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THERMODYNAMIC FUNCTIONS FOR NAPHTHALENE

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ABSTRACT

Thermodynamic functions (heat capacity, enthalpy, entropy and free energy) have been calculated for naphthalene in the ideal gas state from 273.15 K to 1200 K at 1 atm pressure. Obtained results were critically compared with available experimental and calculated data.

INTRODUCTION

The thermodynamic properties of naphthalene in the ideal gas state have been critically studied and calculated by many investigators [1—32]. The most recent study is the work by Chen et al. [9]. Despite the satisfactory application of frequency sum and difference rules [9], there still remains an ambiguity in the certainty of the assigned fundamental frequency values, especially in frequencies representing the A_u, B_{2u} and B_{3u} species **, to warrant further review of the available spectral [1,5,6,8—32] and thermodynamic [33—45] data, and to calculate and re-evaluate the ideal gas state thermodynamic properties [1,6,9—16,18—26] of naphthalene (Tables 2, 3, 5; Figs. 2—6). On the basis of this comparison we have proposed two sets of fundamental assignments, set A and set B (Table 2).

The calculated thermodynamic function values for both sets of assignments (A and B) are found in Table 3. To ease industrial applications, all results presented (Table 3) were fitted to a five-constant polynomial of the form

$$\Lambda = a + bT + cT^2 + dT^3 + eT^4 \qquad (1)$$

where Λ is the thermodynamic function at temperature T (K). The constants a, b, c, d and e [eqn. (1)] were obtained using linear least squares curve fitting methods [1] and are found in Table 4. As already noted, the assigned frequency values for both assignment sets A and B are found in Table 2,

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** In this work the nomenclature of earlier investigations [11] has been retained. In this case the reference axes are set such that the X (longer) and Y axes are oriented in the plane of the naphthalene skeleton.

while the other values of molecular parameters used are the same as those used by McFee and Lielmezs [1].

DISCUSSION

Frequency assignments

Naphthalene forms monoclinic crystals [46a—c] of space group $P2_1/a(C^5_{2h})$ with two molecules in each unit cell located at symmetry sites C_i. Even if the naphthalene molecule is slightly distorted [46a—c] in the crystal, it may be approximated to retain full D_{2h} symmetry. Each molecule has 48 fundamental modes of vibration, of which 24 are Raman active, 20 IR active and four completely inactive. Table 1 gives the summary of selection rules for naphthalene *.

A_g *Fundamentals*

The nine symmetric A_g fundamentals are identified by their high intensity in both the gaseous and solid Raman spectra and by their polarization in the solid, single crystal spectra. Already, in 1955, Luther et al. [12,13] gave frequencies which were very close to the corresponding assignment of Michaelian and Ziegler [1,5] (Table 2). With the exception of the two highest fundamentals of A_g species (which contribute very little to the thermodynamic function values), all recent assignments have included very similar frequencies (Table 2). These assignments appear to be secure.

B_{1u} *Fundamentals*

The four B_{1u} fundamentals have been assigned by McClellan and Pimentel [14] as 176, 475, 780 and 956 cm^{-1}, and have been supported in general by subsequent studies (Table 2). We use, along with Michaelian and Ziegler [5], slightly changed values: 176, 476, 785 and 958 cm^{-1} (Table 2). Again these assignments are considered to be secure.

TABLE 1

Summary of frequency species

Class	No. of vibrations	Gas	Solid
A_g	9	Raman	Raman
A_u	4	Inactive	IR
B_{1g}	8	Raman	Raman
B_{1u}	4	IR	IR
B_{2g}	3	Raman	Raman
B_{2u}	8	IR	IR
B_{3g}	4	Raman	Raman
B_{3u}	8	IR	IR

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* See footnote p. 287.

B_{2u} *Fundamentals*

The assignment made by McClellan and Pimentel [14] of bands at 362, 620, 1125, 1268, 1355, 1601, 2942 and 3034 cm^{-1} has, with the exception of the assignment at 620 cm^{-1} and the two highest fundamentals, been confirmed by later studies (Table 2). Later, normal coordinate analysis treatment [18,19,21] has predicted 793 cm^{-1} for the 620 cm^{-1} value. On this basis, Michaelian and Ziegler [5] and others [18,20] have assigned a frequency of 747 cm^{-1} (this value is also used in this work: assignment set A, Table 2). However, through the application of product rule, Scully and Whiffen [16,17] have predicted a band of 810 cm^{-1}. Following this, we have replaced the frequency of 747 cm^{-1} (used in set A) by the 810 cm^{-1} value as one of the three assignment set B frequency values (see also Table 2).

B_{3u} *Fundamentals*

Early assignments [11,14] based on gas phase contours, solid phase dichroic splitting and on the evaluation of the product rule, differed widely for this class. The first normal coordinate analysis by Scully and Whiffen [16] and Freeman and Ross [18] also differed, but more recent calculations [19—21] have been consistent in assigning frequencies near 619, 870, 1139, 1212, 1362, 1513 cm^{-1} (Michaelian and Ziegler [5]) and 2987, 3076 cm^{-1} (Sharma and Singh [6]) values. However, recent normal coordinate analysis work prefers the value of 1008 cm^{-1} over that of 870 cm^{-1}. In this work, assignment set A contains 870 cm^{-1}, while assignment set B has the value of 1008 cm^{-1} (Table 2), with the remainder of the assignment of B_{3u} species as given by Michaelian and Ziegler [5] and Sharma and Singh [6] (Table 2).

B_{1g} *Fundamentals*

There has been some disagreement over the B_{1g} fundamental frequency assignments (compare with the early values in Table 2) but more recent studies [24—26] have included frequencies similar to those given by Michaelian and Ziegler [5] at 508, 935, 1167, 1242, 1442 cm^{-1}, and 1624, 2978, and 3076 cm^{-1} as proposed by Sharma and Singh [6] (Table 2). The assignment of 1167 cm^{-1} has been given previously [18] as 1099 cm^{-1} but the normal coordinate treatment by Stenman [24] supports the halonaphthalene studies of Michaelian and Ziegler [5]. In this work we accepted the assignments of Michaelian and Ziegler [5] as supplemented by Sharma and Singh [6].

B_{2g} *and* B_{3g} *Fundamentals*

The spectrographic evidence is poorly understood for separation of the seven Raman active out-of-plane B_{2g} and B_{3g} fundamentals [14]. Early assignments differed greatly in these two classes due to this difficulty and to the use of some frequencies above 1000 cm^{-1} (Table 2) which have since been discarded. Normal coordinate analysis [16,22,23] has enabled the

TABLE 2

Summary of frequencies (in cm^{-1}) as suggested by several contributors [a]

Class	Pimentel and McCellan [10] 1952	Lippincott and O'Reilly [11] 1955	Luther et al. [12,13] 1955	McCellan and Pimentel [14] 1955	Mitra and Bernstein [15] 1959		Scully and Whiffen [16] 1960		Freeman and Ross [18] 1960		Scherer [19] 1962
					A [b]	B [b]	Exp. [c]	Calcd. [d]	Exp.	Calcd.	Calcd.
A_g	512	511	512	512	512		512	398	516	508	485
	764	760	763	762	758		763	823	761	762	784
	778	878	1025	943	943		1025	1003	1025	1018	1004
	946	1025	1144	1024	1025		1144	1129	1144	1136	1172
	1025	1240	1379	1240	1158	1239	1379	1299	1379	1375	1380
	1380	1393	1460	1379	1405		1460	1415	1460	1462	1450
	1460	1578	1579	1576	1577		1579	1625	1579	1571	1568
	3001	3028	3004	3001	3031		3025	3049	3004	3008	3022
	3058	3063	3055	3058	3060		3055	3075	3055	3078	3077
Au	581	400	400	400	400	195	195	207			
	726	700	740	842	698	730	581	594			
	841	875	860	1094	730	842	841	807			
	1146	1000	965	1307	915	1094	970	1022			
$B1_g$	390	585	617	611	585		506	372	506	458	480
	726	1144	875	879	1145		936	987	936	921	935
	1144	1337	1168	1145	1320		1168	1127	1099	1064	1116
	1240	1440	1240	1439	1438		1240	1226	1240	1246	1246
	1440	1586	1436	1586	1483		1436	1424	1436	1466	1455
	1575	1628	1624	1625	1624		1624	1639	1624	1679	1621
	2980	3011	2980	2980	2978		3055	3064	2980	2979	3026
	3025	3051	3025	3025	3092		3055	3074	3051	3042	3076
B_{1u}	80	176	176	176	176		176	177			
	747	475	478	475	476		478	445			
	821	782	780	780	782		780	759			
	949	957	955	956	958		955	962			

