

Discussion

## Comment on “prediction of vapor pressures of solid organic compounds with a group contribution method”

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In a recent paper appearing in this journal, Coutsikos et al. [1] presented a group contribution method for estimating vapor pressures of organic solids. The estimation required the compound's molar entropy of fusion,  $\Delta_{\text{fus}}S_{\text{m}}$ , which was also calculated by a group contribution method developed by the authors. The proposed method gave satisfactory vapor pressure predictions for many organic compounds having vapor pressures well below the Pa level. The entropy of fusion estimations was not nearly as good. As noted by the authors, “the obtained predictions are – as expected from a simple method – not very accurate, but sufficient for purposes of this study.” In fairness, the authors' intention was not to develop a group contribution method for estimating entropy of fusion per se. Rather the authors needed a numerical value of the entropy of fusion only for substituting into their predictive vapor pressure expression.

The intent of this short communication is not to criticize the authors' excellent work, but rather to inform journal readers of the existence of a second group contribution method for total solid-to-liquid phase change entropy that gives much better entropy predictions for the database examined. In the second method [2–6], the molar total phase change entropy of a molecule,  $\Delta_{\text{tpce}}S_{\text{m}}$ , is estimated as the sum of three components: the contribution of the hydrocarbon portion of the molecule, the contribution of the carbon(s) bearing the functional group(s), and the contribution of the functional group(s) as summarized by the three terms of Eq. (1):

$$\Delta_{\text{tpce}}S_{\text{m}} = \sum_i n_i G_i + \sum_i n_i C_i G_i + \sum_k n_k C_k G_k \quad (1)$$

where

$$K = \sum_k n_k \quad (2)$$

The subscript  $i$  identifies the hydrocarbon components and the carbons bearing the functional group, and the subscript  $k$  identifies the functional groups. The terms  $n$ ,  $C$ , and  $G$  refer to the number of each group present in the molecule, its group coefficient, and group value, respectively. A complete list of group values and coefficients, as well as numerous illustrational examples, is published elsewhere [5,6] and will not be repeated here.

In Table 1, we have compiled experimental entropy of fusion data for 400 different organic compounds to compare the predictive ability of both the Coutsikos et al. and Chickos et al. (Eq. (1)) group contribution methods. The tabulated experimental values were taken for the most part from our published entropy of fusion database [5,6], with a few recently published values [7–14] also included. In preparing Table 1, we have gathered a large number of the compounds from our database for which both the Coutsikos et al. and Chickos et al. method predictions could be made. The experimental values,  $\Delta_{\text{fus}}S_{\text{m}}$  and  $\Delta_{\text{tpce}}S_{\text{m}}$ , are given in columns 2 and 3. The calculated values are tabulated in the last two columns.

Examination of the numerical entries reveals that the Chickos et al. group contribution method predicts the experimental  $\Delta_{\text{tpce}}S_{\text{m}}$  values to an average absolute deviation of 9.5 J/(mol K). Average absolute deviations for the Coutsikos et al. method are 22.7 J/(mol K) and 21.1 J/(mol K), depending upon whether one compares the predicted values to the experimental entropies of fusion or to the total phase change entropies. Application of the Chickos et al. method of estimating total phase change entropies to estimate fusion entropies results in an absolute average deviation of 18.0 J/(mol K). Irrespective of whether fusion entropies or total phase change entropies are estimated, the Chickos et al. method clearly gives results with the lowest error.

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Table 1  
Comparison of the predictive abilities of the Couttsikos et al. and Chickos et al. group contribution methods

