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1,2-Difluorobenzene: Chemical Thermodynamic Properties and Vibrational Assignment*

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Thermodynamic data were obtained for 1,2-difluorobenzene and correlated by methods of statistical mechanics to derive values of the chemical thermodynamic properties in the ideal-gas state from 0° to 1500°K. A vibrational assignment consistent with the calorimetric data was obtained. The experimental studies provided the following information: values of heat capacity for the solid (14°K to the triple point), the liquid (triple point to 357°K), and the vapor (355° 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 (327° to 367°K); parameters of the equation of state; and vapor pressure (304° to 403°K).

INTRODUCTION

COMPREHENSIVE thermodynamic studies of 1,2-difluorobenzene were made by the Bureau of Mines as part of continuing research on organic fluorine compounds. Experimental data were obtained by low-temperature calorimetry, vapor-flow calorimetry, and comparative ebulliometry. These experimental results and the results of combustion calorimetry reported elsewhere[1] were used with spectral and molecular structure information to calculate a table of chemical thermodynamic properties for the ideal-gas state.

An outcome of these studies was a vibrational assignment for 1,2-difluorobenzene consistent with accurate calorimetric values of the vapor heat capacity and entropy. This reliable assignment for one ortho-disubstituted benzene contributes to understanding the molecular vibrations of ortho-disubstituted benzenes in general.

TABLE I. Observed and calculated thermodynamic properties of 1,2-difluorobenzene.

	Entropy $S°$ cal/deg mole			Heat capacity $C_p°$ cal/deg mole	
T, °K	Obs	Calc	T, °K	Obs	Calc
326.90	79.38	79.39	355.20	29.69	29.68
345.61	80.94	80.96	377.20	31.22	31.23
367.07	82.71	82.76	418.20	33.93	33.93
			459.20	36.41	36.41
			500.20	38.66	38.66

$6C(c, \text{graphite}) + 2H_2(g) + F_2(g) = C_6H_4F_2(g)$

$\Delta Hf°_{298.15} = -67.64$ kcal/mole

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† Contribution No. 120 from the thermodynamics laboratory.

[1] W. D. Good, J. L. Lacina, D. W. Scott, and J. P. McCullough, J. Phys. Chem. 66, 1529 (1962).

TABLE II. Molecular spectra of 1,2-difluorobenzene, cm^{-1}.[a]

Raman liquid			Infrared liquid			Infrared gas			Interpretation
197	s	~0.9							b_2 fundamental
240	vvvw								a_2 fundamental
296	m	0.89							a_1 fundamental
436	w	0.9							b_1 fundamental
453	w	0.9			451	s	*C*		b_2 fundamental
547	m	0.89			548	s	*B*[b]		b_1 fundamental
566	m	0.4			567	m	*A*[b]		a_1 fundamental
585	vw								a_2 fundamental
703	w	0.86							a_2 fundamental
746	m	0.3	750	vs	750	s	*C*[b]		b_2 fundamental
762	vs	0.2	760	vs	762	m	*A*[b]		a_1 fundamental
825	vw								240+585=825 A_1
847	vvw		843	s	?				Fermi resonance, b_1 fundamental and 296+548=844 B_1
			853	s	855	s	*B*		
874	vvw								2×436=872 A_1
906	vw				903	vw			2×451=902 A_1
924	vvw		929	m	929	m	*C*		b_2 fundamental
968	vvw		970	vw					a_2 fundamental
982	vvw		980	vw					436+548=984 A_1
1020	s	0.1	1025	m	1024	m	*A*		a_1 fundamental
1047	vw								296+750=1046 B_2
1103	m	dp	1102	s	1102	s	*B*		b_1 fundamental
1152	m	0.6	1151	w	1155	vw	*A*		a_1 fundamental
			1200	s					a_1 fundamental
			1210	s	1212	s	*B*		b_1 fundamental
1252	vvw								b_1 fundamental or 548+703=1251 B_2
1269	s	0.2	1270	s	1279	s	*A*		a_1 fundamental
1294	w	0.5							585+703=1288 A_1
			1300	w					436+855=1291 A_1
1403	vw		1400	m	1404	w	?		548+855=1403 A_1
1456	vw		1454	m	1464	m	?		Fermi resonance, b_1 fundamental and 436+1024=1460 B_1
1469	vw		1469	m					
1508	w	0.6	1509	s	1518	s	?		a_1 fundamental
			1542	vvw					436+1102=1538 A_1
			1581	vvw					436+1155=1591 B_1
1606	w	~1.0	1604	m	1606	sh			a_1 fundamental
1618	m	0.89	1617	s	1622	s	*B*?		b_1 fundamental
Region above 1630 cm^{-1} omitted									

