273. *Vibrational Frequencies and Thermodynamic Properties of Fluoro-, Chloro-, Bromo-, and Iodo-benzene.*

By D. H. WHIFFEN.

An assignment of all the fundamental vibration frequencies of fluorobenzene, chlorobenzene, bromobenzene, and iodobenzene is given in Table 1, and the spectroscopic thermodynamic properties are given in Table 3.

THE majority of the Raman shifts of the halogeno-benzenes have been assigned by Kohlrausch and Wittik [1] and the infrared and Raman spectra of fluorobenzene have been discussed by Smith, Ferguson, Hudson, and Nielsen.[2] The infrared spectra have been measured by Lecomte [3] who makes a partial assignment, and also at the National Bureau of Standards.[4, 5] The assignment suggested in Table 1 follows these authors to a considerable extent and in it values are suggested for all the thirty fundamental frequencies of each compound, so that the thermodynamic properties can be calculated.

ASSIGNMENT

In the first column of Table 1 is given a code letter designation for the vibration in accordance with the approximate mode diagrams of Randle and Whiffen [6] which is reprinted in the Figure; the next column indicates the symmetry class, and this is followed by the chosen frequencies. The molecules are isomorphous and belong to the C_{2v} symmetry group, and each possesses 11 A_1 class fundamental frequencies, 10 B_1, 3 A_2, and 6 B_2 frequencies, but it is more convenient to discuss the values in terms of the approximate description of the normal modes, rather than to take each symmetry class separately. The more certain assignments will be considered first and the three less well-established frequencies thereafter in sections (9), (10), and (11).

(1) C–H *Stretchings* (*Abbreviation* νC–H).—There are five essentially C–H stretching modes for each compound, whose frequencies must lie in the range 2950—3120 cm.$^{-1}$ by analogy with other aromatic C–H frequencies.[7] But the summation frequencies k + m, k + n, l + m, and l + n are also in this range, and strong Fermi interactions are likely to occur, as in benzene itself.[8] Consequently an extensive investigation with high resolution is likely to be required to establish these frequencies and the suggestions of Table 1 are extremely tentative. Fortunately the thermodynamic properties are not very sensitive to the exact values chosen.

(2) C–C *Stretchings* (νC–C).— There are 2 A_1 and 3 B_1 modes which are essentially C–C stretchings. It is known that one of each class lies near 1600 cm.$^{-1}$, being derived from the degenerate E_{2g} benzene frequency near 1597 cm.$^{-1}$. It is only in the Raman spectrum of fluorobenzene that the two frequencies, k and l, are clearly resolved. The A_1 frequencies related to the E_{1u} frequency of benzene at 1480 cm.$^{-1}$ must be those of the strong infrared absorption of row m and the corresponding B_1 frequencies must be those of row n. These lie some 30 cm.$^{-1}$ lower, since this motion involves some admixture of C–X deformation. For the third B_1 frequency see section (10) below.

(3) *In-plane* C–H *Deformations* (βC–H).—There are two A_1 vibrations whose frequencies are almost unchanged from those of benzene at 1178 and 1033 cm.$^{-1}$ and certainly correspond to rows a and b; these frequencies appear plainly in the Raman spectra. Two of the B_1 frequencies will resemble those of the in-plane C–H deformations of monodeuterobenzene which [9] are at 1158 and 1075 cm.$^{-1}$, and rows c and d list the values. The