Compound	$\Delta_{fus}S_m$ exp	$\Delta_{tpce}S_m$ exp	$\Delta_{fus}S_m$ calc (Coutsikos et al.)	$\Delta_{tpce}S_m$ calc (Chickos et al.)
<i>n</i> -Alkanes				
Ethane	31.8	31.8	30.762	35.2
Propane	41.24	41.24	38.51	42.3
Butane	34.56	53.62	46.259	49.4
Pentane	58.58	58.58	54.008	63.2
Hexane	73.22	73.22	61.756	72.4
Heptane	76.9	76.9	69.505	81.8
Octane	95.86	95.86	77.254	91.1
Nonane	70.29	99.2	85.002	100.5
Decane	117.99	117.99	92.751	109.8
Undecane	89.6	118.6	100.5	119.1
Dodecane	139.75	139.75	108.25	128.5
Tridecane	106.27	136.31	115.997	137.8
Tetradecane	161.54	161.54	123.745	147.1
Pentadecane	122.17	156.02	131.494	156.5
Hexadecane	176.79	176.79	139.243	165.8
Heptadecane	136.11	174.67	146.992	175.1
Octadecane	204.6	204.6	154.74	184.5
Nonadecane	155.9	202.1	162.489	193.8
Eicosane	219.6	219.6	170.237	203.1
Heneicosane	152.06	202.71	177.986	212.4
Docosane	151.36	245	185.735	221.8
Tricosane	168.33	237.39	193.483	231.1
Tetracosane	169.37	266.79	201.232	240.4
Pentacosane	176.76	258.18	208.98	249.8
Hexacosane	180.6	289.3	216.729	259.1
Heptacosane	177.82	265.68	224.478	268.4
Octacosane	193.28	300.26	232.227	277.8
Nonacosane	196.43	286.08	239.975	287.1
Tricontane	203.24	315.06	247.724	296.4
Dotriacontane	223.93	345.11	263.221	315.1
Triatriacontane	305.2	305.2	270.97	324.4
Tetraatriacontane	231.1	316.96	278.719	333.7
Pentatriacontane	248.85	368.04	286.467	343.1
Hexatriacontane	254.41	371.13	294.22	352.4
Tetracontane	377.82	418.4	325.21	389.7
Hentetracontane	402.4	402.4	332.959	397.4
Tetratetracontane	403.1	403.1	356.205	425.8
Pentacontane	504.2	504.2	402.697	481.6
Henpentacontane	466.1	486.8	410.446	469.9
Dopentacontane	468.5	517.1	418.194	500.3
Hexacontane	500.41	500.41	480.18	576.4
Hectaane	854.1	854.1	790.129	946.7
Branched alkanes				
Isobutane	40.11	40.11	38.993	36.4
2-Methylbutane	45.23	45.23	46.741	43.5
2,2-Dimethylpropane	12.69	31.1	35.11	35.5
2,3-Dimethylbutane	5.47	52.96	47.224	37.6
3-Methylpentane	48.17	48.17	54.49	50.6
2-Methylpentane	52.43	52.43	54.49	50.6
2,2-Dimethylbutane	3.31	45.88	42.859	42.6
2,4-Dimethylpentane	44.46	44.46	50.607	44.7
3-Ethylpentane	61.77	61.77	62.239	57.8
2-Methylhexane	59.29	59.29	62.239	57.8
3,3-Dimethylpentane	51.16	51.16	50.607	49.7
2,2,3-Trimethylbutane	8.88	28.53	43.341	36.7
2,2-Dimethylpentane	39.55	39.55	50.607	49.74
2,2,4-Trimethylpentane	54.7	54.7	51.09	43.8
2,3,4-Trimethylpentane	56.65	56.65	55.454	38.8
3-Methylheptane	76.6	76.6	69.987	64.9
2-Methylheptane	72.62	72.62	69.987	64.9
2,2,3,3-Tetramethylbutane	20.16	33.28	39.458	35.8
4-Methylheptane	71.22	71.22	69.987	64.9

Table 1 (Continued)

