at temperatures 100° above 700° the conversion drops off slightly and the products are contaminated.

Preliminary experiments on P₃N₅ alone confirmed the fact that N₂ is evolved when P₃N₅ is heated above 550° *in vacuo*. A similar phenomenon was observed by Moureau and Rocquet.⁵ They also reported the existence of pure PN in a red (α) form and a yellow (β) form. Other workers⁶ have suggested that PN probably exists as a monomeric vapor at elevated temperatures.

Experimental

Materials.—CF₃SF₅ was prepared electrochemically from methyl sulfide in anhydrous HF.⁷ The samples used had a purity of not less than 99% by wt. as established by vapor phase chromatographic analysis and boiled at -20.5°.

(1) This work was supported by the Chemistry Branch, Office of Naval Research. Part or all of this paper may be reproduced for purposes of the United States Government.

(2) F. Seel and J. Langer, *Angew. Chem.*, **68**, 461 (1956).

(3) O. Schmitz-Dumont and H. Kulens, *Z. anorg. allgem. Chem.*, **238**, 189 (1938).

(4) O. Schmitz-Dumont and A. Braschos, *ibid.*, **243**, 113 (1939).

(5) H. Moureau and P. Rocquet, *Bull. soc. chim.*, [V], **3**, 1801 (1936).

(6) E. O. Hoffman, *et al.*, *THIS JOURNAL*, **76**, 6239 (1954); H. Moureau, B. Rosen and G. Wetloff, *Compt. rend.*, **209**, 207 (1939).

(7) A. F. Clifford, H. K. El-Shamy, H. J. Emeleus and R. N. Haszeldine, *J. Chem. Soc.*, 2372 (1953); R. D. Dresdner, *THIS JOURNAL*, **77**, 6633 (1955).

The NF₃ was prepared electrochemically from pyridine in anhydrous HF.⁸ It was freed of acid contaminants by passage through concd. NaOH and of OF₂ by passage through KI solution and a further wash with base to remove any entrained iodine. The gas was dried over P₂O₅ and degassed at considerable length until the vapor pressure of a recondensed sample was less than 2 mm. at liquid air temperatures. Chromatographically, it showed a minor impurity of about 1% by wt. which was presumed to be CF₄. The mol. wt. was 71-72.

P₃N₅ was purchased from Chemicals Procurement Co. (New York). Its purity was questionable as Kjeldahl nitrogen analysis was only 38.5% (theo. 42.9). However, except for the heat treatment noted below, it was used as shipped.

Equipment.—Vapor phase chromatographic analyses were performed on a Perkin-Elmer Fractometer, Model 154. The developer gas was always N₂. The stationary phases used will be indicated at the proper place in this discussion.

Infrared spectra were performed on a Model 21 Beckman Spectroscope using a 5 cm. gas cell with NaCl windows.

Reaction Procedure.—In general, P₃N₅ powder (coarse and fine) was packed snugly into a small volume of a one-inch i.d. nickel tube (0.065" wall). A short tube furnace about 4" long heated the portion of the tube in which the P₃N₅ was packed. The tube was adapted so that the gaseous reagents could be run from a small containing cylinder into the reaction vessel. Flow rates were controlled with a needle valve and measured with a capillary flow meter. Products were collected in cold traps protected from the moisture in the air by drying tubes. The procedure was to purge the system with dried nitrogen until all the air was replaced. Then the system was heated to a predetermined reaction temperature under a positive N₂ flow. The N₂ was shut off and gaseous reagent was slowly let into the system at some predetermined rate. When the run was completed nitrogen again was passed through the system to purge it of products, which were collected.

Reactions.—Numerous trials were made to find some optimum reaction condition. In an initial run at 850°, 30 g. of CF₃SF₅ was passed over excess P₃N₅ at the rate of 10 g./hr. The liquid air condensate was found to contain SF₄, C₂F₆ and other low boiling gases which were acidic. Six grams of material boiling between 54 and 86° remained behind when the low boiling fraction was removed. It had a mol. wt. of from 259 to 297 and hydrolyzed in water. The

(8) J. H. Simons and co-workers, *J. Electrochem. Soc.*, **95**, 47 (1949).