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Fluorobenzene: Thermodynamic Properties in the Solid, Liquid and Vapor States; A Revised Vibrational Assignment[1]

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Studies of fluorobenzene by low temperature calorimetry, comparative ebulliometry, flow calorimetry and combustion calorimetry led to values of the standard entropy, heat capacity and heat of formation of the vapor. A revised vibrational assignment, consistent with the calorimetric values of vapor heat capacity, was made and used with other molecular structure data to compute values of thermodynamic functions at selected temperatures between 0 and 1500°K. Values of the heat, free energy and logarithm of the equilibrium constant of formation were computed for the same selected temperatures. The experimental studies provided the following information. Values of the heat capacity for the solid (14-225°K.), the liquid [$C_{satd} = 39.496 - 0.13777\ T + 5.7113 \times 10^{-4}\ T^2 - 5.3644 \times 10^{-7}\ T^3$ cal. deg.$^{-1}$ mole^{-1} (230-350°K.)] and the vapor [$C_p^\circ = -6.581 + 0.11589\ T - 6.122 \times 10^{-5}\ T^2$ cal. deg.$^{-1}$ mole^{-1} (343-500°K.)]; the heat of fusion [2702.0 cal. mole^{-1}] at the triple point [230.94 ± 0.05°K.]; the entropy of the liquid at 298.16°K. [$S_{satd} = 49.22$ cal. deg.$^{-1}$ mole^{-1}]; the heat of vaporization [$\Delta Hv = 10689 - 3.850\ T - 1.448 \times 10^{-2}\ T^2$ cal. mole^{-1} (318-382°K.)]; the second virial coefficient in the equation of state, $PV = RT(1 + B/V)$, [$B = 212 - 158.6 \exp (750/T)$ cc. mole^{-1} (318-500°K.)]; the vapor pressure [$\log_{10} p$(mm.) $= 6.95208 - 1248.083/(t + 221.827)$, (39-120°)]; and the standard heat of formation of liquid fluorobenzene at 298.16°K. [-34.7_5 kcal. mole^{-1}].

Introduction

The chemical thermodynamics of organic fluorine compounds has received increasing attention in recent years. However, most investigations have been concerned with a single thermodynamic property or a limited set of properties. There are still very few organic fluorine compounds for which enough data are available to calculate the heat and free energy of formation at a single temperature. There are even fewer compounds for which these properties can be calculated over a wide temperature range. Before a really useful body of chemical thermodynamic data can exist for important classes of organic fluorine compounds, the many gaps in the data now at hand must be filled in. Also, compounds that are studied for the first time should be studied comprehensively enough to avoid areas of ignorance that will need to be filled in later.

This paper reports a comprehensive study of fluorobenzene, the simplest member of the class of

aromatic fluorine compounds. Some thermodynamic properties of fluorobenzene had been studied previously,[2] but not with the accuracy attainable by present-day methods. In this research, experimental studies were made by the methods of low temperature calorimetry, comparative ebulliometry, flow calorimetry and combustion calorimetry. The detailed results of these studies are given later in the Experimental section. However, the most significant results were values of the entropy, heat capacity and heat of formation of fluorobenzene vapor, as given in Table I. The values of entropy and heat capacity were used as a check on the calculation of thermodynamic functions by the methods of statistical mechanics. The experimental value of the heat of formation and the calculated values of the thermodynamic functions were then used to calculate the heat, free energy and logarithm of the equilibrium constant of formation, over the entire temperature range for

(2) Low temperature thermal properties, D. R. Stull, THIS JOURNAL, **59**, 2726 (1937); vapor pressure, D. R. Stull, *Ind. Eng. Chem.*, **39**, 517 (1947), and references cited therein; vapor heat capacity, J. B. Montgomery and T. DeVries, THIS JOURNAL, **64**, 2375 (1942); and heat of combustion, F. Swarts, *J. chim. phys.*, **17**, 3 (1919).

which values of these properties are likely to be needed. These calculations of the thermodynamic properties are discussed in detail in the next section.

TABLE I

OBSERVED AND CALCULATED THERMODYNAMIC PROPERTIES OF FLUOROBENZENE VAPOR

	Entropy, $S°$, cal. deg.$^{-1}$ mole^{-1}			Heat capacity, $C°$, cal. deg.$^{-1}$ mole^{-1}	
T, °K.	Obsd.	Calcd.	T, °K.	Obsd.	Calcd.
318.40	73.99	73.86	343.20	25.98	25.97
336.78	75.37	75.26	364.20	27.52	27.50
357.89	76.96	76.85	389.20	29.24	29.25
382.37	78.78	78.70	426.20	31.68	31.71
			463.20	33.98	33.97
			500.20	36.06	36.05

Heat of formation, $\Delta Hf°_{298.16}$ (obsd.): -26.48 kcal. mole^{-1}

Calculation of Thermodynamic Properties

The Vibrational Assignment.—The thermodynamic functions of fluorobenzene were computed by appropriate methods of statistical mechanics. The vibrational assignment used for this purpose was based on the careful study of the Raman and infrared spectra by Smith, Ferguson, Hudson and Nielsen.[3] However, it was necessary to revise the complete vibrational assignment proposed by these workers in the light of the calorimetric vapor heat capacity data of this research. The revised assignment differs from that of Smith, et al., in the frequencies assigned to fundamental vibrations 9b (species b₁), 5(species b₂) and 16a, 10a and 17a (species a₂).[4] Only the assignment of these five frequencies will be discussed in detail here. The revised assignments of four of these are based on regularities in the spectra of monosubstituted benzenes as shown in Table II. All of the monosubstituted benzenes exhibit Raman lines or infrared bands near 405, 830, 990 and 1155 cm.$^{-1}$ that are quite certainly associated with vibrations 16a, 10a, 5 and 9b, respectively. It is noteworthy that vibration 10 in benzene and 10a in the monosubstituted derivatives appear with moderate intensity in the infrared spectra of the liquids, although forbidden by the simple vapor phase selection rules. In the spectra of fluorobenzene the Raman line of 16a is not resolved from that of 18b (405 cm.$^{-1}$), and neither the Raman line nor the infrared band of 9b is resolved from that of 9a (1157 cm.$^{-1}$). Vibrations 16a and 9b of fluorobenzene are therefore assigned the same frequencies as vibrations 18b and 9a, respectively. The fifth reassignment is for vibration 17a, which is inactive in benzene vapor, but for which a frequency of about 970 cm.$^{-1}$ has been assigned by indirect means. (This assignment is supported by the infrared spectrum of crystalline benzene.[5]) The form of vibration 17a does not change in the monosubstituted derivatives, so it would not be expected to be observed spectroscopically for the vapor or liquid states, although formally it is permitted in the Raman