B_{2g}	191	385	195	191	195	285	392	365			
	1168	941	715	715	717	717	715	704			
	1254	1168	812	1167	1239	1158	945	920			
B_{2u}	478	361	362	362	359		362	412	362	387	390
	787	752	618	620	618		810	878	748	793	793
	1129	1139	1125	1125	1128		1125	1144	1125	1083	1116
	1269	1268	1265	1268	1267		1265	1285	1265	1182	1259
	1390	1387	1389	1385	1387		1389	1414	1389	1405	1393
	1590	1595	1595	1601	1592		1595	1586	1595	1535	1589
	2942	2947	2968	2942	3027		3029	3064	3054	2979	3026
	3034	3014	3056	3034	3060		3056	3079	3065	3044	3078
B_{3g}	406	191	392	285	285	386	500	485			
	742	285	591	588	770		778	770			
	972	715	778	774	874		875	881			
	1624	1440	945	1099	1099		980	971			
B_{3u}	620	618	585	581	562		618	794	618	622	637
	779	876	823	742	877		1008	1032	823	816	1000
	975	1012	1008	1012	1011		1144	1144	1008	1080	1135
	1012	1211	1144	1143	1210		1209	1198	1144	1131	1186
	1214	1510	1509	1508	1506		1361	1437	1361	1491	1372
	1508	1680	1718	1723	1715		1509	1543	1509	1546	1509
	2984	2976	3029	2984	2987		3029	3051	3005	3006	3022
	3070	3072	3086	3070	3076		3056	3076	3090	3069	3076

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[a] For other physical constants used, see ref. 1.

[b] Two assignment sets, A and B, proposed.

[c] Exp. = Experimental.

[d] Calcd. = Calculated, refers to NCA.

TABLE 2 (continued)

Summary of frequencies (in cm^{-1}) as suggested by several contributors [a]

Class	Krainov [20] 1964		Neto et al. [21] 1966		Suzuki et al. [22] 1968	Hanson and Gee [23] 1969	Stenman [24] 1971	Sharma and Singh [6] 1973	Michaelian and Ziegler [5] 1973	Karonen et al. [25] 1976	Chen et al. [9] 1979	This work	
	Exp.	Calcd.	Exp.	Calcd.								A [a]	B [a]
A_g	512	491	512	504			513	512	512	513	512	512	512
	758	778	763	767			765	758	762	765	761	762	762
	1025	981	1025	1013			1019	1025	1019	1020	1025	1019	1019
	1145	1125	1144	1173			1148	1145	1145	1148	1145	1145	1145
	1376	1405	1379	1368			1385	1380	1379	1385	1380	1379	1379
	1460	1452	1460	1445			1465	1460	1462	1465	1463	1462	1462
	1577	1564	1579	1577			1578	1577	1574	1578	1577	1574	1574
	3031	3041	3025	3038			3008	3031	3031	3008	3030	3031	3031
	3060	3057	3055	3085			3057	3060	3060	3057	3060	3060	3060
A_u	195	192						400	213		191	213	213
	581	580						698	575		581	575	575
	841	841						730	843		841	843	843
	970	977						915	935		970	935	935
B_{1g}	506	499	506	488			509	506	508	509	506	508	508
	936	961	936	938			938	1145	935	939	936	935	935
	1158	1145	1099	1117			1169	1337	1167	1169	1168	1167	1167
	1239	1226	1240	1253			1246	1438	1242	1246	1242	1242	1242
	1438	1462	1436	1442			1446	1483	1442	1446	1443	1442	1442
	1624	1631	1624	1625			1629	1624	1624	1629	1628	1624	1624
	3060	3056	2980	3019			2975	2978	2978	2976	3060	2978	2978
	3092	3072	3055	3062			3051	3076	3076	3051	3092	3076	3076
B_{1u}	176	175						176	176		176	176	176
	476	471						476	476		472	476	476
	782	784						782	785		782	785	785
	958	958						958	958		958	958	958

B_{2g}	386	390			390	392	389	195	388	389	386	388	388
	717	720			725	727	726	943	724	726	725	724	724
	943	946			933	950	952	1158	945	952	950	945	945
B_{2u}	359	329	362	369				359	361		359	361	361
	747	777	810	795				618	747		877	747	810
	1125	1136	1125	1125				1128	1132		1125	1132	1132
	1265	1271	1265	1258				1267	1270		1265	1270	1270
	1389	1372	1389	1379				1387	1391		1389	1391	1391
	1595	1593	1595	1597				1592	1599		1595	1599	1599
	3058	3052	3029	3020				3027	3027		3058	3027	3027
	3065	3063	3065	3064				3060	3060		3065	3060	3060
B_{3g}	461	459			467	388	469	285	285	469	466	469	469
	846	842			786	468	774	770	783	774	778	783	783
	876	873			878	772	880	874	875	880	876	875	875
	980	979			980	983	983	1099	979	983	980	979	979
B_{3u}	618	606	618	628				562	619		617	619	619
	1008	1016	1008	1007				877	870		1008	870	1008
	1138	1141	1144	1136				1144	1139		1144	1139	1139
	1209	1218	1209	1186				1210	1212		1209	1212	1212
	1361	1360	1361	1357				1506	1362		1361	1362	1362
	1509	1533	1509	1529				1715	1513		1509	1513	1513
	3027	3042	3029	3037				2987	2987		3027	2987	2987
	3090	3066	3056	3084				3076	3076		3090	3076	3076

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[a] For other physical constants used, see ref. 1.

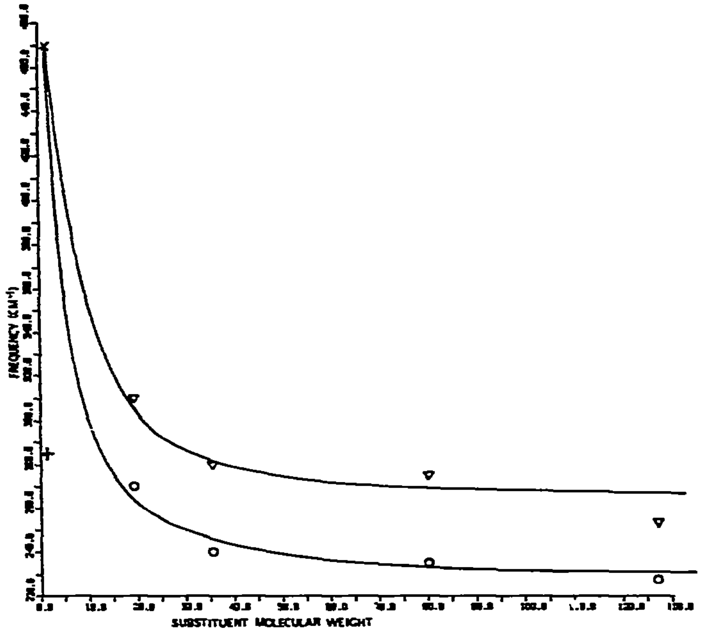

Fig. 1. Frequency (cm^{-1}) and substituent molecular weight relation for ○, α-halonaphthalene; and ▽, β-halonaphthalene.

establishment of B_{2g} assignments of the 3 B_{2g} species close to the assigned Michaelian and Ziegler [5] values of 388, 724 and 945 cm^{-1}. These values have been retained in the present work (Table 2).