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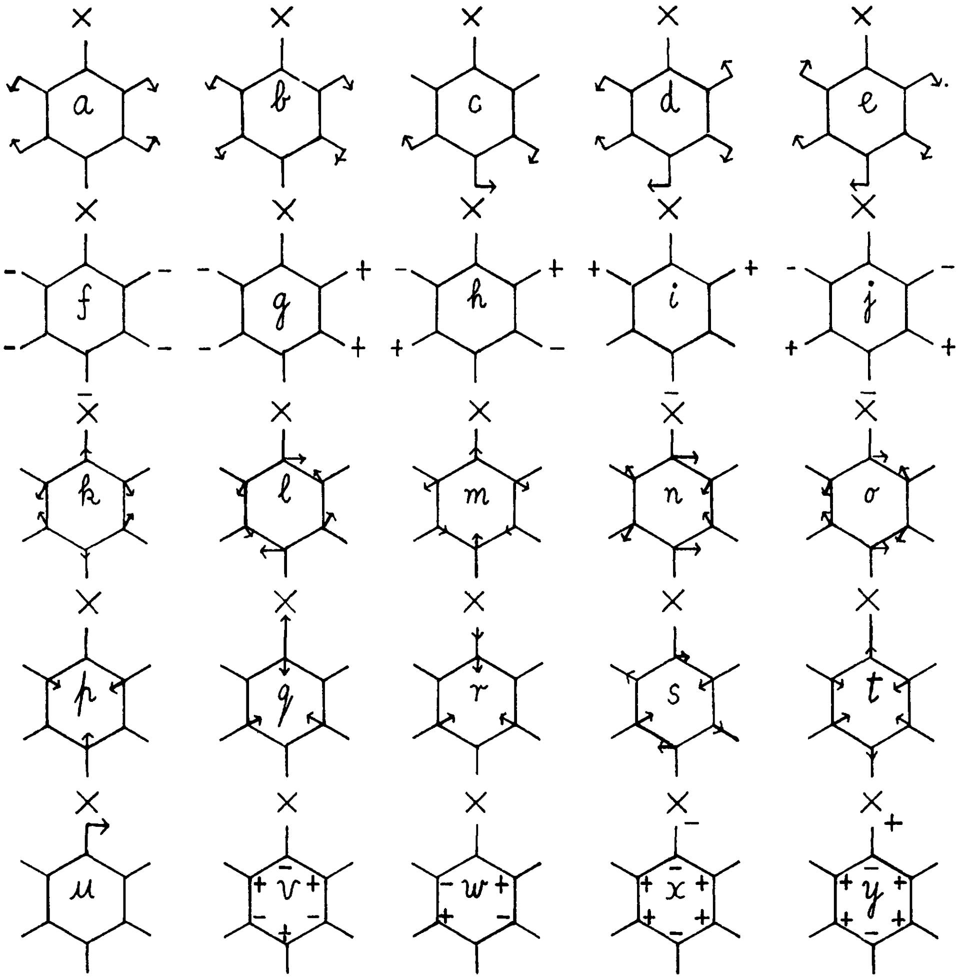
[1] Kohlrausch and Wittik, *Monatsh.*, 1943, **74**, 1.
[2] Smith, Ferguson, Hudson, and Nielsen, *J. Chem. Phys.*, 1953, **21**, 1475.
[3] Lecomte, *J. Phys. Radium*, 1937, **8**, 489.
[4] Amer. Petroleum Inst., Project 44. Infrared spectra contributed by the National Bureau of Standards.
[5] Plyler, *Discuss. Faraday Soc.*, 1950, **9**, 100.
[6] Randle and Whiffen, Molecular Spectroscopy. Conference held by the Institute of Petroleum, London, 1954.
[7] Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 1954.
[8] Herzfeld, Ingold, and Poole, *J.*, 1946, 316.
[9] Bailey, Gordon, Hale, Herzfeld, Ingold, and Poole, *J.*, 1946, 299.

d frequencies are obscured by q in bromo- and iodo-benzene, but there can be little doubt that they are at about 1068 cm.$^{-1}$ as in chlorobenzene and in other monosubstituted benzenes.[6] Indeed in the infrared spectrum [10] of iodobenzene in CS_2 the 1060 cm.$^{-1}$ band is asymmetric in shape and consistent with a medium-intensity band at 1068 cm.$^{-1}$. The frequency 1156 cm.$^{-1}$ for fluorobenzene is assigned to modes in both the A_1 and the B_1 class. There seems to be no reason for the expected B_1 frequency, c, not to lie at this frequency: the A_1 mode, a, would be depressed from its normal value 1175 cm.$^{-1}$ by the adjacent X-sensitive mode, q, at 1220 cm.$^{-1}$ and by the A_1 class energy level v + y at 1183 cm.$^{-1}$. The intensity of the 1156 cm.$^{-1}$ Raman line in fluorobenzene, which is greater than those of row c, adds weight to this suggestion. For the remaining B_1 frequencies see section (11).



[Reprinted, by permission, from Randle and Whiffen, " Molecular Spectroscopy," Institute of Petroleum, London, 1955, pp. 111—123.]

