Glossary

g^E	excess Gibbs energy
n_D	refractive index
P	total pressure
p^0	vapor pressure
R	gas constant
t, T	temperature in °C, K
T_c	critical temperature
v	molar volume $cm^3\ mol^{-1}$

Greek letters

γ	activity coefficient
λ_{ij}	energy interaction
ω	acentric factor

Subscripts

1	1,2-dichloropropane
2	propanal

Literature Cited

(1) d'Avila, S. G., Silva R. S. F., *J. Chem. Eng. Data*, **15**, 421 (1970).
(2) Barker, J. A., *Aust. J. Chem.*, **6**, 207 (1953).
(3) Jose, J., Philippe R., Clechet, P., *Bull. Soc. Chim. Fr.*, **8**, 2860 (1971).
(4) Kay, W. B., *Ind. Eng. Chem.*, **28**, 1014 (1936).
(5) Löffler, H. J., *Kältetechnik*, **20**, 72 (1968).
(6) Matsunaga, I., Katayama, T., *J. Chem. Eng. Jpn.*, **6**, 397 (1973).
(7) Morell, C. E., Carlson, C. S., Mc Ateer, J. H., Robey, R. F., Smith, P. V., *Ind. Eng. Chem.*, **44**, 2839 (1952).
(8) Sundholm, G., *Fin. Kemistamf. Medd.*, **73**, 1 (1964).
(9) TRC Data Project, Texas A&M University (Dec 1961 and Dec 1964).

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Heat Capacities of Liquid Hydrocarbons. Estimation of Heat Capacities at Constant Pressure as a Temperature Function, Using Additivity Rules

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Additivity rules were applied to develop a scheme for estimating constant pressure heat capacity of liquid hydrocarbons as a temperature function. Values for 20 typical hydrocarbon groups and 12 structural features were derived from experimental data on 117 hydrocarbons. The various group values and the structural contributions, which are presented as cubic polynomial expressions, represent the most common groups in hydrocarbons. These group values can be used to estimate the heat capacity of almost any common liquid hydrocarbon below the boiling point. During this research, 1209 independent data points were examined; the standard deviation and the average deviation between the calculated and the observed values were found to be ±0.8 and ±0.64 cal $mol^{-1}\ K^{-1}$, respectively.

The need for data on heat capacities in designing a chemical plant is very obvious. Although experimental data can be very accurate, it is very difficult to provide all the data needed for every single compound. Moreover, in most cases, the accuracy required by the industry is less than ±1 cal $mol^{-1}\ K^{-1}$. For these reasons, several methods have been developed for estimating thermochemical properties and especially methods for estimating liquid heat capacities. Among these methods, it is worth mentioning the simple Kopp's rule (*4*), the Tsien method based on Lennard-Jones and Devonshire theory on normal liquids (*7*), and more recently methods developed by Yuan and Stiel (*8*), by Swenson and Chueh (*6*), and by Amirkhanov et al. (*1*). Although some of these methods are based on some theoretical consideration, they require much experimental input and relatively complicated calculations, their accuracy is marginal, and they are applicable only for a specific property (e.g., liquid heat capacity). A more detailed discussion of these methods, their range of applicability, their accuracy, and their relation to the work presented here is given in a recent manuscript (*9*).

An empirical approach for estimating thermochemical properties was established some 20 years ago by Benson and Buss (*2*), who developed a hierarchy of empirical additivity laws and demonstrated that thermochemical properties of gases, such as entropy, enthalpy, and heat capacity, could be estimated almost to the extent of the experimental uncertainty. Johnson and Huang (*10*), Missenard (*11*), and Shaw (*5*), have applied group methods to the estimation of liquid heat capacities.

Shaw demonstrated that $C_p(l)$ can be estimated to within ±1.0 cal $mol^{-1}\ K^{-1}$ by group methods. The growing need for reliable and simple methods for estimating thermochemical data, mainly for the various energy research programs, has motivated us to extend this method so that heat capacities of liquids as a temperature function can be estimated easily, quickly, and accurately.

