An attempt was made to correlate the values of B with physical properties like the boiling point, molecular weight, number of carbon atoms in a molecule, etc. The square root of the number of carbon atoms in a molecule, Z, gave a reasonably good correlation. The equation

$$B = y_1 + y_2Z + y_3Z^2 + y_4Z^3 + y_5Z^4 \tag{4}$$

is a fourth degree least-squares fit for B in terms of Z. Because of the fewer iso and di-iso substances, a second degree fit was used for these two groups. The constants y_1, y_2, y_3, y_4, and y_5 are tabulated for each group of amines in the third to seventh rows of Table II. Equations 3 and 4 were able to reproduce the 204 experimental viscosity values with a standard deviation of 2.36%.

NOMENCLATURE

A = constant in Equation 1
B = constant in Equation 1; group parameter in Equation 3
D = constant in Equation 2
E = constant in Equation 2
T = absolute temperature, °K.
t = time, sec.
X, Y = group parameters in Equation 3
y_1, y_2, y_3, y_4, y_5 = constants in Equation 4
Z = square root of number of carbon atoms in the liquid molecule

Greek Letters

η = viscosity, cp.
ρ = density, g./cm.^{3}

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Thermodynamic Functions for Halogenated Benzenes

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Thermodynamic functions (heat capacity, enthalpy, entropy, and free energy) are calculated for 38 halogenated benzenes in the ideal gas state from 298.15° to 1000° K. at 1 atm. of pressure. All the functions were obtained by statistical mechanical means. Agreement with experimental results, where such are available, is satisfactory.

THE RECENT availability of molecular structural and spectroscopic data has enabled the calculation of thermodynamic functions—heat capacity, enthalpy, entropy, and free energy—for 38 halogenated benzenes in the ideal gas state at 1 atm. of pressure. The functions for each given halogenated benzene group, including mono- to hexahalobenzenes and some unsymmetrical dihalobenzenes, were calculated by statistical-mechanical methods, using a digital computer program. The accuracy and scope of this work is bound by its purpose, to present a set of calculated thermodynamic function tables for use in chemical engineering problems.

DISCUSSION

Monohalobenzenes. (Table I, more data deposited with ASIS as Table I.). To calculate the thermodynamic functions for fluorobenzene, the data of Scott and coworkers (*37*), Smith and coworkers (*40*), and the microwave structural data of Bak *et al.* (*2*) were used. The anharmonicity corrections of McCullough *et al.* (*24*) were also employed in this calculation, using the same constants as Scott *et al.* (*37*), with similar results.

The thermodynamic functions for chloro-, bromo-, and iodobenzene were calculated using the data of Whiffen (*48*). The principal moments of inertia were taken from the microwave measurements of Rosenthal and Dailey (*32*),

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Table I. Heat Capacity, Entropy, Free Energy Function, and Enthalpy Function, Cal./Mole, ° K.[a, b]

	Temp., °K.	Monohalobenzenes			
		Fluorobenzene[c]	Chlorobenzene[d]	Bromobenzene[e]	Iodobenzene[e]
C_p°	298.15	22.54	23.42	23.82	24.09
S°	298.15	72.32	75.04	77.76	79.85
$(H^\circ - H_0^\circ)/T$	298.15	12.97	13.70	14.13	14.49
$-(G^\circ - H_0^\circ)/T$	298.15	59.35	61.33	63.63	65.37

	Temp., °K.	Polyfluorobenzenes				
		1,2-Difluorobenzene[f]	1,3-Difluorobenzene[g]	1,4-Difluorobenzene[g]	1,3, 5-Trifluorobenzene	1,2, 4-Trifluorobenzene
C_p°	298.15	25.45	25.50	26.06	28.33	28.85
S°	298.15	76.94	76.50	75.30	78.75	82.61
$(H^\circ - H_0^\circ)/T$	298.15	14.76	14.53	14.71	16.24	16.49
$-(G^\circ - H_0^\circ)/T$	298.15	62.19	61.97	60.59	62.51	66.12

	Temp., °K.	1,2,3,5-Tetrafluorobenzene	1,2,4,5-Tetrafluorobenzene	1,2,3,4-Tetrafluorobenzene	Pentafluorobenzene	Hexafluorobenzene[h]
C_p°	298.15	31.08	31.62	30.47	34.29	37.40
S°	298.15	85.29	84.59	83.91	89.63	91.54
$(H^\circ - H_0^\circ)/T$	298.15	18.11	18.48	17.55	20.15	22.47
$-(G^\circ - H_0^\circ)/T$	298.15	67.18	66.11	66.36	69.48	69.07

	Temp., °K.	Polychlorobenzenes					
		1,2-Dichlorobenzene[i]	1,3-Dichlorobenzene[i]	1,4-Dichlorobenzene[i]	1,3,5-Trichlorobenzene	1,2,4-Trichlorobenzene	1,2,3-Trichlorobenzene
C_p°	298.15	27.14	27.21	27.22	30.80	30.88	30.77
S°	298.15	81.66	82.07	80.46	86.64	89.94	88.47
$(H^\circ - H_0^\circ)/T$	298.15	16.07	16.13	16.12	18.54	18.58	18.57
$-(G^\circ - H_0^\circ)/T$	298.15	65.59	65.95	64.34	68.10	71.36	69.90