(3) D. C. Smith, E. E. Ferguson, R. L. Hudson and J. Rud Nielsen, J. Chem. Phys., **21**, 1475 (1953).

(4) Numbering scheme of E. B. Wilson, Jr., Phys. Rev., **45**, 706 (1934). See also K. S. Pitzer and D. W. Scott, THIS JOURNAL, **65**, 803 (1943), Fig. 6.

(5) R. D. Mair and D. F. Hornig, J. Chem. Phys., **17**, 1236 (1949).

TABLE II

REGULARITIES IN SPECTRA OF MONOSUBSTITUTED BENZENES[a]

Vibration	16a	10a	5	9b
C_6H_6	405	849	985	1178
	R	R, (IR)	Inactive	R
C_6H_5D	405	850	995	1158
$C_6H_5CH_3$	405	843	993	1156
$C_6H_5NH_2$	415	833	988	1154
C_6H_5OH	412	829	990	1152
C_6H_5F	..[b]	826	997	..[b]
C_6H_5SH	..[b]	834	991	1158
C_6H_5Cl	..[b]	832	987	1157
C_6H_5Br	409	832	990	1158
C_6H_5I	398	838	988	1158
	R	R, (IR)	R, IR	R, IR

[a] Values mostly from N. Herzfeld, C. K. Ingold and H. G. Poole, J. Chem. Soc., 316 (1946), and K. W. F. Kohlrausch and H. Wittek, Monatsh., **74**, 1 (1941).   [b] Interference from a frequency of another species.

spectrum by the simple selection rules. By the same token, the frequency in a monosubstituted derivative would not be expected to differ much from that in benzene itself, and it is reasonable to use the value 970 cm.$^{-1}$ for fluorobenzene also. The complete vibrational assignment used for thermodynamic calculations is given in Table III. Figure 1 shows that this revised assignment is consistent with the calorimetric values of vapor heat capacity, whereas the original assignment of Smith, et al., is not. The observed frequencies of 818, 874 and ca. 955 cm.$^{-1}$ assigned as fundamentals by Smith, et al., may be interpreted as $2 \times 405 = 810$ (A₁ or B₂) or $1220 - 405 = 815$ (B₁ or A₂), $242 + 242 + 405 = 889$ (B₁ or A₂) or $1499 - 614 = 885$ (B₁) and $1460 - 500 = 960$ (A₂). The interpretation of all other weak Raman lines and infrared bands as combinations or overtones is as satisfactory with the present assignment as with the original assignment of Smith, et al.

NOTE ADDED IN PROOF.—A recent paper by D. H. Whiffen [J. Chem. Soc., 1350 (1956)] gives a vibrational assignment for fluorobenzene that differs only in minor details from that of Table III and gives essentially the same harmonic oscillator contributions to the thermodynamic function.

TABLE III

THE FUNDAMENTAL VIBRATIONAL FREQUENCIES FOR FLUOROBENZENE, CM.$^{-1}$

Species a₁		Species b₁		Species a₂		Species b₂	
6a	519	18b	405	16a	405[a]	11	242
12	808	6b	614	10a	826	16b	500
1	1008	15	1066	17a	970[b]	4	685
18a	1022	9b	1157[a]			10b	754
9a	1157	3	1236			17b	894
7a	1220	14	1323			5	997
19a	1499	19b	1460				
8a	1596	8b	1603				
13	3044	7b	3058				
2	3067	20b	3091				
20a	3101						

[a] Frequency used a second time.   [b] Assumed same as in benzene.

Now that a vibrational assignment for fluorobenzene has been confirmed by accurate calorimetric values of vapor heat capacity, vibrational

assignments may be made for any of the other monosubstituted benzenes by simple analogy with the well-established one for fluorobenzene. The application of this principle to benzenethiol is illustrated in the paper that follows this one.[6]

The Moments of Inertia and Anharmonicity.— The moments of inertia of the fluorobenzene molecule have been determined by McCulloh and Pollnow from microwave studies.[7] The product of the principal moments of inertia is 2.296×10^{-113} g.^{3} cm.^{6} The symmetry number of over-all rotation is 2.

The contributions of anharmonicity to the thermodynamic functions were treated by the empirical method described in an earlier publication from this Laboratory.[8] The parameters, $Z = 0.154$ cal. deg.$^{-1}$ mole^{-1} and $\nu = 550$ cm.$^{-1}$, were selected to give the best fit to the calorimetric values of vapor heat capacity.

The Thermodynamic Functions.— The vibrational assignment, product of the principal moments of inertia and anharmonicity parameters described in the preceding paragraphs were used to compute values of the following thermodynamic functions at selected temperatures from 0 to 1500°K.: $(F° - H_0°)/T$, $(H° - H_0°)/T$, $H° - H_0°$, $S°$ and $C_p°$.[9] The computed values are listed in columns 2–6 of Table IV. The contributions of anharmonicity to the computed functions are small at the lower temperatures, 0.01 and 0.05 cal. deg.$^{-1}$ mole^{-1} in $S°$ and $C_p°$ at 298.16°K., but increase to 0.43 and 0.58 cal. deg.$^{-1}$ mole^{-1} in $S°$ and $C_p°$ at 1500°K.