[a] Supplied by Professor J. Rud Nielsen. The numerical value of frequency is followed by an intensity designation, vs, very strong; s, strong; m, medium; w, weak; vw, very weak; vvw, very very weak; etc., sh; shoulder. The Raman depolarization factors (dp, depolarized) and the contours of the infrared bands of the gas (*A*, *B*, or *C*) are given after the intensity designations.

[b] Overlapped by neighboring band.

TABLE III. Fundamental vibrational frequencies of 1,2-difluorobenzene, cm^{-1}

a_1		b_1		a_2	b_2
Calc	Obs	Calc	Obs	Obs	Obs
319	296	424	436	240	197
567	567	535	548	585	451
794	762	859	855	703	750
1035	1024	1110	1102	(855)[a]	929
1155	1155	1192	1212	969	
1224	1200	1280	1252		
1256	1279	1475	1464		
1508	1518	1625	1622		
1617	1605	3089	(about) 3080		
3091	(about) 3080	3097	(about) 3080		
3092	(about) 3080				

[a] Used second time.

The first section of this paper is on the vibrational assignment and the chemical thermodynamic properties in the ideal-gas state, and the second section is on the experimental measurements. For convenience, the calorimetric values of entropy, heat capacity, and heat of formation[1] needed for discussion in the first section are collected in Table I.

VIBRATIONAL ASSIGNMENT AND CHEMICAL THERMODYNAMIC PROPERTIES

Vibrational Assignment

A complete vibrational assignment was required to correlate the calorimetric values of entropy and heat capacity in Table I by methods of statistical mechanics and to calculate thermodynamic functions at higher temperatures. The assignment made in this work was based on the molecular spectra in Table II, supplied by J. R. Nielsen of the University of Oklahoma. The Raman spectrum in Table II was obtained with some of the same highly purified sample used in the calorimetric studies of this research. The infrared spectra, however, were obtained earlier with a less pure sample; some observed bands obviously caused by fluorobenzene impurity are omitted in Table II.

The assignment for the in-plane symmetry species (a_1 and b_1) was made with the help of force-constant calculations done by Dr. James R. Scherer of the Dow Chemical Company. These calculations were for the Kekulé model of the Urey-Bradley force field. All force constants were transferred from structurally related molecules and were *not* adjusted in any way to improve agreement between the calculated and observed frequencies of 1,2-difluorobenzene. The calculated frequencies are in columns 1 and 3 of Table III, and the observed frequencies assigned by reference to the calculated ones are in columns 2 and 4. The observed frequencies are gratifyingly near to the calculated ones, the maximum difference being 32 cm^{-1}. Only one assignment of an observed frequency to an in-plane symmetry species is not very certain; the 1252 cm^{-1} frequency assigned as a b_1 fundamental appears weakly in the Raman spectrum alone and has an alternative explanation as a sum combination. Another possibility is that the b_1 fundamental coincides with the a_1 fundamental at 1279 cm^{-1} and is obscured by this fundamental in both spectra. The C—H stretching frequencies have the usual uncertainties from incomplete resolution and interference from Fermi resonance. The average frequency of the strong Raman and infrared bands in the C—H stretching region is about 3080 cm^{-1}; this value was used for all four fundamentals in the thermodynamic calculations. These C—H stretching frequencies are unimportant thermodynamically except at higher temperatures.

