72. *Vibrational Spectra and Chemical Thermodynamic Properties of the Difluorobenzenes.*

By J. H. S. Green, W. Kynaston, and H. M. Paisley.

The infrared absorption spectra (liquid, solutions, and vapour phase) and the Raman spectrum (liquid) of *o*-difluorobenzene have been measured and a complete vibrational assignment made. This has been used, together with a revised assignment for *m*-difluorobenzene and a completed assignment for *p*-difluorobenzene, to calculate the chemical thermodynamic properties for all three isomers in the ideal-gas state at 273·16°, 298·16°, and 300—1500°K.

The infrared spectrum (2—15 μ) of *o*-difluorobenzene has been reported [1] but there is no complete record of the Raman displacements apart from a quotation [2] of some frequencies. In the present work the infrared measurements have been extended to 45 μ and the Raman spectrum recorded. The observed frequencies have been fully interpreted and complete assignments made to the normal frequencies. Some revisions of the assignment [3] for *m*-difluorobenzene are now suggested to bring the fundamentals into line more closely with those given recently [4] for other *m*-disubstituted benzenes. The previous assignment for *p*-difluorobenzene [5] has now been completed by an attribution of the lowest b_{3u} fundamental.

Experimental

The original commercial sample of *o*-difluorobenzene was shown by gas chromatography and nuclear magnetic resonance spectroscopy to contain *ca.* 5% of impurity, identified by infrared spectroscopy as *o*-chlorofluorobenzene.[6] Distillation afforded material containing *ca.* 1% of this impurity. The infrared spectra were recorded for the liquid compound and for solutions in carbon tetrachloride and carbon disulphide by using the double-beam prism-grating instrument (4000—560 cm.$^{-1}$) as before; [7] for the liquid and the gaseous state (10 cm. cell at 100°) a Grubb-Parsons GS3 spectrometer (600—400 cm.$^{-1}$) was used, and for the liquid compound a Grubb-Parsons DM3 (25—50 μ) monochromator with a single-beam source unit. Raman spectra were measured photoelectrically and photographically (Kodak 0a—0 plates) with a Hilger source unit and E612 spectrograph.

The spectra are assembled in Table 1. Only one frequency is coincident with frequencies

---

[1] Mecke, D.M.S. Catalogue of Infrared Spectra, Butterworths, London, Nos. 3336, 3337.

[2] Nonnenmacher and Mecke, *Spectrochim. Acta*, 1961, **17**, 1049.

[3] Ferguson, Collins, Nielsen, and Smith, *J. Chem. Phys.*, 1953, **21**, 1470.

[4] Green, *J.*, in the press.

[5] Stojiljkovic and Whiffen, *Spectrochim. Acta*, 1958, **12**, 47; Ferguson, Hudson, Nielsen, and Smith, *J. Chem. Phys.*, 1953, **21**, 1457.

[6] Navasimham, El-Sabban, and Nielsen, *J. Chem. Phys.*, 1956, **24**, 420.

[7] Green, *J.*, 1961, 2236.

belonging to *o*-chlorofluorobenzene;[6] this band, at 441 cm.$^{-1}$, was shown not to change in relative intensity on purification and its relative intensity in both infrared and Raman spectra was too great to be due entirely to impurity.

ASSIGNMENT

o-*Difluorobenzene*.—The molecule has C_{2v} symmetry and, with the z-axis as the twofold axis and the x-axis as that perpendicular to the ring,[8] the thirty fundamentals comprise $(11a_1 + 10b_2)$ planar plus $(5a_2 + 4b_1)$ non-planar modes. With the dimensions C–F = 1·35 Å,[9] C–H = 1·084, C–C = 1·397 Å, and all angles 120°,[10] the moments of inertia are found to be $I_{xx} = 381{\cdot}49$, $I_{yy} = 642{\cdot}97$, $I_{zz} = 261{\cdot}52 \times 10^{-40}$ g. cm.^{2}, so that the least moment coincides with the twofold axis. Hence a_1 fundamentals should yield bands with A-type contours, b_2 fundamentals give B-type contours, and b_1 fundamentals C-type contours. Approximate band envelopes were calculated by using the results of

TABLE 1.

Vibrational frequencies and assignments for *o*-difluorobenzene.