Compound	$\Delta_{\text{fus}}S_{\text{m}} \text{ exp}$	$\Delta_{\text{tpce}}S_{\text{m}} \text{ exp}$	$\Delta_{\text{fus}}S_{\text{m}} \text{ calc}$ (Coutsikos et al.)	$\Delta_{\text{tpce}}S_{\text{m}} \text{ calc}$ (Chickos et al.)
2,2,3,3-Tetramethylpentane	8.9	50.9	47.207	42.9
2,2,4,4-Tetramethylpentane	47.17	47.17	47.207	42.9
3,3-Diethylpentane	42.02	48.2	66.105	64
2-Methyloctane	93.31	93.31	77.736	82.9
3-Methyloctane	102.6	102.6	77.736	80.7
5-Methylnonane	89.19	89.19	85.485	79.2
DL-4-methylnonane	86.94	86.94	85.485	79.2
DL-3-methylnonane	99.22	99.22	85.485	90.0
2-Methylnonane	87.97	87.97	85.485	92.4
2-Methyldecane	111.73	111.73	93.233	101.7
20-Methylnonatricontane	362.1	362.1	317.94	371.24
Cycloalkanes				
Cyclopropane	37.4	37.4	4.939	33.4
Cyclobutane	5.96	45.13	6.585	37.1
Cyclopentane	3.35	45.96	8.23	40.8
Cyclohexane	9.57	45.77	9.877	44.5
Cycloheptane	7.1	47.6	11.523	48.2
Cyclooctane	8.35	48.89	13.169	51.9
Cyclodecane	67.03	67.03	16.52	59.3
Cyclododecane	44.34	47.35	19.754	66.7
Cyclotetradecane	87.51	87.51	23.046	74.1
Cyclopentadecane	25.25	65.71	24.693	77.8
Cyclohexadecane	12.59	86.45	27.985	81.5
Cyclooctadecane	28.52	126.74	29.631	88.9
Cyclotetraicosane	33.54	161.49	39.508	111.1
1-Alkanols				
Methanol	18.3	22.3	56.743	19.3
Ethanol	31	36.2	64.492	26.46
1-Propanol	36.12	36.12	72.24	33.6
1-Butanol	50.46	50.46	79.989	47.3
1-Pentanol	53.7	53.7	87.738	56.7
1-Hexanol	68.56	68.56	95.486	66
1-Heptanol	75.53	75.53	103.235	75.31
1-Octanol	97.28	97.28	110.984	84.62
1-Decanol	134.5	134.5	126.481	103
1-Dodecanol	133.76	133.76	141.978	122
1-Tridecanol	61.09	148.11	149.727	131.3
1-Tetradecanol	70.71	158.75	157.475	140.6
1-Pentadecanol	172.86	172.8	165.207	150
1-Hexadecanol	181.17	181.17	172.973	159.3
1-Heptadecanol	113.29	191.26	180.72	168.12
1-Octadecanol	209.7	209.7	188.47	178
1-Nonadecanol	129.68	217.94	196.22	186.72
1-Eicosanol	129.53	214.18	203.97	196.02
1-Docosanol	134.9	185.6	219.465	214.6
1-Hexacosanol	192.7	243.1	250.459	251.8
Other alcohols				
2-Propanol	29.1	29.1	64.974	27.3
2-Butanol	32.33	32.33	72.723	34.4
2-Methyl-1-propanol	22.42	26.98	61.091	27.7
2-Methyl-2-propanol	36.93	36.93	72.723	31.6
2-Methyl-2-butanol	16.88	31.1	68.84	38.8
2-Pentanol	42.4	42.4	80.471	41.3
3-Pentanol	44.47	44.47	80.471	41.3
2,2-Dimethyl-1-propanol	12.49	30.92	68.84	26.84
1,1-Dimethyl-1-propanol	16.88	31.1	68.84	38.62
Tri- <i>tert</i> -butylmethanol	8.379	32.64	74.136	32.6
3,3-Dimethyl-1-butanol	40.48	40.48	76.589	34.8
Alkanediols				
1,4-Butanediol	63.7	63.2	113.719	73.6
1,5-Pentanediol	63.6	63.6	121.468	82.9
1,6-Hexanediol	79.6	79.6	129.216	92.2
2,3-Dimethyl-2,3-butanediol	46.49	46.49	91.421	60.8

Table 1 (Continued)