No force-constant calculations were made for the out-of-plane symmetry species (a_2 and b_2). However, with the in-plane fundamentals eliminated from the observed spectra, all but one of the out-of-plane fundamentals could be assigned from the selection rules and knowledge of the regions of the spectra in which these fundamentals would be expected. The observed frequencies assigned to species a_2 and b_2 are in columns 5 and 6 of Table III. The reported polarization of the 746 cm^{-1} Raman band was considered to be unreliable because of interference from the much stronger neighboring band at 762 cm^{-1}. The contour of the corresponding infrared band is correct for a b_2 fundamental. Assignment of the very weak Raman bands at 240 and 585 cm^{-1} as a_2 fundamentals is supported by the sum combination, $240+585=825$ A_1. The one out-of-plane fundamental not assigned from the observed spectra was located approximately from the characteristic vibrational frequencies of ortho-disubstituted benzenes tabulated by Randle and Whiffen.[2] These workers find a characteristic frequency of species a_2 near 860 cm^{-1} that appears weakly in the spectra when permitted by the selection rules. In 1,2-difluorobenzene, this characteristic a_2 fundamental must nearly coincide with the b_1 fundamental at 855 cm^{-1} and may be obscured by it in the observed spectra. The a_2 fundamental therefore was assigned the same frequency as the b_1 fundamental. The eleven other characteristic frequencies of ortho-disubstituted benzenes tabulated by Randle and Whiffen are included in the assignment of Table III.

Moments of Inertia

Calculating thermodynamic properties required (in addition to the complete vibrational assignment) a

[2] R. R. Randle and D. H. Whiffen, *Molecular Spectroscopy*, edited by G. Sell (Institute of Petroleum, London, 1955), pp. 111-125.

TABLE IV. The molal thermodynamic properties of 1,2-difluorobenzene in the ideal-gas state.[a]

T, °K	$(F°-H°_0)/T$, cal/deg	$(H°-H°_0)/T$, cal/deg	$H°-H°_0$, kcal	$S°$, cal/deg	$C_p°$, cal/deg	$\Delta Hf°$,[b] kcal	$\Delta Ff°$,[b] kcal	$\log_{10}Kf$[b]
0	0	0	0	0	0	−64.37	−64.37	Infinite
273.15	−60.93	13.87	3.789	74.80	23.51	−67.43	−56.14	44.91
298.15	−62.18	14.76	4.400	76.94	25.46	−67.64	−55.09	40.38
300	−62.28	14.82	4.448	77.10	25.60	−67.65	−55.01	40.08
400	−67.03	18.44	7.375	85.47	32.76	−68.37	−50.68	27.69
500	−71.53	21.91	10.96	93.44	38.65	−68.90	−46.20	20.19
600	−75.81	25.11	15.06	100.92	43.33	−69.29	−41.62	15.16
700	−79.90	27.99	19.59	107.89	47.08	−69.55	−36.98	11.55
800	−83.81	30.57	24.46	114.38	50.12	−69.72	−32.32	8.83
900	−87.55	32.88	29.60	120.43	52.62	−69.80	−27.64	6.71
1000	−91.12	34.97	34.97	126.09	54.72	−69.78	−22.96	5.02
1100	−94.54	36.85	40.53	131.39	56.50	−69.68	−18.28	3.63
1200	−97.82	38.55	46.26	136.37	58.01	−69.53	−13.62	2.48
1300	−100.97	40.10	52.13	141.07	59.31	−69.34	−8.97	1.51
1400	−103.99	41.51	58.12	145.50	60.44	−69.14	−4.33	0.68
1500	−106.90	42.81	64.21	149.71	61.43	−68.91	+0.28	−0.04

[a] To retain internal consistency, some values are given to one more decimal place than is justified by the absolute accuracy.
[b] The standard heat and free energy, and common logarithm of the equilibrium constant of formation by the reaction,

$$6C(c, \text{graphite}) + 2H_2(g) + F_2(g) = C_6H_4F_2(g).$$

value of the product of the principal moments of inertia of the molecule. Moments of inertia were calculated for an assumed structure with all bond angles 120° and the following bond distances: C—C, 1.402 Å; C—H, 1.077 Å; and C—F, 1.299 Å. These distances are based on the fluorobenzene model with a regular hexagon benzene nucleus, consistent with the microwave spectra of fluorobenzene[3]; they differ somewhat from the electron-diffraction values.[4] For the assumed structure, the product of the principal moments of inertia is 6.113×10^{-113} g^3 cm^6. The symmetry number is 2.

