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THERMODYNAMIC FUNCTIONS FOR ANILINE AND HALOGENATED ANILINES

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ABSTRACT

Thermodynamic functions (heat capacity, enthalpy, entropy and free energy) are calculated for aniline and nine halogenated anilines in the ideal gas state from 298.15 to 1200 K at 1 atm pressure. Statistical thermodynamic methods have been used in the calculations, with functions corrected for internal rotation by the method of Pitzer. Agreement with other literature and experimental data, where available, is excellent.

INTRODUCTION

The published molecular structural and spectroscopic data (Tables 3 and 4) have made it possible to estimate the thermodynamic functions (heat capacity, enthalpy, entropy and free energy) for aniline and nine halogenated anilines in the ideal gas state at 1 atm pressure. The functions for each of these compounds were calculated by statistical mechanical methods treating the internal rotational barrier contribution by the method developed by Pitzer [15]. The calculated results are found in Table 1. The functions have all been fitted to a five-constant polynomial of the form

$$\Lambda = a + bT + cT^2 + dT^3 + eT^4 \tag{1}$$

where Λ is any thermodynamic function at temperature T (K). The constants a, b, c, d and e in eqn. (1) have been obtained using linear least-squares curve-fitting methods and are found in Table 2. The molecular structural data needed for the calculation of thermodynamic functions are found in Tables 3 and 4. Table 5 presents a comparison of computed values, this and other work, and available experimental data, while Table 6 gives the possible uncertainties in the calculated final function values. Table 7 presents the calculation of molal entropy for aniline.

The accuracy and scope of this work is set forth by its purpose to present calculated thermodynamic function tables for use in chemical engineering problems.

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TABLE 1

Heat capacity, entropy, free energy function and enthalpy function

Temp. (K)	Aniline	*ortho*-Fluoro-aniline	*meta*-Fluoro-aniline	*para*-Fluoro-aniline	*ortho*-Chloro-aniline	*meta*-Chloro-aniline	*para*-Chloro-aniline	*ortho*-Bromo-aniline	*meta*-Bromo-aniline	*para*-Bromo-aniline
C_p^0 (cal mol^{-1} K^{-1})										
298.15	25.84	28.33	28.47	27.86	29.43	29.70	30.12	30.45	30.65	30.71
300.00	26.00	28.50	28.63	28.03	29.59	29.85	30.27	30.60	30.80	30.86
350.00	30.23	32.89	33.00	32.43	33.73	33.92	34.34	34.58	34.75	34.88
400.00	34.17	36.91	37.00	36.48	37.55	37.69	38.07	38.28	38.43	38.57
450.00	37.71	40.51	40.59	40.10	41.00	41.11	41.43	41.63	41.76	41.90
500.00	40.89	43.70	43.77	43.30	44.07	44.16	44.43	44.62	44.75	44.86
550.00	43.70	46.53	46.59	46.12	46.81	46.89	47.09	47.29	47.40	47.48
600.00	46.20	49.02	49.09	48.61	49.24	49.31	49.45	49.66	49.77	49.81
650.00	48.45	51.23	51.30	50.80	51.40	51.47	51.54	51.78	51.88	51.87
700.00	50.46	53.20	53.28	52.77	53.33	53.40	53.43	53.67	53.77	53.73
750.00	52.28	54.96	55.05	54.52	55.07	55.14	55.11	55.37	55.48	55.39
800.00	53.94	56.55	56.64	56.11	56.64	56.71	56.65	56.91	57.01	56.90
850.00	55.46	57.98	58.08	57.55	58.06	58.13	58.03	58.31	58.41	58.27
900.00	56.85	59.29	59.40	58.86	59.36	59.43	59.30	59.58	59.68	59.52
950.00	58.13	60.48	60.59	60.06	60.55	60.61	60.47	60.75	60.84	60.67
1000.00	59.31	61.57	61.69	61.16	61.63	61.70	61.54	61.81	61.91	61.72
1050.00	60.41	62.57	62.70	62.18	62.62	62.70	62.52	62.79	62.89	62.69
1100.00	61.42	63.50	63.62	63.11	63.55	63.62	63.44	63.70	63.79	63.59
1150.00	62.36	64.35	64.47	63.98	64.40	64.46	64.28	64.54	64.63	64.42
1200.00	63.23	65.13	65.26	64.78	65.18	65.25	65.06	65.32	65.40	65.20
$(H^0 - H_0^0)/T$ (cal mol^{-1} K^{-1})										
298.15	14.50	15.64	15.52	15.65	16.91	17.17	17.39	18.04	18.26	18.19
300.00	14.57	15.72	15.60	15.72	16.98	17.25	17.46	18.12	18.33	18.27
350.00	16.51	17.86	17.78	17.80	19.09	19.35	19.59	20.19	20.40	20.36
400.00	18.47	19.99	19.93	19.89	21.16	21.41	21.67	22.22	22.43	22.41

450.00	20.42	22.08	22.03	21.93	23.18	23.41	23.68	24.20	24.39	24.40
500.00	22.31	24.09	24.05	23.91	25.11	25.33	25.61	26.09	26.28	26.30
550.00	24.13	26.00	25.98	25.81	26.97	27.17	27.45	27.90	28.09	28.11
600.00	25.87	27.82	27.80	27.61	28.72	28.92	29.18	29.62	29.80	29.82
650.00	27.52	29.54	29.53	29.31	30.39	30.57	30.83	31.24	31.42	31.44
700.00	29.09	31.16	31.15	30.92	31.96	32.14	32.37	32.78	32.95	32.97
750.00	30.57	32.69	32.69	32.43	33.44	33.61	33.83	34.23	34.39	34.41
800.00	31.98	34.13	34.14	33.86	34.84	35.01	35.21	35.60	35.76	35.77
850.00	33.32	35.49	35.50	35.21	36.17	36.33	36.51	36.89	37.05	37.05
900.00	34.58	36.78	36.80	36.49	37.42	37.58	37.47	38.12	38.28	38.26
950.00	35.79	37.99	38.02	37.70	38.61	38.76	38.91	39.28	39.43	39.41
1000.00	36.94	39.14	39.17	38.84	39.73	39.88	40.02	40.38	40.53	40.50
1050.00	38.03	40.24	40.27	39.93	40.80	40.94	41.06	41.42	41.57	41.53
1100.00	39.07	41.27	41.31	40.96	41.81	41.95	42.06	42.42	42.56	42.51
1150.00	40.06	42.26	42.30	41.94	42.78	42.91	43.01	43.36	43.50	43.45
1200.00	41.01	43.19	43.24	42.88	43.69	43.83	43.91	44.26	44.40	44.34
$-(F^0 - H_0^0)/T$ (cal mol^{-1} K^{-1})										
298.15	61.59	63.74	63.57	64.14	66.24	66.63	66.56	69.22	69.68	69.53
300.00	61.68	63.84	63.66	64.24	66.34	66.74	66.67	69.33	69.80	69.64
350.00	64.07	66.42	66.23	66.81	69.12	69.55	69.52	72.28	72.78	72.61
400.00	66.40	68.95	68.74	69.33	71.80	72.27	72.27	75.11	75.64	75.47
450.00	68.69	71.42	71.21	71.79	74.41	74.91	74.95	77.84	78.39	78.23
500.00	70.94	73.86	73.64	74.21	76.96	77.47	77.54	80.49	81.06	80.89
550.00	73.15	76.24	76.02	76.58	79.44	79.98	80.07	83.06	83.65	83.48
600.00	75.33	78.58	78.36	78.90	81.86	82.42	82.53	85.56	86.17	86.00
650.00	77.46	80.88	80.66	81.18	84.22	84.80	84.93	88.00	88.62	88.46
700.00	79.56	83.13	82.90	83.40	86.53	87.12	87.27	90.37	91.00	90.84
750.00	81.62	85.33	85.11	85.59	88.79	89.39	89.56	92.68	93.33	93.17
800.00	83.64	87.48	87.26	87.73	90.99	91.60	91.79	94.94	95.59	95.43
850.00	85.62	89.60	89.37	89.82	93.15	93.77	93.96	97.13	97.80	97.64
900.00	87.56	91.66	91.44	91.88	95.25	95.88	96.09	99.28	99.95	99.79
950.00	89.46	93.68	93.46	93.88	97.30	97.94	98.16	101.37	102.05	101.89
1000.00	91.33	95.66	95.44	95.84	99.31	99.96	100.18	103.41	104.10	103.94