(4) *Ring Frequencies.*—The extremely strong, polarized, Raman lines of row p certainly arise from the A_1 trigonal ring breathings in which the substituent scarcely moves.

(5) *Out-of-plane* C–H *Deformations* (γC–H).—The lowest of the three B_2 C–H out-of-plane deformation frequencies, row *f*, is known to give very strong infrared absorption. The lower of the two A_2 frequencies is almost unchanged from the corresponding benzene

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[10] Randle and Whiffen, *Trans. Faraday Society*, 1956, **52**, 9.

vibration at 849 cm.$^{-1}$ and is indicated by the medium-intensity Raman shifts of row g. Row i corresponds to medium infrared absorption and accounts for a second B_2 mode; the frequencies are slightly below the corresponding deuterobenzene value[9] of 922 cm.$^{-1}$. Rows h and j are less evident in the fundamental spectra, but the evidence of the summation tones from 1700 to 2000 cm.$^{-1}$ indicates that these have been correctly chosen, as has been discussed in detail elsewhere.[11]

(6) *Out-of-plane Ring Deformations* (φC–C).—The strong infrared bands of row v clearly correspond to the B_2 ring deformation in agreement with the calculated value[12] of 698 cm.$^{-1}$ and the deuterobenzene value[9] also of 698 cm.$^{-1}$. The A_2 frequencies are discussed in section (9).

TABLE 1. *Assignment of fundamentals of* C_6H_5X.

Nature of X			F				Cl		Br		I	
Spectrum			I–r[2]	I–r[4, 5]	R[2]	R[1]	I–r[4, 5]	R[2]	I–r[4, 5]	R[2]	I–r[4, 5]	R[2]
z_1	A_1	νC–H	3067	3065	3072	3084	3071	3067	3069	3065	3064	3070
z_2	A_1	νC–H	3053	3049	—	—	— (3050) —		— (3050) —		— (3050) —	
z_3	A_1	νC–H	3040	3036	—	—	3029	—	3029	—	3031	—
z_4	B_1	νC–H	3100	3095	—	—	3071	—	3069	—	3064	—
z_5	B_1	νC–H	—	—	—	3072	—	3052	—	3056	—	3048
k	A_1	νC–C	1597	1592	1602	1603	1580	1583	1580	1577	1575	1571
l	B_1	νC–C	1597	1592	—	1596	1580	1583	1580	1577	1575	1571
m	A_1	νC–C	1499	1492	1496	1496	1477	1479	1473	1472	1473	1469
n	B_1	νC–C	1460	—	1457	xx	1445	1443	1445	1441	1435	1436
o	B_1	νC–C	1326	1324	xx	xx	1326	1322	1323	1319	1321	1318
e	B_1	βC–H	1290	1282	xx	1295	1271	1263	1264	1263	1261	1255
a	A_1	βC–H	—	—	1156	1157	1174	1174	1175	1176	1178	1175
c	B_1	βC–H	1156	1155	—	—	1157	1157	1159	1158	1159	1156
d	B_1	βC–H	1066	1065	1065	1068	1068	—	— (1068) —		— (1068) —	
b	A_1	βC–H	1020	1020	1021	1024	1026	1024	1021	1020	1015	1017
p	A_1	ring	—	—	1009	1010	1003	1002	1001	1001	998	999
j	B_2	γC–H	980	982	—	—	985	987	988	990	987	988
h	A_2	γC–H	955	955	xx	xx	965	xx	963	xx	963	xx
i	B_2	γC–H	896	896	896	900	902	xx	903	906	904	xx
g	A_2	γC–H	831	—	829	831	830	832	832	832	835	838
f	B_2	γC–H	752	752	754	759	740	741	735	737	730	731
v	B_2	φC–C	685	682	687	xx	682	xx	681	—	684	xx
s	B_1	αC–C–C	615	615	613	612	616	615	615	614	613	613
w	A_2	φC–C	—	— (400) —		—	— (400)	xx	—	409	—	398
q	A_1	X sens.	1220	1219	1217	1218	1085	1083	1070	1071	1060	1060
r	A_1	X sens.	806	806	806	807	701	702	669	673	654	654
t	A_1	X sens.	520	519	519	519	415	418	314	315	—	266
u	B_1	X sens.	405	406	407	407	297	297	—	254	—	220
y	B_2	X sens.	501	499	499	496	467	467	458	460	448	450
x	B_2	X sens.	—	—	242	241	—	196	—	181	—	166

Symbols: xx frequency not observed, — spectrum obscured or not measured, () frequency inferred, see text.