Thermodynamic Functions

Thermodynamic functions were computed from the usual formulas of statistical mechanics. An empirical anharmonicity function[5] with $\nu=1250$ cm^{-1} and $Z=0.97$ cal/deg mole was used to obtain better agreement with the vapor heat capacity data. The contributions of anharmonicity, according to this empirical function, are only 0.0004 and 0.004 cal/deg mole in $S°$ and C_p at 298.15°K but increase to 0.74 and 1.45 cal/deg mole at 1500°K. The calculated values of entropy and heat capacity are compared with the observed values in Table I. The excellent agreement shows that the vibrational assignment in Table III is substantially correct. Liquid-state values were used for the lowest frequencies in Table III because gas-state values have not been determined. Sometimes liquid-state values of low frequencies differ enough from the gas-state values to affect the calculated entropy significantly,[6] but seemingly that does not occur for 1,2-difluorobenzene. The calculated values of the thermodynamic functions for selected temperatures up to 1500°K are in columns 2–6 of Table IV.[7]

Heat, Free Energy, and Equilibrium Constant of Formation

The calculated values of the thermodynamic functions, the experimental value of $\Delta Hf°_{298.15}$ (Table I), and values of the thermodynamic functions of C (c, graphite),[8] H_2 (g),[8] and F_2 (g)[9] were used in calcu-

[3] B. Bak, D. Christensen, L. Hansen-Nygaard, and E. Tannenbaum, J. Chem. Phys. 26, 134 (1957).
[4] H. Oosaka, Bull. Chem. Soc. Japan 15, 31 (1940).
[5] J. P. McCullough, H. L. Finke, W. N. Hubbard, W. D. Good, R. E. Pennington, J. F. Messerly, and G. Waddington, J. Am. Chem. Soc. 76, 2661 (1954).
[6] D. W. Scott, G. B. Guthrie, J. F. Messerly, S. S. Todd, W. T. Berg, I. A. Hossenlopp, and J. P. McCullough, J. Phys. Chem. 66, 911 (1962).
[7] The contributions of vibration and anharmonicity were computed by the Bureau of Mines Electronic Computer Service, Pittsburgh, Pennsylvania.
[8] D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer, and F. D. Rossini, J. Research Natl. Bur. Standards 34, 143 (1945).
[9] W. H. Evans, T. R. Munson, and D. D. Wagman, J. Research Natl. Bur. Standards 55, 147 (1955).

TABLE V. The molal heat capacity of 1,2-difluorobenzene in cal/deg.

T, °K[a]	C_s[b]	T, °K[a]	C_s[b]	T, °K[a]	C_s[b]
Crystal		64.49	10.967	207.78	26.681
13.84	1.471	70.85	11.595	214.31	27.625[c]
15.35	1.873	77.38	12.228	Liquid	
16.93	2.323	84.05	12.910	229.03	34.013
16.97	2.337	90.77	13.547	234.46	34.291
18.71	2.830	90.89	13.553	239.16	34.545
18.78	2.848	97.47	14.143	242.29	34.698
20.79	3.417	104.37	14.778	252.43	35.255
20.85	3.434	110.99	15.408	262.90	35.851
23.10	4.064	118.32	16.125	273.21	36.468
23.16	4.076	126.31	16.922	283.37	37.081
25.60	4.735	133.99	17.708	293.81	37.739
25.65	4.747	141.38	18.495	294.04	37.751
28.31	5.404	148.51	19.274	304.96	38.429
28.35	5.408	155.41	20.047	315.96	39.126
31.35	6.109	162.09	20.819	326.28	39.768
34.55	6.782	168.94	21.624	326.51	39.792
37.93	7.418	176.27	22.524	336.71	40.382
42.01	8.094	183.36	23.415	336.89	40.433
46.80	8.800	190.24	24.313	346.99	40.947
51.75	9.468	196.92	25.200	347.13	41.023
53.74	9.720	199.14	25.497	357.12	41.498
56.99	10.105	200.57	25.688	357.23	41.570
58.82	10.324	205.12	26.337		