TABLE 1 (continued)

Temp. (K)	Aniline	*ortho*-Fluoro-aniline	*meta*-Fluoro-aniline	*para*-Fluoro-aniline	*ortho*-Chloro-aniline	*meta*-Chloro-aniline	*para*-Chloro-aniline	*ortho*-Bromo-aniline	*meta*-Bromo-aniline	*para*-Bromo-aniline
1050.00	93.16	97.60	97.38	97.76	101.28	101.93	102.16	105.41	106.10	105.94
1100.00	94.95	99.49	99.28	99.65	103.20	103.86	104.09	107.36	108.06	107.90
1150.00	96.71	101.35	101.14	101.49	105.08	105.74	105.98	109.26	109.97	109.81
1200.00	98.44	103.17	102.96	103.30	106.92	107.59	107.83	111.13	111.84	111.67
S^0 (cal mol^{-1} K^{-1})										
298.15	76.10	79.38	79.08	79.79	83.14	83.80	83.95	87.26	87.94	87.72
300.00	76.25	79.56	79.26	79.96	83.33	83.99	84.14	87.45	88.13	87.91
350.00	80.58	84.28	84.00	84.61	88.20	88.90	89.11	92.47	93.18	92.98
400.00	84.88	88.94	88.68	89.22	92.96	93.68	93.95	97.33	98.07	97.88
450.00	89.11	93.50	93.24	93.73	97.59	98.32	98.63	102.04	102.79	102.62
500.00	93.25	97.94	97.69	98.12	102.07	102.81	103.15	106.58	107.34	107.19
550.00	97.28	102.24	102.00	102.38	106.40	107.15	107.52	110.97	111.74	111.59
600.00	101.20	106.40	106.16	106.51	110.58	111.34	111.72	115.18	115.97	115.82
650.00	104.98	110.41	110.18	110.49	114.61	115.37	115.76	119.24	120.03	119.90
700.00	108.65	114.28	114.06	114.32	118.49	119.26	119.65	123.15	123.95	123.81
750.00	112.19	118.02	117.79	118.02	122.23	123.00	123.39	126.91	127.72	127.57
800.00	115.62	121.61	121.40	121.59	125.84	126.61	127.00	130.54	131.35	131.20
850.00	118.94	125.09	124.88	125.04	129.31	130.09	130.48	134.03	134.85	134.69
900.00	122.15	128.44	128.23	128.37	132.67	133.45	133.83	137.40	138.22	138.05
950.00	125.26	131.67	131.48	131.58	135.91	136.70	137.07	140.65	141.48	141.30
1000.00	128.27	134.80	134.62	134.69	139.04	139.84	140.20	143.79	144.63	144.44
1050.00	131.19	137.83	137.65	137.70	142.08	142.87	143.22	146.83	147.68	147.48
1100.00	134.02	140.77	140.59	140.61	145.01	145.81	146.15	149.78	150.62	150.41
1150.00	136.77	143.61	143.43	143.44	147.85	148.66	148.99	152.63	153.48	153.26
1200.00	139.44	146.36	146.20	146.18	150.61	151.42	151.75	155.39	156.24	156.02

TABLE 2

Calculated constants *a*, *b*, *c*, *d* and *e*

Compound	C_p^0					S^0				
	a	$b \times 10^{-2}$	$c \times 10^{-4}$	$d \times 10^{-8}$	$e \times 10^{-11}$	a	$b \times 10^{-2}$	$c \times 10^{-4}$	$d \times 10^{-8}$	$e \times 10^{-11}$
Aniline	−12.25388	16.95434	−1.637077	8.241015	−1.669237	49.41467	8.836312	0.1263157	−3.399207	1.184651
ortho-Fluoroaniline	−11.58871	17.94168	−1.783831	9.034133	−1.822858	49.34239	10.30429	−0.0067067	−2.727131	1.035856
meta-Fluoroaniline	−11.04083	17.71113	−1.746060	8.792263	−1.770900	48.82819	10.42459	−0.0273719	−2.558159	0.985671
para-Fluoroaniline	−12.79584	18.40115	−1.877370	9.820013	−2.052984	50.43034	9.96545	0.0392992	−3.068271	1.135381
ortho-Chloroaniline	−7.472380	16.35154	−1.545318	7.423027	−1.412394	51.18080	11.39651	−0.1952254	−1.286471	0.628340
meta-Chloroaniline	−6.155577	15.73923	−1.435546	6.572748	−1.171969	51.43908	11.62479	−0.2350040	−0.971504	0.536312
para-Chloroaniline	−6.443638	16.32239	−1.587874	7.939990	−1.586462	50.78164	12.04074	−0.2940060	−0.614901	0.455675
ortho-Bromoaniline	−4.757860	15.47659	−1.419733	6.560974	−1.184200	53.64402	12.28437	−0.3341394	−0.280485	0.352339
meta-Bromoaniline	−4.139350	15.24507	−1.380814	6.273872	−1.106916	54.03471	12.43610	−0.3565857	−0.118480	0.307762
para-Bromoaniline	−5.563597	16.22237	−1.588353	7.997763	−1.609348	53.62831	12.51053	−0.3593503	−0.178295	0.342419
	$(H^0 - H_0^0)/T$					$-(F^0 - H_0^0)/T$				
Aniline	2.853884	3.54253	0.211024	−3.422545	1.177706	46.55273	5.29847	−0.0856795	0.031616	0.004438
ortho-Fluoroaniline	1.906017	4.56754	0.080013	−2.624718	0.980511	47.43772	5.73529	−0.0863485	−0.106151	0.056638
meta-Fluoroaniline	1.359580	4.80939	0.037889	−2.289247	0.881978	47.47120	5.61328	−0.0648549	−0.272453	0.104786
para-Fluoroaniline	2.654205	4.16362	0.145395	−3.124900	1.125876	47.77040	5.80498	−0.1067316	0.061896	0.079570
ortho-Chloroaniline	3.245108	4.66616	0.024335	−2.060120	0.798880	47.93748	6.72859	−0.2191207	0.769272	−0.169040
meta-Chloroaniline	3.520178	4.69217	0.011134	−1.919498	0.751499	47.92095	6.93092	−0.2457593	0.944548	−0.214086
para-Chloroaniline	3.230415	4.98202	−0.038668	−1.591802	0.674605	47.54983	7.05893	−0.2553024	0.975900	−0.218424
ortho-Bromoaniline	4.439441	4.71509	−0.006986	−1.754539	0.703099	49.20653	7.56745	−0.3267063	1.469676	−0.349276
meta-Bromoaniline	4.667876	4.72475	−0.013011	−1.689839	0.681136	49.36894	7.70964	−0.3432014	1.568005	−0.372313
para-Bromoaniline	4.300206	4.87079	−0.029614	−1.642515	0.687487	49.32694	7.63983	−0.3296792	1.463085	−0.344535