	Temp., °K.	1,2,3,5-Tetrachlorobenzene	1,2,4,5-Tetrachlorobenzene	1,2,3,4-Tetrachlorobenzene	Pentachlorobenzene	Hexachlorobenzene
C_p°	298.15	34.60	34.61	34.46	38.24	41.90
S°	298.15	95.50	94.03	94.91	101.65	104.13
$(H^\circ - H_0^\circ)/T$	298.15	21.20	21.18	21.07	23.74	26.26
$-(G^\circ - H_0^\circ)/T$	298.15	74.30	72.84	73.84	77.91	77.88

	Temp., °K.	Polybromobenzenes			
		1,2-Dibromobenzene	1,3-Dibromobenzene	1,4-Dibromobenzene	1,3,5-Tribromobenzene
C_p°	298.15	27.99	28.04	28.94	32.21
S°	298.15	86.43	87.69	86.33	95.30
$(H^\circ - H_0^\circ)/T$	298.15	16.92	17.15	17.44	20.29
$-(G^\circ - H_0^\circ)/T$	298.15	69.51	70.54	68.89	75.01

	Temp., °K.,	Mixed Polyhalogenated Benzenes				
		Chloropentafluorobenzene	Bromopentafluorobenzene	Iodopentafluorobenzene	1,2-Chlorofluorobenzene	1,3-Chlorofluorobenzene
C_p°	298.15	38.37	38.89	39.15	26.46	26.30
S°	298.15	97.90	100.82	102.94	80.74	81.02
$(H^\circ - H_0^\circ)/T$	298.15	23.35	24.02	24.40	15.43	15.48
$-(G^\circ - H_0^\circ)/T$	298.15	74.55	76.80	78.54	65.30	65.54

	Temp., °K.	1,4-Chlorofluorobenzene	1,2-Bromofluorobenzene	1,2-Fluoroiodobenzene	1,2-Bromochlorobenzene
C_p°	298.15	25.19	27.28	27.19	28.85
S°	298.15	76.90	83.59	85.60	86.58
$(H^\circ - H_0^\circ)/T$	298.15	14.24	16.00	16.28	17.13
$-(G^\circ - H_0^\circ)/T$	298.15	62.66	67.59	69.32	69.45

[a] Rest of the calculated values (from 300° to 1000° K. at 50° intervals) are placed with ASIS as Tables I-V. [b] Molecular parameters needed (selected) for the calculation of the presented thermodynamic functions are placed with ASIS as Tables VII-XI. [c] Previous calculations by Scott *et al.* (*37*) and Whiffen (*48*). [d] Previous calculations by Whiffen (*48*) and Godnev and Sverdlin (*14*). [e] Previous calculation by Whiffen (*48*). [f] Previous calculations by Scott *et al.* (*38*) and Green *et al.* (*15*). [g] Previous calculations by Green *et al.* (*15*). [h] Previous calculation by Counsell *et al.* (*5*). [i] Previous calculation by Godnev and Sverdlin (*13*).

while for iodobenzene, the vapor microwave structural data of Johansson *et al.* (*20*) were used. Agreement with the experimental data, referred to by Whiffen (*48*), and previous calculations (*14, 48*) is satisfactory.

Polyfluorobenzenes. (Table I, more data deposited with ASIS as Table II.) DIFLUOROBENZENES. The thermodynamic functions for *o*-difluorobenzene have already been calculated by Scott *et al.* (*38*) and Green *et al.* (*15*). Green *et al.* use the vapor state frequencies, while Scott *et al.* use liquid state frequencies and correct semiempirically for the anharmonicity contribution. Using the frequencies and other data proposed by Scott *et al.* and correcting for anhar-

Table II. Comparison of Computed and Experimental Values, Cal./Mole, °K.[a]

Compound	Temp., °K.	Heat Capacity, C_p° Exptl.	Heat Capacity, C_p° This Work	Entropy, S° Exptl.	Entropy, S° This Work
1,2-Difluorobenzene	326.90			79.38 (*38*)	79.39
	345.61			80.94 (*38*)	80.96
	355.20	29.69 (*38*)	29.68		
	367.07			82.71 (*38*)	82.75
	418.20	33.93 (*38*)	33.90		
	459.20	36.41 (*38*)	36.36		
	500.20	38.66 (*38*)	38.60		

[a] This table is also deposited (as Table VI) with ASIS.

monicity, the present thermodynamic functions are obtained. Although these compare excellently with the selected experimental values (Table II) obtained by Scott *et al.* (*38*), their values are somewhat lower at high temperatures (>1000° K.); the entropy at 1000° K. in this work is 0.12% lower than the original calculated values of Scott *et al.* This deviation at higher temperatures may be due to differing calculation methods.

The thermodynamic functions for the *m*-difluorobenzene computed by Green *et al.* (*15*) were recalculated using corrected products of moments of inertia. Few liquid state frequencies (vapor state not available) were used in the calculation; see Table VIII, placed with ASIS. Note that Green *et al.* reported the product of principal moments of inertia as: $I_{ABC} = 7.255 \times 10^{-113}$ gram^3 cm.^{6}. In this work, using the same structural data, the same product of moments of inertia is $I_{ABC} = 7.4137 \times 10^{-113}$ gram^3 cm.^{6}.