[a] T is the mean temperature of each heat capacity measurement.
[b] C_s is the heat capacity of the condensed phase at saturation pressure.
[c] Values of C_s for crystals are *not* corrected for the effects of premelting caused by impurities.

lating values of $\Delta Hf°$, $\Delta Ff°$, and $\log_{10}Kf$. The results are in columns 7–9, Table IV.

EXPERIMENTAL

The basic experimental techniques are described in published accounts of apparatus and methods for low-temperature calorimetry,[10] vapor-flow calorimetry,[11] and comparative ebulliometry.[12] The reported values are based on a molecular weight of 114.092 g/mole (1951 International Atomic Weights),[13] the 1951 values of fundamental physical constants,[14] and the relations 0°C = 273.15°K[15] and 1 cal = 4.184 J (exactly). Measurements of temperature were made with platinum resistance thermometers calibrated in terms of the International Temperature Scale[16] between 90° and 500°K and the provisional scale[17] 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.

Material

The sample of 1,2-difluorobenzene used for low-temperature calorimetry and comparative ebulliometry had a purity of 99.998 mole %, as determined by calorimetric studies of melting point as a function of fraction melted. The source and purification of this sample, which was used also for combustion calorimetry, are reported elsewhere.[1] A sample of somewhat lower purity was used for vapor-flow calorimetry.

Heat Capacity in the Solid and Liquid States

Low temperature calorimetric measurements were made with 0.54821 mole of sample sealed in a platinum calorimeter with helium (34 mm pressure at room temperature) added to promote thermal equilibration. The observed values of heat capacity at saturation pressure C_s are given in Table V. Temperature increments used in the measurements were small enough to obviate corrections for curvature; that is, 10% of the

TABLE VI. 1,2-difluorobenzene: Melting point summary. $T_{tp} = 226.01 \pm 0.05$°K; $N_2^o = A_F(T_{tp} - T_F) = 0.00002_4$ $A = 0.02601$ deg^{-1}; $B = 0.00356$ deg^{-1}.

F	$1/F$	T_F, °K	T_{calc},[a] °K
0.1104	9.058	226.0065	226.0065
0.2513	3.979	226.0109	226.0111
0.5021	1.992	226.0133	226.0130
0.7058	1.417	226.0135	226.0135
0.9092	1.100	226.0136	226.0138
1.0000	1.000		226.0139
Pure	0.000		226.0148

[a] Calculated from a straight line through points at $F = 0.1104$ and 0.7058.

[10] H. M. Huffman, Chem. Rev. **40**, 1 (1947); H. M. Huffman, S. S. Todd, and G. D. Oliver, J. Am. Chem. Soc. **71**, 584 (1949); D. W. Scott, D. R. Douslin, M. E. Gross, G. D. Oliver, and H. M. Huffman, *ibid.* **74**, 883 (1952).
[11] G. Waddington, S. S. Todd, and H. M. Huffman, J. Am. Chem. Soc. **69**, 22 (1947); J. P. McCullough, D. W. Scott, R. E. Pennington, I. A. Hossenlopp, and G. Waddington, *ibid.* **76**, 4791 (1954).
[12] G. Waddington, J. W. Knowlton, D. W. Scott, G. D. Oliver, S. S. Todd, W. N. Hubbard, J. C. Smith, and H. M. Huffman, J. Am. Chem. Soc. **71**, 797 (1949).
[13] E. Wichers, J. Am. Chem. Soc. **74**, 2447 (1952). Use of the unified atomic weight scale [Chem. Eng. News, November 20, 1961, p. 43] would not change any of the results significantly.
[14] F. D. Rossini, F. T. Gucker, Jr., H. L. Johnston, L. Pauling, and G. W. Vinal, J. Am. Chem. Soc. **74**, 2699 (1952).
[15] Some of the results originally were computed with constants and temperatures in terms of the relation 0°C = 273.16°K. Only results affected significantly by the newer definition of the absolute temperature scale [H. F. Stimson, Am. J. Phys. **23**, 614 (1955)] were recalculated. Therefore, numerical inconsistencies, much smaller than the accuracy uncertainty, may be noted in some of the reported data.
[16] H. F. Stimson, J. Research Natl. Bur. Standards **42**, 209 (1949).
[17] H. J. Hoge and F. G. Brickwedde, J. Research Natl. Bur. Standards **22**, 351 (1939).