Compound	$\Delta_{\text{fus}}S_m$ exp	$\Delta_{\text{tpce}}S_m$ exp	$\Delta_{\text{fus}}S_m$ calc (Coutsikos et al.)	$\Delta_{\text{tpce}}S_m$ calc (Chickos et al.)
2,2-Dimethyl-1,3-propanediol	10.77	53.3	103.052	49.9
1,7-Heptanediol	72.15	72.15	136.965	101.6
1,8-Octanediol	108.47	108.47	144.713	111
1,9-Nonanediol	113.89	113.89	152.462	120.2
1,10-Decanediol	120.69	120.69	160.211	129.5
1,13-Tridecanediol	50.71	137.6	183.456	156.2
1,14-Tetradecanediol	171.8	171.8	191.205	165.6
1,15-Pentadecanediol	65.8	165.8	198.954	174.9
1,16-Hexadecanediol	175.7	175.7	206.7	184.2
1,17-Heptadecanediol	83.9	182.3	214.45	193.5
1,18-Octadecanediol	90.4	196.1	222.2	202.7
1,19-Nonadecanediol	95.5	198.9	229.949	212.1
1,20-Eicosanediol	105.6	206	237.697	221.3
1,21-Heneicosanediol	107.8	218.3	245.446	230.7
1,22-Docosanediol	122.6	230.3	253.195	239.9
1,23-Tricosanediol	122.1	236.2	260.943	249.2
1,24-Tetracosanediol	134.2	248.8	268.692	258.5
2-Butyl-2-ethyl-1,3-propanediol	65.55	65.55	133.564	78.36
2,2,4-Trimethyl-1,3-pentanediol	73.71	73.71	111.283	51.92
<b>Alkenes</b>				
Ethene	32.24	32.24	8.929	34.7
Propene	34.18	34.18	27.029	40.2
1-Butene	43.84	43.84	34.777	47.3
<i>cis</i> -2-Butene	54.43	54.43	45.128	45.7
<i>trans</i> -2-Butene	58.22	58.22	45.128	45.7
1-Pentene	53.82	53.82	42.526	54.4
<i>cis</i> -2-Pentene	58.39	58.39	52.877	52.8
<i>trans</i> -2-Pentene	62.82	62.82	52.877	52.8
3-Methyl-1-butene	51.19	51.19	35.26	41.4
1- <i>cis</i> -3-Pentadiene	42.61	42.61	41.395	50.7
<i>trans</i> -1,3-Pentadiene	38.46	38.46	41.395	50.7
1,4-Pentadiene	49.41	49.41	32.707	52.3
1-Hexene	70.1	70.1	50.275	61.6
<i>cis</i> -2-Hexene	67.27	67.27	60.626	59.9
4-Methylpent-1-ene	41.5	41.5	43.008	48.5
1-Heptene	82.5	82.5	58.023	77.5
1-Octene	89.29	89.29	65.772	86.8
1-Nonene	104.23	104.23	73.521	96.1
1-Decene	66.73	106.8	81.269	105.5
1-Undecene	75.84	118.2	89.018	114.8
1-Dodecene	83.54	104.92	96.766	124.1
1-Hexadecene	108.86	124.39	127.761	161.5
<b>Alkanones</b>				
Acetone	32.34	32.34	26.156	39.7
2-Butanone	45.27	45.27	33.904	46.9
2-Pentanone	54.14	56.32	41.653	54
3-Pentanone	49.5	50.5	41.653	54
2-Hexanone	68.42	68.42	49.402	61.1
3-Hexanone	61.89	66.61	49.402	61.1
3,3-Dimethyl-2-butanone	51.04	51.04	30.504	52
2-Heptanone	82.9	82.9	57.15	77
3-Heptanone	74.3	74.3	57.15	74.8
4-Heptanone	67.3	67.3	57.15	68.2
Di-isopropyl ketone	54.6	54.6	42.618	55.3
2-Octanone	96.57	96.57	64.899	86.4
5-Nonanone	24.94	117.5	72.648	82.5
2-Undecanone	99.07	99.07	88.145	114.4
2-Tetradecanone	160.16	160.16	111.391	142.4
2-Pentadecanone	174.8	174.8	119.14	151.7
9-Heptadecanone	205.87	205.87	134.637	170.4
2-Nonadecanone	209.3	209.3	150.13	188.7
10-Nonadecanone	202.04	202.04	150.13	188.7
11-Heneicosanone	226.31	226.31	165.632	207.7
2-Heneicosanone	232.55	232.55	165.632	207.7

Table 1 (Continued)