Data Sources

Heat capacity data as a temperature function are usually presented in the literature in intervals of 10 K. In this study, we

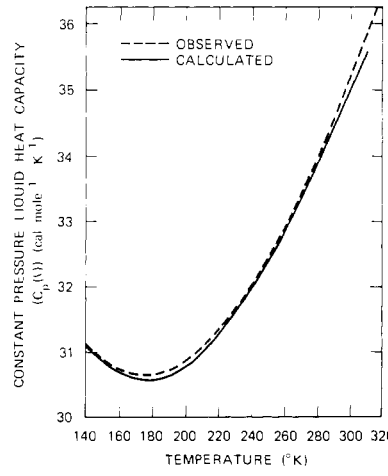

Figure 1. Schematic presentation of the agreement between observed calculated $C_p(l)$ for the case of 1-*cis*-3-pentadiene [$C_p(l) = a + f + g + 2j + \alpha$].

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Table I. Cubic Polynomial Group Values Used to Calculate Constant Pressure Heat Capacity of Liquid Hydrocarbons [C_p(l) (group) = $A + BT + CT^2 - DT^3$], cal mol^{-1} K^{-1}

Group	Group symbol	Polynomial coefficient				Temperature range (°K)	
		A	B	C	D	Evaluated	Extrapolated
$C(C)(H)_3$	a	8.459	2.113E-3	-5.605E-5	1.723E-7	90-380	90-400
$C(C)^2(H)_2$	b	-1.383	7.049E-2	-2.063E-4	2.269E-7	90-380	
$C(C)_3(H)$	c	2.489	-4.617E-2	3.181E-4	-4.565E-7	120-380	
$C(C)_4$	d	9.116	-2.354E-1	1.287E-3	-1.906E-6	150-320	
$C_d(C_d)(C)_2$	e	8.005	-9.456E-2	4.620E-4	-6.547E-7	200-320	140-320
$C_d(C_d)(H)_2$	f	8.754	1.776E-2	-1.526E-4	2.542E-7	110-320	
$C_d(C_d)(C)(H)$	g	5.792	-1.228E-2	6.036E-5	-1.926E-8	140-300	110-320
$C(C_d)(C)(H)_2$	h	3.497	-1.568E-1	1.808E-4	-3.277E-7	140-300	110-320
$C(C_d)(C)_2(H)$	i	-2.232	-1.773E-2	2.812E-4	-4.199E-7	140-300	
$C_d(C_d)(C_d)(H)$	j	8.127	-7.171E-2	3.894E-4	-5.462E-7	140-310	140-330
$C_d(C_d)_2$	k	13.756	-1.338E-1	6.553E-4	-9.447E-7	140-310	
$C(C_d)_2(H)_2$	l	9.733	-1.100E-1	5.522E-4	-6.852E-7	140-300	140-320
$C_d(C_a)_1(C_a)(C)$	m	5.745	-1.085E-1	5.898E-4	-6.983E-7	140-300	
$C_a(C_a)_2(H)$	n	-1.842	5.778E-2	-1.716E-4	1.995E-7	280-350	180-400
$C_a(C_a)_2(C)$	o	28.807	-2.824E-1	9.779E-4	-1.103E-6	180-400	
$C(C_a)(H)_2$	p	30.192	-2.812E-1	1.002E-3	-1.115E-6	180-380	
$C_a(C_a)_3$	q	-3.780	2.563E-2	1.190E-5	-9.774E-8	250-400	
$C_t(C_t)(C)$	r	-10.407	1.662E-1	-5.679E-4	6.667E-7	250-290	150-290
$C_t(C_t)(H)$	s	30.122	-2.081E-1	5.945E-4	-3.430E-7	150-280	

Table II. Cubic Polynomial Corrections Used to Calculate Constant Pressure Liquid Heat Capacity of Some Liquid Hydrocarbons