	Infrared			
Raman $\Delta\nu$ (liquid)	(Liq. and solns.)	(Vapour)		Interpretation
196vs	—	—		a_1 and a_2 fund.
298s	289s	—		b_1 fund.
439m	441m			b_2 fund.
456m	451m	444 450 456	C	b_1 fund.
551m	546s	541 553	B	b_2 fund.
568s	566m	565 571	A	a_1 fund.
596w	588w	—		a_2 fund.
705m	701sh	—		a_2 fund.
748w	749vvs	741 749 757	C	b_1 fund.
762vvs	762vs	762 767	A	a_1 fund.
	840m	838sh		a_2 fund.; 551 + 289 = 840 (B_1)
851w	856m	851 862	B	b_2 fund.
906w	904w	920		2 × 451 = 902 (A_1)
	930m	929	C	b_1 fund.
	982 vw	938		a_2 fund.
1025vs	1024m	1020 1025 1031	A	a_1 fund.
1102m	1101s	1098 1109	B	b_2 fund.
1152m	1152w	1148 1155 1162	A	a_1 fund.
1215w	1206s	1209 1219	B	b_2 fund.
1270s	1272vs	1272 1277 1283	A	a_1 fund.
1296w	1292m	—		b_2 fund.
1316vw	1313sh			a_1 fund.
	1385sh			451 + 930 = 1381 (A_1)
1402w	1403m	1401 1406 1410	A	2 × 701 = 1402 (A_1)
	1456m			701 + 749 = 1450 (B_2)
1464w	1472m	1458 1471	B	b$_2$ fund.
1511m	1511vs	1509 1514 1519	A	a_1 fund.
	1525m			2 × 762 = 1524 (A_1)
1565vw	1561m			856 + 701 = 1557 (B_1)
1609s	1610sh	1609		a_1 fund.
1620s	1619m	1625		b_2 fund.
	1694	1688		2 × 840 = 1680 (A_1)
	1777m	1763 1774	B	840 + 929 = 1769 (B_2)
	1816vw	1806		982 + 840 = 1822 (A_1)
	1860w	1850		2 × 929 = 1858 (A_1)
	1897m	1886 1895	B	929 + 982 = 1911 (B_2)
	1948w	1931		1101 + 856 = 1957 (A_1)
3010w	3013w			2 × 1511 = 3022 (A_1)
3045s	3060s	3076		
3085vs	3081s			$2a_1$ and $2b_2$ fund.

fund. = fundamental. w = weak; m = medium; s = strong; v = very; sh = shoulder. Region 2000—3000 cm.$^{-1}$ omitted; additional weak Raman lines were observed at 2825, 2915, and 2977 cm.$^{-1}$.

---

[8] Mulliken, *J. Chem. Phys.*, 1955, **23**, 1997.

[9] Sutton, " Tables of Interatomic Distances," Chem. Soc., London, 1958. *Special Publ.* No. 11.

[10] Stoicheff, *Canad. J. Phys.*, 1954, **32**, 339.

Badger and Zumwalt [11] and the *PR* separations found to be 12, 8, and 11 cm.$^{-1}$ for the *A*, *B*, and *C* types respectively.

The CH stretching fundamentals are not all adequately resolved and are assigned schematically as summarised in Table 2. However, the expected pair of frequencies derived from the benzene vibration at 1600 cm.$^{-1}$ are resolved and the lower is placed in the a_1 class and the higher in the b_2 class as for other *o*-disubstituted benzenes and in accord with the calculations for *o*-xylene.[12] Also in the a_1 class must be placed the bands with *A*-type contours centred at 1514, 1277, 1155, and 1025 cm.$^{-1}$. The contours around 750 cm.$^{-1}$ are somewhat confused since the *P* branch of the *A*-type contour centred at 762 cm.$^{-1}$ is overlapped by the *R* branch of the adjacent, extremely strong, b_1 fundamental at 749 cm.$^{-1}$. The Raman intensities support the assignments to a_1 and b_1 modes. Similarly, the pair of frequencies at 546 and 566 cm.$^{-1}$ are overlapped but the lower appears to have a *B*-type and the higher an *A*-type contour, and the Raman intensities again support this. The lowest a_1 fundamental is expected at about 200 cm.$^{-1}$ and is assigned to the strong Raman displacement of 196 cm.$^{-1}$ (cf. *o*-xylene, 180 cm.$^{-1}$; *o*-fluorotoluene, 186 cm.$^{-1}$; *o*-cresol, 190 cm.$^{-1}$). A final a_1 mode is derived from ν_{14} of benzene and therefore expected at around 1300 cm.$^{-1}$, though it is often only a weak band and somewhat elusive. The shoulder at 1313 cm.$^{-1}$ is a reasonable attribution though the fundamental may be coincident with the b_2 mode suggested at 1292 cm.$^{-1}$. There are also three other B_2 levels in this region, namely $1206 + 196 = 1302$, $566 + 749 = 1315$, and $450 + 856 = 1336$.