(7) *In-plane Ring Deformation* (αC–C–C).—One component of the degenerate E_{2g} class vibration of benzene at 606 cm.$^{-1}$ is scarcely changed in mode for C_6H_5X and appears as the B_1 class frequency in row s; it is especially strong in the Raman spectra.

(8) X-*Sensitive Vibrations* (X *sens.*).—There are six vibrational modes in which the substituent, X, moves with appreciable amplitude and consequently the frequencies are sensitive to the mass of X. The three A_1 frequencies give rise to strongly polarized Raman lines[1] and have the frequencies given in rows q, r, and t. The alternative assignments by Plyler[5] are unacceptable as they place polarized Raman line frequencies in the B_2 class. Modes q, r, and t all involve appreciable C–X stretching and it would not be justified to call any particular row the C–X stretching frequencies. In contrast only one B_1 mode is sensitive to the mass of X and may be called the C–X in-plane deformation mode. The values given in row u agree with Garg's approximate calculations.[13] The two sensitive B_2 frequencies for each molecule are given in rows y and x; the fluorobenzene frequencies

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[11] Whiffen, *Spectrochim. Acta*, 1955, **7**, 253.

[12] Whiffen, discussion, see ref. 6.

[13] Garg, *Current Sci.*, 1953, **22**, 298.

at 499 and 241 cm.$^{-1}$ agree with the approximate calculations[12] which gave 490 and 247 cm.$^{-1}$. The heavier halogens have rather lower frequencies, as is to be expected. Also the lowest B_2 frequency, row x, lies below the lowest B_1, row u, which is consistent with a lower out-of-plane than in-plane deformation force constant; for aromatic C–H links the values[14] are 0·286 and 0·864 × 10^5 dynes/cm. respectively.

The discussion above has accounted for twenty-seven of the fundamentals in each case and discussion of the remaining modes has been postponed to this point since the evidence involves summation frequencies of the more certain modes already given.

(9) *Out-of-plane* A$_2$ *Ring Deformation.*—The missing A_2 ring deformation frequency, row w, cannot, from its symmetry class, involve any motion of the substituent. Departures from the corresponding E_{2u} benzene frequency at 405 cm.$^{-1}$ are therefore likely to be small since the C–C twisting force constant remains essentially unchanged. Kohlrausch and Wittik[1] adduce experimental evidence for frequencies near 400 cm.$^{-1}$ from the Raman spectra, while Table 2 shows that summation bands may be explained as 2w, v + w, w + g, w + i, and w + j, by use of this value. The last three are important evidence since the corresponding bands in the infrared spectrum of benzene[8] at 1248 and 1381 cm.$^{-1}$ are interpreted as summation bands of the 405 cm.$^{-1}$ E_{2u} frequency with the benzene equivalents[11] of rows g, i, and j, namely, the degenerate E_{1g} frequency at 849 cm.$^{-1}$ and the B_{2g} frequency at 985 cm.$^{-1}$. This evidence seems stronger than that for the value 330 cm.$^{-1}$ in fluorobenzene.[2] The summation bands thought to require the value 330 cm.$^{-1}$ have alternative explanations, namely: 565 (d − u = 561, d − w = 565); 653 (x + w = 642, x + u = 647); 955 (A_2 fundamental); 1190 (v + y = 1186); 1789 (2i = 1792); 3373 (m + n + u = 3360 cm.$^{-1}$).

TABLE 2. *Some summation frequencies of* C_6H_5X.