Compound	$\Delta_{\text{fus}}S_{\text{m exp}}$	$\Delta_{\text{tpce}}S_{\text{m exp}}$	$\Delta_{\text{fus}}S_{\text{m calc}}$ (Coutsikos et al.)	$\Delta_{\text{tpce}}S_{\text{m calc}}$ (Chickos et al.)
12-Tricosanone	228.04	228.04	181.129	226.4
13-Pentacosanone	277.1	277.1	199.63	244.4
16-Hentricontanone	328.56	328.56	243.118	300.228
20-Nonatricontanone	418.5	418.5	305.107	374.6
Alkanoic acids				
Acetic acid	39.24	39.24	28.218	31
Propanoic acid	42.2	42.2	35.966	38.1
Butanoic acid	41.82	41.82	43.715	45.2
Pentanoic acid	59.14	59.14	51.464	58.9
2,2-Dimethylpropanoic acid	36.74	36.74	32.566	43.3
Heptanoic acid	58.07	67.15	66.961	77.6
Ocanoic acid	73.8	73.8	74.71	86.9
Nonanoic acid	71.13	92.05	82.458	96.3
Decanoic acid	91.28	91.28	90.207	105.6
Undecanoic acid	86.15	114.22	97.956	114.9
Dodecanoic acid	115.7	115.7	105.704	124.3
Tridecanoic acid	107.11	135.52	113.453	133.6
Tetradecanoic acid	137.92	137.92	121.201	142.9
Pentadecanoic acid	127.49	152.97	128.95	152.3
Hexadecanoic acid	163.27	163.27	136.699	161.6
Heptadecanoic acid	153.55	176.15	144.447	170.9
Octadecanoic acid	178.66	178.66	152.196	180.2
Nonadecanoic acid	168.87	195.93	159.94	189.6
Eicosanoic acid	198.7	198.7	167.69	198.9
Alkanedioic acids				
Malonic acid	56.7	56.7	33.422	39.53
Succinic acid	72.1	72.1	41.171	46.5
Glutaric acid	56.33	63.4	48.92	60.2
Adipic acid	81.73	81.73	56.668	69.6
Pimelic acid	73.17	73.17	64.417	78.9
Suberic acid	69.4	69.4	72.166	88.2
Azelaic acid	85.97	85.97	79.914	97.5
Sebaic acid	101	101	87.663	106.9
1,11-Undecanedioic acid	102.99	102.99	95.411	116.2
1,12-Dodecanedioic acid	125.64	125.64	103.16	125.5
1,13-Tridecanedioic acid	116.9	116.9	110.909	134.9
1,14-Tetradecanedioic acid	142.22	142.22	118.658	144.3
1,16-Hexadecanedioic acid	132.02	132.02	134.16	163.1
Tetramethylsuccinic acid	13.95	49.02	34.37	56.89
PAHs				
Benzene	35.4	35.4	38.51	44.5
Naphthalene	53.75	53.75	47.473	44.4
Anthracene	60.08	60.08	56.452	44.2
Phenanthrene	44.21	44.83	56.452	44.2
Chrysene	49.21	55.5	65.348	44.1
Perylene	57.87	57.87	54.789	43.7
Coronene	27.02	27.02	33.672	42.8
Acenaphthene	58.55	58.55	53.625	41.09
Acenaphthylene	30.28	42.4	40.248	37.8
Biphenyl	54.81	54.81	51.996	59.2
Pyrene	40.97	43.36	61.357	43.8
Triphenylene	52.53	52.53	65.398	44.1
Benz[ <i>a</i> ]anthracene	49.23	49.23	65.348	44.1
1,2:3,4-Dibenzanthracene	46.65	46.65	74.328	44
1,2:5,6-Dibenzanthracene	57.26	57.26	74.328	44
1,2-Benzofluorene	39.76	49.26	65.681	50.9
2,3-Benzofluorene	47.78	47.78	65.681	50.9
1,2:4,5-Dibenzopyrene	58.63	58.63	63.786	42.5
3,4,9,10-Dibenzopyrene	50.05	50.05	63.786	42.5
1,2:3,4-Dibenzopyrene	49.24	49.24	63.786	42.5
Picene	55.22	55.22	74.36	44
Corannulene	31.9	31.9	28.06	34
<i>m</i> -Terphenyl	62.76	62.76	65.481	73.9

Table 1 (Continued)

