

ESTIMATION OF HEAT CAPACITY OF ORGANIC COMPOUNDS FROM GROUP CONTRIBUTIONS

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A group contributions procedure has been developed for estimating the heat capacity of organic compounds at different temperatures. Using a four-constant equation for C_p° as a function of temperature, the values of the constants have been estimated for a variety of groups in hydrocarbon as well as nonhydrocarbon compounds. The values of these constants for any compound can then be obtained by adding the figures for the component groups. The proposed method has been tested for a large number of organic compounds at different temperatures. The average deviation at 300° K. is of the order of 3%, while in the range 400° to 1500° K. it is less than 2%.

THE most accurate method of calculating the heat capacity of an ideal vapor involves the use of spectroscopic data. Since for a large number of organic molecules such data are not available, several other methods of estimation have been proposed.

The majority of these methods are based on the approximation that the ideal heat capacity of a substance may be estimated from the vibrational contributions to thermodynamic properties. A given bond is assumed to possess two characteristic fundamental frequencies which are independent of the nature of the molecule in which the bond occurs—viz., those of bending and stretching. Using the most general form of the heat capacity equation,

$$C_p^\circ = a + bT + cT^2 \quad (1)$$

Fugassi and Rudy (14) have tabulated the contributing values of the constants a , b , and c for the two characteristic fundamental frequencies.

Dobratz (12) derived a more accurate equation by accounting for free rotation:

$$C_p^\circ = 4R + \frac{MR}{2} + \sum qiC_{vi} + \frac{3n - 6 - M - \sum qi}{\sum qi} \sum qiC_{\delta i} \quad (2)$$

Stull and Mayfield (34) have re-evaluated this equation by calculating the vibrational contributions in the light of more recent spectroscopic data, and found an error of about 4% when applied to hydrocarbons.

Janz (20) has suggested the use of the derivatives of Equation 1 for estimating the temperature dependence of C_p° from data at three temperatures.

Kothari and Doraiswamy (29) showed from dimensional analysis that

$$C_p^\circ = f(T_r) \quad (3)$$

and that plots of C_p° vs. $\log T_r$ give perfect straight lines for all compounds except hydrogen. For any homologous series they also derived a general expression from which the C_p° of any member of the series at any desired temperature may be calculated from fragmentary data.

The heat capacity of organic compounds, like any other thermodynamic function, can also be estimated by the method of group contributions (1, 13, 31, 33). Among the several

methods proposed, that of Anderson, Beyer, and Watson (7) gives data for estimating the constants of Equation 1 by this procedure. The method of Souders, Matthews, and Hurd (33) is applicable to hydrocarbons only.

An examination of the heat capacities of several compounds at different temperatures has shown that a four-constant equation gives a far better representation of the data than the three-constant Equation 1. A group contributions procedure is presented in this paper for estimating the four constants of the heat capacity equation.

Development of Method

On the basis of Pitzer's statistical mechanical treatment (37), Franklin (13) showed that any thermodynamic function of a paraffin hydrocarbon can be expressed as the sum of contributions from characteristic groups and corrections plus a correction term for the symmetry of the molecule. Thus the equation for any thermodynamic property, P , may be expressed as

$$P = \sum \text{contribution of composing groups} + \sum \text{corrections where necessary} + RT \ln \sigma \quad (4)$$

From the limited data available for nonhydrocarbon groups, Franklin suggested that Equation 4 may also be used for these compounds.

In developing a procedure for heat capacity from group contributions, Equation 4 can be modified as:

$$C_p^\circ = \sum \text{contribution of composing groups} + \sum \text{corrections where necessary} \quad (5)$$

since the symmetry effect is nonexistent in dealing with heat capacity. The contribution from each group to the heat capacity of a compound may be expressed as:

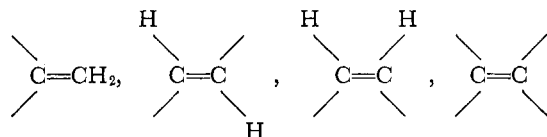
$$(C_p^\circ)_{\text{group}} = a + bT + cT^2 + dT^3 \quad (6)$$

in which constants a , b , c , and d are characteristic of that particular group. It is possible to obtain the values of C_p° for any group (or correction) at different temperatures from published data on appropriate compounds, and to fit an equation of the form denoted by Equation 6. The heat capacity of any compound can then be determined by the equation,