Correction parameter for:	Correction symbol	Polynomial coefficient				Temperature range (°K)
		A	B	C	D	
Cis around double bond	α	14.299	-1.646E-1	6.069E-4	-7.716E-7	140-300
Cyclopentane ring	β	34.261	-3.803E-1	1.161E-3	-1.118E-6	140-370
Cyclohexane ring	γ	13.021	-1.468E-1	2.802E-4	-3.185E-8	150-380
Cyclopropane ring	δ	28.469	-2.696E-1	6.534E-4	-1.636E-7	150-240
Cyclobutane ring	ϵ	6.060	-3.114E-2	-2.461E-4	8.349E-7	190-280
Spiropentane ring	η	32.469	-1.991E-1	1.820E-4	4.090E-7	170-310
Cyclopentene ring	θ	13.650	-1.126E-1	7.257E-5	3.400E-7	140-300
Cyclohexene ring	κ	5.360	-3.456E-2	-2.232E-4	7.324E-7	170-300
Cycloheptane ring	λ	210.72	-2.344E 0	8.235E-3	-9.500E-6	270-300
Cycloheptatriene ring	μ	-22.158	3.985E-1	-2.059E-3	2.863E-6	200-320
Cyclo-octane ring	ν	1691.9	-1.680E+1	5.523E-2	-6.033E-5	290-330
Cyclo-octatetraene ring	ρ	-1.060	2.739E-1	-1.972E-3	3.167E-7	270-330
Cis- and trans-decahydro-naphthalene ring	σ	141.85	-1.510E 0	4.773E-3	-4.872E-6	240-350
1,2,3,4-Tetra-hydronaphthalene	φ	-212.65	2.203E 0	-7.571E-3	8.565E-6	240-340

treat every value at the 10 K intervals as one data point even though this value may arise from two or three different experimental points. With the aid of the polynomial expressions C_p(l), values can be calculated at any temperature at the normal liquid range from 100 to 400 K.

Method of Calculation

The principle of group additivity has been explained in detail elsewhere (*3, 5*). The definition of a group is a polyvalent atom

Table III. Comparison of Calculated and Observed Values of Heat Capacity at Constant Pressure for Straight Chain Liquid Alkanes as a Temperature Function (in cal mol^{-1} K^{-1})