Compound	$\Delta_{\text{fus}}S_m$ exp	$\Delta_{\text{tpe}}S_m$ exp	$\Delta_{\text{fus}}S_m$ calc (Coutsikos et al.)	$\Delta_{\text{tpe}}S_m$ calc (Chickos et al.)
<i>p</i> -Terphenyl	72.5	74.1	65.481	73.9
1,3,5-Triphenylbenzene	74.89	74.89	78.966	88.6
<i>p</i> -Quaterphenyl	64.37	66.15	78.966	88.6
Halogenated benzenes				
Bromobenzene	44.2	44.2	33.273	47.1
1,2-Dibromobenzene	45.58	45.58	28.035	49.8
1,3-Dibromobenzene	49.61	49.61	28.035	49.8
1,4-Dibromobenzene	55.54	55.54	34.919	49.8
1,2,4-Tribromobenzene	56.47	56.47	22.797	52.2
1,3,5-Tribromobenzene	54.99	54.99	22.797	52.2
1,2,4,5-Tetrabromobenzene	61.53	62.62	17.559	55.1
Chlorobenzene	41.92	41.92	40.157	40.4
1,2-Dichlorobenzene	50.41	50.41	41.803	47.1
1,3-Dichlorobenzene	50.89	50.8	41.803	47.1
1,4-Dichlorobenzene	55.65	55.65	41.803	47.1
1,2,3-Trichlorobenzene	62.71	62.71	43.482	48.4
1,3,5-Trichlorobenzene	54.05	54.05	43.482	48.4
1,2,3,4-Tetrachlorobenzene	53.13	53.13	45.095	49.6
1,2,4,5-Tetrachlorobenzene	57.22	57.22	45.095	49.6
1,2,3,5-Tetrachlorobenzene	58.66	58.66	45.095	49.6
Pentachlorobenzene	57.59	57.59	46.747	50.9
Hexachlorobenzene	47.23	47.23	48.387	52.2
Fluorobenzene	48.95	48.95	38.735	46.2
1,2-Difluorobenzene	48.95	48.95	38.959	48
1,3-Difluorobenzene	42.05	46.48	38.959	48
1,2,3,4-Tetrafluorobenzene	46.85	46.85	39.408	51.4
1,2,3,5-Tetrafluorobenzene	47.01	47.01	39.408	51.4
1,2,4,5-Tetrafluorobenzene	54.31	54.31	39.408	51.4
Pentafluorobenzene	48.24	48.24	39.633	53.2
Hexafluorobenzene	41.67	41.67	39.857	54.9
1-Bromo-2-chlorobenzene	47.47	47.47	34.919	48.4
1-Bromo-3-chlorobenzene	48.77	48.77	34.919	48.4
1-Bromo-4-chlorobenzene	55.54	55.54	34.919	48.4
1,3,5-Trichloro-2,4,6-trifluorobenzene	59.2	59.2	44.122	53.6
Chloropentafluorobenzene	32.45	55.55	41.279	54.5
1-Chloro-4-fluorobenzene	56.73	56.73	47.697	47.4
Alkylated benzenes				
Toluene	37.15	37.15	43.191	45
1,2-Dimethylbenzene	54.9	54.9	47.872	45.6
1,3-Dimethylbenzene	51.4	51.4	47.872	45.6
1,4-Dimethylbenzene	59.77	59.77	47.872	45.6
1,2,3-Trimethylbenzene	33.01	41.81	52.553	46.2
1,2,4-Trimethylbenzene	57.53	57.53	52.553	46.2
1,3,5-Trimethylbenzene	41.66	41.66	52.553	46.2
1,2,3,4-Tetramethylbenzene	42.31	42.31	57.234	46.7
1,2,3,5-Tetramethylbenzene	52.01	52.01	57.234	46.7
1,2,4,5-Tetramethylbenzene	59.25	59.25	57.234	46.7
Pentamethylbenzene	32.51	39.33	61.939	47.3
Hexamethylbenzene	47.02	51.6	66.595	47.9
Ethylbenzene	51.43	51.43	50.94	52.2
Propylbenzene	53.39	53.39	58.688	59.3
Isopropylbenzene	41.34	41.34	49.343	46.3
Butylbenzene	60.56	60.56	66.429	66.5
<i>tert</i> -Butylbenzene	39.1	39.1	70.76	45.4
Benzoic acid derivatives				
Benzoic acid	45.45	45.45	43.698	43
2-Methylbenzoic acid	53.51	53.51	48.379	43.5
3-Methylbenzoic acid	41.19	41.19	48.379	43.5
4-Methylbenzoic acid	50.17	50.17	48.379	43.5
2,3-Dimethylbenzoic acid	43.8	43.8	53.043	44.1
3,5-Dimethylbenzoic acid	51	51	53.043	44.1
4-Ethylbenzoic acid	36.4	36.4	56.12	50.7
4-Propylbenzoic acid	55.21	66.51	63.868	57.8