The thermodynamic functions for 1,4-difluorobenzene were calculated, using the vibrational frequency assignments of Ferguson *et al.* (*8*) as corrected by Stojiljkovic and Whiffen (*44*). The results (Table II, deposited with ASIS) are close to those calculated by Green *et al.* (*15*), even if the value of 163 cm.$^{-1}$ was assigned to a b_{2u} fundamental frequency, whereas in the work of Green *et al.* (*15*) and Steele *et al.* (*42*) it was specified as 186 cm.$^{-1}$.

TRIFLUOROBENZENES. For 1,3,5-trifluorobenzene, the vapor state fundamental frequencies of Nielsen *et al.* (*28*) and revisions by Ferguson (*7*) and Scherer *et al.* (*34*) were used to calculate the vibrational contributions to the thermodynamic properties. See also Steele (*41*) and Nonnenmacher and Mecke (*29*) for vibrational data.

Halogenated benzenes may be considered planar molecules (*7, 11, 12, 45, 46*); therefore, planar bond distances and all bond angle values of 120° were assumed. There is probably no repulsion of fluorine atoms and a resultant distortion of bond angles—as in ortho bonds (*46*)—since these bonds are not adjacent on the carbon ring.

The C—F bond distance was assumed to be 1.30 A., as in meta- and paradifluorobenzene (*45*). If the atoms of the molecule are crowded, as in ortho compounds, the C—F bond is stretched to 1.35 A. (*38*). In hexafluorobenzene, however, the bond is stretched only to 1.327 A. (*1, 5*). The C—C bond distance was assumed to be 1.397 A. (*1, 2, 5, 45, 46*), while the C—H bond was 1.08 A.

The thermodynamic functions for 1,2,4-trifluorobenzene were calculated (Tables I and II, placed with ASIS) using the available vibrational assignments by Ferguson *et al.* (*9*) and the above structural data (Table VIII, placed with ASIS).

The ortho fluorines are thought to be connected to the ring by bonds of the same type as found in orthodifluorobenzene (i.e., C—F = 1.35 A.) and the "4-position" fluorine atom is bonded by C—F = 1.30 A., as in other difluorobenzenes (*45*). As before, C—H = 1.08 A., while the C—C bond = 1.397 A.

TETRAFLUOROBENZENES. To calculate the thermodynamic properties of 1,2,3,5-tetrafluorobenzene, the nearly complete vibrational assignments of Steele (*41*) were used. Steele, however, has not assigned the a_1 frequency corresponding to 1157 cm.$^{-1}$ and the b_2 frequency corresponding to 215 cm.$^{-1}$ in C_6F_6. Following Steele (*41*), by analogy, we assign these frequencies as 1200 and 220 cm.$^{-1}$, respectively. See Table VIII, placed with ASIS, footnote (*j*). Note that an error of ±40 cm.$^{-1}$ in this value would change C_p° by less than 0.02 cal. per mole °K. and S° by 0.01 e.u. at 273.15° K.; at 1000° K., the changes would be less than 0.03 cal. per mole °K. and 0.05 e.u., respectively. Note also that in assigning this low frequency value, the effect of vapor-liquid shift (*6*) is considered. No published structural data of the tetrafluorobenzenes were found. These molecules were assumed to be planar, with all bond angles of 120°. By analogy with the chlorobenzenes, it was assumed that the bond lengths are approximately the same for the tetra- as for the hexa-compounds. The C—F bond distance of 1.327 A. found in hexafluorobenzene (*1, 5*) was considered the distance for the tetrafluorobenzenes. The other bond distances used were C—C = 1.394 A. (*1, 5, 45*) and C—H = 1.08 A.

The vibrational frequency assignment by Ferguson *et al.* (*10*), as modified by Steele and Whiffen (*43*), was used to calculate the thermodynamic functions of 1,2,4,5-tetrafluorobenzene (Table I, more data deposited with ASIS as Tables II and VIII).

The two unassigned frequencies were estimated (Figure 1) from the known vibrational frequencies of the same mode. In Figure 1, the fundamental *X* sensitive frequency (*X* = F, Cl, Br, I) corresponding to 443 cm.$^{-1}$ in C_6F_6 is plotted against the increasing sequence of isomers 1,2,4,5-(para), 1,2,3,5-(meta) and 1,2,3,4-(ortho), yielding a straight line. The desired a_1 frequency, however, corresponds to the 315 cm.$^{-1}$ vibration for C_6F_6. These frequencies for the 1,2,3,5- and 1,2,3,4- isomers are 445 and 460 cm.$^{-1}$, respectively. In Figure 1, the straight line between the points given by these two known frequencies is extrapolated to predict the desired a_1 frequency for the 1,2,3,4- isomer as approximately 420 cm.$^{-1}$. This is a reasonable estimate, if compared with the values of the same fundamental frequency for similar molecules, C_6HF_5, C_6DF_5, and C_6F_6, as shown by Steele (*43*). The other previously unassigned vibrational frequency was approximated, by the same method, as 270 cm.$^{-1}$. At least four of the low frequencies (420, 270, 140, and 240 cm.$^{-1}$) used in the vibrational contribution calculation are of doubtful accuracy (*43*). The moments of inertia of this molecule were calculated, using the data for the 1,2,3,5-tetrafluorobenzene already assumed and discussed (by analogy with chlorobenzenes).