Calculated values of $S°$ and $C_p°$ are compared with the experimental values in Table I. It may be seen that the values of $C_p°$ agree within 0.1% over a 157° temperature range. The differences in the values of $S°$, 0.08 to 0.14 cal. deg.$^{-1}$ mole^{-1} are well within the combined uncertainties of the observed and calculated values. It should be noted that the observed and calculated values of $S°$ are strictly independent; that is, the experimental values of entropy were not used to evaluate any parameters used in the calculation of thermodynamic functions. The agreement of the observed and calculated values therefore is a *bona fide* check of the third law of thermodynamics.

The Heat, Free Energy and Equilibrium Constant of Formation.— The calculated values of the thermodynamic functions, the experimental value of $\Delta Hf°_{298.16}$ (Table I) and values of the thermodynamic functions of C(graphite),[10] $H_2(g)$[10] and
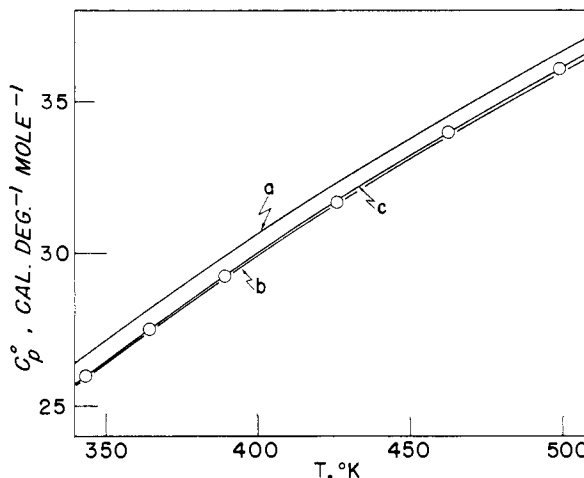

Fig. 1.—The vapor heat capacity of fluorobenzene: circles, experimental value; curves, calculated, a, with vibrational assignment of Smith, *et al.*, harmonic oscillator approximation; b, with vibrational assignment of this research, harmonic oscillator approximation; c, with vibrational assignment of this research and empirical correction for anharmonicity.

$F_2(g)$[11] were used to compute values of $\Delta Hf°$, $\Delta Ff°$ and $\log_{10}Kf$ at selected temperatures from 0 to 1500°K. The computed values are listed in columns 7–9 of Table IV.

Experimental

The 1951 International Atomic Weights[12] and the 1951 values of the fundamental physical constants[13] were used in all calculations described in this paper. The reported values are based on a molecular weight of 96.100 for fluorobenzene and the following relations: 0° = 273.16°K. and 1 cal. = 4.1840 abs. j. = 4.1833 int. j. Measurements of temperature were made with platinum resistance thermometers calibrated in terms of the International Temperature Scale[14] between 90 and 500°K. and the provisional scale[15] of the National Bureau of Standards between 11 and 90°K. Measurements of mass, energy and temperature were made in terms of standard devices calibrated at the National Bureau of Standards. Density data used for liquid fluorobenzene were from unpublished determinations at the Laramie, Wyoming, station of the Bureau of Mines, which also included determinations of viscosity, surface tension and refractive index, all with the same highly purified sample used in this research.

The Material.— Fluorobenzene, supplied by the Illinois State Geological Survey Division through the courtesy of Dr. G. C. Finger, was distilled in an efficient fractionating column by the Chemistry and Refining Branch of this station. Selected fractions were combined to give the sample used for low temperature calorimetry, comparative ebulliometry and combustion calorimetry. This sample had a purity of 99.95 ± 0.03 mole %, as determined by a calorimetric study of melting point as a function of fraction melted. For flow calorimetry, which required a larger volume of material, a composite of other fractions from the plateau of the same distillation was used. The purity of this second sample, as determined by the time–temperature freezing point method, was 99.94 ± 0.05 mole %. Before use in any of the experimental determinations, the fluorobenzene samples were dried by passage of the vapor through anhydrous magnesium perchlorate.

(6) D. W. Scott, J. P. McCullough, W. N. Hubbard, J. F. Messerly, I. A. Hossenlopp, F. R. Frow and Guy Waddington, THIS JOURNAL, **78**, 5463 (1956).

(7) K. E. McCulloh and G. F. Pollnow, *J. Chem. Phys.*, **22**, 1144 (1954).

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

(9) The vibrational contributions were computed by use of the tables of H. L. Johnston, L. Savedoff and J. Belzer, "Contributions to the Thermodynamic Functions by a Planck–Einstein Oscillator in One Degree of Freedom," Office of Naval Research, Department of the Navy, Washington, D. C., July, 1949; the empirical anharmonicity contributions were computed by use of the tables of R. E. Pennington and K. A. Kobe, *J. Chem. Phys.*, **22**, 1442 (1954).

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

(11) "Selected Values of Chemical Thermodynamic Properties," Series III, Natl. Bur. Standards, Table issued March 1, 1954.