Table 1 (Continued)

Compound	$\Delta_{\text{fus}}S_{\text{m}} \text{ exp}$	$\Delta_{\text{tpce}}S_{\text{m}} \text{ exp}$	$\Delta_{\text{fus}}S_{\text{m}} \text{ calc (Coutsikos et al.)}$	$\Delta_{\text{tpce}}S_{\text{m}} \text{ calc (Chickos et al.)}$
2-Bromobenzoic acid	58.89	58.89	38.461	48.31
3-Bromobenzoic acid	57.92	57.92	38.461	48.31
4-Bromobenzoic acid	58.65	58.65	38.461	48.31
2-Chlorobenzoic acid	62.34	62.34	45.345	47
3-Chlorobenzoic acid	55.65	55.65	45.345	47
4-Chlorobenzoic acid	62.76	62.76	45.345	47
3,5-Dichlorobenzoic acid	50.01	50.01	46.99	62.2
2,3,6-Trichlorobenzoic acid	59.23	59.23	48.637	63.5
2-Nitrobenzoic acid	66.8	66.8	50.05	48.5
3-Nitrobenzoic acid	46.66	46.66	50.05	48.5
4-Nitrobenzoic acid	72.02	72.02	50.05	48.5
4-Fluorobenzoic acid	46.32	46.32	43.923	47.41
4-Methoxybenzoic acid	61.1	61.1	58.971	53.1
4-Ethoxybenzoic acid	62.18	62.18	66.72	60.2
2-Hydroxybenzoic acid	56.97	56.97	32.549	51.1
3-Hydroxybenzoic acid	55.15	55.15	53.434	51.1
4-Hydroxybenzoic acid	63.31	63.31	53.434	51.1
2,4,5-Trimethoxybenzoic acid	74.54	74.54	89.52	81.88
3,4,5-Trimethoxybenzoic acid	67.27	67.27	89.52	81.88
Nitrated benzenes				
Nitrobenzene	43.5	43.5	44.829	47.3
1,2-Dinitrobenzene	57.66	57.66	51.148	50.2
1,3-Dinitrobenzene	47.82	47.82	51.148	50.2
1,4-Dinitrobenzene	62.93	62.93	51.148	50.2
1,3,5-Trinitrobenzene	38.95	44.08	57.466	53
4-Nitrotoluene	51.76	51.76	49.51	47.9
2,4-Dinitrotoluene	58.61	58.61	55.829	50.7
2,6-Dinitrotoluene	72.82	72.82	55.829	50.7
2,3-Dinitrotoluene	53.27	53.27	55.829	50.7
3,4-Dinitrotoluene	57.15	57.15	55.829	50.7
2,4,6-Trinitrotoluene	66.52	66.52	62.147	53.5
Phenols				
Phenol	36.82	36.82	48.246	49.9
1,2-Benzenediol	58.39	58.39	16.212	55.2
1,3-Benzenediol	49.41	52.64	57.949	55.2
1,4-Benzenediol	59.5	59.5	57.949	55.2
2-Methylphenol	52.01	52.01	46.883	50.4
3-Methylphenol	37.53	37.53	52.96	50.42
4-Methylphenol	41.25	41.25	52.96	50.42
2,3-Dimethylphenol	60.75	60.75	51.563	51
2,5-Dimethylphenol	67.18	67.18	51.563	51
2,6-Dimethylphenol	59.27	59.27	51.563	51
3,4-Dimethylphenol	54.28	54.28	57.616	51
3,5-Dimethylphenol	53.44	53.44	57.616	51
4- <i>tert</i> -Butylphenol	38.9	38.9	80.496	50.7
4-Bromophenol	49.32	49.32	43.008	52.5
2,4,6-Tribromophenol	56.87	56.87	14.343	57.6
Pentabromophenol	58.75	58.75	3.908	62.8
2-Chlorophenol	44.24	44.57	31.743	51.2
3-Chlorophenol	48.76	48.76	49.892	51.2
4-Chlorophenol	44.54	44.54	49.892	51.2
2,3-Dichlorophenol	64.73	64.73	39.807	52.4
2,4-Dichlorophenol	63.18	63.18	39.807	52.4
2,5-Dichlorophenol	67.76	67.76	39.807	52.4
2,6-Dichlorophenol	65.12	65.12	39.807	52.4
3,4-Dichlorophenol	61.38	61.38	51.538	52.4
3,5-Dichlorophenol	60.15	60.15	51.538	52.4
Pentachlorophenol	37.08	37.8	38.328	56.3
3-Nitrophenol	51.7	51.7	54.564	52.7
4-Nitrophenol	47.02	47.02	54.564	52.7
Miscellaneous				
Benzil	64.02	64.52	46.391	68.4
Thymol	67.88	67.88	59.778	52.2