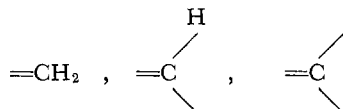
$$(C_p^\circ)_{\text{compound}} = \sum a + \sum bT + \sum cT^2 + \sum dT^3 \quad (7)$$

Methods for Estimating Values of Contributing Groups

Hydrocarbons. The heat capacities of the composing groups of paraffin hydrocarbons in the temperature range 298° to 1500° K. have been estimated from published data (32). For the olefins the following basic structural group types have been taken:



rather than the apparently more simple arrangements



since the former takes into account the complicating factors of hyperconjugation and cis-trans isomerism. The introduc-

Table I. Aliphatic Hydrocarbon Groups

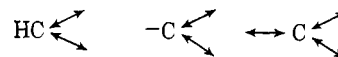
Group	<i>a</i>	<i>b</i> × 10 ²	<i>c</i> × 10 ⁴	<i>d</i> × 10 ⁶
—CH ₃	0.6087	2.1433	−0.0852	0.001135
—CH ₂	0.3945	2.1363	−0.1197	0.002596
=CH ₂	0.5266	1.8357	−0.0954	0.001950
—C—H	−3.5232	3.4158	−0.2816	0.008015
—C—	−5.8307	4.4541	−0.4208	0.012630
H C=CH ₂	0.2773	3.4580	−0.1918	0.004130
C=CH ₂	−0.4173	3.8857	−0.2783	0.007364
H H \ / C=C	−3.1210	3.8060	−0.2359	0.005504
H / C=C \ H	0.9377	2.9904	−0.1749	0.003918
\ H C=C	−1.4714	3.3842	−0.2371	0.006063
C=C	0.4736	3.5183	−0.3150	0.009205
H C=C=CH ₂	2.2400	4.2896	−0.2566	0.005908
C=C=CH ₂	2.6308	4.1658	−0.2845	0.007277
H / H C=C=C	−3.1249	6.6843	−0.5766	0.017430
≡CH	2.8443	1.0172	−0.0690	0.001866
—C≡	−4.2315	7.8689	−0.2973	0.00993

Table II. Aromatic Hydrocarbon Groups

Group	<i>a</i>	<i>b</i> × 10 ²	<i>c</i> × 10 ⁴	<i>d</i> × 10 ⁶
HC↔	−1.4572	1.9147	−0.1233	0.002985
—C↔	−1.3883	1.5159	−0.1069	0.002659
↔C↔	0.1219	1.2170	−0.0855	0.002122

tion of the —C≡ group makes it possible to apply this method to several acetylenes as well (though with an error of the order of 3%). The values of *a*, *b*, *c*, and *d* for each of these groups, obtained by fitting equations of the form denoted by Equation 6 by the method of least squares, are summarized in Table I.

For the aromatic hydrocarbons the basic structures suggested



have been retained, and the values of *a*, *b*, *c*, and *d* for these groups are summarized in Table II.

Ring Formation. While dealing with cycloalkanes and cycloalkenes, it is necessary to calculate corrections for the formation of rings. Corrections for the three-membered ring were calculated from the heat capacity values of CH₂—CH₂



(ethylene oxide) (28). Corrections for the five-membered alkane and alkene rings were calculated from the heat capacity

data for (cyclopentane) and (cyclopentene).

Corrections for the six-membered alkane and

alkene rings were calculated from the values of (cyclohexane) and (cyclohexene). The values

of *a*, *b*, *c*, and *d* for ring correction, calculated by the method of least squares, are summarized in Table III.

In calculating the corrections for the four-membered ring, nonavailability of an appropriate compound of known thermodynamic properties made it necessary to estimate this correction by an empirical procedure. The values of *a*, *b*, *c*, and *d* were plotted as functions of ring number, and from these plots the corresponding values for the four-membered ring were interpolated.