Although Steele (*41*) has assigned most of the fundamental vapor phase frequencies of 1,2,3,4-tetrafluorobenzene to calculate the thermodynamic functions of this compound, the authors still had to assign four of the five a_1 fundamental vibrations. These frequencies were assigned by analogy with

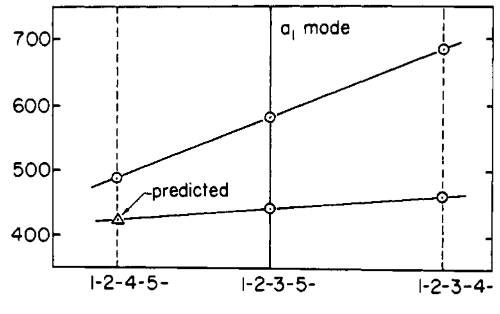

Figure 1. The prediction of the unknown frequency for 1,2,4,5-tetrafluorobenzene by analogy with similar frequencies of the same mode

the change in frequency of the highest (already assigned) a_2 vibration, over the series o—$C_6H_4F_2$, 1,2,3,4-$C_6F_4H_2$, and C_6F_6 [see also Steele (*41*)].

The frequency assignments for 1,2,4,5-tetrafluorobenzene (Figure 2) were made using a method similar to that employed in Figure 1. A series of different molecules was employed, rather than a series of positional isomers of a single molecule, as was the case for 1,2,4,5-tetrafluorobenzene.

Note that the lowest frequency, corresponding to 175 cm.$^{-1}$ in C_6F_6, was predicted by this method as 335 cm.$^{-1}$, but was assigned to be 305 cm.$^{-1}$, since it was observed that the lower frequencies—<500 cm.$^{-1}$—for 1,2,3,4-tetrafluorobenzene were relatively closer to those of C_6F_6 than the higher frequencies.

The structural data for the tetrafluorobenzenes were used to calculate the product of the moments of inertia.

PENTAFLUOROBENZENE. To calculate the thermodynamic properties for pentafluorobenzene, the vibrational assignments by Steele and Whiffen (*43*) and Long and Steele [normal coordinate analysis, (*22*)] were utilized. Steele and Whiffen do not assign the highest a_2 vibration, but, following the behavior of similar compounds, $C_6H_2F_4$, C_6HF_5, and C_6F_6, suggest that it is 600 cm.$^{-1}$. However, in the b_1 mode there are two unassigned frequencies. That corresponding to 249 cm.$^{-1}$ in hexafluorobenzene is assigned as 300 cm.$^{-1}$, following the recommendation of Steele and Whiffen that it must be lower than 350 cm.$^{-1}$ and higher than the corresponding C_6F_6 frequency, 249 cm.$^{-1}$. Similarly, the lowest a_2 frequency corresponding to 175 cm.$^{-1}$ in C_6F_6 is assigned as 200 cm.$^{-1}$. The structural data for pentafluorobenzene is the same as for hexafluorobenzene, with C—H = 1.08 A.

HEXAFLUOROBENZENE. The thermodynamic functions for hexafluorobenzene were calculated from the vibrational frequency assignments of Counsell *et al.* (*5*), who also include third law data. Comparing the calculated and observed entropies over a 30° experimental range, from 290° to 320° K., Counsell *et al.* proposed that the lowest e_{2u} mode (doubly degenerate) should have a frequency value of 125 cm.$^{-1}$, as opposed to the Steele and Whiffen value of 175 cm.$^{-1}$. This agrees well with the values calculated by normal coordinate analysis, 121 cm.$^{-1}$ (*13*) and 119 cm.$^{-1}$ (*29*). Note that Counsell *et al.* report a value of I_{ABC} = 8.870 × 10^{-112} gram^3 cm.^{6} for a planar molecule having bond angles of 120°. Using the same structural data (*1*), we calculate the value of I_{ABC} = 10.901 × 10^{-112} gram^3 cm.^{6} If the proposed larger value of the product of the principal moments of inertia is used, we find that the lowest e_{2u} mode frequency to give the best fit to the experimental entropy and heat capacity is 133 cm.$^{-1}$, not 125 cm.$^{-1}$, as suggested by Counsell and his coworkers (*5*). If the calculated entropy values, this work, Table I (Table II deposited with ASIS), and Counsell *et al.* (*5*) (Table VIII) are plotted using third law methods (Figure 3), it appears that there is an error in the experimental work.