TABLE 3

Frequency assignments (key to types of vibration: IP, in plane; OP, out of plane vibration; GING, wagging or rocking characteristic motion of inversion; TWIST, twisting; X SENS, of amino group; ASYMM, asymmetric stretch of amino group; TORSION, frequency related

Aniline [a]			Fluoroaniline					
Mode	Freq.	Mode	*ortho*		*meta*		*para*	
			Freq.	Ref.	Freq.	Ref.	Freq.	Ref.
CH BEND IP	1312	CH STRETCH	3048	30	3030	29	3053	27
CC STRETCH	1330	CH STRETCH	3072	30	3088	29	3032	31
X SENS	1278	CH STRETCH	3055	27	3068	27	3078	31
CH BEND IP	1173	CH STRETCH	3035	[b]	3040	27	3061	31
CH BEND IP	1154	CH BEND IP	1272	30	1330	27	1275	27
CH BEND IP	1084	CH BEND IP	1155	30	1170	27	1150	31
NH TWIST	1050	CH BEND IP	1136	30	1142	27	1115	27
CH BEND IP	1028	CH BEND IP	1075	[b]	1060	28	1025	27
CC BREATH	990	CH BEND OP	924	30	840	27	916	27
CH BEND OP	970	CH BEND OP	848	30	765	27	820	27
CH BEND OP	959	CH BEND OP	825	27	740	27	745	27
CH BEND OP	874	CH BEND OP	745	27	950	27	940	27
CH BEND OP	825	CC STRETCH	1584	30	1625	29	1620	27
X SENS	812	CC STRETCH	1510	30	1490	29	1519	31
CH BEND OP	751	CC STRETCH	1472	30	1412	[b]	1451	31
CC DEFO OP	690	CC STRETCH	1328	30	1000	29	1020	31
NH WAGGING	664	CC STRETCH	816	[b]	847	[b]	852	31
CC DEFO IP	618	CC STRETCH	1028	30	1372	29	1327	31
X SENS IP	527	CC DEFO IP	1002	[b]	1000	29	1008	27
X SENS OP	500	CC DEFO IP	556	30	590	29	638	[b]
CC DEFO OP	415	CC DEFO IP	436	30	530	29	756	31
X SENS IP	390	CC DEFO OP	404	30	515	29	690	[b]
X SENS OP	233	CC DEFO OP	498.5	25	449.8	25	162	31
NH STRETCH	3500	CC DEFO OP	723	[b]	315	29	502	25
NH STRETCH	3418	NH ASYMM	3493	3	3492	3	3474	3
CH STRETCH	3089	NH SYMM	3404	3	3405	3	3394	3
CH STRETCH	3072	NH BEND	1632	30	1600	27	1630	27
CH STRETCH	3050	NH SCISSOR	1068	30	1060	27	1072	27
CH STRETCH	3047	NH ROCK	690.5	25	719.4	28	679.7	25
CH STRETCH	3025	CN STRETCH	1305	27	1315	27	1325	27
NH BENDING	1619	CN BEND IP	500	[b]	510	[b]	520	31
CC STRETCH	1600	CN BEND OP	422	[b]	432	[b]	442	31
CC STRETCH	1586	CC STRETCH	1270	27	1288	27	1240	31
CC STRETCH	1503	CF BEND IP	438.8	[b]	443.7	[b]	437	31
CC STRETCH	1468	CC BEND OP	184.4	28	293.4	25	270.4	25
NH TORSION	216							

[a] All frequencies assigned by Evans [1].

[b] Estimated, this work.

BEND, bending vibration; STRETCH, stretching vibration; DEFO, deformation; WAG-
vibration which is sensitive to the substituent (X) in the molecule; SYMM, symmetric stretch
to internal rotation in the molecule)