Assignment of the B_{3g} species has been less certain. Michaelian and Ziegler [5] have assigned 285, 783, 875 and 979 cm^{-1} as fundamentals, although several authors [16,22,24—26], using normal coordinate treatment, have placed the lowest frequency near 469 cm^{-1} (Table 2). The correctness of 469 cm^{-1} as the assignment value over the 285 cm^{-1} value is also strengthened through Fig. 1, which shows for the α- and β-halonaphthalene series this particular B_{3g} frequency [5] plotted against the weight of the substituent atom X (X = H, F, Cl, Br and I). Figure 1 shows that by using 469 cm^{-1} as the naphthalene fundamental frequency we obtain a smooth inverse relation between the frequency change and the corresponding weight of the substituent halogen atom. If we substitute the 285 cm^{-1} value for 469 cm^{-1}, this plot (Fig. 1) becomes nearly discontinuous. Considering that this inverse frequency—atomic weight relation (Fig. 1) is valid, we would expect higher B_{3g} species values for naphthalene than for the halogen substituted α- and β-halonaphthalenes [5], i.e., assignment of 469 cm^{-1} is the preferred value. This is indirectly confirmed by Lielmezs and Vogt's [47] finding that for a series of normal paraffins, the fundamental frequencies varied inversely with the increase of n-paraffin chain length. In this work, for both sets of assignments (A and B), the proposed Michaelian and Ziegler [5] values were accepted except for the lowest B_{3g} frequency which was set at 469 cm^{-1}.

A_u *Fundamentals*

The four A_u frequencies are inactive in both the Raman and IR spectra (Table 1) but may be seen in the solid IR spectra. Because of this it was not until 1960 that Scully and Whiffen [16] were able to predict the A_u frequencies by normal coordinate analysis and not until the studies of Bree and Kydd [27], Chantry et al. [28] and Michaelian and Ziegler [5] that the lowest A_u frequency first predicted [6] at 207 cm^{-1} was suggested to be at 213 cm^{-1}. The data of Michaelian and Ziegler [5] with frequencies of 213, 575, 843 and 935 cm^{-1} fit the predictions of Scully and Whiffen [16] and the more recent work of Krainov [20], and are incorporated in our work (assignment sets A and B, Table 2).

Naphthalene vapour—liquid phase frequency shift

While there is evidence [48] that in the low frequency region of the IR spectrum (below about 300 cm^{-1}), gas phase frequencies may have considerably less value than those of the condensed states, this does not seem to be true for naphthalene. Careful studies [10,23,29] indicate that in the frequency range 473—1629 cm^{-1}, the average frequency shift is less than 1% (only a small number of frequencies changed as much as 1%) and this shift is not at all associated with any particular phase, but rather, the observed frequency shift associated with any phase change appears to be nearly randomly distributed. Even if vapour phase assignment values are to be preferred, these studies [10,23,29] assure that the proposed naphthalene frequency sets A and B (Table 2) containing the averaged solid state low frequencies [10,27—29] of 176, 213 and 361 cm^{-1} are sufficiently accurate to yield acceptable ideal gas state thermodynamic functions (Tables 3 and 4) which fall well within the range of experimental certainty (Tables 5—7, Figs. 2—6).

Comparison and accuracy

To determine the degree of reliability and accuracy of the presented thermodynamic properties (Tables 3 and 4), we have compared the spectroscopically calculated values with the available experimental vapour heat capacities and the third law entropies. Table 5 presents a comparison between the available experimental data for naphthalene vapour heat capacity and third law entropies and the corresponding calculated results for a series of investigators. Tables 6 and 7 list the calorimetric measurements and vapour pressure data used to obtain the experimental thermodynamic properties shown in Table 5 and Figs. 2—6. Comparison of the experimental results (Table 5; Figs. 2—6) reveals considerable measured value disagreement. For instance, in the case of enthalpy of sublimation measurements (Tables 6 and 7), recent sublimation enthalpy values calculated from saturated vapour pressure data at 298.15 K are: 17.328 ± 0.0598 kcal $mole^{-1}$ [44]; 17.328 kcal $mole^{-1}$ [43]; 17.366 ± 0.08 kcal $mole^{-1}$ [39]; while the calorimetric measurements at 298.15 K are: 17.447 ± 0.069 kcal $mole^{-1}$ [34] and 17.220 ± 0.06 kcal

TABLE 3

Heat capacity, entropy, free energy function and enthalpy function for naphthalene

Temp. (K)	C_p° (cal g^{-1} mole^{-1} K^{-1})		S° (cal g^{-1} mole^{-1} K^{-1})		$-(F^\circ - H_o^\circ)/T$ (cal g^{-1} mole^{-1} K^{-1})		$(H^\circ - H^\circ)/T$ (cal g^{-1} mole^{-1} K^{-1})	
	A	B	A	B	A	B	A	B
451.00	48.52	48.24	96.10	95.85	71.35	71.26	24.75	24.59
522.70	54.77	54.51	103.72	103.44	75.27	75.16	28.45	28.28
273.15	28.88	28.62	76.89	76.79	61.50	61.48	15.39	15.32
298.15	31.90	31.62	79.55	79.43	62.90	62.87	16.65	16.56
300.00	32.12	31.84	79.75	79.63	63.00	62.97	16.75	16.65
350.00	37.98	37.68	85.15	84.98	65.78	65.73	19.36	19.24
400.00	43.45	43.16	90.58	90.37	68.54	68.48	22.04	21.89
450.00	48.43	48.15	95.99	95.75	71.29	71.21	24.70	24.54
500.00	52.90	52.64	101.33	101.06	74.03	73.93	27.30	27.13
550.00	56.89	56.65	106.56	106.26	76.75	76.63	29.81	29.63
600.00	60.45	60.23	111.67	111.35	79.45	79.31	32.22	32.04
650.00	63.64	63.44	116.63	116.30	82.12	81.97	34.52	34.33
700.00	66.50	66.32	121.46	121.11	84.76	84.59	36.70	36.51
750.00	69.08	68.92	126.13	125.77	87.36	87.18	38.77	38.59
800.00	71.43	71.28	130.67	130.30	89.92	89.74	40.74	40.56
850.00	73.55	73.42	135.06	134.69	92.45	92.25	42.61	42.43
900.00	75.49	75.37	139.32	138.94	94.94	94.73	44.39	44.21
950.00	77.27	77.16	143.45	143.06	97.38	97.17	46.07	45.90
1000.00	78.90	78.79	147.46	147.06	99.79	99.56	47.67	47.50
1050.00	80.39	80.29	151.34	150.94	102.15	101.92	49.19	49.03
1100.00	81.76	81.68	155.12	154.71	104.47	104.23	50.64	50.48
1150.00	83.03	82.95	158.78	158.37	106.75	106.51	52.02	51.86
1200.00	84.20	84.12	162.34	161.92	109.00	108.74	53.34	53.18

TABLE 4

Calculated constants a, b, c, d and e in eqn. (1) (all values of constants in cal g^{-1} mole^{-1} K^{-1})