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

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

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

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

TABLE IV

THE MOLAL THERMODYNAMIC PROPERTIES OF FLUOROBENZENE[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.$^{-1}$	$\Delta Hf°$,[b] kcal.	$\Delta Ff°$,[b] kcal.	$\log_{10} Kf$[b]
0	0	0	0	0	0	-22.72	-22.72	Infinite
273.16	-58.24	12.19	3.330	70.43	20.65	-26.21	-16.03	12.82
298.16	-59.35	12.97	3.868	72.33	22.57	-26.48	-15.12	11.08
300	-59.43	13.03	3.910	72.47	22.72	-26.50	-15.05	10.97
400	-63.64	16.38	6.554	80.02	29.99	-27.46	-11.09	6.06
500	-67.66	19.73	9.866	87.39	36.04	-28.21	- 6.90	3.02
600	-71.54	22.87	13.72	94.40	40.86	-28.78	- 2.59	0.94
700	-75.28	25.72	18.01	101.00	44.70	-29.22	1.82	-0.57
800	-78.89	28.30	22.64	107.19	47.83	-29.54	6.27	-1.71
900	-82.35	30.61	27.55	112.96	50.42	-29.77	10.77	-2.61
1000	-85.69	32.70	32.70	118.39	52.58	-29.88	15.28	-3.34
1100	-88.90	34.60	38.06	123.50	54.42	-29.91	19.79	-3.93
1200	-91.98	36.32	43.58	128.30	55.99	-29.88	24.30	-4.43
1300	-94.95	37.88	49.25	132.83	57.32	-29.83	28.82	-4.85
1400	-97.81	39.31	55.04	137.12	58.48	-29.75	33.32	-5.20
1500	-100.57	40.63	60.94	141.20	59.49	-29.64	37.81	-5.51

[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 fluorobenzene by the reaction: $6C(graphite) + 5/2H_2(g) + 1/2F_2(g) = C_6H_5F(g)$.

The Heat Capacity in the Solid and Liquid States.—The low temperature thermal studies (14 to 350°K.) were made in an adiabatic calorimeter system similar to that described in previous publications.[16] A platinum calorimeter with internal heat-distributing disks of gold was used. The calorimeter contained 0.54912 mole of compound. About 40 mm. helium pressure, at room temperature, was left in the calorimeter to promote thermal equilibration at low temperatures.

The observed values of the heat capacity at saturation pressure, C_{satd}, are listed in Table V. No adjustment for the effects of hetero-phase premelting has been applied to these values. The temperature increments used in the measurements (about 10% of the absolute temperature below 60°K. and 6 to 11° above 60°K.) were small enough that corrections for non-linear variation of heat capacity with temperature were unnecessary. As there was no detectable influence of thermal history on the measured values of heat capacity, the chronological sequence of the measurements is not indicated in Table V. Generally, the precision of the results was within ±0.1%; it is estimated that above 30°K. the accuracy uncertainty is not greater than 0.2%. The heat capacity of crystalline fluorobenzene varies regularly with temperature over the whole range studied. However, immediately below the melting point, it increases unusually rapidly with increasing temperature; this rapid increase cannot be attributed to hetero-phase premelting. The heat capacity of liquid fluorobenzene may be represented by the empirical equation

$$C_{satd}(liq) = 39.496 - 0.13777T + 5.7113 \times 10^{-4} T^2$$
$$- 5.3644 \times 10^{-7} T^3 \quad cal. deg.^{-1} mole^{-1} \quad (1)$$

which reproduces the observed values between the melting point and 350°K. with a maximum deviation of 0.05%.

The Heat of Fusion.—Measurements were made of the enthalpy change over a finite temperature interval that included the triple point. Subtraction of the energy absorbed non-isothermally by the crystals and liquid gave the heat of fusion. Corrections for the effects of premelting were applied. Three determinations yielded an average value for the heat of fusion, $\Delta H_{fusion} = 2702.0 \pm 0.2$ cal. mole^{-1}; the indicated uncertainty is the maximum deviation from the mean.

The Triple Point Temperature, Cryoscopic Constants and Sample Purity.—For determination of the triple point temperature and sample purity, a study of the equilibrium melting temperature, T_{obsd}, as a function of fraction of total sample melted, F, was made by the procedure outlined in an

TABLE V

THE MOLAL HEAT CAPACITY OF FLUOROBENZENE IN CAL. DEG.$^{-1}$

T, °K.[a]	C_{satd}[b]	T, °K.[a]	C_{satd}[b]	T, °K.[a]	C_{satd}[b]
Crystals		74.80	11.032	212.37	25.173[c]
		80.42	11.487	216.23	26.111[c]
14.63	1.506	86.31	11.959	219.21	26.961[c]
15.87	1.797	92.88	12.434	220.69	27.408[c]
16.93	2.060	99.60	12.913	222.38	28.150[c]
17.25	2.138	106.08	13.372	225.20	29.877[c]
18.75	2.522	112.35	13.840		
18.86	2.551	118.42	14.301	Liquid	
20.61	2.996	124.32	14.767		
20.70	3.012	130.61	15.272	235.13	31.71
22.64	3.507	137.27	15.823	240.86	31.95
22.81	3.557	143.75	16.379	242.40	32.02
25.49	4.219	150.05	16.938	248.09	32.29
28.14	4.850	156.67	17.548	248.95	32.33
28.46	4.917	163.61	18.231	257.11	32.72
31.70	5.622	170.34	18.916	267.37	33.24
35.10	6.310	176.88	19.646	277.29	33.77
38.67	6.949	183.30	20.425[c]	277.31	33.76
42.55	7.581	189.88	21.300[c]	287.48	34.34
46.84	8.189	192.94	21.757[c]	297.99	34.97
51.71	8.834	197.06	22.372[c]	308.33	35.59
54.23	9.131	199.48	22.729[c]	318.51	36.22
58.25	9.552	203.02	23.301[c]	328.98	36.89
63.32	10.060	205.79	23.825[c]	339.73	37.57
68.97	10.555	209.25	24.481[c]	350.30	38.25

[a] T is the mean temperature of each heat capacity measurement. [b] C_{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.

earlier publication.[17] The results are summarized in Table VI. The values of T_{obsd} were plotted as a function of $1/F$, and the triple point temperature, $T_{T.P.} = 230.94 \pm 0.05$°K., was obtained by linear extrapolation to zero value of $1/F$. If the impurities present form ideal solutions in the liquid phase and are insoluble in the solid phase, the relation between mole fraction of total impurity, N_2^* and the melting point depression, $\Delta T = T_{T.P.} - T_{obsd}$ is[18]

$$- \ln(1 - N_2) = A\Delta T(1 + B\Delta T + \ldots) \quad (2)$$

(16) R. A. Ruehrwein and H. M. Huffman, THIS JOURNAL, **65**, 1620 (1943); H. M. Huffman, S. S. Todd and G. D. Oliver. *ibid.*, **71**, 584 (1949); D. W. Scott, D. R. Douslin, M. E. Gross, G. D. Oliver and H. M. Huffman, *ibid.*, **74**, 883 (1952).