Four b_2 fundamentals can be assigned clearly on a basis of the observed *B*-type contours of bands centred at 1464, 1214, 1103, and 857 cm.$^{-1}$ and a fifth is evidently at 546 cm.$^{-1}$. The b_2 fundamental derived from ν_4 is that proposed at 1292 cm.$^{-1}$, and the lowest is expected at *ca.* 400 cm.$^{-1}$ and is assigned to the 439 cm.$^{-1}$ medium-intensity Raman line which appears as a definite shoulder in the infrared spectrum.

The five a_2 modes are forbidden in the infrared spectrum of the vapour and are usually only weak in the Raman effect. The two highest are essentially out-of-plane hydrogen-bonding modes, γ(CH), and are expected at *ca.* 980 and 860 cm.$^{-1}$; the former can therefore be readily assigned to the weak infrared band in the liquid at 982 cm.$^{-1}$. A band of medium intensity is observed in the liquid-state spectrum at 840 cm.$^{-1}$ but it is too strong to be entirely due to an a_2 fundamental and, further, it appears as a shoulder on the 856 cm.$^{-1}$ band in the vapour spectrum. This presumably arises from $551 + 289 = 840$ (B_1). The a_2 fundamental is assumed to be at about this position and some support for this is found in the usual analysis of the bands in the 1600—1900 cm.$^{-1}$ region in terms of combination and overtones of the γ(CH) modes. Two further a_2 fundamentals are assigned as weak bonds at 705 and 596 cm.$^{-1}$, whilst the lowest involving essentially out-of-plane bending of the C–F bonds is the strong Raman displacement of 196 cm.$^{-1}$; as in *o*-xylene,[4,12] the lowest a_1 and a_2 frequencies are accidentally coincident.

Three of the b_1 fundamentals, at 929, 749, and 450 cm.$^{-1}$, are readily identified by the *C*-type contours and the fourth is assigned to the strong infrared band and Raman line at 298 cm.$^{-1}$. These assignments of the out-of-plane classes are in reasonable accord with the results of calculations.[2,13]

m-*Difluorobenzene.*—The revisions of the assignment [3] for *m*-difluorobenzene are made as follows. In the a_1 class it is clear that two fundamentals cannot be placed at 1257 and 1279 cm.$^{-1}$. One of these frequencies is acceptable as the fundamental and is the latter, with its *Q* branch at 1286 cm.$^{-1}$; the former is $736 + 524 = 1260$ (A_1) which has probably borrowed intensity from the fundamental. The required new fundamental is certainly at 1608 cm.$^{-1}$ where it is evidently unresolved from its b_2 counterpart. The *Q* branches of other a_1 fundamentals are taken as 1456, 1066, and 735 cm.$^{-1}$; the ring breathing mode

---

[11] Badger and Zumwalt, *J. Chem. Phys.*, 1938, **6**, 711.

[12] Kovner and Bogomoloff, *Optika i Spektroskopiya*, 1959, **7**, 751.

[13] Whiffen, "Molecular Spectroscopy," Conference held by the Institute of Petroleum, London, 1954, p. 126.

which appears as a very strong Raman line at 1008 cm.$^{-1}$ is absent from the infrared spectrum.

In the b_2 class (b_1 of ref. 3) the Q branch of the lower ν(CC) mode is taken at 1493 cm.$^{-1}$. The next two fundamentals are derived from ν_3 and ν_4 of benzene and are lost in the infrared spectrum beneath the strong bands at 1257 and 1279 cm.$^{-1}$. They are taken to be at 1290 and 1265 cm.$^{-1}$ on a basis of their values in other *m*-disubstituted benzenes where the X-sensitive a_1 fundamental has moved to lower frequencies and left the other fundamentals exposed (*e.g. m*-dichlorobenzene, 1295 and 1255 cm.$^{-1}$; *m*-dibromobenzene, 1292 and 1256 cm.$^{-1}$). Bands at 458 and 478 cm.$^{-1}$ were previously both candidates for the lowest b_2 mode and the former was preferred; however, it is now[2] known that it has a C-type contour and must be assigned to the infrared-active out-of-plane class, b_1; the b_2 mode is now placed at 478 cm.$^{-1}$.