TABLE VII. The molal thermodynamic properties of 1,2-difluorobenzene in the solid and liquid states.[a]

T, °K	$-(F_s-H^\circ_0)/T$, cal/deg	$(H_s-H^\circ_0)/T$, cal/deg	$H_s-H^\circ_0$, cal	S_s, cal/deg	C_s, cal/deg
		Crystal			
10	0.051	0.152	1.52	0.203	0.601
12	0.088	0.258	3.10	0.346	1.002
14	0.138	0.399	5.59	0.537	1.496
16	0.202	0.571	9.14	0.773	2.058
18	0.280	0.768	13.82	1.048	2.628
20	0.372	0.983	19.65	1.355	3.195
25	0.653	1.565	39.12	2.218	4.577
30	0.992	2.171	65.13	3.163	5.803
35	1.372	2.768	96.89	4.140	6.872
40	1.779	3.339	133.57	5.118	7.772
45	2.203	3.876	174.40	6.079	8.544
50	2.638	4.378	218.88	7.016	9.239
60	3.519	5.292	317.5	8.811	10.463
70	4.397	6.109	427.6	10.506	11.515
80	5.262	6.845	547.6	12.107	12.497
90	6.107	7.529	677.6	13.636	13.475
100	6.934	8.168	816.8	15.102	14.374
110	7.741	8.775	965.2	16.516	15.313
120	8.530	9.360	1123.2	17.890	16.291
130	9.302	9.932	1291.1	19.234	17.296
140	10.059	10.495	1469.3	20.554	18.346
150	10.801	11.055	1658.2	21.856	19.439
160	11.533	11.614	1858.2	23.147	20.575
170	12.254	12.175	2069.8	24.429	21.753
180	12.965	12.742	2293.5	25.707	22.988
190	13.671	13.314	2529.7	26.985	24.279
200	14.368	13.896	2779.1	28.264	25.609
210	15.061	14.486	3042	29.547	26.981
220	15.750	15.086	3319	30.84	28.457
226.01	16.158	15.455	3498	31.61	29.295
		Liquid			
226.01	16.158	27.136	6138	43.29	33.860
230	16.636	27.252	6268	43.89	34.06
240	17.803	27.546	6611	45.35	34.59
250	18.931	27.840	6960	46.77	35.11
260	20.029	28.131	7314	48.16	35.68
270	21.095	28.422	7674	49.52	36.27
273.15	21.427	28.512	7788	49.94	36.46
280	22.136	28.711	8039	50.85	36.88
290	23.149	29.003	8411	52.15	37.50
298.15	23.954	29.244	8719	53.20	38.01
300	24.137	29.297	8789	53.43	38.12
310	25.100	29.594	9174	54.69	38.75
320	26.046	29.888	9564	55.93	39.38
330	26.976	30.180	9961	57.16	40.01
340	27.879	30.480	10364	58.36	40.6
350	28.765	30.780	10773	59.55	41.18
360	29.633	31.08	11188	60.71	41.71
367.07	30.24	31.29	11484	61.53	42.08
370	30.49	31.37	11608	61.86	42.23