Chloroaniline						Bromoaniline					
ortho		*meta*		*para*		*ortho*		*meta*		*para*	
Freq.	Ref.	Freq.	Ref.	Freq.	Ref.	Freq.	Ref.	Freq.	Ref.	Freq.	Ref.
3018	39	3051	37	3059	37	3059	39	3060	39	3085	42
3065	37	3054 (R)	37	3040	37	3053	39	3051	39	3040	42
3051 (R)	37	3037	39	3051	39	3026	39	3052	39	3053	39
3035	39	3065	39	3053	39	3053	39	3055	39	3051	39
1262	37	1314	37	1317	39	1316	39	1295	46	1331	39
1155	37	1166	37	1180	37	1158	47	1178	39	1182	42
1145	37	1078	37	1118	37	1142	47	1070	39	1055	42
1083	37	1171 (R)	37	1089	37	1072	39	1120	39	1021	39
847	39	962	37	819	37	847	39	894	39	904	39
756	37	925	37	853	39	895	39	876	39	853	39
875	37	863	37	889 (R)	37	877	39	824	39	851	39
966	37	774	37	850	39	839	47	848	39	816	45
1600	39	1608	[b]	1602	37	1602	39	1597	46	1597	45
1589	39	1592	37	1596	37	1575	47	1586	46	1587	39
1492	37	1473	37	1496	37	1486	47	1480	46	1490	42
1455	37	1447	37	1426	37	1451	47	1447	46	1420	45
1316	47	1305	39	1297	39	1299	39	1303	39	1285	39
1031	39	900	37	1097	39	1045	39	865	39	1075	39
814	39	997	39	788	39	801	39	990	46	817	39
559	37	530	37	624	39	549	39	678	39	625	39
471	37	489	37	640	39	655	39	530	39	630	39
727	[b]	705	[b]	496	39	289	48	237	39	494.8	25
538.8	25	438	25	400	39	468	48	433.9	25	400	39
261	37	245	39	223 (R)	37	248	48	233	48	135	39
3452	37	3490	3	3497	3	3491	3	3492	3	3485	3
3351	37	3402	3	3412	3	3397	3	3404	3	3399	3
1617	37	1617	37	1623	37	1618	45	1621	45	1627	39
1052	37	1005	39	1052	37	1020	39	1004	39	1009	39
745.9	25	716.9	25	662	[b]	742.8	25	717.9	25	645.9	25
1312	37	1260	37	1292	37	1260	45	1260	45	1270	45
365	[b]	349	[b]	415	39	430	39	421	39	405	[b]
218	[b]	212	[b]	210	[b]	169.8	[b]	168.5	[b]	165	[b]
677	37	694 (R)	37	637 (R)	[b]	650	48	665	[b]	595 (R)	48
372	37	315	[b]	305	[b]	215	39	207	39	230	39
155.2	25	178.1	25	189.5	25	140	25	162	25	124	39

TABLE 4

Molecular structural data

	Aniline	Fluoroaniline			Chloroaniline			Bromoaniline		
		ortho	*meta*	*para*	*ortho*	*meta*	*para*	*ortho*	*meta*	*para*
C–X (X = F, Cl, Br) Bond length (Å)		1.354	1.354	1.354	1.720	1.720	1.720	1.850	1.850	1.850
(reference)		20	20	20	21	21	21	21	21	21
θ (degrees) [a]	37.40	40.88	36.20	46.40	33.05	35.90	40.41	31.09	35.91	40.36
(reference)	19	23	22	20	f	f	f	f	f	f
ψ (degrees) [b]	113.3	113.1	115.0	112.0	113.5	115.0	112.0	114.0	115.0	112.0
(reference)	18, 19	23	22	20	g	g	g	g	g	g
I_{ABC} ($g^3\,cm^6$) [c] $\times 10^{-117}$	22682.8	61917.6	74742.4	63290.9	128415.3	163630.9	130938.8	276063.3	369249.4	284259.1
I_r ($g\,cm^2$) [c] $\times 10^{-40}$	2.695	2.748	2.703	2.843	2.625	2.699	2.737	2.603	2.699	2.739
V^0 ($cal\,mol^{-1}$)	4000	5541	6206	4182	5688	6086	4803	5765	6128	4840
(reference)	1	h	i	i	h	i	h	h	i	h
σ [d]	1	1	1	1	1	1	1	1	1	1
n [e]	2	2	2	2	2	2	2	2	2	2

[a] θ, angle between the plane of amino group and the plane of the aromatic ring. [b] ψ, angle between hydrogens of the amino group, HNH. [c] Calculated, this work. [d] This work; C_s-symmetry class, ref. 16. [e] This work; ref. 1. [f] Obtained, this work, using refs. 24 and 25. [g] Obtained, this work, using ref. 26. [h] Estimated, this work. [i] Calculated, this work, using ref. 25.

DATA USED (TABLES 3 AND 4)

Aniline and general physical data

Among several recent investigations of the Raman and infrared spectra of aniline reported in the literature [1–7] the work of Evans [1] appears to be the most complete. Even if Larsen et al. [6], and Kydd and Krueger [7] in their far-infrared investigations of aniline in the vapour phase have indicated that some corrections to the vibrational assignment of aniline as given by Evans [1] may follow, none has been forthcoming; and so, in view that the assignments made by Evans [1] are in close agreement with the results of normal coordinate analysis work of Berezin and Elkin [2], we have retained in this work the vibrational assignments of Evans [1] except for the value of the barrier to the internal rotation (Tables 3 and 4). To obtain the height of the internal rotational barrier the spectroscopically calculated ideal gas state entropy of aniline was compared to the third law entropy at 298.15 K.

Table 7 presents the calculation of the third law entropy at 298.15 K. Table 7 shows that the calculated third law entropy value is subject to the choice of the vaporization heat and the low vapour pressure values for aniline at 298.15 K. Figure 1 points out the prevailing uncertainty in the choice of the appropriate experimental vapour pressure value from the given data sets [10–13]; while Fig. 2 indicates the strong, calculated (at fixed S(liq) and H_v values) third law entropy dependence on the saturated vapour pressure.

Using the frequency assignments of aniline made by Evans [1], a potential barrier to internal rotation of 4.0 kcal mol^{-1} was calculated so as to give the same entropy value as determined from the third law entropy calculations. In view that Evans' [1] assignments agree with the majority of the frequencies predicted by normal coordinate analysis [2], the fitted barrier of 4.0 kcal mol^{-1} is assumed to be significantly accurate for the determination of

TABLE 5

Comparison of calculated and experimental ideal gas heat capacity and entropy values for aniline [a]

Investigator	S^0 (e.u.)		C_p^0 (cal mol^{-1} K^{-1})	
	298.15 K	800.00 K	298.15 K	800.00 K
This work, experimental	76.100 [b]	–	–	–
This work, calculated	76.10	115.62	25.84	53.94
Hatton et al. [8]	76.28	115.76	25.91	53.79

[a] Other available literature values such as calculated thermodynamic functions of Gadagin and Sheshidhar for the three isomeric fluoroanilines [60] and Seshadri et al.'s work for aniline [14] were not included in this Table.

[b] See appropriate discussion in the text as well as Table 7.