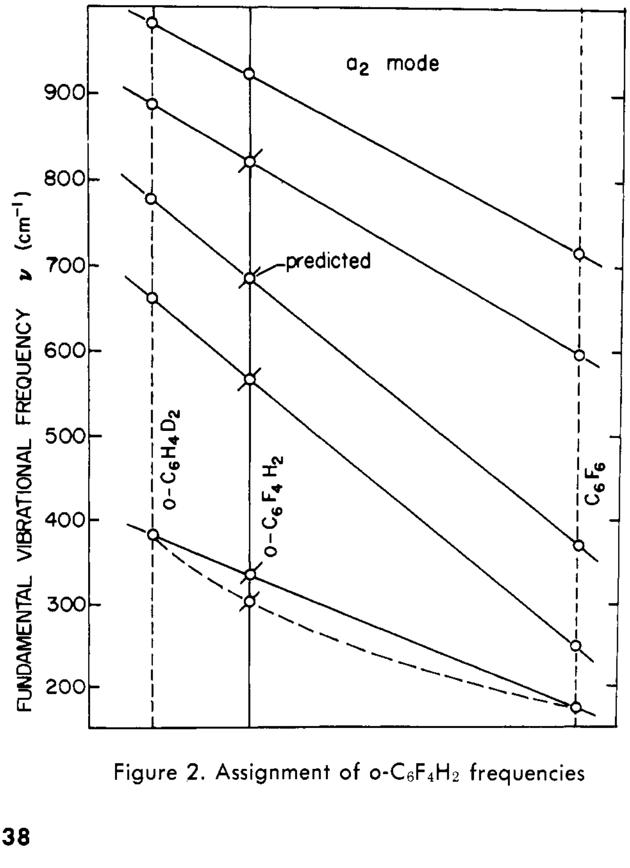

Figure 2. Assignment of o-$C_6F_4H_2$ frequencies

Figure 3 shows that for the experimental work (*5*), the slope $(\partial S/\partial T)_p$ is increasing with temperature rather than decreasing, as would be expected from the general entropy-temperature behavior and from the experimental results for other compounds. It seems very unlikely that, with the fundamental frequencies and structure of hexafluorobenzene as well known and as accurate as they are, there should be such a large deviation between the calculated and the "third law" values as shown in Figure 3.

Polychlorobenzenes. (Table I, more data deposited with ASIS as Table III). DICHLOROBENZENES. The thermodynamic functions of 1,2-, 1,3-, and 1,4-dichlorobenzene were calculated, using the liquid state vibrational frequency assignments suggested by Scherer and Evans (*33*).

The calculated thermodynamic functions in Table I (Table II deposited with ASIS) agree well with those proposed in an earlier work by Godnev and Sverdlin [older vibrational frequency assignments (*13*)] except for the entropy of 1,4-dichlorobenzene. This work finds an entropy about 0.5 e.u. higher, while the heat capacity is only slightly lower (by 0.04 cal. per gram mole ° K.) than that of Godnev and Sverdlin. This work uses lower low frequencies—125 and 226 cm.$^{-1}$ instead of 200 and 240 cm.$^{-1}$—so that there is a large change in entropy, but little effect on the heat capacity (*18*).

TRICHLOROBENZENES. The vibrational assignments of Scherer *et al.* (*35*) were used to calculate the thermodynamic properties for 1,3,5-trichlorobenzene. Three of the frequencies used in the assignment (a_2 mode) are the calculated (normal coordinate) values and are of very limited reliability. The bond lengths used were the same as in meta- and paradichlorobenzene.

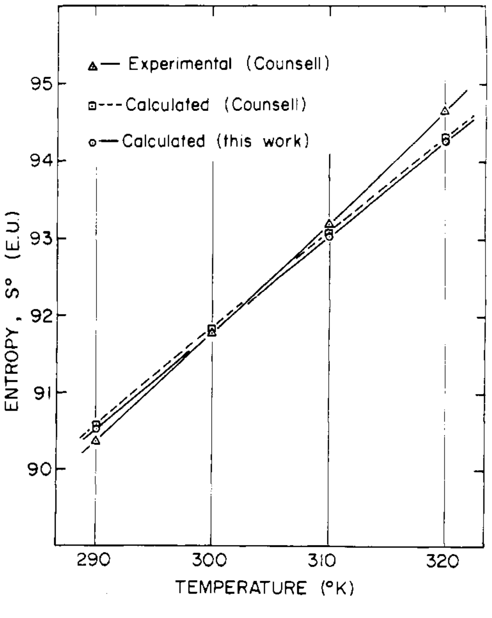

Figure 3. Entropy (S°) for hexafluorobenzene

For 1,2,3- and 1,2,4-trichlorobenzene thermodynamic function value calculation, the vibrational frequency assignments made by Scherer and Evans (*33*) were used. The bond lengths are as in ortho-dichlorobenzene for adjacent C—Cl bonds, other bond lengths being the same as those given above.

TETRACHLOROBENZENES. The thermodynamic functions for tetrachlorobenzenes were calculated using the liquid state frequency assignments proposed by Scherer and Evans (*33*).

The needed structural data were obtained from the vapor electron-diffraction work of Strand and Cox (*46*). In the case of 1,2,4,5-tetrachlorobenzene, Strand and Cox specify that the length of the C—C bond is 1.395 A., C—Cl = 1.724 A., and C—H = 1.08 A., where the radial angle between the C—Cl bonds is 62.8°, as opposed to the symmetric 60°. As the experimental data for the other two tetrachlorobenzenes was missing, the C—C and C—H bond distances were assumed to be the same as in the 1,2,4,5-isomer. Since the C—Cl bonds in the 1,2,3,4- form are closer than in the 1,2,4,5- isomer, the C—Cl distance should be closer to that of hexachlorobenzene, so that C—Cl = 1.721 A. was chosen for this isomer. Although the two outer C—Cl bonds may be at a larger radial angle than 60°, this angular change will probably have a negligible effect in the calculation of the moments of inertia; thus, it was not considered. For 1,2,3,5-tetrachlorobenzene, the bond distances (*45*) were 1.722 A. for the 1, 2, and 3 chlorine atoms, and 1.725 A. for the 5-position chlorine atom.