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

TABLE VIII. Vapor pressure of 1,2-difluorobenzene

Boiling point, °C Reference compound[a]	1,2-Difluoro-benzene	p(obs),[b] mm	p(obs) − p(calc), mm Antoine Eq. (2)	Cox Eq. (3)
19.061	31.168	71.87	+0.01	−0.01
21.720	33.916	81.64	0.00	−0.01
24.388	36.668	92.52	+0.01	+0.01
27.068	39.436	104.63	0.00	+0.02
29.757	42.210	118.06	0.00	+0.02
32.460	44.996	132.95	+0.01	+0.03
...	...	...	...	...
60.000	47.803	149.41	−0.06	−0.03
65	53.423	187.57	−0.06	−0.02
70	59.084	233.72	−0.04	−0.01
75	64.787	289.13	−0.02	0.00
80	70.530	355.22	+0.01	+0.01
85	76.314	433.56	+0.06	+0.04
90	82.142	525.86	+0.07	+0.02
95	88.009	633.99	+0.10	+0.04
100	93.921	760.00	+0.09	+0.03
105	99.874	906.06	+0.02	−0.01
110	105.869	1074.6	0.0	0.0
115	111.903	1268.0	−0.1	0.0
120	117.980	1489.1	−0.1	0.0
125	124.099	1740.8	−0.2	0.0
130	130.256	2026.0	0.0	0.0

[a] The reference compound from 71.87 to 132.95 mm was pure benzene and that from 149.41 to 2026.0 mm was pure water.

[b] From vapor pressure data for benzene [F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Braun, and G. C. Pimentel, *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds* (Carnegie Press, Pittsburgh, Pennsylvania, 1953), Table 21*k*] and for water [N. S. Osborne, H. F. Stimson, and D. C. Ginnings, J. Research Natl. Bur. Standards **23**, 261 (1939)].

absolute temperature below 50°K, 5° to 6° from 50°K to the triple point, and 10° or less above the triple point. Above 30°K, the accuracy uncertainty of the results is estimated to be no greater than 0.2%. The heat capacity values for the liquid may be represented between the triple point and 357°K by the empirical equation

$$C_s(\text{liq}) = 46.535 - 0.20805T + 8.9687\times10^{-4}T^2 - 9.8958\times10^{-7}T^3, \text{ cal/deg mole} \quad (1)$$

with an average deviation of 0.04%.

Heat of Fusion, Triple-Point Temperature, Cryoscopic Constants, and Purity of Sample

Three determinations of the heat of fusion ΔHm gave the average value 2639.8±0.3 cal/mole with the maximum deviation from the mean taken as the uncertainty. A correction for premelting caused by impurities was applied in obtaining the foregoing value. The results of a study of the melting temperature, T_F, as a function of the fraction of total sample melted F are in Table VI. Also in Table VI are the values obtained for the triple-point temperature T_{tp}, the mole fraction of impurity in the sample N_2^*, and the cryoscopic constants[18] $A = \Delta Hm/RT_{tp}^2$ and $B = 1/T_{tp} - \Delta Cm/2\Delta Hm$, calculated from the observed values of T_{tp}, ΔHm, and ΔCm (4.565 cal/deg mole).

Thermodynamic Properties in the Solid and Liquid States

Values of thermodynamic functions for the condensed phases were computed from the calorimetric data for selected temperatures between 10° and 370°K. The results are given in Table VII. The values from 10° to 14°K were computed from a Debye function for 5 degrees of freedom with $\theta = 108.2°$; these parameters were evaluated from the heat capacity data between 15° and 21°K. Corrections for the effects of premelting have been applied to the "smoothed" data in Table VII.

Vapor Pressure

Values of vapor pressure determined by comparative ebulliometry are in Table VIII. The condensation temperature of the sample was 0.004° lower than the ebullition temperature at 1 atm pressure. The Antoine and Cox equations selected to represent the results are

$$\log_{10}p = 7.00003 - 1298.053/(t+221.197) \quad (2)$$

and

$$\log_{10}(p/760) = A(1-367.072/T)$$

$$\log_{10}A = 0.841936 - 6.77698\times10^{-4}T + 6.52099\times10^{-7}T^2. \quad (3)$$

In these equations, p is in mm, t is in °C, and T is in °K. The observed and calculated vapor pressure for both the Antoine and Cox equations are compared in Table VIII. The normal boiling point is 93.92°C (367.07°K).