Temp, °K		ethane	propane	n-butane	n-pentane	n-hexane	n-heptane	n-octane	n-nonane	n-decane	n-undecane	n-dodecane	n-tridecane	n-tetradecane	n-pentadecane	n-hexadecane	n-heptadecane	n-octadecane
90	O	16.30	20.21															
	C	16.64	20.09															
	Δ	−0.34	0.12															
100	O	16.38	20.30															
	C	16.56	20.39															
	Δ	−0.18	−0.09															
110	O	16.47	20.42															
	C	16.49	20.67															
	Δ	−0.02	−0.25															
120	O	16.55	20.55															
	C	16.11	20.91															
	Δ	0.11	−0.36															
130	O	16.61	20.70															
	C	16.33	21.12															
	Δ	0.28	−0.42															
140	O	16.69	20.86	27.16														
	C	16.26	21.32	26.39														
	Δ	0.43	−0.46	0.77														
150	O	16.78	21.06	27.50	33.83													
	C	16.19	21.50	26.82	32.13													
	Δ	0.60	−0.44	0.68	1.70													
160	O	16.93	21.26	27.71	33.86													
	C	16.14	21.64	27.23	32.77													
	Δ	0.79	−0.42	0.51	1.09													
170	O	17.08	21.50	27.86	33.94													
	C	16.10	21.85	27.62	33.36													
	Δ	0.98	−0.35	0.25	0.56													
180	O	17.26	21.75	28.03	34.04	40.64												
	C	16.06	22.00	27.95	33.89	39.84												
	Δ	1.20	−0.25	0.08	0.15	0.80												
190	O		22.02	28.28	34.23	40.76	48.27											
	C		22.16	28.28	34.40	40.52	48.61											
	Δ		−0.14	0.00	−0.17	0.24	1.63											
200	O		22.34	28.58	34.50	40.97	48.15											
	C		22.32	28.60	34.88	41.18	47.44											
	Δ		0.02	−0.02	−0.38	−0.19	0.71											
210	O		22.70	28.90	34.82	41.26	48.43											
	C		22.48	28.90	35.32	41.75	48.17											
	Δ		0.22	0.00	−0.50	−0.49	0.26											
220	O		23.08	29.23	35.20	41.63	48.49	55.53	63.19									
	C		22.65	29.21	35.76	42.32	48.87	55.43	61.99									
	Δ		0.43	0.02	−0.56	−0.69	−0.38	0.10	1.44									
230	O		23.53	29.63	35.64	42.09	48.88	55.78	63.19									
	C		22.82	29.49	36.16	42.83	49.49	56.16	62.83									
	Δ		0.71	0.14	−0.52	−0.74	−0.61	−0.38	0.36									
240	O			30.02	36.15	42.66	49.38	56.19	63.36									
	C			29.82	36.80	43.39	50.18	56.97	63.76									
	Δ			0.20	−0.65	−0.73	−0.80	−0.78	−0.40									
250	O			30.53	36.71	43.27	49.98	56.74	63.81	71.10	78.75							
	C			30.13	37.02	43.91	50.81	57.69	64.58	71.47	78.37							
	Δ			0.11	−0.31	−0.64	−0.83	−0.95	−0.77	−0.37	0.38							
260	O			31.10	37.29	43.91	50.66	57.41	64.47	71.66	79.11							
	C			30.47	37.46	44.49	51.41	58.42	65.41	72.40	79.38							
	Δ			0.63	−0.17	−0.58	−0.78	−0.98	−0.94	−0.74	−0.27							
270	O			31.65	37.92	44.59	51.39	58.22	65.26	72.38	79.72	87.18	94.93					
	C			30.82	37.90	44.98	52.05	59.13	66.20	73.28	80.36	87.13	94.51					
	Δ			0.83	0.02	−0.39	−0.66	−0.91	−0.94	−0.90	−0.64	−0.25	0.42					
280	O				38.61	45.31	52.19	59.07	66.13	73.24	80.52	87.92	95.37	102.92				
	C				38.36	45.52	52.66	59.84	67.00	74.17	81.33	88.49	95.65	102.81				
	Δ				0.25	−0.21	−0.49	−0.77	−0.87	−0.93	−0.81	−0.57	−0.28	0.11				
290	O				39.34	46.07	53.04	59.98	67.11	74.26	81.55	88.91	96.31	103.91	111.50			
	C				38.85	46.09	53.34	60.58	67.82	75.07	82.31	89.55	96.80	104.04	111.28			
	Δ				0.49	−0.02	−0.30	−0.60	−0.71	−0.81	−0.76	−0.64	−0.49	−0.13	0.22			
300	O				40.13	46.86	53.93	60.90	68.16	75.37	82.68	90.09	97.47	105.01	112.53	120.07	127.87	
	C				39.37	46.70	54.02	61.34	68.66	75.98	83.31	90.63	97.96	105.28	112.80	119.93	127.25	
	Δ				0.73	0.16	−0.09	−0.44	−0.50	−0.61	−0.63	−0.54	−0.49	−0.27	−0.07	0.14	0.62	
310	O						54.85		69.25	76.52	83.90	91.32	98.72		113.82	121.43	129.09	136.77
	C						54.74		69.55	76.95	84.35	91.76	99.16		113.96	121.37	128.77	136.17
	Δ						0.11		−0.30	−0.43	−0.45	−0.44	−0.44		−0.14	0.06	0.32	0.60
320	O						55.78		70.40	77.75		92.82				123.05	130.67	138.30
	C						55.51		70.47	77.96		92.93				122.86	130.35	137.83
	Δ						0.27		−0.07	−0.21		−0.11				0.19	0.32	0.47
330	O						56.75										132.38	140.02
	C						56.32										131.98	139.55
	Δ						0.43										0.40	0.47
340	O						57.76										134.17	141.87
	C						57.21										133.74	141.39
	Δ						0.55										0.42	0.48
350	O						58.79										136.04	143.85
	C						58.17										135.62	143.36
	Δ						0.62										0.42	0.49
360	O						59.89										137.93	145.77
	C						59.21										137.64	145.48
	Δ						0.68										0.29	0.29
370	O						61.04										139.85	147.77
	C						60.34										139.82	147.76
	Δ						0.70										0.03	0.01
380	O																141.76	149.93
	C																142.20	150.26
	Δ																−0.44	−0.33
390	O																143.69	
	C																	
	Δ																	
Source		1	2	3	4	4	4	4	4	4	4	4	4	4	4	4	4	4