Assignment set A or B	C°_{p} (rms, root mean square)				
	a (rms)	b (rms)	$c \times 10^{-3}$ (rms)	$d \times 10^{-7}$ (rms)	$e \times 10^{-11}$ (rms)
A	−18.03435 (0.6873604)	0.2155649 (0.4651032×10^{-2})	−0.1820894 (0.108798×10^{-4})	0.7439797 (0.1053801×10^{-7})	−1.0969430 ($0.3606865 \times 10^{-11}$)
B	−17.78467 (0.7331244)	0.2118440 (0.4960697×10^{-2})	−0.1735525 (0.1160417×10^{-4})	0.6694938 (0.1123962×10^{-7})	−0.8691946 ($0.3847008 \times 10^{-11}$)
	S° (rms, root mean square)				
	a (rms)	$b \times 10^{-1}$ (rms)	$c \times 10^{-4}$ (rms)	$d \times 10^{-7}$ (rms)	$e \times 10^{-10}$ (rms)
A	48.71632 (0.3323961)	0.9285736 (0.2249163×10^{-2})	0.5485272 (0.5261292×10^{-5})	−0.7177181 (0.5096005×10^{-8})	0.2279522 ($0.1744219 \times 10^{-11}$)
B	49.05392 (0.3285136)	0.9064615 (0.2222892×10^{-2})	0.5751093 (0.5199840×10^{-5})	−0.7328896 (0.5036483×10^{-8})	0.2313094 ($0.1723847 \times 10^{-11}$)
	$(H^{\circ}-H^{\circ}_{0})/T$ (rms, root mean square)				
	a (rms)	$b \times 10^{-1}$ (rms)	$c \times 10^{-4}$ (rms)	$d \times 10^{-7}$ (rms)	$e \times 10^{-10}$ (rms)
A	2.087996 (0.3686550)	0.4004266 (0.2494510×10^{-2})	0.4575870 (0.5835213×10^{-5})	−0.6009981 (0.5651899×10^{-8})	0.1987142 ($0.1934486 \times 10^{-11}$)
B	2.372436 (0.3695545)	0.3798670 (0.2500596×10^{-2})	0.4901539 (0.5849450×10^{-5})	−0.6233006 (0.5665687×10^{-8})	0.2044519 ($0.1939205 \times 10^{-11}$)
	$-(F^{\circ}-H^{\circ}_{0})/T$ (rms, root mean square)				
	a (rms)	$b \times 10^{-1}$ (rms)	$c \times 10^{-5}$ (rms)	$d \times 10^{-7}$ (rms)	$e \times 10^{-11}$ (rms)
A	46.62813 (0.4674780×10^{-1})	0.5281619 (0.3163195×10^{-3})	0.9091033 (0.7399422×10^{-6})	−0.1166925 (0.7166967×10^{-9})	0.2922894 ($0.2453051 \times 10^{-12}$)
B	46.68156 (0.5120276×10^{-1})	0.5265903 (0.3464641×10^{-3})	0.8497158 (0.8104579×10^{-6})	−0.1096078 (0.7849963×10^{-9})	0.2686478 ($0.2686821 \times 10^{-12}$)

TABLE 5

Comparison of experimental and calculated properties

Ref.	C_p^o (cal g^{-1} mole^{-1} K^{-1})							
	298.15 K		451.0 K		522.7 K		1000.0 K	
	Exp. [a]	Calcd. [b]	Exp.	Calcd.	Exp.	Calcd.	Exp.	Calcd.
7			48.18 [c] ± 0.48		54.17 [c] ± 0.54			
10		31.03		48.01		54.38		78.01
11		31.94		47.72		53.83		78.27
12,13		32.78		49.24		55.34		79.07
14		32.07		48.14		54.27		78.55
15: Assignment A		32.09		48.23		54.37		78.55
Assignment B		31.68		47.80		53.98		78.38
16: Exp.		31.55		48.20		54.48		78.76
Calcd.		31.63		48.09		54.34		78.61
6		31.49		47.40		53.56		78.14
9		31.53		48.13		54.40		78.67
This work:								
Assignment A		31.90		48.53		54.77		78.90
Assignment B		31.62		48.24		54.51		78.79
36								
45a								
37								
38								
40								
41								
34								
35								
42b								
43								
44								

[a] Exp. = Experimental.

[b] Calcd. = Calculated from spectroscopic data, also NCA.

[c] Values proposed by author(s). Complete evaluation of experimental data.

[d] The "third law" entropy value was calculated using: (i) the corresponding calorimetric value of the entropy for the crystal state taken from McCullough et al. [33], and (ii) the sublimation entropy value was obtained from this work.

[e] The compression correction was made using the vapour pressure data of this work.

[f] Gas imperfection correction (Berthelot equation of state) neglected for this work.

mole^{-1} [35]. The measurement uncertainties range from ±0.0598 to ±0.08 kcal mole^{-1}; the listed enthalpy of sublimation values disagree as much as 1.30%.

In view of this disagreement, it was felt advisable to compare the calculated spectroscopic thermodynamic functions (Table 3) with thermodynamic property values taken from the work of several investigators (Tables 5—7; Figs. 2—6). Figures 2—5 compare the calculated ideal gas state entropies of McFee and Lielmezs [1] and those of this work (assignments A and B, Tables 2 and 3) with selected "third law" entropy values obtained from vapour

S° (cal g^{-1} mole^{-1} K^{-1})							
298.15 K		451.0 K		522.7 K		1000.0 K	
Exp.	Calcd.	Exp.	Calcd.	Exp.	Calcd.	Exp.	Calcd.
		96.85 ± 0.44		104.41 ± 0.44			
	80.30		96.55		104.11		147.73
	80.71		97.08		104.57		147.75
	80.19		97.08		104.79		148.75
	80.43		96.92		104.47		147.91
	80.37		96.89		104.46		147.93
	80.23		96.56		104.07		147.36
	79.48		95.89		103.46		147.07
	79.89		96.28		103.84		147.35
	80.25		96.45		103.90		146.97
	79.62						147.12
	79.55		96.10		103.72		147.46
	79.43		95.85		103.44		147.06
79.89^{d,e,f}							
		96.62^{d,e,g,i}		104.08^{d,e,g,i}		155.70^{d,e,g,h,i}	
79.67^{d,e,f}							
79.78^{d,e,f}							
75.15^{d,e,f}							
		96.49^{d,e,g,l}		104.27^{d,e,g,l}		155.55^{d,e,g,h,l}	
80.42^{d,e,f}							
79.67^{d,e,f}							
80.38^{d,e,f}							
79.98^{c,f}							
80.04^{d,e,f,j}		96.54^{d,e,g,k}		104.22^{d,e,g,k}		146.63^{d,e,g,h,k}	

[g] Gas imperfection correction included using Berthelot equation of state. The naphthalene critical state property values were taken from Weast [51].

[h] Estimate, temperature beyond the range of validity of given vapour pressure data.

[i] Entropy needed for liquid based on extrapolation of equation for heat capacity of liquid as given by McCullough et al. [33]: $C_{\text{satd.}} = 19.212 + 0.092572\,T$.

[j] Use made of low temperature vapour pressure equation [44].

[k] Use made of high temperature vapour pressure equation [44].

[l] Heat of sublimation used was taken from Ambrose et al. [44].

pressure and calorimetric data (Tables 5—7). Unexpectedly, several of the experimental data sets yielded erratic entropy—temperature behaviour patterns. Figures 2 and 3 show that for the Ambrose et al. [44] low temperature (range: 230—344 K) vapour pressure equation and, to a lesser extent, high temperature (range: 353—750 K) vapour pressure equation, the slope of the "third law" entropy vs. temperature curve is increasing with temperature rather than decreasing. Figure 5 indicates that the same "third law" entropy—temperature curvature change (temperature range: 270—310 K) is also displayed by the results of Bradley and Cleasby [36], Sherwood and

TABLE 6

Summary of vapour pressure data used

Ref.	Temp. range (K)	Sample purity and/or method of purification	Vapour pressure measurement method	Experimental accuracy	Experimental precision	Comments
Below triple point (353.43 K)						
36	279.85—293.85	Vacuum sublimation	Effusion	Not discussed	Not discussed	
37	273.15—311.15	Not discussed	Weight loss of packed bed in air stream	Not discussed	Not discussed	
38	289.15—323.15					Vapour pressure equation. See ref.
39	230—260	99.7 mole %, zone melting	Effusion	±5% in middle of range	Not discussed	
40	283.15—323.15	Zone melting	Effusion	±3%	Within 1%	Accuracy questionable
41	313.15—353.15	99.99 mole %, zone melting	Equilibrium	Not discussed	±0.033 Torr	
42b	285.15—297.06	Recrystallization	Effusion	±2.25%	Not discussed	
43	275	99.99 mole %	Gas saturation	±2%		Single vapour pressure measurement
44	230—343 (low temperature range)	99.95 mole %	Equilibrium	(±2% for $T > 280$ K (±5% for $T < 280$ K	±1.6%	
Above triple point (353.43 K)						
45	399.15—491.15	99.97 mole %	Equilibrium	Not discussed	$\rho = 6.36$ [a]	
41	353.43—453	99.99 mole %	Equilibrium	Not discussed	±0.088 Torr	
44	353.43—748.4 [b] (high temperature range)		Pooled vapour pressure data	Not discussed	[c]	

[a] RMS (root mean square) value of ratio of deviations of observed points from Antoine equation to expected standard deviation.