PENTA- AND HEXACHLOROBENZENE. Using the liquid state frequency assignments proposed by Scherer and Evans (*33*), the thermodynamic functions were calculated for both pentachlorobenzene and hexachlorobenzene. The structural data needed to compute the product of the moments of inertia for hexachlorobenzene were taken from the electron-diffraction work of Strand and Cox (*46*). For pentachlorobenzene, however, a selection of bond lengths intermediate between those of tetrachloro- and hexachlorobenzene (*46*) was made: C—C = 1.40 A., C—Cl = 1.72 A., C—H = 1.08 A. It was further assumed that all bond angles are 120°, and that the molecule is planar.

Polybromobenzenes. (Table I, part as Table IV, placed with ASIS). DIBROMOBENZENES. The liquid state vibrational frequency assignments of Shurvell *et al.* (*39*) and the suggested structural data by Strand (*45*) were used to calculate the thermodynamic functions of 1,2-dibromobenzene. For 1,2-dibromobenzene, Strand (*45*) gives the structural data as follows: C—C = 1.402 A., C—Br = 1.883 A., and the radial angle between the C—Br bonds = 63.6°. Using these data, I_{ABC} was calculated to be 12.555 $\times 10^{-112}$ gram^{3} cm.^{6}. To determine the effect of neglecting the distortion of the structure owing to the repulsion of the bromine atoms, I_{ABC} was also calculated using a radial angle of 60° between the bonds. This gave I_{ABC} = 12.562 $\times 10^{-112}$ gram^{3} cm.^{6}. The difference in the two values has a negligible effect on the thermodynamic functions. This approximation was used in the calculations for other molecules mentioned in the work.

To calculate the thermodynamic functions for 1,4-dibromobenzene, the vibrational frequency assignments made by Shurvell *et al.* were supplemented by the more recent 1,4-dibromobenzene solid solution data of Griffiths and Thompson (*16*). They give the two lowest missing frequencies as 103 cm.$^{-1}$ (b_{3u}) and 173 cm.$^{-1}$ (b_{2u}). These values are for solid solutions; there may, therefore, arise an appreciable frequency shift between these and the needed vapor state vibrational frequencies. The gaseous electron-diffraction structural data of Bastiansen and Hassel (*3*) and Strand (*45*) was used in the calculation of the principal moments of inertia.

The thermodynamic function calculations for 1,3-dibromobenzene were performed, employing the vibrational frequency assignments of Shurvell *et al.* (*39*). Since the bond lengths in ortho- and paradibromobenzene are the same (*3, 45*), it was assumed that they would be also unchanged in the meta- isomer. C—C = 1.482 A. and C—Br = 1.883 A. were used to calculate the product of the moments of inertia for 1,3-dibromobenzene.

TRIBROMOBENZENES. The vibrational assignment of Scherer *et al.* (*34*), agreeing well with the fundamental frequencies given by Nonnenmacher and Mecke (*29*) and Mooney (*25*), was used to calculate the thermodynamic functions for 1,3,5-tribromobenzene. To compute the principal moments of inertia, first it was assumed that the atoms are coplanar, and that the bond angles are 120°. Then, following the suggestion by Scherer *et al.*, the C—Br distance was assumed to be 1.88 A. This value is intermediate between the bond distances in di- and hexabromobenzene (*3, 45*). The C—C and C—H bond lengths were the same as those for dibromobenzene (*45*).

Mixed Polyhalogenated Benzenes. (Table I, more data deposited with ASIS as Table V). HALO-PENTAFLUOROBENZENES. The thermodynamic functions for chloro-, bromo-, and iodo-pentafluorobenzene were calculated using the liquid state fundamental frequencies assigned by Hyams *et al.* (*19*) and considering the previous work of Long and Steele (*22, 23*). For those compounds, there are two unassigned fundamental frequencies, an a_2 and a b_1 mode. Following the suggestion of Hyams *et al.*, the missing a_2 frequency was assigned as 600 cm.$^{-1}$ for all the three compounds, since the a_2 frequencies are not X-sensitive (*19*). The b_1 frequency—also X-insensitive—was assigned as 550 cm.$^{-1}$, since it should be about 50 cm.$^{-1}$ lower than the corresponding C_6H_6 value (*19*).

The structural data used to calculate the products of moments of inertia for these halo-pentafluorobenzenes were generally chosen for those occurring in hexafluorobenzene. However, the C—Cl distance, 1.717 A., was that found in hexachlorobenzene (*46*) and the C—Br distance, 1.879 A., was taken from Strand's (*45*) data for hexabromobenzene. The choice of C—I bond length, 2.10 A., is justified through the observation that in iodobenzene (*20*) the determined C—I length is 2.08 A. The crowding of the halogen atoms may increase their distance, and although there is no data to verify this, the C—I bond distance of 2.10 A. appears to be a reasonable selection for iodo-pentafluorobenzene.