Nature of X		F				Cl		Br		I	
Spectrum		I–r[2]	I–r[4, 5]	R[2]	R[1]	I–r[4, 5]	R[2]	I–r[4, 5]	R[2]	I–r[4, 5]	R[2]
t − x	B_2	—	—	277	274	—	—	—	—	—	—
t + x	B_2	—	—	—	—	—	—	xx	502	—	—
2x	A_1	—	—	—	—	390 ?	382	—	365	—	321
t + u	B_1	925	925	xx	xx	—	—	545	xx	—	xx
x + y	A_1	—	—	—	—	—	xx	628	—	—	—
x + w	B_1	653	651	—	—	xx	—	xx	—	—	—
2w	A_1	—	—	—	—	810	—	812	—	790	—
m–s, e–w	B_1, B_2	875	874	xx	xx	860	xx	862	xx	862	xx
2y, f + x	A_1, A_1	996	995	997	997	936	934	912	xx	—	xx
r + t	A_1	—	—	—	—	1123	1121	—	—	919	xx
v + w	B_1	1105	1104	xx	xx	—	—	1095	xx	1095	xx
v + y	A_1	1190	1185	xx	xx	—	—	1133	xx	1125	xx
f + y	A_1	1255	—	xx	xx	1212	xx	1196	xx	1186	—
w + g	A_1	1235	—	—	—	1234	xx	1233	xx	1231	xx
w + i	B_1	1302	1299	xx	1301	1299	1294	1299	xx	1302	xx
i + y	A_1	1397	1393	—	—	1374	—	1362	—	1351	—
2v	A_1	—	—	1369	1370	—	1372	—	1365	—	1361
j + w	A_1	1397	1393	—	—	1389	1399	1385	—	1379	—
v + g	B_1	1531	—	xx	xx	—	xx	—	xx	1522	xx
s + p	B_1	1624	—	1623	1626	1626	1614	—	1614	—	1619
i + f	A_1	1652	—	—	—	1647	—	1639	—	1636	—
2g	A_1	—	—	xx	xx	—	xx	—	1667	—	1666
g + i	B_1	1714	1709	—	—	1736	xx	1736	xx	1739	xx
g + h	A_1	1778	1773	1789	xx	1795	xx	1795	xx	1798	xx
i + h	B_1	1855	1855	xx	xx	1873	xx	1873	xx	1872	xx
h + j	B_1	1939	1938	—	xx	1949	xx	1949	xx	1949	xx

Symbols as in Table 1.

(10) B_1 C–C *Stretching Frequency.*—If Mair and Hornig[15, 16] are followed in placing the

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[14] Whiffen, *Phil. Trans.*, 1955, **248**, 131.

[15] Mair and Hornig, *J. Chem. Phys.*, 1949, **17**, 1236.

[16] Additional argument in favour of the new assignment was given by F. A. Miller at the Ohio State Meeting on Molecular Spectroscopy, 1955; *J. Chem. Phys.*, in the press.

B_{2u} frequency of benzene at 1310 cm.$^{-1}$ the missing B_1 C–C stretching frequencies of the substituted benzenes must have similar values. The infrared spectra show two possible bands for each compound near 1320 cm.$^{-1}$, row o, and near 1300 cm.$^{-1}$. The Raman evidence[1] is in favour of the former set which corresponds to Raman frequencies in three of the spectra; w + i is an acceptable attribution to the 1300 cm.$^{-1}$ frequencies. The fluorobenzene frequency at 1326 cm.$^{-1}$ might be r + t = 1326 cm.$^{-1}$, but no explanation other than B_1 fundamental could be found for the other frequencies of row o.

(11) B_1 C–H *In-plane Deformation.*—There remain the highest B_1 C–H deformations which are likely to be only a little lower than 1292 cm.$^{-1}$, the value[9] for deuterobenzene, and the values in row e are suggested. Possible alternative candidates nearer 1230 cm.$^{-1}$ are more probably w + g. The suggestion[2] that the missing frequency is 875 cm.$^{-1}$ in fluorobenzene would imply that this compound has C–H deformation force constants which are very different from those in benzene, which is improbable. The summation frequencies thought to involve 875 cm.$^{-1}$ can all be otherwise explained: 1190 (v + y = 1186); 1485 (j + y = 1480); 1676 (t + a = 1676, t + c = 1676); 1939 (h + j = 1936); 2375 (a + q = 2377, c + q = 2377). The 875 cm.$^{-1}$ frequency itself is less satisfactorily explained, but the frequencies m − s = 881, e − w = 890, e − u = 884 cm.$^{-1}$, are all available. Nor is 1236 cm.$^{-1}$ essential as a fundamental,[2] for the frequencies that might involve this value can be explained as: 1735 (g + i = 1727, q + t = 1740); 2491 (n + d = 2480); 2846 (z_4 − y = 2848 cm.$^{-1}$). 1236 cm.$^{-1}$ itself is probably w + g = 1231 cm.$^{-1}$, which involves transition to an A_1 level, and the infrared band could derive part of its intensity by interaction with the 1220 cm.$^{-1}$ fundamental.