[b] High temperature values questionable.

[c] Estimate of experimental precision of data tied to: (i) ±0.35% RMS fit to Fowler et al. [41] data, and (ii) ±0.57% RMS fit to Camin and Rossini [45a,b] data.

TABLE 7

Summary of calorimetric data used

Ref.	Sample purity	Measurement			Comments
		Heat capacity	Vaporization heat	Sublimation heat	
33	99.99 mole %	Measurements from 10 to 370 K			Measurements for both solid and liquid states used in "third law" entropy calculations (Table 5, Fig. 2–6)
7	Not specified		11.110 ± 0.030 * kcal/deg mole at 440.9 K		
34	Reagent grade			17.45 ± 0.06 * kcal/deg^{-1} mole^{-1} at 298.15 K	
35	Organic analytic standard			17.22 ± 0.06 * kcal/deg^{-1} mole^{-1} at 298.15 K	Non-equilibrium measurement

* Single temperature measurement.

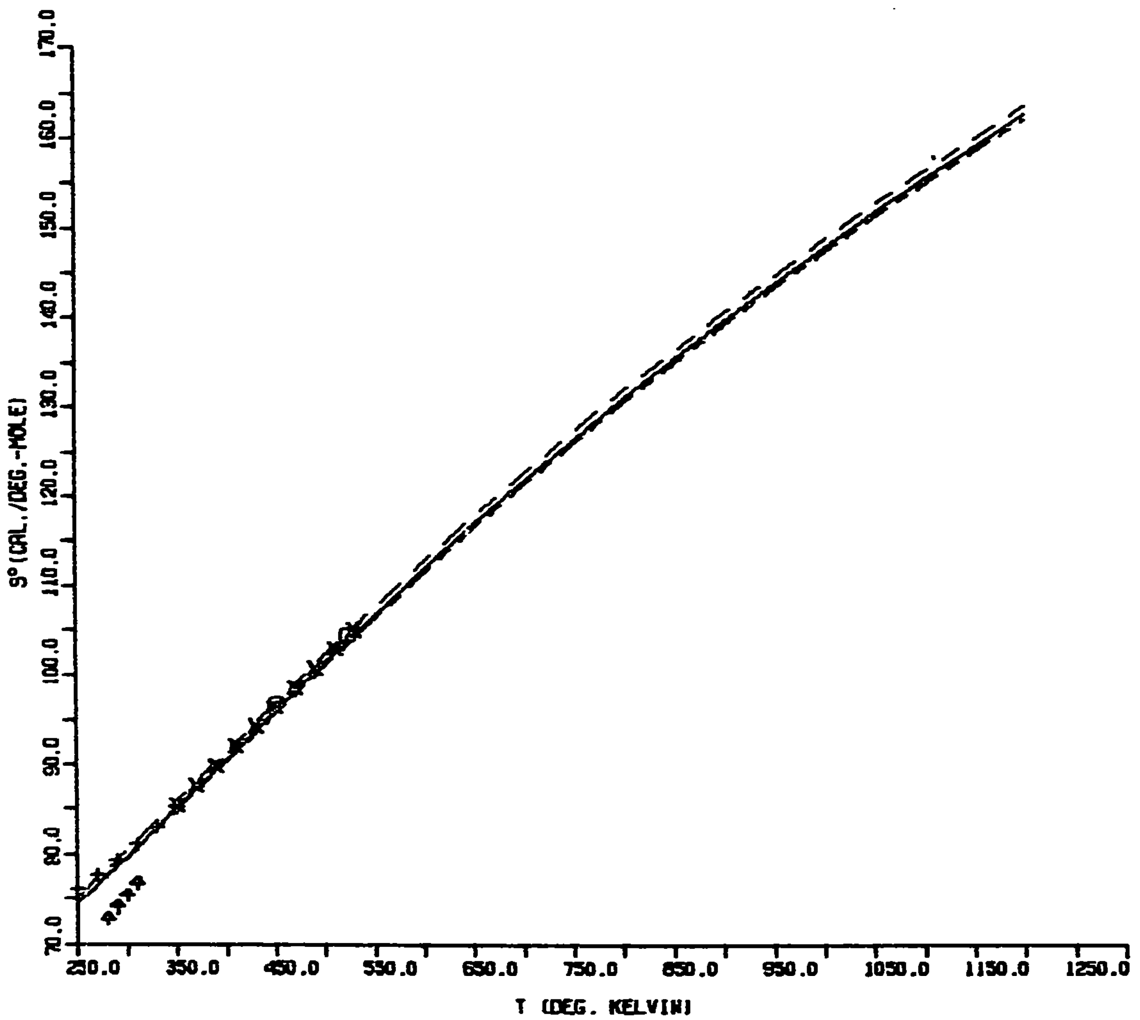

Fig. 2. Comparison of the spectroscopic calculated entropy (S^0) obtained by McFee and Lielmezs [1] (— — —), and this work (assignment A: ———; assignment B: — - — -); and the "third law" entropy obtained from the data of Ambrose et al. [44] (+, solid range), (X, liquid range); Karyakin et al. [40] (↑); and Barrow and McClellan [7] (□], in the temperature range 250—1250 K.

Bryant [37], and Radchenko and Kitaigorodskii [42a, b].

The disagreement between the single vapour pressure measurement value of Sinke [43] at 298.15 K and the single calorimetric measurement values of Irving [34] and Morawetz [35] at the same temperature of 298.15 K, has been noted (Fig. 5). It is of interest, however, to note that the non-equilibrium single state measurements of Morawetz [35] have yielded one of the lowest "third law" entropy values at 298.15 K (Table 5; Fig. 5). We also note that ideal gas state entropy values as calculated in this work, the work