(17) S. S. Todd, G. D. Oliver and H. M. Huffman, *ibid.*, **69**, 1519 (1947).

(18) A. R. Glasgow, A. J. Streiff and F. D. Rossini, *J. Research Natl. Bur. Standards*, **35**, 355 (1945).

T, °K.	$(F°_{satd} - H°_0)/T$, cal. deg.$^{-1}$	$(H°_{satd} - H°_0)/T$, cal. deg.$^{-1}$	$H_{satd} - H°_0$, cal.	S_{satd}, cal. deg.$^{-1}$	C_{satd}, cal. deg.$^{-1}$
160	10.495	10.411	1665.7	20.906	17.867
170	11.140	10.879	1849.3	22.019	18.881
180	11.775	11.354	2043.7	23.129	20.011
190	12.402	11.843	2250.1	24.245	21.300
200	13.023	12.351	2470.2	25.374	22.754
210	13.638	12.887	2706.3	26.525	24.518
220	14.250	13.465	2962.2	27.715	26.734
230	14.862	14.094	3241	28.956	29.120
230.94	14.920	14.155	3269	29.075	29.343
		Liquid			
230.94	14.920	25.855	5971	40.77	31.56
240	15.91	26.077	6258	41.99	31.91
250	16.98	26.320	6579	43.30	32.37
260	18.02	26.562	6906	44.58	32.86
270	19.03	26.804	7237	45.83	33.37
273.16	19.34	26.881	7342	46.22	33.54
280	20.01	27.049	7573	47.06	33.92
290	20.96	27.296	7915	48.26	34.49
298.16	21.72	27.499	8199	49.22	34.98
300	21.89	27.546	8263	49.44	35.08
310	22.80	27.799	8617	50.60	35.69
320	23.68	28.055	8977	51.74	36.32
330	24.55	28.315	9343	52.87	36.95
340	25.40	28.578	9716	53.98	37.59
350	26.23	28.845	10095	55.08	38.23

[a] The values tabulated are the free energy function, heat content function, heat content, entropy and heat capacity of the condensed phases at saturation pressure.

TABLE VI

FLUOROBENZENE: MELTING POINT SUMMARY

Triple point temperature, $T_{T.P.}$ = 230.94 ± 0.05° K.; cryoscopic constant, A = 0.02549 deg.$^{-1}$; impurity = 0.05 ± 0.03 mole %.

Melted, %	1/F	Obsd.	Graph.[a]
8.86[b]	11.29	230.720	230.705
9.12	10.96	230.735	230.712
22.98[b]	4.352	230.852	230.852
23.04	4.341	230.855	230.852
45.73	2.187	230.900	230.897
46.75[b]	2.139	230.899	230.898
63.41	1.577	230.909	230.910
70.57[b]	1.417	230.910	230.914
82.30	1.214	230.917	230.918
89.62[b]	1.116	230.920	230.920
100.00	1.000		230.922
Pure	0.000		230.944

T, °K.

[a] Temperatures read from a straight line through a plot of T_{obsd} vs. $1/F$. [b] Repeat determination.

where $N_2 = N_2*/F$. The cryoscopic constants, $A = \Delta H_{fusion}/RT_{T.P.}^2$ = 0.02549 deg.$^{-1}$ and $B = 1/T_{T.P.} - \Delta C_{fusion}/2\Delta H_{fusion}$ = 0.00392 deg.$^{-1}$, were calculated from the values of $T_{T.P.}$ (230.94°K.), ΔH_{fusion} (2702.0 cal. mole^{-1}) and ΔC_{fusion} (2.22 cal. deg.$^{-1}$ mole^{-1}). Application of eq. 2 in its simplified form (for $N_2* <<1$), $N_2* = AF\Delta T$, yielded a value of 0.05 ± 0.03 mole % for the liquid-soluble, solid-insoluble impurity in the fluorobenzene sample.

The Thermodynamic Properties in the Solid and Liquid States.—Values of the free energy function, heat content function, heat content, entropy and heat capacity at selected temperatures between 10 and 350°K. were computed from the low temperature calorimetric data for fluorobenzene. The values at 10°K. were calculated from a Debye function for 4.5 degrees of freedom with θ = 108.9°; these parameters were evaluated from the heat capacity data between 14 and 23°K. The thermodynamic properties above 10°K. were computed by numerical integration of values of C_{satd} read from a large scale plot of the data of Table V and use of the observed values of ΔH_{fusion} and $T_{T.P.}$. The results are given in Table VII. Corrections for the effects of premelting have been applied to the "smoothed" data recorded in Table VII.