Oxygen-Containing Groups. The most important oxygen-containing groups are —OH, —O—, —CHO, , —COOH, , and . The contributions of these groups were calculated from the values of ethanol (8, 26) and phenol (9, 17), dimethyl and diethyl ethers (2), acetaldehyde (7, 28), acetone (22, 23), acetic acid (38), ethyl acetate (12), and furan (18), respectively.

The thermodynamic properties of the ether group, —O—, have so far been determined from the experimental work of Valentin (35) on the equilibrium constant of the reaction,

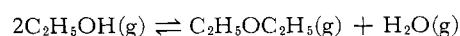


Table III. Contributions Due to Ring Formation

Ring	<i>a</i>	<i>b</i> × 10 ²	<i>c</i> × 10 ⁴	<i>d</i> × 10 ⁶
3-membered ring	-3.5320	-0.0300	0.0747	-0.005514
4-membered ring	-8.6550	1.0780	0.0425	-0.000250
5-membered ring				
Pentane	-12.2850	1.8609	-0.1037	0.002145
Pentene	-6.8813	0.7818	-0.0345	0.000591
6-membered ring				
Hexane	-13.3923	2.1392	-0.0429	-0.001865
Hexene	-8.0238	2.2239	-0.1915	0.005473

In the present development the thermodynamic properties of dimethyl and diethyl ethers calculated by Banerjee and Doraiswamy (2) were used to estimate the contribution of the ether group.

The calculated values of the constants for these groups are summarized in Table IV.

Nitrogen-Containing Groups. The values of *a*, *b*, *c*, and *d* for the principal nitrogen-containing groups are listed in Table V. The contributions of the $\text{—C}\equiv\text{N}$ group were obtained from the mean of the values for methyl cyanide and acrylonitrile (27). The contributions of the $\text{—N}\equiv\text{C}$ group were obtained from the data on methyl isocyanide (40). The contributions of the primary, secondary, and tertiary amino groups were obtained from the values of aniline (19) and methylamine (24), dimethylamine (24), and trimethylamine (24), respectively. The contributions of the $\text{N} \begin{smallmatrix} \nearrow \\ \searrow \end{smallmatrix}$ and —NO_2 groups were obtained from the data for pyridine (21) and nitromethane (30).

Sulfur- and Halogen-Containing Groups. The values of *a*, *b*, *c*, and *d* for the sulfur-containing groups are summarized in Table VI. The contributions of the —SH , —S— , and $\text{S} \begin{smallmatrix} \nearrow \\ \searrow \end{smallmatrix}$ groups were obtained from the thermodynamic properties of methanethiol (3, 5, 10), dimethyl sulfide (3, 5, 11), and thiophene (37), respectively. The contributions of the $\text{—SO}_3\text{H}$ group were estimated from the recent work of Bigg, Banerjee, and Doraiswamy (4).

In the case of halogen-containing compounds, a large volume of data is available. The values for the —F group were calculated as the mean of the thermodynamic properties for CH_2F_2 and CH_3F (15); of the —Cl group from those of CHCl_3 and CH_2Cl_2 (15); of the —Br group from CH_3Br and CH_2Br_2 (15); and of the —I group from CH_3I (15). The heat capacities calculated from these contributions hold with surprising accuracy for a variety of halogenated compounds.

Discussion

It was originally thought that different values of group contributions would be necessary for aliphatic and aromatic compounds. When assignments were made, however, this was found to be unnecessary. This fact greatly simplifies the application of the proposed method. Another feature of this procedure is that the several correction factors used by earlier investigators (13, 36) and shown in Equation 5 were found to be unnecessary.

The contributions of $\text{S} \begin{smallmatrix} \nearrow \\ \searrow \end{smallmatrix}$ and $\text{O} \begin{smallmatrix} \nearrow \\ \searrow \end{smallmatrix}$ were calculated from the heat capacity functions of thiophene (37) and furan (18) on the assumption that these groups would account for the correction caused by resonance, as in the case of the other resonating groups listed in Table II.