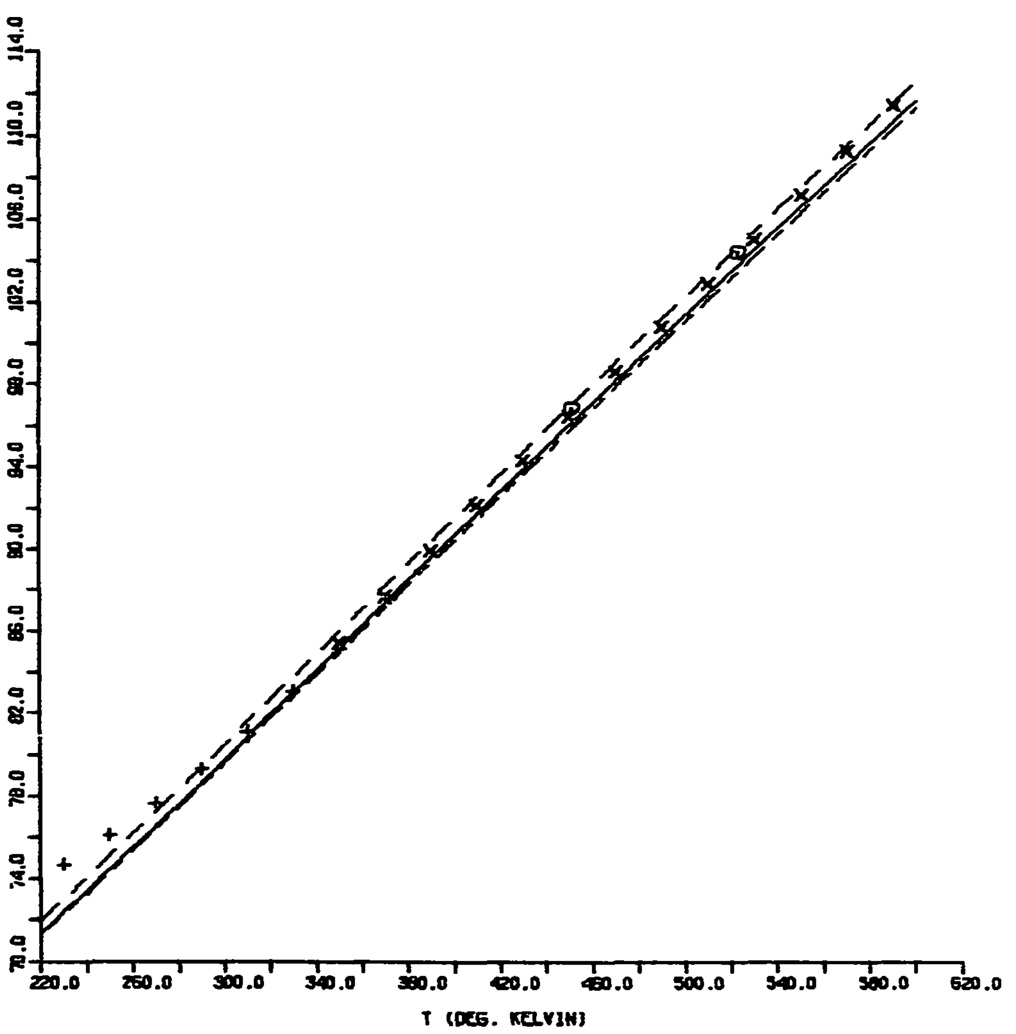

Fig. 3. Comparison of the spectroscopic calculated entropy (S^0) obtained by McFee and Lielmezs [1] (— — —), and this work (assignment A: ———; assignment B: — - — -); and the "third law" entropy obtained from the data of Ambrose et al. [44], and Barrow and McClellan [7] (see Fig. 2 for data notation), in the temperature range 220—620 K.

of Chen et al. [9], Scully and Whiffen [16], and calculations (this work) using assignments by Krainov [20], are all below the "third law" entropy value of Morawetz [35] at 298.15 K (Fig. 6). Whether this indicates that the "third law" entropy value is still too high is an open question subject to further experimental work, not merely at low but also at moderate and elevated temperatures.

In view of the presented comparisons (Tables 5—7; Figs. 2—5), it appears that assignment set A in this work (Table 2) yields the most realistic ideal gas state thermodynamic function values. Figure 6 compares the percent deviattion in entropy values as a function of temperature for a series of calculated ideal gas state and selected "third law" entropies with respect to calculated

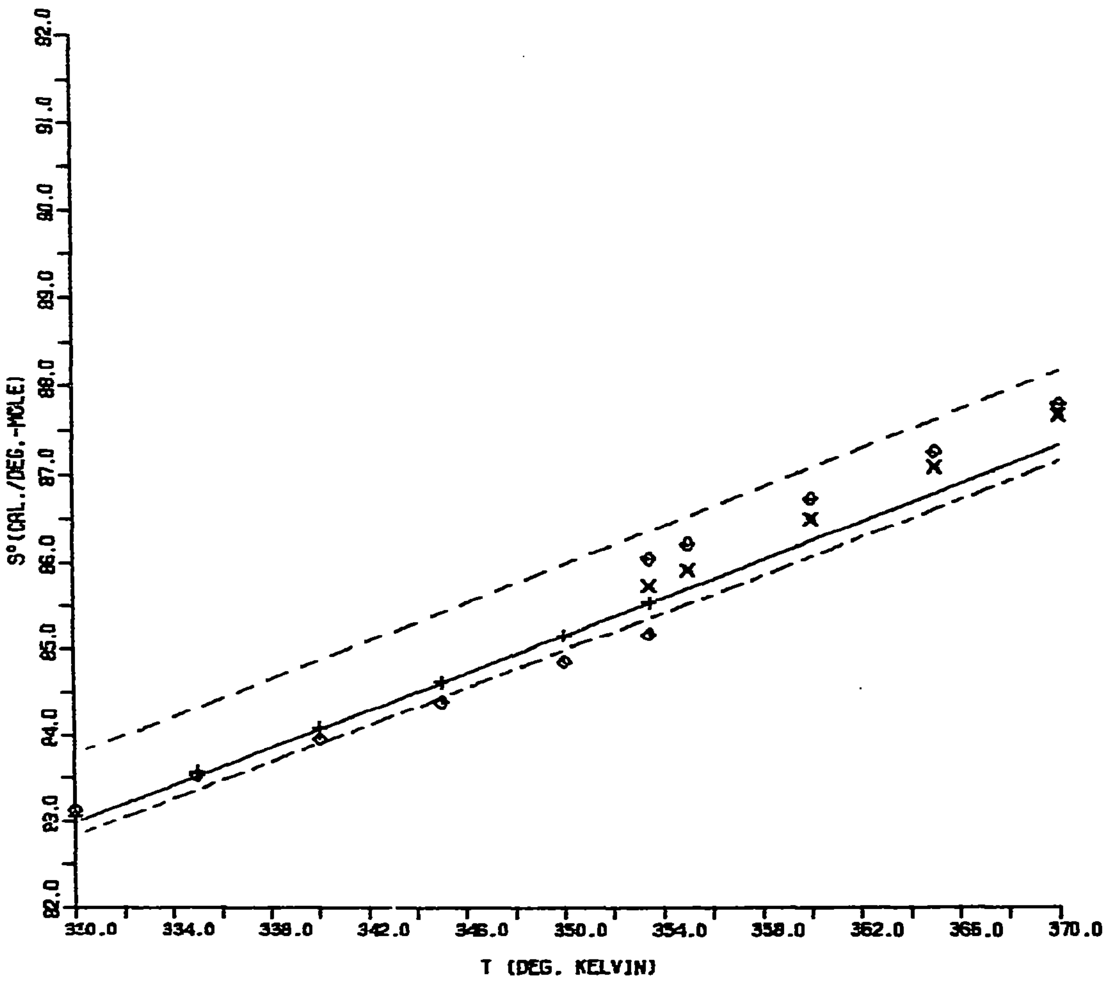

Fig. 4. Comparison of the spectroscopic calculated entropy (S^0) obtained by McFee and Lielmezs [1] (— — —), and this work (assignment A: ————; assignment B: — - — -); and the "third law" entropy obtained from the data of Ambrose et al. [44] (×, liquid range), (+, solid range); and Fowler et al. [41] (◇, liquid range), (◇, solid range), in the temperature range 330—370 K.

entropy values of this work (assignment set A, Table 2). The strong "third law" entropy upward curving, shown in Fig. 6, accentuates the already implied possibility that some of the vapour pressure equations may have an error in the experimental work (Figs. 2—5).

In this work, all values are in cal g^{-1} $mole^{-1}$ K^{-1} units and apply to the ideal gas state at 1 atm. For internal consistency and precision, tabulated values are given in ±0.1 cal g^{-1} $mole^{-1}$ K^{-1}. However, probable errors may be larger than this. Although in general there is a reasonable agreement between the calculated spectroscopic ideal gas state thermodynamic functions and thermodynamic property values obtained from the experimental data (Table 5; Figs. 2—6), the noted disagreement of experimental results (Table 5;