TABLE 6

Effect of various changes in the input parameters in the calculation of the thermodynamic functions of *para*-fluoroaniline and *ortho*-bromoaniline at 298.15 and 800.00 K

Percentage change in input parameters		*para*-Fluoroaniline							
		298.15 K				800.00 K			
		ΔC_p^0	$\Delta\frac{(H^0-H_0^0)}{T}$	$\Delta\frac{-(F^0-H_0^0)}{T}$	ΔS^0	ΔC_p^0	$\Delta\frac{(H^0-H_0^0)}{T}$	$\Delta\frac{-(F^0-H_0^0)}{T}$	ΔS^0
All frequencies	−1%	0.97	0.70	0.11	0.23	0.45	0.68	0.28	0.39
3 Lowest frequencies	−2%	–	–	–	–	–	–	–	–
3 Lowest frequencies	+2%	0.11	0.26	0.09	0.13	< 0.00	0.09	0.10	0.10
Product of principal moments of inertia	+10%	< 0.00	< 0.00	0.16	0.11	< 0.00	< 0.00	0.11	0.08
Reduced moments of inertia, I_r	+1%	< 0.00	< 0.00	0.02	0.01	< 0.00	< 0.00	0.01	0.01
	+2%	< 0.00	< 0.00	0.02	0.03	< 0.00	< 0.00	0.02	0.02
Potential barrier, V_0	−5%	0.07	0.13	0.06	0.08	−0.09	< 0.00	0.06	0.04
	+5%	0.10	0.19	−0.05	−0.08	0.07	< 0.00	−0.05	−0.03
Potential barrier, V_0 and all frequencies	+5% −1%	0.86	0.58	0.06	0.16	0.52	0.68	0.23	0.35

Percentage change in input parameters		*ortho*-Bromoaniline							
		298.15 K				800.00 K			
		ΔC_p^0	$\Delta\frac{(H^0-H_0^0)}{T}$	$\Delta\frac{-(F^0-H_0^0)}{T}$	ΔS^0	ΔC_p^0	$\Delta\frac{(H^0-H_0^0)}{t}$	$\Delta\frac{-(F^0-H_0^0)}{T}$	ΔS^0
All frequencies	−1%	0.79	0.67	0.13	0.31	0.42	0.59	0.27	0.36
3 Lowest frequencies	−2%	0.03	0.22	0.12	0.14	< 0.00	0.06	0.11	0.09
3 Lowest frequencies	+2%	−0.07	−0.22	−0.10	−0.13	< 0.00	−0.06	−0.11	−0.09
Product of principal moments of inertia	10%	< 0.00	< 0.00	0.14	0.18	< 0.00	< 0.00	0.09	0.08
Reduced moments of inertia, I_r	+1%	< 0.00	< 0.00	0.01	0.08	< 0.00	< 0.00	< 0.00	0.01
	+2%	< 0.00	0.06	0.01	0.09	< 0.00	< 0.00	0.01	0.01
Potential barrier, V_0	−5%	0.07	0.17	0.04	0.13	−0.05	0.03	0.04	0.05
	+5%	−0.10	−0.11	−0.03	0.01	0.04	−0.06	−0.05	−0.05
Potential barrier, V_0 and all frequencies	+5% −1%	–	–	–	–	–	–	–	

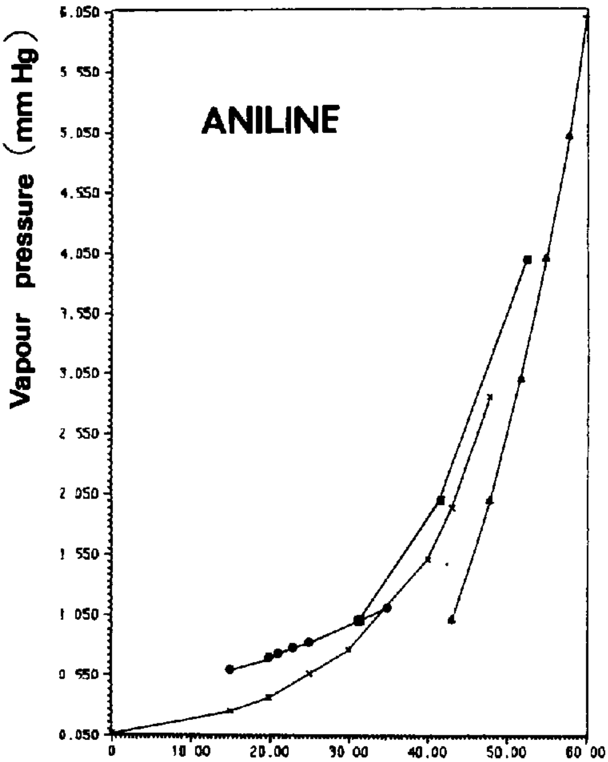

Fig. 1. Saturated vapour pressure–temperature plot for aniline. (×) Ref. 10, (■) ref. 11, (▲) ref. 12, (●) ref. 13.

TABLE 7

The molar entropy of aniline in the ideal gas state (e.u.) at 298.15 K

ΔS(liq) [a]	45.721
$\Delta H_v/T$ [b]	44.692
$R \ln P$ [c]	-14.313
S(ideal) $-$ S(real) [d]	0
S^0(obs)	76.100

[a] Taken directly from ref. 8.

[b] Taken from ref. 8. It should be noted that the direct measurement of Kusano and Wadsö [9] yields a supporting value of 13.345 kcal mol^{-1} at 298.15 K. Because of weighted averaging, it appeared that Hatton et al.'s [8] data are more reliable than the measured value of Kusano and Wadsö [9].

[c] While Hatton et al. [8] have given with some assurance the extrapolated value of heat of vaporization at 298.15 K, the extrapolation of saturated vapour pressure data from the given value of 304.7 K (Hatton et al. [8] give the smoothed vapour pressure data from 304.7 to 457.55 K) down to 298.15 K is a rather questionable practice. Figure 1 compares several low vapour pressure data sets [10–13]. The vapour pressure (P_{vap} = 0.566 mmHg at 298.15 K) used in this work, and with the closest experimental data point at 298.07 K, was taken from the data set of Gurevich and Sigalovskaja [10], not considered by Hatton et al. [8].

[d] Noting the deviations in the low vapour pressure values, the real gas entropy correction was considered to be negligible (compare with ref. 14).

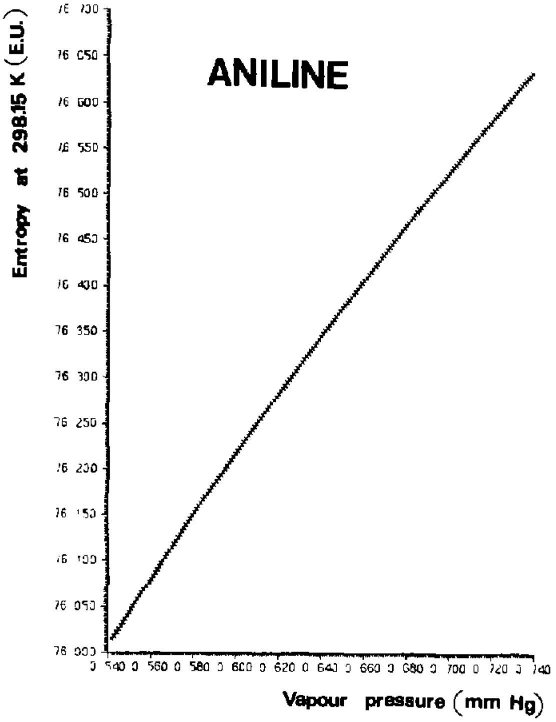

Fig. 2. Entropy at 298.15 K versus the saturated vapour pressure plot at the same temperature for aniline.

thermodynamic functions. Figure 3 illustrates the change of entropy of aniline as an ideal gas at 298.15 K versus the potential barrier to internal rotation at the given vibrational assignment set [1].