Table IV. Oxygen-Containing Groups

Group	<i>a</i>	<i>b</i> × 10 ²	<i>c</i> × 10 ⁴	<i>d</i> × 10 ⁶
—OH	6.5128	-0.1347	0.0414	-0.001623
—O—	2.8461	-0.0100	0.0454	-0.002728
$\begin{smallmatrix} \text{H} \\ \\ \text{—C=O} \end{smallmatrix}$	3.5184	0.9437	0.0614	-0.006978
$\begin{smallmatrix} & \text{O} \\ & \\ \diagup & \text{C=O} \\ & \diagdown \end{smallmatrix}$	1.0016	2.0763	-0.1636	0.004494
$\begin{smallmatrix} \text{O} \\ \\ \text{—C—O—H} \end{smallmatrix}$	1.4055	3.4632	-0.2557	0.006886
$\begin{smallmatrix} \text{O} \\ \\ \diagup & \text{C} \\ & \\ & \text{O—} \end{smallmatrix}$	2.7350	1.0751	0.0667	-0.009230
$\text{O} \begin{smallmatrix} \nearrow \\ \searrow \end{smallmatrix}$	-3.7344	1.3727	-0.1265	0.003789

Table V. Nitrogen-Containing Groups

Group	<i>a</i>	<i>b</i> × 10 ²	<i>c</i> × 10 ⁴	<i>d</i> × 10 ⁶
$\text{—C}\equiv\text{N}$	4.5104	0.5461	0.0269	-0.003790
$\text{—N}\equiv\text{C}$	5.0860	0.3492	0.0259	-0.002436
—NH_2	4.1783	0.7378	0.0679	-0.007310
$\begin{smallmatrix} \diagdown \\ \text{NH} \end{smallmatrix}$	-1.2530	2.1932	-0.1604	0.004237
$\begin{smallmatrix} \diagdown \\ \text{N—} \end{smallmatrix}$	-3.4677	2.9433	-0.2673	0.007828
$\text{N} \begin{smallmatrix} \nearrow \\ \searrow \end{smallmatrix}$	2.4458	0.3436	0.0171	-0.002719
—NO_2	1.0898	2.6401	-0.1871	0.004750

Table VI. Sulfur-Containing Groups

Group	<i>a</i>	<i>b</i> × 10 ²	<i>c</i> × 10 ⁴	<i>d</i> × 10 ⁶
—SH	2.5597	1.3347	-0.1189	0.003820
—S—	4.2256	0.1127	-0.0026	-0.000072
$\text{S} \begin{smallmatrix} \nearrow \\ \searrow \end{smallmatrix}$	4.0824	-0.0301	0.0731	-0.006081
$\text{—SO}_3\text{H}$	6.9218	2.4735	0.1776	-0.022445