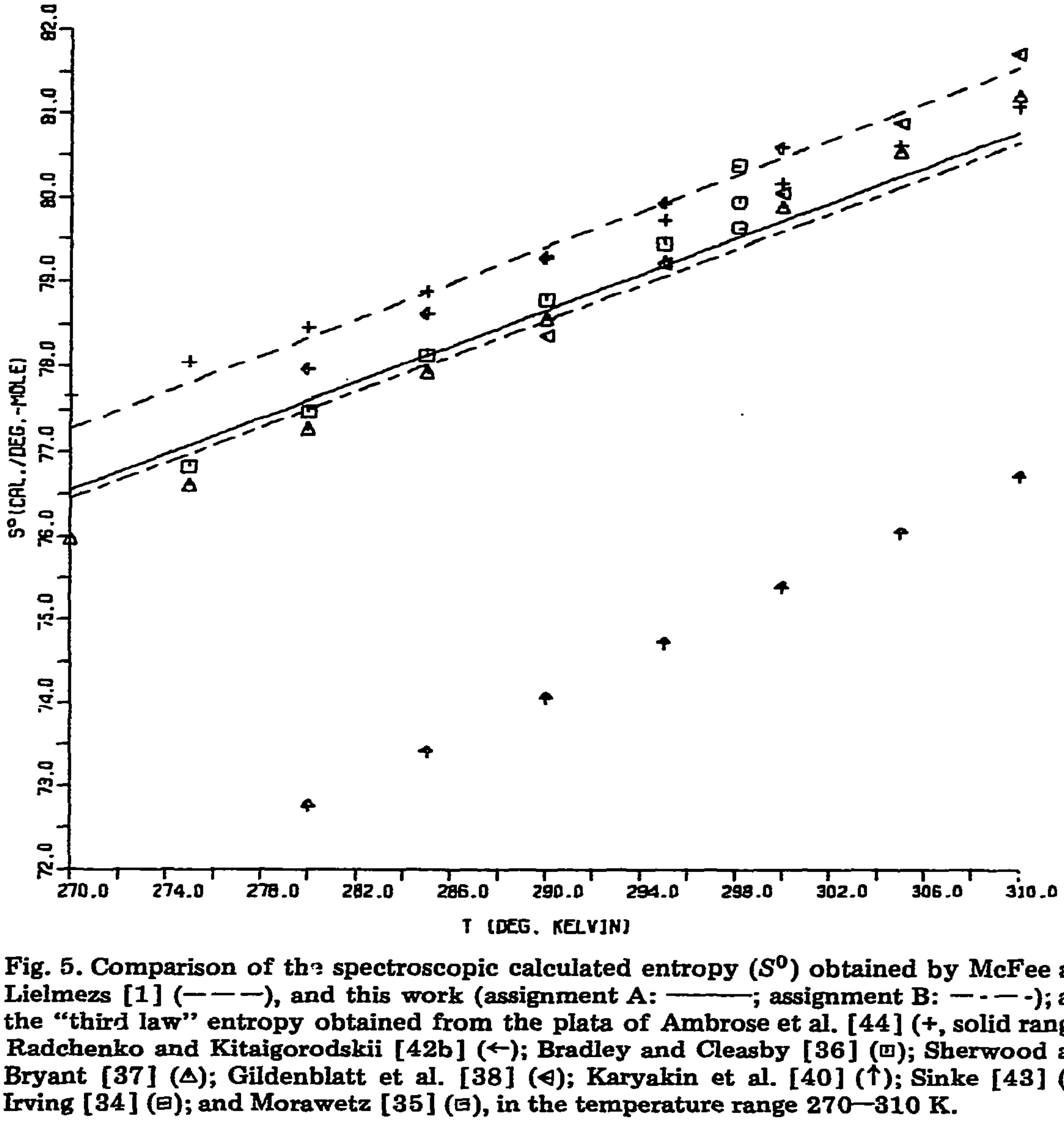

Fig. 5. Comparison of the spectroscopic calculated entropy (S^0) obtained by McFee and Lielmezs [1] (— — —), and this work (assignment A: ———; assignment B: — · — -); and the "third law" entropy obtained from the plata of Ambrose et al. [44] (+, solid range); Radchenko and Kitaigorodskii [42b] (←); Bradley and Cleasby [36] (⊡); Sherwood and Bryant [37] (Δ); Gildenblatt et al. [38] (◁); Karyakin et al. [40] (↑); Sinke [43] (▢); Irving [34] (⊟); and Morawetz [35] (⊟), in the temperature range 270—310 K.

Figs. 2—6), and the complexity of the IR and Raman spectra of naphthalene (especially A_u, B_{2u}, B_{3u} species) have as yet affected the evaluation of the certainty and reliability of the presented thermodynamic function values (assignment sets A and B, Tables 2 and 3). The percentage error ascribed below to the calculated thermodynamic functions (Table 3) is therefore an estimate. This estimate * was obtained considering errors in the molecular and structural data used, mathematical errors due to the round-off in the computer, and errors due to the inapplicability of the basic assumptions, for

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* For more detailed discussion see McFee and Lielmezs [1], and Butler and Lielmezs [49].

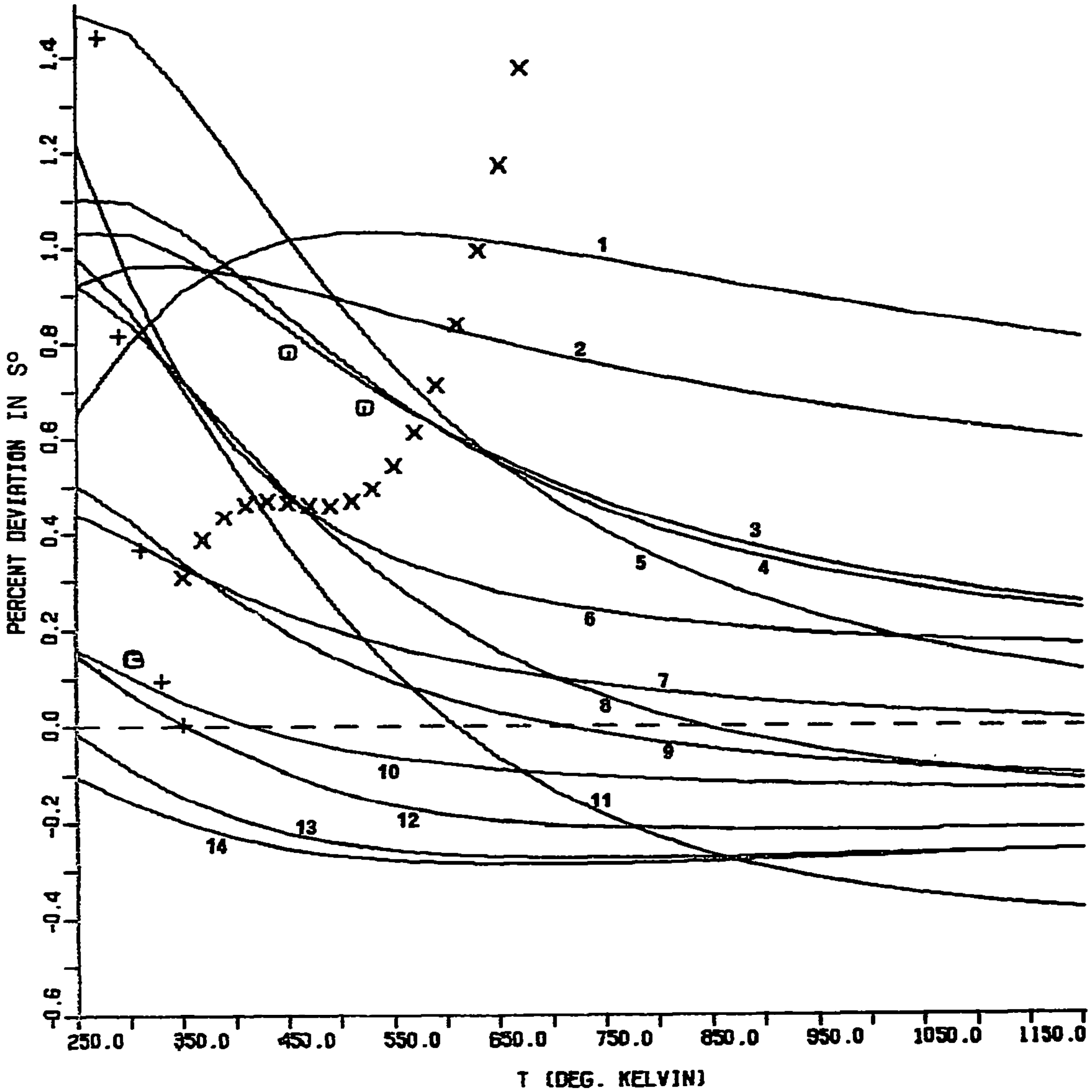

Fig. 6. Comparison of percent deviation in entropy (S^0) between the calculated spectroscopic value of 1, Luther et al. [12,13]; 2, McFee and Lielmezs [1]; 3, Mitra and Bernstein [15] (A); 4, McClellan and Pimentel [14]; 5, Lippincott and O'Reilly [11]; 6, Pimentel and McClellan [10]; 7, this work (Krainov's [20] assignments, calc.); 8, Mitra and Bernstein [15] (B); 9, Scully and Whiffen [16] (calc.); 10, this work (Krainov's [20] assignments, exp.); 11, Sharma and Singh [6]; 12, Chen et al. [9]; 13, Scully and Whiffen [16] (exp.); 14, this work (assignment B); zero line, this work (assignment A); and the "third law" percent deviation in entropy obtained from the data of Morawetz [35] (⊟); Barrow and McClellan [7] (▣); Ambrose et al. [44] (+, low temperature), (×, high temperature), in the temperature range 250—1150 K.