The aniline and its derivatives have a high, double minimum inversion barrier [1,6,7,15–19]. On the other hand planar aniline belongs to the point symmetry group C_{2v}. Subsequent internal rotation of the amino group to ring bond reduces this symmetry to C_2 while aniline with pyramidal bonds at the nitrogen center has C_s point symmetry at rotational angles $\varphi = 0$ and 90° and no symmetry for all other angles.

Although a complete estimation of thermodynamic properties of aniline and its derivatives should consider all aniline conformers and the associated implications of the existence of a double inversion barrier; in this work, following Pitzer [15] and Evans [1] we neglect the possibility of inversion (since the barrier to inversion is high [1,6,7,15], take the lower symmetry number (i.e., C_s point symmetry, $\sigma = 1$) for external rotation and assume single rather than doubly degenerate vibrational levels).

To calculate the values of the products of the principal moments of inertia and the reduced moments of inertia (Table 5), the structure for each of the compounds considered was assumed to be the same as that of aniline [19]. Hence, the input data for each compound differed in each case by the bond

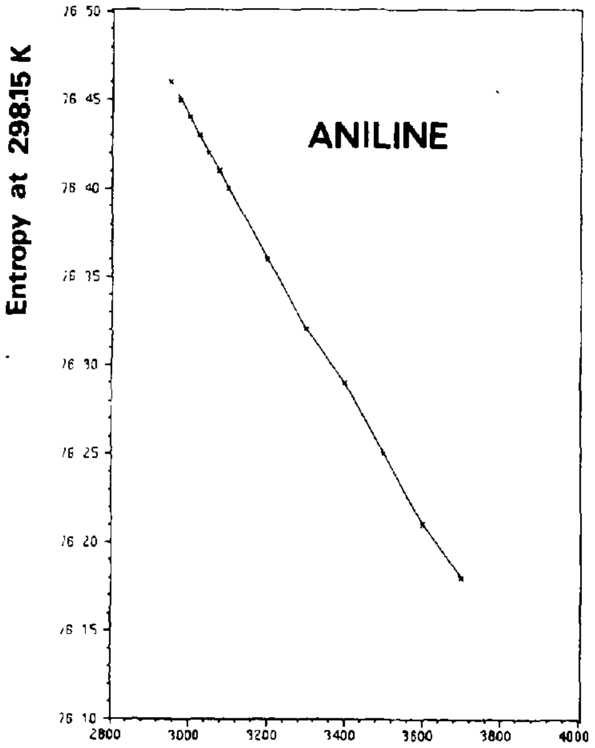

Fig. 3. Ideal gas state entropy at 298.15 K versus the potential energy barrier to internal rotation plot for aniline.

lengths of the respective carbon–halogen (substituent) bond, the angle between the plane of the amino group and the plane of the aromatic ring, and the angle between the hydrogen atoms of the amino groups. Table 5 summarizes these input data. The bond lengths of C–F, C–N, C–H and N–H were obtained from ref. 20, while the C–Cl and C–Br bond lengths were from ref. 21. The angle between the plane of the aromatic ring and the plane of the amino group has been found for aniline [19], *para*-fluoroaniline [20], *meta*-fluoroaniline [22] and *ortho*-fluoroaniline [23]. However, Kydd [24] states that ϕ, the angle between the plane of the amino group and the planar aromatic ring, is linearly related to the inversion barriers. This was accepted in this work to estimate values of ϕ for the haloanilines using the inversion barriers as calculated by Kydd and Krueger [25].

For aniline there are several quoted values of ϕ varying from 37 to 42° [18]. The value used in this work is 37.48° [19].

For the angle between the hydrogens of the amino group, θ, only values for aniline and *p*-, *m*- and *o*-fluoroanilines were available. For the other haloanilines, except for *o*-haloanilines, the angles were transferred from the corresponding positional analogues of fluoroanilines. For the *o*-haloanilines however, it was assumed that the angle increased in the order F, Cl, Br as stated in ref. 26, and the values were found by adding a small difference of 0.5° to each succeeding *o*-haloaniline in the above order as a first approximation although it is likely that the difference will be higher.

The calculated products of the principal moments of inertia and the reduced moments of inertia are listed in Table 5.

In this work the barrier height of the internal rotation for aniline (Table 5) was deduced by comparing the third law entropy with the spectroscopically obtained entropy value. However, for the haloanilines there are no available thermodynamic data but only a series of assigned torsional frequency values [1,6,25]. (Recently Belorgeot et al. [4,5] presented values for the barriers of internal rotation for some of the haloanilines. However the presented values, when cross-evaluated, appeared to be too low and were not substantiated by any other of the available data. Hence, we did not consider these values for use in this work.)

Assuming that the torsional frequency can be approximated to represent a harmonic oscillation, the corresponding potential barrier to internal rotation may be found using the following equation

$$\nu = \left(\frac{n}{2\pi}\right)\sqrt{\frac{V_0}{2I_r}} \tag{2}$$

where ν = torsional frequency, I_r = reduced moment of inertia, V_0 = potential barrier height, n = symmetry number of the rotating group.

In this work to calculate the internal rotational barriers via harmonic oscillator approximation (eqn. 2) we used the assignments made by Kydd and Krueger [25] for torsional frequencies of *para*-fluoroaniline and the *meta*-haloanilines. These assignments were well supported by the independent work of Larsen et al. [6] for aniline and *para*-fluoroaniline (Table 4). As a matter of fact the torsional frequency for aniline of 277 cm^{-1} was deduced by Kydd and Krueger [25] from the amino group out of plane wag of 216.5 cm^{-1} while Evans [1] assigned 216 cm^{-1} to the torsional frequency. Larsen et al.'s [6] independent work did yield a value of 277.3 cm^{-1} for the torsional frequency of aniline thus substantially supporting Kydd and Krueger's [25] findings.

Since torsional frequencies for the *ortho*-haloanilines and *para*-bromoanilines were not found in the literature; the barrier heights to internal rotation were estimated through the general observation that the deduced torsional frequencies are inversely related to the amino group out of plane wag for the anilines (compare with Kydd and Krueger [25]). The potential barriers to internal rotation determined in this manner and used in this work, are listed in Table 5.

Fluoroanilines

The liquid state fundamental frequencies for the isomeric fluoroanilines have been assigned by several workers [27–30], while vapour and liquid phase assignments have been made by Tiwari and Upadhya [31].