Table VIII. Comparison of Calculated and Reported Heat Capacities

S No.	Compound	300° K.			500° K.			1000° K.			Ref.
		Calcd.	Rept.	Error, %	Calcd.	Rept.	Error, %	Calcd.	Rept.	Error, %	
1	Neopentane	29.29	29.21	0.27	44.85	45.00	0.33	67.91	67.80	0.16	(32)
2	Isobutane	23.31	23.25	0.25	35.53	35.62	0.25	54.48	54.40	0.14	(32)
3	Isopentane	29.11	28.97	4.83	43.94	44.23	0.66	66.83	66.90	0.10	(32)
4	Ethylbenzene	30.67	30.88	0.68	48.65	49.35	1.41	74.55	74.77	0.29	(32)
5	Styrene	27.59	29.35	5.99	44.17	45.94	3.85	67.26	67.92	0.97	(26)
6	Ethylene oxide	11.53	11.60	0.60	17.73	18.03	1.66	27.05	27.47	1.53	(27)
7	Cyclopentene	16.89	18.08	6.58	32.74	31.62	3.54	52.54	51.94	1.15	(32)
8	Cyclohexane	27.06	25.58	5.78	46.14	45.47	1.47	75.85	75.80	0.06	(32)
9	Isopropyl alcohol	23.37	21.64	7.99	32.89	31.78	3.49	47.49	46.80	1.47	(9)
10	Phenol	25.00	24.90	0.40	37.61	38.64	2.66	55.60	55.49	0.19	(9, 17)
11	Dimethyl ether	15.76	15.89	0.81	22.27	22.08	0.86	33.90	33.84	0.17	(2)
12	Diethyl ether	27.35	27.01	1.25	39.09	38.98	2.82	58.69	58.71	0.03	(2)
13	Dihexyl ether	73.76	71.49	3.17	106.58	106.49	0.08	158.64	153.19	3.55	(2)
14	Benzaldehyde	25.27	26.07	3.07	39.77	40.23	1.14	59.58	59.56	0.03	(12)
15	Ketene	11.08	11.43	3.00	15.42	15.05	2.45	21.19	20.03	5.80	(22, 27)
16	Acetic acid	16.08	15.97	0.68	22.53	...	...	32.28	31.99	0.90	(38)
17	Methyl cyanide	12.34	12.53	1.51	16.79	16.71	0.47	23.67	23.58	0.38	(27)
18	Methyl isocyanide	12.60	12.68	0.63	16.51	16.48	0.18	23.39	23.44	0.21	(40)
19	Aniline	25.36	26.07	2.72	39.54	40.80	3.08	58.05	59.18	1.90	(19)
20	Monomethylaniline	28.86	28.33	1.87	46.46	45.62	1.84	71.00	70.20	1.14	(12)
21	Dimethylaniline	34.06	32.75	4.00	53.85	53.04	1.52	83.85	82.18	2.03	(12)
22	Pyridine	19.84	19.85	0.05	31.28	31.68	1.26	46.59	46.76	0.37	(21)
23	Methyl mercaptan	11.89	12.09	1.65	16.07	15.96	0.68	22.49	22.56	0.31	(10)
24	Dimethyl sulfide	18.07	17.77	1.68	23.77	24.24	1.94	35.46	35.17	0.81	(11)
25	Ethylene dichloride	18.78	18.27	2.79	24.48	24.81	1.32	33.05	33.43	1.13	(25)
26	1,1,1-Trichloroethane	20.66	22.40	7.76	27.86	28.32	1.62	36.03	35.33	1.98	(25)
27	1,1,2-Trichloroethane	20.72	21.34	2.90	26.20	27.92	6.16	35.43	35.42	0.03	(25)
28	Hexachloroethane	33.08	32.74	1.06	38.41	38.32	2.34	44.07	42.13	4.60	(25)
29	Carbon tetrachloride	18.47	20.08	8.07	22.86	23.27	1.75	26.01	25.52	1.92	(6)
30	Chlorobenzene	22.15	23.56	5.98	34.73	36.48	4.79	51.67	52.48	1.54	(16, 39)
31	Methyl bromide	10.11	10.17	0.59	13.50	13.55	3.67	19.02	19.01	0.52	(15)
32	Methyl tetrabromide	19.29	21.83	1.16	24.03	24.02	0.04	25.71	25.33	1.50	(15)
33	Bromobenzene	22.36	23.96	6.69	35.04	36.69	4.49	51.79	52.54	1.42	(39)
34	Vinyl iodide	14.39	13.86	3.82	17.58	17.89	1.73	21.49	21.30	0.88	(15)
35	Iodobenzene	22.85	24.22	5.65	35.47	36.86	3.77	51.85	52.59	1.40	(39)
36	Fluorobenzene	20.87	22.65	7.85	33.68	35.86	6.08	51.31	52.18	1.67	(39)

Table IX. Typical Estimations of Heat Capacity

Group	No. of Each Group	a	b × 10 ²	c × 10 ⁴	d × 10 ⁶
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{H} \text{ (Isopropyl alcohol)} \\ \\ \text{OH} \end{array}$					
—CH ₃	2	1.2174	4.2866	—0.1704	0.00227
—C—H	1	—3.5232	3.4158	—0.2816	0.00802
—OH	1	6.5128	—0.1347	0.0414	—0.00162
CH ₃ CHOHCH ₃ ^a		4.2070	7.5677	—0.4106	0.00867
$\text{C}_6\text{H}_5\text{Br} \text{ (Bromobenzene)}$					
CH	5	—7.2860	9.5735	—0.6165	0.01493
—C—	1	—1.3883	1.5159	—0.1069	0.00266
—Br	1	2.7605	0.4731	—0.0455	0.00142
C ₆ H ₅ Br ^b		—5.9138	11.5625	—0.7689	0.01901

^a $C_p^\circ = 4.207 + 7.5677 \times 10^{-2} T - 0.4106 \times 10^{-4} T^2 + 0.00867 \times 10^{-6} T^3$. ^b $C_p^\circ = -5.914 + 11.5625 \times 10^{-2} T - 0.7689 \times 10^{-4} T^2 + 0.01901 \times 10^{-6} T^3$. Calculated and reported values given in Table VIII.