TABLE VII

THE MOLAL THERMODYNAMIC PROPERTIES OF FLUOROBENZENE IN THE SOLID AND LIQUID STATES[a]

T, °K.	$(F°_{satd} - H°_0)/T$, cal. deg.$^{-1}$	$(H°_{satd} - H°_0)/T$, cal. deg.$^{-1}$	$H_{satd} - H°_0$, cal.	S_{satd}, cal. deg.$^{-1}$	C_{satd}, cal. deg.$^{-1}$
			Crystals		
10	0.045	0.134	1.342	0.179	0.531
15	.149	.427	6.411	.576	1.591
20	.330	.872	17.442	1.202	2.838
25	.579	1.393	34.81	1.972	4.101
30	.881	1.943	58.28	2.824	5.259
35	1.223	2.492	87.22	3.715	6.290
40	1.590	3.023	120.92	4.613	7.173
45	1.975	3.528	158.75	5.503	7.937
50	2.372	4.003	200.14	6.375	8.616
60	3.180	4.869	292.14	8.049	9.738
70	3.989	5.631	394.1	9.620	10.641
80	4.786	6.308	504.6	11.094	11.452
90	5.565	6.924	623.1	12.489	12.226
100	6.324	7.490	749.0	13.814	12.941
110	7.063	8.018	881.9	15.081	13.662
120	7.783	8.520	1022.4	16.303	14.426
130	8.483	9.005	1170.6	17.488	15.219
140	9.168	9.478	1326.9	18.646	16.053
150	9.838	9.945	1491.7	19.783	16.930

[a] The values tabulated are the free energy function, heat content function, heat content, entropy and heat capacity of the condensed phases at saturation pressure.

The Vapor Pressure.—The vapor pressure of fluorobenzene at temperatures between 39 and 121° was measured with a twin ebulliometer system that was a somewhat improved modification of the one described in an earlier publication.[19] Observations were made of the boiling and condensation temperatures of fluorobenzene and water as the two compounds boiled simultaneously at a common pressure. The pressures corresponding to the observed boiling points of the water were obtained from the tabulation of Osborne, Stimson and Ginnings.[20] The results are presented in Table VIII. The difference between the boiling and condensation temperatures of the sample was only 0.001° at 1 atm. pressure; this observation indicates that the material was essentially free of impurities of different volatility. The constants of an Antoine equation

$$\log_{10} p(\text{mm}). = 6.95208 - 1248.083/(t + 221.827) \quad (3)$$

were obtained from the data of Table VIII by a least squares treatment.[21] Also, to provide a more accurate means of extrapolation to temperatures beyond the range of the experiments, the following Cox equation[22] was derived

$$\log_{10} P(\text{atm}.) = A(1 - 357.892/T) \quad (4)$$

$$\log_{10} A = 0.840607 - 7.0956 \times 10^{-4} T + 7.0443 \times 10^{-7} T^2$$

In these equations, t is in °C. and T is in °K. Comparisons of the observed and calculated vapor pressure for both the Antoine and Cox equations are given in Table VIII. The normal boiling point of fluorobenzene, calculated from either equation, is 84.73° (357.89°K.).

The Heat of Vaporization.—The heat of vaporization and vapor heat capacity of fluorobenzene were studied in the flow calorimeter described in previous publications.[23] The results of measurements of the heat of vaporization at boiling points corresponding to $^1/_4$, $^1/_2$, 1 and 2 atm. pressure are

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

(20) N. S. Osborne, H. F. Stimson and D. C. Ginnings, J. Research Natl. Bur. Standards, **23**, 261 (1939).

(21) C. B. Willingham, W. J. Taylor, J. M. Pignocco and F. D. Rossini, ibid., **35**, 219 (1945).

(22) E. R. Cox, Ind. Eng. Chem., **28**, 613 (1936).

(23) (a) Guy Waddington, S. S. Todd and H. M. Huffman, THIS JOURNAL, **59**, 22 (1947); (b) J. P. McCullough, D. W. Scott, R. E. Pennington, I. A. Hossenlopp and Guy Waddington, ibid., **76**, 4791 (1954).

Table VIII

The Vapor Pressure of Fluorobenzene

Boiling point, °C. Water	Fluorobenzene	p(obsd),[a] mm.	p(obsd) − p(calcd), mm. Eq. 3	Eq. 4
60.000	39.404	149.41	0.00	0.00
65	44.920	187.57	− .01	.00
70	50.480	233.72	− .01	.00
75	56.081	289.13	.00	+ .01
80	61.726	355.22	+ .01	.00
85	67.412	433.56	+ .03	+ .01
90	73.141	525.86	+ .05	+ .03
95	78.916	633.99	.00	− .01
100	84.734	760.00	− .05	− .05
105	90.590	906.06	+ .01	+ .04
110	96.497	1074.6	− .1	.0
115	102.438	1268.0	.0	+ .1
120	108.431	1489.1	− .1	.0
125	114.462	1740.8	.0	+ .1
130	120.538	2026.0	+ .1	.0

[a] From vapor pressure data for water given in ref. 20.

summarized in Table IX. The estimated accuracy uncertainty of the values of ΔHv in Table IX is ±0.1%. The following empirical equation was derived for interpolation in the temperature range of the measurements (318 to 382°K.)

Table IX

The Molal Heat of Vaporization and Second Virial Coefficient of Fluorobenzene

T, °K.	P, atm.	ΔHv, cal.	B_{obsd}. cc.	B_{calcd}. cc.[a]
318.40	0.250	7996 ± 1[b]	−1446	−1460
336.78	0.500	7748 ± 2[b]	−1275	−1259
357.89	1.000	7457 ± 1[b]	−1086	−1077
382.37	2.000	7098 ± 2[b]	− 909	− 916

[a] Calculated with eq. 7. [b] Maximum deviation from the mean of three determinations.

$$\Delta Hv = 10689 - 3.850T - 1.448 \times 10^{-2}T^2$$
$$\text{cal. mole}^{-1} \quad (5)$$

The Vapor Heat Capacity and the Effects of Gas Imperfection.—The vapor heat capacity of fluorobenzene was measured at two or more pressures at each of six temperatures between 343 and 500°K. The results are summarized in Table X.