The one other change in the b_1 class is the choice of 978 cm.$^{-1}$ rather than 862 cm.$^{-1}$ for the highest, γ(CH) mode. The a_2 class remains as before.

p-*Difluorobenzene.*—The revised assignment[5] for this molecule has received confirmation from intensity measurements[14] and from further band contour studies.[15] A band at 163 cm.$^{-1}$ in the vapour and 164 cm.$^{-1}$ in the liquid has been observed by one of us[16] and may be assigned to the missing b_{3u} fundamental; the calculated value[14] was 168 cm.$^{-1}$. A very weak Raman shift of 165 cm.$^{-1}$ had been reported[5] but not interpreted

TABLE 2.

Fundamental vibrational frequencies (cm.$^{-1}$) of the difluorobenzenes.

ortho (*a*)			*meta* (*a*)			*para* (*b*)		
a_1	ν(CH)	3081	a_1	ν(CH)	3096	a_g	ν(CH)	3084
	ν(CH)	3060		ν(CH)	3087		ν(CC)	1617
	ν(CC)	1609		ν(CH)	3087		β(CH)	1245
	ν(CC)	1514		ν(CC)	1608		β(CH)	1142
	ν(CC)	1313		ν(CC)	1456		ν(CC)	858
	X-sens.	1277		X-sens.	1286		α(CCC)	451
	β(CH)	1152		β(CH)	1066	b_{1u}	ν(CH)	3065
	β(CH)	1025		Ring	1008		ν(CC)	1511
	X-sens.	762		X-sens.	735		Ring	1225
	X-sens.	568		X-sens.	524		β(CH)	1012
	X-sens.	196		X-sens.	331		(CX)	737
b_2	ν(CH)	3081	b_2	ν(CH)	3096	b_{3g}	ν(CH)	3084
	ν(CH)	3060		ν(CC)	1608		ν(CC)	1617
	ν(CC)	1625		ν(CC)	1493		β(CH)	1285
	ν(CC)	1464		ν(CC)	1290		α(CCC)	635
	β(CH)	1294		β(CH)	1265		β(CX)	427
	X-sens.	1214		β(CH)	1158	b_{2u}	ν(CH)	3074
	β(CH)	1103		β(CH)	1123		ν(CC)	1437
	X-sens.	857		X-sens.	954		ν(CC)	1285
	Ring	546		Ring	514		Ring	1085
	X-sens.	440		X-sens.	478		β(CX)	350
a_2	γ(CH)	982	a_2	γ(CH)	879	b_{1g}	γ(CH)	800
	γ(CH)	840		X-sens.	599	a_u	γ(CH)	943
	ϕ(CC)	703		X-sens.	271		ϕ(CC)	405
	X-sens.	592	b_1	γ(CH)	978	b_{2g}	γ(CH)	928
	X-sens.	196		γ(CH)	853		ϕ(CC)	692
b_1	γ(CH)	929		γ(CH)	769		γ(CX)	375
	γ(CH)	749		ϕ(CC)	672	b_{3u}	γ(CH)	833
	ϕ(CC)	450		ϕ(CC)	458		ϕ(CC)	509
	X-sens.	298		X-sens.	235		γ(CX)	163

(*a*) Approximate description of mode based on symmetry co-ordinates and behaviour in other compounds.[4] (*b*) Cf. refs. 5, 17.

---

[14] Steele and Whiffen, *Trans. Faraday Soc.*, 1960, **56**, 8, 177.

[15] Personal communication from Dr. T. M. Dunn.

[16] Gebbie, Kynaston, and Steele, unpublished measurements.

[17] Albrecht, *J. Mol. Spectroscopy*, 1960, **5**, 256.

as a fundamental. The complete assignment, together with a revised description of the modes,[17] is given in Table 2.

A sum rule for the square of the out-of-plane frequencies was used by Nielsen *et al.* to justify their assignments[3] for *m*-difluorobenzene. With the present values, $\sum\nu^2$ is 4·26, 4·19, and 4·15 × 10^6 for the *o*-, *m*-, and *p*-isomers, respectively; this agreement seems satisfactory.