instance the excluded anharmonicity effect: small and indeed negligible at temperatures below 500 K, but larger at higher temperatures [50]. Noting the overall reliability of the spectroscopic input data used (Table 2), it is estimated that the accuracy of the calculated thermodynamic functions (this work, sets A and B) is less than ±0.5% up to temperatures of 1000 K.

NOMENCLATURE

Å	Angstrom
C_p^0	heat capacity (cal mole^{-1} K^{-1})
e.u.	entropy unit (cal mole^{-1} K^{-1})
$-(F^0 - H_0^0)/T$	free energy function (cal mole^{-1} K^{-1})
$(H^0 - H_0^0)/T$	enthalpy function, where $H_0^0 = H^0$ at 0 K cal mole^{-1} K^{-1}
S^0	entropy e.u.
ν	wave number (cm^{-1})
Superscript	
0	reference state, referring to the hypothetical state of an ideal gas at 1 atm
Subscript	
p	pressure (atm)

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REFERENCES

1 D.C. McFee and J. Lielmezs, Thermochim. Acta, 30 (1979) 173.
2 D.G. McFee and J. Lielmezs, Thermochim. Acta, 24 (1978) 39.
3 D.G. McFee and J. Lielmezs, Thermochim. Acta, 24 (1978) 55.
4 D.G. McFee and J. Lielmezs, Thermochim. Acta, 25 (1978) 21.
5 K.H. Michaelian and S.M. Ziegler, Appl. Spectrosc., 27 (1973) 13.
6 R.P. Sharma and R.S. Singh, Ind. J. Appl. Phys., 11 (1973) 618.
7 G.M. Barrow and A.L. McLellan, J. Am. Chem. Soc., 73 (1951) 573.
8 D.H. Whiffen, J. Chem. Soc., (1956) 1350.
9 S.S. Chen, S.A. Kudchadker and R.C. Wilhoit, J. Phys. Chem. Ref. Data, 8 (1979) 527.
10 G.C. Pimentel and A.L. McClellan, J. Chem. Phys., 20 (1952) 270.
11 E.R. Lippincott and E.J. O'Reilly, Jr., J. Chem. Phys., 23 (1955) 238.
12 H. Luther, K. Feldmann and B. Hampel, Z. Electrochem., 59 (1955) 1008.
13 H. Luther, G. Brandes, H. Günzler and B. Hampel, Z. Elektrochem., 59 (1955) 1012.
14 A.L. McClellan and G.C. Pimentel, J. Chem. Phys., 23 (1955) 245.
15 S.S. Mitra and H.J. Bernstein, Can. J. Chem., 57 (1959) 553.
16 D.B. Scully and D.H. Whiffen, Spectrochim. Acta, 16 (1960) 1409.
17 D.B. Scully and D.H. Whiffen, J. Mol. Spectrosc., 1 (1957) 257.
18 D.E. Freeman and I.G. Ross, Spectrochim. Acta, 16 (1960) 1393.
19 J.R. Scherer, J. Chem. Phys., 36 (1962) 3308.
20 E.P. Krainov, Opt. Spectroscopy, 16 (1964) 415.
21 N. Neto, M. Scrocco and S. Califano, Spectrochim. Acta, 22 (1966) 1981.
22 M. Suzuki, T. Yokoyama and M. Ito, Spectrochim. Acta, Part A, 24 (1968) 1091.
23 D.M. Hanson and A.R. Gee, J. Chem. Phys., 51 (1969) 5052.
24 F. Stenman, J. Chem. Phys., 54 (1971) 4217.
25 A. Karonen, J. Rasanen and F. Stenman, Commentat. Phys. Math. Soc. Sci. Fenn., 46 (1976) 69.
26 A. Karonen and F. Stenman, Commentat. Phys. Math. Soc. Sci. Fenn., 46 (1976) 85.
27 A. Bree and R.A. Kydd, Spectrochim. Acta, Part A, 26 (1970) 1791.

28 G.W. Chantry, A. Anderson and H.A. Gebbie, Spectrochim. Acta, 20 (1964) 1465.
29 G.C. Pimentel, A.L. McClellan, W.B. Person and O. Schnepp, J. Chem. Phys., 23 (1955) 234.
30 W.B. Person, G.C. Pimentel and O. Schnepp, J. Chem. Phys., 23 (1955) 230.
31 P.N. Prasad and R. Kopelman, J. Chem. Phys., 57 (1972) 856.
32 M. Hineno and H. Yoshinaga, Spectrochimica Acta, Part A, 31 (1975) 617.
33 J.P. McCullough, H.L. Finke, J.F. Messerly, S.S. Todd, T.C. Kincheloe and G. Waddington, J. Phys. Chem., 61 (1957) 1105.
34 R.J. Irving, J. Chem. Thermodyn., 4 (1972) 793.
35 E. Morawetz, J. Chem. Thermodyn., 4 (1972) 455.
36 R.J. Bradley and T.G. Cleasby, J. Chem. Soc., (1953) 1690.
37 T.K. Sherwood and H.S. Bryant, Jr., Can. J. Chem. Eng., 35 (1957) 51.
38 I.A. Gildenblatt, A.S. Furmanov and N.M. Zhavoronkov, Zh. Prikl. Khim., 33 (1960) 246.
39 G.A. Miller, J. Chem. Eng. Data, 3 (1963) 69.
40 N.V. Karyakin, I.B. Rabinovich and L.G. Pakhomov, Russ. J. Phys. Chem., 42 (1968) 9521.
41 L. Fowler, W.N. Trump and C.E. Vogel, J. Chem. Eng. Data, 13 (1968) 209.
42 (a) L.G. Radchenko, Russ. J. Phys. Chem., 45 (1971) 747. (b) L.G. Radchenko and A.I. Kitaigorodskii, Russ. J. Phys. Chem., 48 (1974) 1695.
43 G.C. Sinke, J. Chem. Thermodyn., 6 (1974) 311.
44 D. Ambrose, I.J. Lawrenson and C.H.S. Sprake, J. Chem. Thermodyn., 7 (1975) 1173.
45 (a) D.L. Camin and F.D. Rossini, J. Phys. Chem., 59 (1955) 1173. (b) D.M. Speros and F.D. Rossini, J. Phys. Chem., 64 (1960) 1723.
46 (a) D.W. Cruikshank, Acta Crystallogr., 10 (1957) 504. (b) D.W. Cruikshank and R.A. Sparks, Proc. R. Soc. London, Ser. A, 258 (1961) 1056. (c) A. Almenningen, O. Bastiansen and F. Dyvik, Acta Crystallogr., 14 (1961) 1056.
47 J. Lielmezs and H.J. Vogt, Thermochim. Acta, 6 (1973) 27.
48 W.G. Fateley, I. Matsubara and R.E. Witkowski, Spectrochim. Acta, 20 (1964) 1461.
49 J.B. Butler and J. Lielmezs, J. Chem. Eng. Data, 14 (1969) 335.
50 R.E. Pennington and K.A. Kobe, J. Chem. Phys., 22 (1954) 1442.
51 R.C. Weast (Ed.), Handbook of Chemistry and Physics, CRC Press, Cleveland, 58th edn., 1977.