O = observed
C = calculated
Δ = C_p(I) [observed-calculated]

[1] R. K. Witt and J. D. Kemp, J. Amer. Chem. Soc., 59, 273 (1937).
[2] J. D. Kemp and C. J. Egan, J. Amer. Chem. Soc., 60, 1521 (1938).
[3] J. G. Aston and G. H. Messerly, J. Amer. Chem. Soc., 62, 1917 (1940).
[4] J. F. Messerly, G. B. Guthrie, S. S. Todd, and H. L. Finke, J. Chem. and Eng. Data, 12, 338 (1967).

together with its ligands. (Of these ligands, at least one is another polyvalent atom; otherwise, the whole molecule is composed from one group, e.g., CH_4, H_2O.) The easiest way to demonstrate this principle is to consider an example. Let us estimate C_p(l) of 1-hexadecene at 280 K. The molecule is composed of five groups: (1) a double bonded C atom attached to a double bonded C atom and to two H atoms ($C_d(C_d)(H)_2$, group f), (2) a double bonded C atom attached to a double bonded C atom, to one H atom, and one single bonded C atom (C_d-(C_d)(C)(H), group g), (3) a single bonded C atom attached to double and single bonded C atoms and to two H atoms ($C(C_d)(C)(H)_2$, group h), (4) 12 groups of single bonded C atoms each attached to another two single bonded C atoms and to two H atoms ($C(C)_2(H)_2$, group b), and (5) a single bonded C atom attached to three H atoms and one single bonded C atom ($C(C)(H)_3$, group a). Using the parameters for the groups a, b, g, f, and h, which are given in Table I, substituting 280 for T, and summing a + 12b + f + g + h, we obtain the value of 113.87 cal mol^{-1} K^{-1}, which compares well with the value of 114.03 cal mol^{-1} K^{-1} observed experimentally. Note that we have represented the central C atom in allene as C_a in

Table IV. Comparison of Calculated and Observed Values of Heat Capacity at Constant Pressure for Tertiary Liquid Alkanes as a Temperature Function (in cal mol^{-1} K^{-1})