Table XI

The Molal Entropy of Fluorobenzene, Cal. Deg.$^{-1}$

0–10°K.	Debye extrapolation[a]	0.179
10–230.94°	Crystals, numerical $\int C_{satd} \, d \ln T$	28.896
230.94°	Fusion, 2702.0/230.94	11.700
230.94–298.16°	Liquid, numerical $\int C_{satd} \, d \ln T$	8.449

S_{satd} (liq.), 298.16°K. (±0.10)[b]			49.22

T, °K.	318.40	336.78	357.89	382.37
S_{satd} (liq.)	51.56[c]	53.63[c]	55.94[d]	58.50[d]
$\Delta Hv/T$[e]	25.11	23.00	20.84	18.56
S (ideal) − S (real)[f]	0.07	0.12	0.18	0.28
$R \ln (p/760)$[g]	−2.75	−1.38	0.00	1.38
$S°$ (obsd.) (±0.15)[b]	73.99	75.37	76.96	78.78

[a] $1.5D(108.9/T)$. [b] Estimated accuracy uncertainty. [c] Interpolated from Table VII. [d] Extrapolated by use of eq. 1. [e] Entropy of vaporization. [f] Entropy of gas imperfection from eq. 3 and 7. [g] Entropy of compression from eq. 3.

The numerical constants of the following empirical equation for B were determined by the method described in ref. 23b.

$$B = 212 - 158.6 \exp (750/T) \text{ cc. mole}^{-1} (318-500°K.) \quad (7)$$

Values of B, computed by use of eq. 7, and values of $C_p(1 \text{ atm.}) - C_p°$, computed by use of eq. 6 and 7, are compared with the experimental values in Tables IX and X, respectively.

To determine the "observed" values of $C_p°$ listed in Table X, the last term in eq. 6 was evaluated for each experimental point by use of eq. 7, and subtracted from C_p(obsd.).[24] The adjusted values of C_p at each temperature were then extrapolated linearly to zero pressure to obtain $C_p°$(obsd.). The accuracy uncertainty of the values of $C_p°$(obsd.) listed in Table X should not exceed 0.2%. The following empirical equation represents these data within ±0.05% from 343 to 500°K.

$$C_p° = -6.581 + 0.11589 T - 6.122 \times 10^{-5} T^2$$
$$\text{cal. deg.}^{-1} \text{ mole}^{-1} \quad (8)$$

The Entropy in the Ideal Gaseous State.—The experimental and derived results given in the foregoing sections were used to compute "observed" values of the entropy in the ideal gaseous state at 1 atm. pressure. These calculations are summarized in Table XI.

The Heat of Formation and Related Properties.—The heat of formation of fluorobenzene was determined by a ro-

Table X

The Molal Vapor Heat Capacity of Fluorobenzene in Cal. Deg.$^{-1}$

T, °K.	343.20	364.20	389.20	426.20	463.20	500.20
C_p (2.000 atm.)			30.452			36.446
C_p (1.000 atm.)		28.263	29.791	32.036	34.224	36.244
C_p (0.500 atm.)	26.449					
C_p (0.250 atm.)	26.208	27.691	29.386	31.766	34.038	36.113
$C_p°$ (obsd.)	25.98	27.52	29.24	31.68	33.98	36.06
$[C_p$ (1 atm.) − $C_p°$](obsd.)		0.74	0.55	0.36	0.24	0.18
$[C_p$ (1 atm.) − $C°$](calcd.)[a]		0.75	0.55	0.36	0.25	0.18

[a] Calculated with eq. 6 and 7.

To correlate the thermal data, an equation of state for fluorobenzene was obtained from data for the vapor pressure, heat of vaporization and vapor heat capacity. Values of the second virial coefficient, B, in the equation of state, $PV = RT(1 + B/V)$, were computed by use of the exact Clapeyron equation. Values of d^2B/dT^2 were determined from the thermodynamic relationship, $(\partial^2 V/\partial T^2)_P = -1/T(\partial C_p/\partial P)_T$, in terms of which the variation of vapor heat capacity with the pressure is represented, with slight approximations,[23b] by

$$C_p = C° - T\left(\frac{d^2B}{dT^2}\right)P + 2\left(\frac{B}{R}\right)\left(\frac{d^2B}{dT^2}\right)\left(1 - \frac{3BP}{RT}\right)P^2$$
$$(6)$$

tating-bomb method of combustion calorimetry. The detailed experimental results have been reported elsewhere.[25] The observed value of $\Delta Hf°_{298.16}$ for liquid fluorobenzene is −34.7$_5$ kcal. mole^{-1}. The standard heat of vaporization at 298.16°K., $\Delta Hv°_{298.16}$, was calculated to be 8.27 kcal. mole^{-1} by use of eq. 4, 5 and 7 and the relationship, $\Delta Hv° = \Delta Hv - BRT/V + (dB/dT)RT^2/V$. The foregoing values of $\Delta Hf°_{298.16}$ and $\Delta Hv°_{298.16}$ lead to the value of $\Delta Hf°_{298.16}$ for fluorobenzene vapor, −26.4$_8$ kcal. mole^{-1}, as given in Table I.

(24) The maximum value of the last item in eq. 6 was 0.15 cal. deg.$^{-1}$ mole^{-1} at 2 atm. pressure and 389.20°K.

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

The value of S_{satd}(liq.) from Table XI, and values of the entropy of graphite,[10] hydrogen[10] and fluorine[11] were used to compute values of the entropy, free energy and logarithm of the equilibrium constant of formation of liquid fluorobenzene.

$$6C(\text{graphite}) + 5/2H_2(g) + 1/2F_2(g) = C_6H_5F(\text{liq})$$
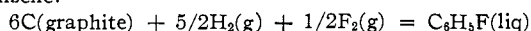
$$\Delta Hf°_{298.16} = -34.7_5 \text{ kcal. mole}^{-1}$$

$$\Delta Sf°_{298.16} = -61.19 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta Ff°_{298.16} = -16.5_1 \text{ kcal. mole}^{-1} \qquad \log_{10} Kf = +12.1_0$$

BARTLESVILLE, OKLA.