In this work, comparative studies were made with all the above assignments and with those of the isomeric fluoro-toluene assignments by Green [32–34], the difluoro anilines by Singh and co-workers [35], and the isomeric fluoro-*N*-methylanilines by Kumar [36].

In selecting the frequencies from assignments of various researchers, the vapour state fundamental frequencies were preferred, and those frequencies which were found to be strongly deviating from the majority of assignments of the same mode of vibration by different researchers were replaced by most frequently occurring frequencies of the same mode.

The missing frequencies were assigned by comparison. In *para*-fluoroaniline one C–C in-plane deformation, one out-of-plane deformation, and one C–C vibration were missing. The first two were transferred from the assignment of the same modes in *para*-fluoro-*N*-methylaniline [36] as most of the frequencies of the latter compound are very similar to *para*-fluoroaniline; i.e., the methyl group is substituted in the amino group while the aromatic ring has the same atoms attached to it.

Similarly, in *meta*-fluoroaniline, one C–C stretching vibration was transferred from *meta*-fluoro-*N*-methylaniline [36]. For *ortho*-fluoroaniline a C–H stretch, a C–H in-plane bend, a C–C stretch, a C–C in-plane deformation and a C–C out-of-plane deformation were transferred from *ortho*-fluoro-*N*-methylaniline [36].

To complete the set of vibrational assignments for the isomeric fluoroanilines (Table 4), the following frequencies were also estimated.

(i) in *meta*-fluoroaniline, the C–N in-plane and out-of-plane bending vibrational modes,

(ii) in *ortho*-fluoroaniline, the C–N in-plane and out-of-plane bending modes and the C–F in-plane bending vibration.

To estimate these missing frequencies, it was noted that the known C–N stretching modes in the isomeric fluoroanilines are linearly related to the position in the ring in the order *para*, *meta* and *ortho*. If so, the C–N in-plane and out-of-plane bending modes were also assumed to be linearly related because they all involve the same atoms. Subsequently, the frequencies for the C–N in-plane bending modes in *meta*- and *ortho*-fluoroanilines were obtained by extrapolation from the corresponding vibrational mode in *para*-fluoroaniline. Similarly, the C–N out-of-plane bending mode frequencies were estimated for the *meta*- and *ortho*-fluoroanilines.

In estimating the C–F in-plane bending mode frequencies for *ortho*-fluoroaniline, it was assumed that the ratio of the frequencies is of the same mode in *ortho*-fluoroaniline and *ortho*-fluoro-*N*-methylaniline.

The vapour state NH_2 wag (or rock) and C–F out-of-plane bending mode frequencies were selected from Kydd and Krueger [25]. Table 4 presents all frequency assignments.

Chloroanilines

Singh et al. [37] investigated the infrared spectra of *ortho-* and *meta*-chloroanilines in the liquid state, and of *para*-chloroaniline in the solid state. Tripathi and Katon [38] studied the infrared spectrum of crystalline *para*-chloroaniline at low temperatures, while Kumpawat et al. [39] studied the infrared spectra of the isomeric chloroanilines in the liquid state and performed normal coordinate analysis of these compounds.

To select the fundamental frequencies of the isomeric chloroanilines for use in this work, comparative studies, similar to those performed for the fluoroanilines, were made with the fundamental frequency assignments of the chloro-methylanilines by Sharma and Dwivedi [40], the dichloroanilines by Goel et al. [41] and Tripathi [42], 2,4,6,-trichloroaniline by Tripathi and Pandey [44].

Also some frequencies were selected from assignments of Katritzky et al. [45–47] of *para-*, *meta-* and *ortho*-disubstituted benzenes. The frequencies estimated in this work are as follows:

(i) *para*-chloroaniline, the N–H rock, C–N out-of-plane and C–Cl in-plane bending,

(ii) *meta*-chloroaniline, C–C out-of-plane deformation, the C–N in-plane and out-of-plane and C–Cl in-plane bending modes,

(iii) *ortho*-chloroaniline, C–C out-of-plane deformation, C–N in-plane and out-of-plane bending vibrational modes.

In the chloro-methylanilines, the aromatic ring molecular vibrations that are not X-sensitive (i.e., sensitive to the substituent in the ring) have been noted to be similar to the chloroanilines. In view of this, the frequencies for the missing C–C out-of-plane deformation modes in *meta-* and *ortho*-chloroanilines were transferred from the same modes in corresponding 3-chloro-2-methyl- and 6-chloro-2-methylaniline.

The C–Cl in-plane bending vibrational modes for *para-* and *meta*-chloroanilines were taken from their respective chloro-methylaniline analogues as it was assumed that the carbon–halogen vibrational mode was not significantly affected by a methyl substituent in the aromatic ring.

Similarly, the C–N in-plane and out-of-plane bending modes in *para-* and *meta*-chloroanilines were transferred from their corresponding chloromethylanilines as this is not a ring vibration that would be sensitive to a ring substituent. As there were no assignments of the remaining missing modes in *ortho*-chloroaniline, the C–N in-plane and out-of-plane bending modes were transferred from 2,6-dichloroaniline (which is *ortho*-disubstituted aniline). This estimate is expected to be close to the "true" frequencies as the C–N stretching vibrational mode in 2,6-dichloroaniline is within 3 cm^{-1} of the same mode in *ortho*-chloroaniline.

The N–H rocking mode in *para*-chloroaniline was also transferred from 2,4,6-trichloroaniline as this vibration is practically unchanged from that in aniline and is in a similar range in the dichloroanilines. Although Kumpawat et al. [39] did assign the above estimated frequencies from their normal coordinate analyses we did not use their assigned values in this work since it was found that these were too low in comparison to the spectroscopic data of the other chloro-substituted anilines. It was noted that the error in higher frequencies calculated by these authors was much less than the error in their lower calculated frequencies and thus, where possible, in this work the latter were either transferred from analogous compounds or estimated.

Bromoanilines

Rao [48] studied the ultraviolet spectra of the isomeric bromoanilines in the vapour state. Tripathi [42] also assigned some fundamental frequencies for *para*-bromoaniline in the vapour state while Katritzky et al. [45–47] included some of the fundamental vibrations of the isomeric bromoanilines in their study of disubstituted benzenes. In 1980 Kumpawat et al. [39] studied the isomeric haloanilines and assigned complete sets of fundamental frequencies, most of which were obtained from their normal coordinate analyses.

Due to lack of data, the comparative studies of frequencies for the isomeric bromoanilines were more difficult and limited. Comparisons of similar modes were done with the assignments of 2,6-dibromoaniline in the solid state by Verma [49] and of 2,4,6-tribromoaniline by Faniran et al. [43].