ASYMMETRICAL DIHALOBENZENES. The thermodynamic functions for the 1,2-, 1,3-, and 1,4- isomers of chlorofluorobenzene were calculated utilizing the vibrational assignments made by Nielsen and coworkers (*17, 26, 27*). All the fundamental vibrations except the low frequencies—liquid state—are for the vapor state and should be reliable, provided there are no large vapor-liquid shifts in the low frequencies. The only published structural data for these three compounds is the vapor state microwave (moments of inertia) study of Rachman (*31*) for the 1,3- (meta) isomer. To calculate the principal moments of inertia for 1,4-(para)-chlorofluorobenzene, bond distances similar to those observed by Rachman for the meta isomer (*31*) were assumed since, in general, meta and para halobenzenes have similar bond lengths: C—C = 1.397 A., C—H = 1.08 A., C—Cl = 1.699 A., and C—F = 1.329 A., again in a planar molecule. In the 1,2-(ortho) isomer, some bond stretching due to crowding of atoms probably takes place. The bond distances were assumed to be as follows (*47*): C—F = 1.33 A., C—Cl = 1.71 A., C—C = 1.397 A., and C—H = 1.08 A., where all the angles are 120° in a planar configuration. Of these three structures, that of the meta isomer is the most reliable [Rachman's microwave measurements (*31*)], and the assumed ortho structure the most doubtful, since the crowding effect between two halogen atoms is difficult to predict.

In the calculations of thermodynamic properties for the ortho compounds bromofluoro-, fluoroiodo- and bromochlorobenzene, the vibrational assignments of Krishnamachari (*21*) were used. The fundamental frequency assignments for these liquid film measurements were made by analogy with similar substituted benzenes, using infrared vapor phase contours, Raman lines and the relative intensities of the vibrational spectra. As there is no indication what the possible accuracy of these assignments may be and no vapor state frequency measurements, it is difficult to assess the magnitude of the vapor-liquid shift. As published structural data were not available, the bond lengths were assumed to be analogous to the other disubstituted benzenes—i.e., C—C = 1.397 A., C—H = 1.08 A. All the molecules were assumed to be planar and to have bond angles of 120°. The ortho C—F distance, like that for 1,2-difluorobenzene (*47*), was 1.35 A.; the C—Cl distance, like that for 1,2-dichlorobenzene, was 1.71 A.; similarly, C—Br = 1.883 A. (*45*). The C—I distance for these ortho-compounds was assumed to be 2.10 A. See the discussion regarding iodo-pentafluorobenzene.

ACCURACY

In this work, all values are in cal. per gram mole °K. units and apply to the ideal gas state at 1 atm. For internal consistency and precision, tabulated values are given to ±0.1 cal. per gram mole °K. However, probable errors may be larger than this.

The percentage errors ascribed below to the calculated thermodynamic functions (Table I and Tables I, II, III, IV, and V, placed with ASIS) are really estimates. These estimates were obtained considering errors in the molecular structural and spectroscopic data needed to compute the presented thermodynamic properties. This consideration of contributing errors excluded the effect of anharmonicity—small at temperatures below 500° K. (experimental region), but larger at higher temperatures (*30*), such as 2% at 1000° K.—and mathematical errors—for instance, round-off error generated in the computer calculations of vibrational contributions and in the moments of inertia.

In the compounds for which there exist experimental structural data for the molecule, the accuracy of the bond lengths is usually within ±0.01 A. (*2, 45, 46*), although sometimes ±0.05 A. deviation is reported [Sutton (*47*)]. The available data show that for the compounds whose bond lengths have been predicted by analogy with known bond distances, the error seldom exceeds ±0.05 A.; for example, the structure of pentachlorobenzene can be reasonably predicted if tetrachloro- and hexachlorobenzene structures are known (*46*). Errors in the bond lengths should not greatly change the calculated thermodynamic properties—an error of 10% in product of the principal moments of inertia (I_{ABC}) for 1,2-difluorobenzene changes the entropy S° by ±0.09 e.u., or about ±0.12% at 298.15° K., and ±0.07% at 1000° K.

The calculated thermodynamic function values may be affected by two types of inaccuracies in the vibrational frequency assignments: the use of liquid state frequencies instead of those for the vapor state (vapor-liquid shift) and by incorrect assignments. This last type of error does not appear too often—most authors [such as Scherer and Evans, (*33*)] also give the assignment of the combination bands observed in the spectrum, so that the fundamental frequency assignments could be verified.

In accordance with the Fateley *et al.* (*6*) study of the low-frequency vapor-liquid shift for halogenated toluenes and other aromatic compounds, the frequency shift from liquid to vapor decreases the frequency for vibrations below 700 cm.$^{-1}$ and increases the frequency above this. They found that the higher frequency shifts are usually less than ±5 cm.$^{-1}$ (above 700 cm.$^{-1}$), while the low frequency shifts range from 10 to 20 cm.$^{-1}$ (below 700 cm.$^{-1}$). However, it is difficult to know without an experiment if an appreciable vapor-liquid frequency shift takes place in any given compound (*6*).