Benzenethiol: Thermodynamic Properties in the Solid, Liquid and Vapor States; Internal Rotation of the Thiol Group[1]

BY D. W. SCOTT, J. P. McCULLOUGH, W. N. HUBBARD, J. F. MESSERLY, I. A. HOSSENLOPP, F. R. FROW
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Studies of benzenethiol by low temperature calorimetry, comparative ebulliometry, flow calorimetry and combustion calorimetry led to values of the standard entropy, heat capacity and heat of formation of the vapor. The calorimetric results were used with molecular structure information to evaluate the contributions of internal rotation and anharmonicity to the thermodynamic functions. Internal rotation of the thiol group is essentially free, and the contributions of anharmonicity are significant even at ordinary temperatures. Thermodynamic functions were computed by the methods of statistical mechanics for selected temperatures between 0 and 1000°K. Values of the heat, free energy and logarithm of the equilibrium constant of formation were computed for the same temperatures. The experimental studies provided the following information: Values of the heat capacity for the solid (12-258°K.), the liquid [$C_{satd} = 34.985 + 2.175 \times 10^{-3} T + 6.500 \times 10^{-5} T^2$ cal. deg.$^{-1}$ mole^{-1} (258-375°K.)] and the vapor [$C_p° = -5.541 + 0.12212 T - 6.577 \times 10^{-5} T^2$ cal. deg.$^{-1}$ mole^{-1} (427-500°K.)]; the heat of fusion [2736 cal. mole^{-1}] at the triple point [258.27 ± 0.05°K.]; the entropy of the liquid at 298.16°K. [$S_{satd} = 53.25$ cal. deg.$^{-1}$ mole^{-1}]; the heat of vaporization [$\Delta Hv = 15808.5 - 13.620 T - 1.586 \times 10^{-3} T^2$ cal. mole^{-1} (375-417°K.)]; the second virial coefficient in the equation of state, $PV = RT(1 + B/V)$, [$B = -588 - 28.50 \exp(1500/T)$ cc. mole^{-1} (375-500°K.)]; the vapor pressure [$\log_{10} p$(mm.) $= 6.99019 - 1529.454/(t + 203.048)$ (114-212°)]; and the standard heat of formation [$6C(\text{graphite}) + 3H_2(g) + S(\text{rhombic}) = C_6H_5SH (\text{liq})$, $\Delta Hf°_{298.16} = +15.02 ± 0.27$ kcal. mole^{-1}]. The heat capacity of solid benzenethiol has a λ-like anomaly near 128°K.
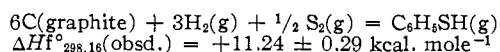
Introduction

An integrated experimental and computational program is conducted in this Laboratory to obtain thermodynamic data for organic sulfur compounds of interest in petroleum technology. As part of this program a comprehensive investigation was made of the thermodynamic properties of benzenethiol (thiophenol). Experimental studies were made by the methods of low temperature calorimetry, comparative ebulliometry, flow calorimetry and combustion calorimetry. The detailed results of these studies are given later in the Experimental section. The most significant results were values of the entropy, heat capacity and heat of formation of benzenethiol vapor, as given in Table I. The values of entropy and heat capacity were used with an assignment of the fundamental vibrational frequencies of the molecule to evaluate the contributions of internal rotation and anharmonicity to the thermodynamic functions. The functions $(F° - H_0°)/T$, $(H° - H_0°)/T$, $H° - H_0°$, $S°$ and $C_p°$ were computed by the methods of statistical mechanics for selected temperatures between 0 and 1000°K. Values of the appropriate thermodynamic functions were used with the experimental value of the heat of formation to compute the heat, free energy and logarithm of the equilibrium constant of formation for the same selected temperatures. These calculations of the thermodynamic properties are discussed in detail in the next section.

(1) This investigation was part of American Petroleum Institute Research Project 48A on "The Production, Isolation and Purification of Sulfur Compounds and Measurement of their Properties," which the Bureau of Mines conducts at Bartlesville, Okla., and Laramie, Wyo.

TABLE I

OBSERVED AND CALCULATED THERMODYNAMIC PROPERTIES
OF BENZENETHIOL VAPOR

T, °K.	Entropy, $S°$, cal. deg.$^{-1}$ mole^{-1}		T, °K.	Heat capacity, $C_p°$, cal. deg.$^{-1}$ mole^{-1}	
	Obsd.	Calcd.		Obsd.	Calcd.
375.24	86.98	86.96	427.20	34.63	34.62
394.74	88.57	88.56	448.20	35.97	35.98
407.34	89.59	89.59	473.20	37.53	37.52
416.90	90.36	90.37	500.20	39.08	39.08

$$6C(\text{graphite}) + 3H_2(g) + 1/2 S_2(g) = C_6H_5SH(g)$$
$$\Delta Hf°_{298.16}(\text{obsd.}) = +11.24 ± 0.29 \text{ kcal. mole}^{-1}$$

Calculation of Thermodynamic Properties

The Vibrational Assignment.—The calculation of thermodynamic functions by the methods of statistical mechanics required an assignment of the fundamental vibrational frequencies of the benzenethiol molecule. The assignment used for that purpose was based on the spectroscopic data in Table II.[2-4] The data of ref. 2 and 4 were obtained from samples of the same highly purified benzenethiol that was used in this research. The vibrational assignment is given in Table III. The benzenethiol molecule has approximately C_{2v} symmetry, and the vibrations, exclusive of the two associated with the S–H group, are classified according to C_{2v} symmetry in Table III. In the

(2) American Petroleum Institute Research Project 44 at the Carnegie Institute of Technology, Catalog of Raman Spectral Data, Serial No. 228.

(3) K. W. F. Kohlrausch, "Ramanspektren," Akademische Verlagsgesellschaft, Becker & Erler, Leipzig, 1943, p. 280.

(4) American Petroleum Institute Research Project 44 at the Carnegie Institute of Technology, Catalog of Infrared Spectral Data, Serial Nos. 1680 and 1681.