The last two B_1 assignments are also supported by calculations for deuterobenzene using force constants[14] appropriate to the Mair and Hornig assignment for benzene. The calculations lead to frequencies of 1314 and 1291 cm.$^{-1}$, but the normal co-ordinates show that there is considerable mixing of the C–C stretching and C–H deformation co-ordinates. w + i is a third B_1 energy level in this frequency region, and the description of the three frequencies as C–C stretching fundamental, w + i summation, and C–H deformation fundamental is a gross simplification of the true state of affairs.

The more important summation frequencies and their interpretation are given in Table 2. Some of the assignments have already been discussed and other comments are to be found in the references cited.[1, 2, 11] The remaining points are not of sufficient importance or certainty to warrant detailed discussion, but Table 2 does show that the frequencies are capable of at least one explanation in terms of the chosen fundamentals.

It can be seen that the assignment of any one halogenobenzene has been made more certain by considering together the analogous vibrations of all four compounds. This approach could readily be extended to other monosubstituted benzenes. If a general rather than a particular substituent were considered the result would be essentially Table 1 of reference 6. This Table is in agreement with the present interpretations except in a few minor particulars: (i) Line 2 contains a misprint in the class designation which should read B_1 for the s mode. (ii) The frequency near 962 cm.$^{-1}$ is[11] that of the A_2 mode h and that near 982 cm.$^{-1}$ belongs to the B_2 mode j. (iii) The highest B_1 C–H deformation mode, e, seems to be near 1270 cm.$^{-1}$ rather than 1240 cm.$^{-1}$ which is the value for the summation tone w + g. (iv) The last row with frequencies near 1663 cm.$^{-1}$ is more probably[11] f + i than either o or s + b.

It is interesting that the frequencies of the halogenobenzenes are in many cases essentially unchanged in passing from fluoro- to iodo-benzene despite the change of electronegativity[17] from 4·0 to 2·5. This implies that the force constants governing the carbon and hydrogen motions are also unchanged. Apart from the specifically X-sensitive motions, the greatest frequency deviation seems to be 22 cm.$^{-1}$ in row f which is analogous to the modes discussed in relation to Hammett's σ values by Bellamy.[18] Rows k, l, m, and n are also more sensitive than the average, but they correspond to ring frequencies which are more likely to be mass-sensitive than the hydrogen frequencies.

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[17] Pauling, " Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, 1945.
[18] Bellamy, *J.*, 1955, 2818.

THERMODYNAMIC PROPERTIES

These fundamental frequencies were used to calculate the vibrational contributions to the thermodynamic properties; an average value between the infrared and Raman frequencies was used if these differed. For determining the rotational contributions accurate moments of inertia are available for fluoro-[19] and chloro-benzene.[20] For bromo- and iodo-benzene the distances[21] 1·86 ± 0·03 Å for C–Br and 2·08 ± 0·04 Å for C–I were assumed and the moments of inertia calculated with the aid of the additional assumption that the moment of inertia of benzene itself could be assumed to be $148 \cdot 0 \times 10^{-40}$ about an axis in the plane of the ring. This is the value found by Erlandsson[19, 20] for the smallest moment of chloro- and fluoro-benzene and is consistent with the Raman value for benzene obtained by Stoicheff.[22] The limits of error given correspond to ±0·02 in $(H^\circ_0 - G^\circ)/\mathbf{R}T$ and $S^\circ/\mathbf{R}$. The total contributions are given in Table 3 which relates to 1 mole of perfect gas at 1 atmosphere. Spin contributions are excluded, except through the intervention of the symmetry number, as are isotopic mixing terms. The usual high-temperature and harmonic oscillator approximations were made, and the computation was shortened by the use of the tables quoted by Pitzer;[23] values of the fundamental constants were taken from the same source.