If the vapor state vibrational frequencies are available and the molecular structure is determined by known (experimental) data, the possible error should be less than ±0.5% of the thermodynamic functions in the region where experimental data is available (less than 500° K.). This evaluation of the error is also strengthened by Table II, in which the computed and experimental thermodynamic property values are compared. If the assignment of frequencies is considered reliable, but only the liquid state frequencies are available, the error in the computed values of the thermodynamic functions is estimated as ±1.0%. Half of this error (±0.5%) corresponds to a possible vapor-liquid shift of 10 cm.$^{-1}$ in six frequencies spaced evenly between 110 and 700 cm.$^{-1}$. In the halogenated benzenes, there are about six to 10 frequencies below 700 cm.$^{-1}$, but not all have vapor-liquid shifts (*6, 36*).

If the frequency assignments have been made by analogy with other compounds or other frequencies of the same mode (Figures 1, 2), or if the structure is doubtful, the error in the calculated thermodynamic property values is established as ±1.5%. This, when recalculated, corresponds to a possible error of 20 cm.$^{-1}$ in six frequencies below 700 cm.$^{-1}$. In the case of calculations using liquid state frequencies, it is probable that the estimated errors will take the positive values rather than the negative; since the low liquid frequencies will be too high, entropy and heat capacity will tend to be too low.

Accuracy of the thermodynamic functions for monohalobenzene is good, less than ±0.5% (*14, 37, 48*). Calculations for polyfluorobenzenes are of varying accuracy—it is excellent (<±0.5%) for the computed thermodynamic property values of difluorobenzenes (Table II); for trifluorobenzenes, however, the over-all inaccuracy is estimated from ±0.5 to 1.0%. Structural data need to be predicted, and errors may be caused by the liquid stat frequency assignments for 1,2,4-trifluorobenzene.

For tetrafluorobenzenes, some of spectroscopic and structural data were missing, and so the use of these values gives an over-all error in the thermodynamic functions of ±1.5%.

Although for the pentafluorobenzenes some spectroscopic and structural data are missing, it is estimated that the error should not exceed ±1.5%. In the case of hexafluorobenzene, there is a good agreement (Figure 3) between the calculated and previously calculated (*5*) values. Deviation from calculated and experimental values (Figure 3) may be due to an experimental error. Table I (Table III deposited with ASIS) gives calculated values for polychlorobenzenes. As the agreement between the available calculations (Table III, deposited with ASIS, footnote *a*) and this work is good, the calculated thermodynamic functions for dichlorobenzenes should be reasonably accurate—±0.5 to 1.0%. In the case of trichlorobenzenes, some of the frequency assignments are of limited reliability, and some of the structural data are missing. The estimated error is ±1.5%. The accuracy of the tetra-, penta- and hexachlorobenzenes is estimated as ±1.0%.

The polybromobenzene series (Table I, Table IV placed with ASIS) consists of 1,2-, 1,3-, and 1,4-dibromobenzenes, and 1,3,5-tribromobenzene. For ortho- and meta-dibromobenzene, the accuracy of the results is estimated to be ±1.0%, while for the para isomer, owing to the use of two solid state frequencies, an accuracy of only ±1.5% can be ascribed to the thermodynamic functions. For 1,3,5-tribromobenzene, however, several frequency assignments are not certain [three a_1 mode frequencies (*34*)], and the structural data are assigned by analogy. The accuracy of results, therefore, is estimated to be within the ±1.5%.

The accuracy for the calculated thermodynamic functions of mixed polyhalogenated benzenes (Table I, Table V placed with ASIS) is estimated as follows: In the case of halopentafluorobenzenes, the chloro- and bromopentafluorobenzene have an error of ±1.0% (liquid state frequencies used), while for the iodo-pentafluorobenzene (additional uncertainty in the structure), 1.5% appears to be a reasonable error limit of the presented calculations. In the case of unsymmetrical dihalobenzenes, the calculations for the chlorofluorobenzene isomers appear to be more accurate than those for the ortho-compounds of bromofluoro-, fluoroiodo- and bromochlorobenzene.

For the 1,3- and 1,4-chlorofluorobenzene (low frequencies in liquid state) the accuracy is ±1.0%, while for the 1,2-chlorofluorobenzene liquid state low frequencies (uncertainty in the structure), the accuracy is estimated to be ±1.5%.

For the second series (ortho compounds of chlorofluoro-, fluoroiodo- and bromofluorobenzene), owing to larger uncertainties in the vibrational frequency assignments and the missing structural data, the use of predicted values may have led to larger errors. For these compounds, we estimate the over-all accuracy of thermodynamic functions to be within ±2 to 3% range.

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NOMENCLATURE

A. = Angstrom
C_p° = heat capacity, cal. per mole, ° K.
e. u. = entropy unit, cal. per mole, ° K.
$-(G - H_0^\circ)/T$ = free energy function
$(H - H_0^\circ)/T$ = enthalpy function, where $H_0^\circ = H^\circ$ at 0° K.
I_A, I_B, and I_C = principal moments of inertia along the axis A, B, and C
I_{ABC} = principal moments of inertia product
S° = entropy
ν = wave number, cm.$^{-1}$

Superscript

$^\circ$ = reference state, referring to the hypothetical state of an ideal gas at 1 atm.

Subscript

p = pressure, atm.

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