To test the accuracy of the procedure, heat capacities of several organic compounds were calculated at different temperatures. The principal difficulty in testing the method was the nonavailability of heat capacity data over the required temperature range (300° to 1500° K.) for the more complicated compounds. For purposes of comparison where spectroscopic data were not available, the method of Dobratz (12) has been used. Calculated and reported values for over 30 representa-

tive compounds are summarized in Table VIII. Values at only three temperatures are recorded in this table: 300°, 600°, and 1000° K. The agreement at all temperatures for all the compounds is remarkably good. In general, the accuracy of the method appears to be greater at higher temperatures. From several calculations (including some not listed in Table VIII), it may be stated that at 300° K. the average deviation is about 3%, while in the temperature range 400° to 1500° K.

Table VII. Halogen-Containing Groups

Group	a	b × 10 ²	c × 10 ⁴	d × 10 ⁶
—F	1.4382	0.3452	—0.0106	—0.000034
—Cl	3.0660	0.2122	—0.0128	0.000276
—Br	2.7605	0.4731	—0.0455	0.001420
—I	3.2651	0.4901	—0.0539	0.001782

estimated deviation is less than 2%; and for hydrocarbons the average error is about 1.5%, while for nonhydrocarbons it is about 4%. Sample calculations for isopropyl alcohol and bromobenzene are shown in Table IX.

Nomenclature

a, b, c, d = constants of heat capacity equation
 C_p° = ideal heat capacity, cal./° K./gram-mole
 C_{v_i} = contribution to heat capacity from stretching vibrations of bond i
 C_{b_i} = contribution to heat capacity from bending vibrations of bond i
 M = number of single bonds about which internal rotation of groups can take place
 n = number of atoms in molecule
 P = any thermodynamic function
 $\sum q_i$ = total number of bonds in molecule
 R = gas constant, cal./° K./gram-mole
 T = temperature, ° K.
 T_r = reduced temperature
 σ = symmetry number

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PARTICLE-TO-FLUID HEAT TRANSFER IN WATER-FLUIDIZED SYSTEMS

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Stainless steel and lead spheres were fluidized in water and heated by an induction heating field. Reynolds numbers based on particle diameter and superficial velocity ranged between 240 and 14,000. The heat transfer from the spherical particles to the water was correlated with: $Nu = 1.28 \times 10^{-5} (ReF_e)^{2.0} Pr^{0.67} (D_T/D_p)^{0.5} (\rho_f/\rho_p)^2 (\mu/\mu_0)^{0.83}$. The velocity correction factor, F_e , is used to account for variations in porosity. The data of the present investigation compare favorably with previous particle-to-gas and particle-to-water heat transfer studies, although a different correlation from the one above is necessary for comparison, since porosity data were not available for the previous studies.

MANY studies of fluidization heat transfer have been reported. Most of these studies are concerned with heat transfer from an exposed surface to a fluidized medium and suitable empirical correlations are available for predicting the heat transfer rates under conditions similar to those reported in the various investigations. Only a few studies consider the heat transfer from the fluidized particles to the fluidizing medium. It is necessary to know these heat transfer rates in order to design a fluidized nuclear reactor as proposed (11, 12).

The experimental study described in this paper was initiated to determine the heat transfer coefficients for solid spheres fluidized in water and it is anticipated that the data will be applicable to natural-uranium-water fluidized nuclear reactors.

Previous Work

Heat transfer in fluidized systems has been studied for both particulate and aggregative fluidization and for both gas and liquid systems, although the data for the liquid systems are