Temp., °K		methyl-propane	methyl-butane	2-methyl-pentane	3-methyl-pentane	2,3-dimethyl-butane	2-methyl-hexane	2,4-dimethyl-pentane	3-ethyl-pentane	2-methyl-heptane	3-methyl-heptane	2-methyl-nonane	3-methyl-nonane	4-methyl-nonane	5-methyl-nonane	2-methyl-decane
120	O	23.97	29.55	35.16	34.90											
	C	25.35	29.85	34.35	34.35											
	Δ	-1.38	-0.30	0.81	0.55											
130	O	24.28	29.95	35.49	35.25											
	C	25.36	30.15	34.94	34.94											
	Δ	-1.08	-0.20	0.55	0.31											
140	O	24.63	30.34	35.87	35.62											
	C	25.40	30.48	35.53	35.53											
	Δ	-0.77	-0.12	0.34	0.09											
150	O	25.05	30.74	36.24	36.00	34.83										
	C	25.47	30.79	36.10	36.10	34.75										
	Δ	-0.42	-0.05	0.14	-0.10	0.08										
160	O	25.52	31.14	36.69	36.41	35.36	43.06	40.49	41.59		48.98					
	C	25.59	31.13	36.67	36.67	35.04	42.22	40.58	42.25		47.80					
	Δ	-0.07	0.01	0.02	-0.26	0.32	0.84	-0.09	-0.66		1.18					
170	O	26.03	31.55	37.15	36.87	35.90	43.53	41.24	42.18	50.69	49.45					
	C	25.73	31.48	37.23	37.23	35.36	42.99	41.10	42.99	48.74	48.74					
	Δ	0.30	0.07	-0.08	-0.36	0.54	0.54	0.14	-0.81	1.95	0.71					
180	O	26.50	32.00	37.66	37.36	36.46	44.04	42.01	42.80	51.00	49.94			63.17		
	C	25.91	31.85	37.80	37.80	35.76	43.74	41.70	43.74	49.69	49.69			61.58		
	Δ	0.59	0.15	-0.14	-0.44	0.70	0.30	0.31	-0.94	1.31	0.25			1.59		
190	O	26.84	32.46	38.16	37.87	37.05	44.58	42.81	43.46	51.39	50.72		62.98	63.32	63.29	
	C	26.13	32.25	38.37	38.37	36.22	44.49	42.34	44.49	50.61	50.61		62.85	62.85	62.85	
	Δ	0.61	0.21	-0.21	-0.50	0.83	0.09	0.47	-1.03	0.78	0.11		0.13	0.47	0.44	
200	O	27.33	33.00	38.74	38.41	37.64	45.19	43.65	44.14	51.81	51.19	66.59	63.70	64.17	63.90	
	C	26.39	32.67	38.94	38.94	36.74	45.22	43.01	45.22	51.50	51.50	64.06	64.06	64.06	64.06	
	Δ	0.94	0.33	-0.20	-0.53	0.90	-0.03	0.64	-1.08	0.31	-0.31	2.53	-0.36	0.11	-0.16	
210	O	27.81	33.50	39.36	38.99	38.24	45.83	44.51	44.85	52.34	51.83	66.70	64.48	65.02	64.65	
	C	26.68	33.05	39.47	39.47	37.30	45.95	43.73	45.95	52.37	52.37	65.22	65.22	65.22	65.22	
	Δ	1.13	0.45	-0.11	-0.48	0.94	-0.12	0.78	-1.10	-0.03	-0.54	1.48	-0.76	-0.20	-0.57	
220	O	28.37	34.04	40.00	39.62	38.88	46.51	45.42	45.59	52.97	52.56	66.95	65.17	65.84	65.44	
	C	27.01	33.57	40.12	40.12	37.93	46.68	44.48	46.68	53.23	53.23	66.35	66.35	66.35	66.35	
	Δ	1.36	0.47	-0.12	-0.50	0.95	-0.17	0.94	-1.09	-0.26	-0.67	0.60	-1.18	-0.47	-0.91	
230	O	28.99	34.60	40.70	40.26	39.56	47.22	46.36	46.35	53.72	53.32	67.42	65.91	66.73	66.38	74.32
	C	27.37	34.05	40.72	40.72	38.59	47.40	45.27	47.40	54.08	54.08	67.43	67.43	67.43	67.43	74.14
	Δ	1.62	0.55	-0.02	-0.46	0.97	-0.18	1.11	-1.05	-0.36	-0.76	-0.01	-1.52	-0.70	-1.05	0.18
240	O	29.71	35.20	41.41	40.95	40.28	48.00	47.37	47.15	54.54	54.10	68.04	66.79	67.70	67.43	75.13