TABLE IX. The molal heat of vaporization and second virial coefficient of 1,2-difluorobenzene.

T, °K	P, atm	ΔHv, cal	B(obs), cc	B(calc), cc[a]
326.90	0.250	8261±1[b]	−1625	−1636
345.61	0.500	8003±2[b]	−1423	−1399
367.07	1.000	7699±3[b]	−1186	−1194

[a] Maximum deviation from the mean of three determinations.

[b] Calculated from Eq. (5).

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

Heat of Vaporization, Vapor Heat Capacity, and Effects of Gas Imperfection

The experimental values of heat of vaporization and vapor heat capacity are in Tables IX and X. The estimated accuracy uncertainties of the values of ΔHv and C_p° are 0.1% and 0.2%, respectively. The heat of vaporization may be represented by the empirical equation

$$\Delta Hv = 11710 - 7.487T - 0.937\times10^{-2}T^2 \text{ cal/mole} \quad (327°\text{–}367°\text{K}). \quad (4)$$

The effects of gas imperfection were correlated by the procedure described in an earlier paper.[19] The empirical equation for B, the second virial coefficient in the equation of state, $PV = RT(1+B/V)$, is

$$B = -80 - 73.05\exp(1000/T) \quad \text{cc/mole} (327°\text{–}500°\text{K}). \quad (5)$$

Observed values of B and

$$-T(d^2B/dT^2) = \lim_{p\to0}(\partial C_p/\partial P)_T$$

TABLE X. The molal vapor heat capacity of 1,2-difluorobenzene in cal/deg.

T, °K	355.20	377.20	418.20	459.20	500.20
C_p(1.000 atm)		32.105	34.426	36.735	38.887
C_p(0.500 atm)	30.278	31.630			
C_p(0.250 atm)	29.977	31.436	34.047	36.492	38.712
C_p°	29.69	31.22	33.93	36.41	38.66
$-T(d^2B/dT^2)$,[a]					
obs	1.12	0.81	0.47	0.31	0.22
calc[b]	1.13	0.82	0.48	0.31	0.21

[a] Units: cal/deg mole atm.
[b] Calculated from Eq. (5).

[19] J. P. McCullough, H. L. Finke, J. F. Messerly, R. E. Pennington, I. A. Hossenlopp, and G. Waddington, J. Am. Chem. Soc. 77, 6119 (1955).

TABLE XI. The molal entropy of 1,2-difluorobenzene in the ideal-gas state in cal/deg.

T, °K	326.90	345.61	367.07
S_s(liq)[a]	56.78	59.03	61.53
$\Delta Hv/T$	25.27	23.15	20.97
S(ideal) − S(real)[b]	0.09	0.14	0.21
$R\ln P^s$	−2.76	−1.38	0.00
S°(obs)±0.16[d]	79.38	80.94	82.71

[a] By interpolation in Table VII.
[b] The entropy in the ideal-gas state less that in the real-gas state calculated from Eq. (5).
[c] Entropy of compression, calculated from Eq. (3).
[d] Estimated accuracy uncertainty.

and those calculated from Eq. (5) are compared in Tables IX and X.

The heat of vaporization at 298.15°K was calculated by extrapolation with Eq. (4) (8.64 kcal/mole), by use of the Clapeyron equation with Eqs. (3) and (5) (8.64 kcal/mole), and by use of a thermodynamic network with the thermodynamic functions of Table IV (8.63 kcal/mole). The last value was selected as most reliable. By use of Eq. (5), the standard heat of vaporization (to the hypothetical ideal gas) is calculated to be 0.02 kcal/mole greater than the heat of vaporization (to the real gas); thus, $\Delta Hv^\circ_{298.15} = 8.65$ kcal/mole.

Entropy in the Ideal-Gas State

The entropy in the ideal-gas state at 1 atm pressure was calculated as shown in Table XI.

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