TABLE 3.

The molal thermodynamic properties of the difluorobenzenes in the ideal-gas state.

T (°K)	$-(G^\circ - H_0^\circ)/T$ (cal./deg.)	$(H^\circ - H_0^\circ)/T$ (cal./deg.)	$(H^\circ - H_0^\circ)$ (kcal.)	S° (cal./deg.)	C_p° (cal./deg.)	$-\Delta H_f^\circ$ [a] (kcal.)	$-\Delta G_f^\circ$ [a] (kcal.)	$\log_{10} K_f^\circ$ [a]
o-*Difluorobenzene*								
273·16	61·20	13·99	3·82	75·19	23·51	67·44	56·23	44·99
298·16	62·45	14·87	4·43	77·32	25·41	67·65	55·22	40·48
300	62·54	14·93	4·48	77·47	25·67	67·67	55·14	40·17
400	67·32	18·50	7·40	85·82	32·61	68·39	51·16	27·95
500	71·83	21·94	10·97	93·77	38·39	68·93	46·39	20·27
600	76·08	25·04	15·03	101·12	42·95	69·37	41·83	15·23
700	80·18	27·89	19·52	108·07	46·59	69·67	37·03	11·56
800	84·09	30·41	24·33	114·50	49·50	69·89	32·59	8·90
900	87·79	32·67	29·40	120·46	51·88	70·04	27·91	6·78
1000	91·33	34·69	34·69	126·02	53·85	70·10	23·22	5·07
1100	94·74	36·51	40·16	131·25	55·50	70·10	18·54	3·68
1200	97·98	38·25	45·91	136·23	56·89	69·92	13·85	2·52
1300	101·09	39·64	51·53	140·73	58·07	69·98	9·17	1·54
1400	104·09	41·00	57·40	145·09	59·07	69·90	4·52	0·71
1500	106·95	42·23	63·34	149·18	59·96	69·82	−0·32	−0·05
m-*Difluorobenzene*								
273·16	60·78	13·64	3·73	74·42	23·42	71·16	59·74	47·80
298·16	62·02	14·55	4·34	76·57	25·40	71·37	58·71	43·03
300	62·11	14·63	4·39	76·74	25·54	71·38	58·63	42·71
400	66·81	18·27	7·31	85·08	32·72	72·10	54·58	29·82
500	71·27	21·77	10·88	93·04	38·55	72·64	49·74	21·74
600	75·53	24·96	14·98	100·49	43·13	73·04	45·12	16·43
700	79·59	27·82	19·48	107·41	46·74	73·34	40·22	12·55
800	83·49	30·40	24·32	113·89	49·67	73·53	35·74	9·76
900	87·19	32·65	29·38	119·84	51·99	73·68	30·99	7·53
1000	90·74	34·68	34·68	125·42	53·94	73·73	26·24	5·73
1100	94·13	36·51	40·16	130·64	55·57	73·72	21·50	4·27
1200	97·37	38·16	45·79	135·53	56·94	73·66	16·75	3·05
1300	100·49	39·65	51·54	140·14	58·11	73·60	12·00	2·02
1400	103·48	41·01	57·41	144·49	59·11	73·52	7·28	1·14
1500	106·35	42·24	63·36	148·59	59·97	73·42	2·56	0·37
p-*Difluorobenzene*								
273·16	59·50	13·78	3·77	73·28	23·57	70·49	58·76	47·01
298·16	60·74	14·69	4·38	75·43	25·53	70·70	57·70	42·29
300	60·83	14·75	4·43	75·59	25·67	70·71	57·62	41·98
400	65·58	18·40	7·36	83·98	32·80	71·42	53·46	29·21
500	70·06	21·88	10·94	91·95	38·60	71·95	48·50	21·19
600	74·34	25·06	15·04	99·40	43·16	72·35	43·78	15·94
700	78·42	27·92	19·54	106·34	46·76	72·64	38·78	12·11
800	82·32	30·46	24·37	112·78	49·65	72·85	34·17	9·33
900	86·04	32·72	29·45	118·76	52·01	72·98	29·32	7·12
1000	89·59	34·75	34·75	124·34	53·96	73·03	24·46	5·34
1100	92·99	36·58	40·23	129·57	55·59	73·02	19·62	3·90
1200	96·24	38·22	45·86	134·46	56·97	72·96	14·76	2·69
1300	99·37	39·71	51·62	139·08	58·14	72·88	9·92	1·67
1400	102·36	41·06	57·49	143·42	59·14	72·81	5·07	0·79
1500	105·24	42·29	63·44	147·53	60·00	72·71	0·25	0·04

[a] Standard heat, standard free energy, and common logarithm of the equilibrium constant for the formation of the difluorobenzene by the reaction: 6C (graphite) + $2H_2$(g) + F_2(g) = $C_6H_4F_2$(g).