Table 1 (Continued)

Compound	$\Delta_{\text{fus}}S_{\text{m}} \text{ exp}$	$\Delta_{\text{tpce}}S_{\text{m}} \text{ exp}$	$\Delta_{\text{fus}}S_{\text{m}} \text{ calc}$ (Coutsikos et al.)	$\Delta_{\text{tpce}}S_{\text{m}} \text{ calc}$ (Chickos et al.)
4-Bromotoluene	50.2	50.2	37.953	47.1
4-Chlorotoluene	48.29	48.29	44.837	40.9
2-Fluorotoluene	46.51	46.51	43.416	46.8
3-Fluorotoluene	45.11	45.11	43.416	46.8
4-Fluorotoluene	43.18	43.18	43.416	46.8
2,3,4,5,6-Pentafluorotoluene	54.48	54.48	44.314	53.7
Anisole	48	48	53.783	51.9
1-Bromonaphthalene	55.86	55.86	42.235	47
2-Bromonaphthalene	43.76	61.85	42.235	47
1-Chloronaphthalene	47.65	47.65	49.086	40.2
2-Chloronaphthalene	44.28	44.28	49.086	40.2
1-Nitronaphthalene	55.87	55.87	53.758	47.2
1-Naphthol	62.34	62.34	57.209	49.7
2-Naphthol	47.7	47.7	57.209	49.7
1-Methylnaphthalene	28.62	49.3	52.154	44.9
2-Methylnaphthalene	39.43	58.87	52.154	44.9
1,8-Dimethylnaphthalene	46.9	46.9	56.835	45.5
2,6-Dimethylnaphthalene	65.39	65.39	56.835	45.5
2,7-Dimethylnaphthalene	63.3	63.3	56.835	45.5
1,4-Dimethylnaphthalene	37.87	37.87	56.835	45.5
2,3-Dimethylnaphthalene	42.06	42.06	56.835	45.5
1-Naphthoic acid	45.7	45.7	52.628	42.8
2-Naphthoic acid	51.15	51.15	52.628	42.8
1,2,3,6,7,8-Hexahydroxyrene	44.37	57.69	17.21	45
2,3,4,5-Tetrachlorobiphenyl	69.25	69.25	52.711	64.3
2,2',4,4',6,6'-Hexachlorobiphenyl	45.25	45.25	38.411	66.9
2,2',3,3',5,5',6,6'-Octachlorobiphenyl	52.56	52.56	41.653	69.5
Decachlorobiphenyl	68.1	68.1	44.979	72.1
Diphenylmethane	62.34	62.34	63.352	62.1
Triphenylmethane	60.13	60.13	76.323	66
1-Chloroanthracene	39.81	39.81	58.082	39.9
9-Chloroanthracene	49.21	49.21	58.082	39.9
Benzophenone	56.67	56.67	54.041	63.8
<i>p</i> -Benzoquinone	47.56	47.56	36.166	29.4
Phenylacetic acid	41.41	41.41	48.396	48
Diphenylacetic acid	74.34	74.34	61.304	58.7
9,10-Anthraquinone	58.7	58.7	44.713	52
4,4'-Di- <i>tert</i> -butylbiphenyl	46.77	49.88	116.49	61

Our past experience using Eq. (1) indicates that the method should be able to predict  $\Delta_{\text{tpce}}S_{\text{m}}$  values to within approximately 13 J/(mol K) for simple organic compounds, which should be adequate for most applications. Slightly larger deviations would be expected for the more structurally complex organic molecules.

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