Of the selected frequencies (Table 4), those that were estimated are as follows:

(i) in *para*-bromoaniline, the C–N out-of-plane and C–Br out-of-plane bending vibrational modes;

(ii) in *meta*-bromoaniline, the C–N out-of-plane and C–Br out-of-plane stretching molecular vibrations;

(iii) in *ortho*-bromoaniline, the C–N out-of-plane bending vibrational mode.

On the other hand, the C–Br in-plane bending vibrational frequencies for the bromoanilines were selected from the work of Kumpawat et al. [39]. This was done since their frequency for this mode in para-bromoaniline is similar to that in 2,4,6-tribromoaniline [43]. The calculated C–Br out-of-plane bending vibrational frequencies of Kumpawat et al. [39] were thought to be too high and these were estimated by the methods discussed below.

The C–Br out-of-plane bending mode for *para*-bromoaniline was transferred from bromobenzene as assigned by Whiffen [50]. It was found that the out-of-plane bending modes for the chloroanilines were linearly related (correlation coefficient, $r^2 = 0.982$) in the increasing order with position of *ortho, meta* and *para*, and when a similar linear relation was established for the bromoanilines with the same positional order, the estimated frequency was very close to that in bromobenzene.

The C–N in-plane bending vibrational frequencies for the *ortho-* and *meta*-bromoanilines were selected from the assignments of Kumpawat et al. [39]. This choice was strengthened by noting that the experimental frequency for this mode in *para*-bromoaniline compared favourably to that calculated by them [39] and it was assumed to hold for the other bromoanilines (Table 4).

The frequencies of the C–N out-of-plane bending modes were estimated in this work noting that as these were low frequencies, they would be linearly related on a log–log basis with the respective ionization potentials of the halogen atoms as first indicated by Lielmezs [51,52]. This linearity on a log–log basis of the low frequencies with ionization potential was verified for the low frequencies of the halobenzenes via the assigned values of Brown et al. [53].

The C–Br stretch in *meta*-bromoaniline was estimated by assuming that frequencies of this mode for the isomeric bromoanilines were linear with position in the increasing order of *para, ortho* and *meta* positions. This relation agrees with that found for the fluoro- and chloroanilines.

DISCUSSION AND ERROR ANALYSIS

The thermodynamic functions of aniline (Table 1) have been re-evaluated. Table 5 compares the calculated values for C_p^0 and S^0 with those obtained by Hatton et al. [8]. For instance, at 298.15 K the differences in the functions from Hatton et al.'s [8] values were 0.27 and 0.25% in heat capacity and entropy, respectively. These differences chiefly arise as Hatton et al. used a value of 3.43 kcal mol^{-1} for the internal rotational potential barrier while in this work we used a value of 4.00 kcal mol^{-1} (Table 4). This latter barrier obtained by fitting the chosen value of the rotational barrier to obtain the experimental entropy value (Table 7) at 298.15 K by statistical mechanical means. As the presented Evan's assignments [1] agree with the majority of the frequencies predicted by Berezin and Elkin [2] with their NCA work, the fitted barrier is assumed to be significantly accurate for the determination of the thermodynamic functions.

For isomeric halo-anilines (Table 1), the heat capacities at 298.15 K for the fluoro-, chloro- and bromo-anilines lie within 1.7, 1.4 and 1.1% of each other, respectively. Similarly, the entropies at 298.15 K lie within 0.9, 1.0 and 1.4% of each other, respectively. With this narrow margin of difference in the thermodynamic functions, any significant trend with position within the isomeric halo-anilines cannot be stated with certainty as small function errors could upset the supposed trend. The only noticeable order would appear to be that for the corresponding positional halo-anilines in which each of the thermodynamic functions follow the order of fluoro < chloro < bromo. This order agrees with that present in the halonitrobenzenes and halonaphthalenes.

Due to the relative lack of gaseous state frequencies, the authors had to use liquid and some solid state frequencies to complete the assignment sets (Table 3). Allowance for this state shift effect [54–56] has been made in the function error analysis (compare with Table 6). The effect of the uncertainty in the determination of internal rotational barrier values is shown in Table 6. As a matter of fact, a variation of ±5% (Table 6) indicates relatively small changes in the calculated thermodynamic functions.

The two main sources of errors are the input data values and the calculation assumptions made. An estimate of the input data errors is found in Table 6. Input parameters were changed by a certain amount and the resulting changes in the final thermodynamic function values noted. The errors made in frequency assignments cause the most significant changes in the thermodynamic function values. For instance (Table 6), a decrease in all the frequencies by 1% causes a change of about 0.8%, 0.7%, 0.1% and 0.3% in the heat capacity, enthalpy, free energy and entropy values, respectively, of *ortho*-bromoaniline at 298.15 K. At increased temperatures, this error effectively decreases (Table 6). Only large magnitudes in the uncertainties of the internal potential barrier, principal moments of inertia, reduced moments of inertia and the bond lengths used, will noticeably affect the calculated thermodynamic function values.

The main calculation assumption made was to neglect the unharmonicity effects [57]. Lielmezs et al. [58] and Bennett and Lielmezs [59] in their calculations of thermodynamic functions for naphthalene and halogenated naphthalenes, and methylhalosilanes, respectively, noted that the effects due to unharmonicity will change the function values by 1–2% at about 1000 K, and about 0.5% at 298.15 K. Therefore, in consideration of these estimates, the conventions for unharmonicity have been neglected in this work.

The overall differences due to changes in input parameters reduce at higher temperatures (Table 6), but with high temperatures, the magnitude of errors made in calculation assumptions, increases. It is estimated that the overall accuracy of the thermodynamic functions (Tables 1 and 2) are within ±1.5%.

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NOMENCLATURE

a, b, c, d, e	curve-fitting constants (dimensions vary)
C_p^0	ideal gas heat capacity function (cal mol^{-1} K^{-1})
$-(F^0 - H_0^0)/T$	ideal gas free energy function (cal mol^{-1} K^{-1})
$(H^0 - H_0^0)/T$	ideal gas enthalpy function (cal mol^{-1} K^{-1})
I_{ABC}	product of principal moments of inertia (g^3 cm^6)
I_A, I_B, I_C	principal moments of inertia (g cm^2)
M	molecular weight (g mol^{-1})
n	number of potential minima per revolution of a top
P	pressure (atm)
Q_f	free rotation partition function (dimensionless)
R	universal gas constant (1.98719 cal mol^{-1} K^{-1})
S^0	ideal gas entropy function (cal mol^{-1} K^{-1})
T	temperature (K)
V_0	internal rotation barrier (cal mol^{-1})

Greek letters

θ	azimuthal angle of internal rotation (degrees)
σ	symmetry number (dimensionless)
ν_i	ith fundamental vibration frequency (cm^{-1})
α_i	direction cosine between axis of rotation and ith principal axis.

Superscripts

0	ideal gas state

Subscripts

0	function at 0 K

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