THERMODYNAMIC PROPERTIES

The values for the fundamental vibrational frequencies given in Table 2 were used with the aid of tables[18] to calculate the vibrational contribution to the thermodynamic functions: the free-energy function $(G^\circ - H_0^\circ)/T$, heat-content function $(H^\circ - H_0^\circ)/T$, entropy S°, and heat capacity C_p°. For the rotational contributions, the product of the principal moments of inertia of the *o*-isomer using the above values is $6{\cdot}414 \times 10^{-113}$ g.^{3} cm.^{6}. For the *m*- and the *p*-isomer, the C–F distance was taken[9] as 1·30 Å, other distances and angles as in the *o*-compound, and the products of the principal moments of inertia were found to be 7·255 and $6{\cdot}364 \times 10^{-113}$ g.^{3} cm.^{6}, respectively. The symmetry number is 2 for the *o*- and the *m*- and 4 for the *p*-isomer. The resulting total values for the thermodynamic functions for 273·16, 298·16, and 300—1500°K are given in Table 3; all relate to one mole of the difluorobenzene in the ideal-gas state at one atmosphere pressure.

Values for the heats of formation of the gaseous difluorobenzenes at 298·16°K have been reported[19] and were used with the present results, and values of the thermodynamic functions for C (graphite),[20] H_2(g)[20], and F_2 (g)[21] to find ΔH_f° at 0°K; the values were *o*-, —64·42; *m*-, —68·04; *p*-, —67·41 kcal./mole. From these, the heat ΔH_f°, free energy ΔG_f°, and logarithm of the equilibrium constant $\log_{10} K_f^\circ$, of formation, of the difluorobenzenes were calculated for the whole temperature range. At each temperature the mole fraction, N, of each isomer present at equilibrium was calculated; the values are given in Table 4.

TABLE 4.

Equilibrium mole fractions of the difluorobenzenes.

T (°K)	273·16	298·16	300	400	500	600	700	800	900	1000	1100	1200	1300	1400	1500
N_o	0·002	0·002	0·002	0·011	0·025	0·046	0·070	0·092	0·11	0·13	0·15	0·17	0·19	0·20	0·21
N_m	0·859	0·844	0·842	0·792	0·760	0·720	0·683	0·661	0·64	0·62	0·59	0·58	0·56	0·55	0·54
N_p	0·139	0·154	0·156	0·197	0·215	0·234	0·247	0·247	0·25	0·25	0·25	0·25	0·25	0·25	0·25

The entropies are sufficiently close to equality that the relative free energies are determined by the enthalpy term. As with the xylenes,[22] the order of thermodynamic stability throughout the temperature range is *m*- > *p*- > *o*-; in the cresols, however, the order has been found[23] to be *m* > *o*- > *p*.

We thank Mr. R. R. Collerson and Mr. D. Harrop for the gas chromatographic examination, and Dr. I. J. Lawrenson for the nuclear magnetic resonance measurements.

NATIONAL CHEMICAL LABORATORY,
TEDDINGTON, MIDDLESEX.

[*Received, July* 13*th*, 1962.]

---

[18] Johnston, Savedoff, and 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., 1949.

[19] Good and Scott, *Pure Appl. Chem.*, 1961, **2**, 77.

[20] Wagman, Kilpatrick, Taylor, Pitzer, and Rossini, *J. Res. Nat. Bur. Stand.*, 1945, **34**, 143.

[21] Evans, Munson, and Wagman, *J. Res. Nat. Bur. Stand.*, 1955, **55**, 147.

[22] Taylor, Wagman, Williams, Pitzer, and Rossini, *J. Res. Nat. Bur. Stand.*, 1946, **37**, 95.

[23] Green, *Chem. and Ind.*, 1962, 1575.