Calorimetric values for the liquid-state entropies and specific heats have been given by Stull.[24] From these, gas-state entropies can be obtained by using the latent-heat data suggested by Jones and Bowden[25] and interpolating the vapour pressures from Stull's data.[26] If gas imperfections are neglected, the resulting entropies at 25° C are those given in Table 4, where they are compared with the spectroscopic values at the same temperature. The calorimetric values are consistently lower by 2—5 e.u. This difference is rather

TABLE 3. *Thermodynamic properties.*

Temp. (K)	200°	273·16°	298·16°	300°	400°	500°	600°	800°	1000°
				Fluorobenzene					
$(H^\circ_0 - G^\circ)/\mathbf{R}T$	27·58	29·31	29·87	29·91	32·02	34·04	35·98	39·67	43·08
$(H^\circ - H^\circ_0)/\mathbf{R}T$	5·09	6·13	6·52	6·55	8·23	9·90	11·67	14·18	16·37
$S^\circ/\mathbf{R}$	32·67	35·44	36·39	36·46	40·25	43·94	47·65	53·85	59·45
$C^\circ_p/\mathbf{R}$	7·61	10·37	11·33	11·40	15·03	18·05	20·45	23·91	26·26
				Chlorobenzene					
$(H^\circ_0 - G^\circ)/\mathbf{R}T$	28·38	30·22	30·81	30·85	33·07	35·18	37·19	40·97	44·44
$(H^\circ - H^\circ_0)/\mathbf{R}T$	5·40	6·49	6·90	6·93	8·61	10·28	11·83	14·50	16·67
$S^\circ/\mathbf{R}$	33·78	36·71	37·70	37·78	41·68	45·45	49·02	55·47	61·11
$C^\circ_p/\mathbf{R}$	8·13	10·84	11·79	11·86	15·41	18·36	20·71	24·10	26·41
				Bromobenzene					
$(H^\circ_0 - G^\circ)/\mathbf{R}T$	29·50	31·40	32·01	32·05	34·34	36·49	38·53	42·36	45·87
$(H^\circ - H^\circ_0)/\mathbf{R}T$	5·61	6·71	7·12	7·15	8·82	10·47	12·01	14·65	16·80
$S^\circ/\mathbf{R}$	35·11	38·12	39·13	39·20	43·16	46·96	50·54	57·01	62·67
$C^\circ_p/\mathbf{R}$	8·43	11·07	11·99	12·06	15·56	18·47	20·79	24·15	26·44
				Iodobenzene					
$(H^\circ_0 - G^\circ)/\mathbf{R}T$	30·31	32·28	32·90	32·94	35·27	37·45	39·52	43·39	46·92
$(H^\circ - H^\circ_0)\mathbf{R}T$	5·79	6·89	7·29	7·32	8·98	10·61	12·13	14·76	16·89
$S^\circ/\mathbf{R}$	36·10	39·16	40·18	40·26	44·25	48·07	51·66	58·14	63·80
$C^\circ_p/\mathbf{R}$	8·62	11·21	12·12	12·19	15·65	18·55	20·85	24·19	26·47

TABLE 4. *Standard vapour entropy,* S° (e.u.) *at* 298·16° K.

	C_6H_5F	C_6H_5Cl	C_6H_5Br	C_6H_5I
Calorimetric	69·9	71·8	74·5	74·7
Spectroscopic	72·32	74·92	77·76	79·85

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[19] Erlandsson, *Arkiv Fys.*, 1953, **7**, 189.
[20] *Idem, ibid.*, 1954, **8**, 341.
[21] Schoppe, *Z. phys. Chem.*, 1936, **34**, *B*, 461.
[22] Stoicheff, *J. Chem. Phys.*, 1953, **21**, 1410.
[23] Pitzer, "Quantum Chemistry," Constable, London, 1953.
[24] Stull, *J. Amer. Chem. Soc.*, 1937, **59**, 2726.
[25] Jones and Bowden, *Phil. Mag.*, 1946, **37**, 480.
[26] Stull, *Ind. Eng. Chem.*, 1947, **39**, 517.

larger than Stull's[24] estimate of 3% as his error, though some allowance must be made for errors in the vapour pressures and latent heats. But the main uncertainty is possibly in the reliability of Stull's extrapolation for the entropy change from 0° to 91° K, and a direct determination of specific heats below 91° K would be desirable. It is not easy to estimate errors in the spectroscopic values, which are uncertain owing to neglect of anharmonicity and the use of liquid-state frequencies; also there is uncertainty of about 10 cm.^{-1} in the exact values of row w of Table 1. Providing there is no major error of assignment, the properties in Table 3 are probably correct within ±0·2 in the quantities listed.

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