	C	27.78	34.57	41.36	41.36	39.25	48.15	46.12	48.15	54.94	54.94	68.52	68.52	68.52	68.52	75.31
	Δ	1.93	0.63	0.05	-0.41	1.03	-0.15	1.25	-1.00	-0.40	-0.84	-0.48	-1.73	-0.82	-1.09	-0.18
250	O	30.38	35.80	42.21	41.68	41.02	48.81	48.38	47.99	55.45	54.86	68.99	67.81	68.92	68.51	75.96
	C	28.23	35.12	42.01	42.01	40.10	48.90	47.00	48.90	55.79	55.79	69.57	69.57	69.57	69.57	76.46
	Δ	2.15	0.68	0.20	-0.33	0.92	-0.09	1.38	-0.91	-0.34	-0.81	-0.58	-1.76	-0.65	-1.06	-0.50
260	O	31.00	36.48	43.02	42.44	41.80	49.67	49.43	48.88	56.33	55.82	70.03	68.01	70.26	69.69	76.89
	C	28.71	35.70	42.69	42.69	40.93	49.67	47.92	49.67	56.66	56.66	70.63	70.63	70.63	70.63	77.62
	Δ	2.29	0.78	0.33	-0.25	0.87	0.00	1.51	-0.79	-0.33	-0.74	-0.60	-1.62	-0.37	-0.94	-0.73
270	O		37.10	43.82	43.22	42.64	50.55	50.51	49.78	57.30	56.89	71.19	70.28	71.56	71.09	78.00
	C		36.32	43.39	43.39	41.81	50.47	48.88	50.47	57.54	57.54	71.69	71.69	71.69	71.69	78.77
	Δ		00.78	0.43	-0.17	0.83	0.08	1.63	-0.69	-0.24	-0.65	-0.50	-1.41	-0.13	-0.63	-0.77
280	O			44.67	44.02	43.50	51.49	51.60	50.70	58.31	57.90	72.49	71.57	72.94	72.42	79.20
	C			44.12	44.12	42.72	51.28	49.88	51.28	58.44	58.44	72.72	72.77	72.77	72.77	79.93
	Δ			0.55	-0.10	0.78	0.21	1.72	-0.58	-0.13	-0.54	-0.23	-1.20	0.17	-0.35	-0.73
290	O			45.59	44.84	44.37	52.47	52.70	51.66	59.38	58.93	73.79	72.84	74.56	73.80	80.45
	C			44.89	44.89	43.69	52.14	50.93	52.13	59.38	59.38	73.86	73.86	73.86	73.86	81.11
	Δ			0.70	-0.05	0.68	0.33	1.77	-0.47	-0.02	-0.45	-0.07	-1.02	0.70	-0.06	-0.66
300	O			46.50	45.74	45.28	53.48	53.79	52.66	60.43	60.01					81.82
	C			45.69	45.69	44.69	53.02	52.01	53.01	60.34	60.34					82.31
	Δ			0.81	0.05	0.59	0.46	1.78	-0.38	0.09	-0.33					-0.49
310	O			47.20	46.64			54.87		61.55	61.14					83.25
	C			46.54	46.54			53.15		61.35	61.35					83.56
	Δ			0.66	0.10			1.72		0.20	-0.21					-0.31
320	O				47.56					62.70	62.26					84.69
	C				47.43					62.46	62.40					84.85
	Δ				0.13					0.24	-0.14					-0.16
330	O				48.50					63.87	63.43					86.14
	C				48.36					63.49	63.49					86.19
	Δ				0.14					0.38	-0.06					-0.05
340	O									65.10	64.63					87.60
	C									64.65	64.65					87.61
	Δ									0.45	-0.02					-0.01
350	O									66.35	65.76					89.10
	C									65.86	65.86					89.10
	Δ									0.49	-0.10					0.00
360	O									67.64	66.94					90.67
	C									67.16	67.16					90.69
	Δ									0.48	-0.22					-0.02
370	O									68.92	68.20					92.30
	C									68.52	68.52					92.37
	Δ									0.40	-0.32					-0.07
380	O										69.54					93.96
	C										69.96					93.73
	Δ										-0.42					0.23
390	O															95.68
	C															
	Δ															
Source		1	2	3	4	5	3	6	6	3	4	7	7	7	7	8

O = observed
C = calculated
Δ = $C_p(l)$ [observed-calculated]

[1] J. G. Aston, R. M. Kennedy, and S. C. Schumann, J. Amer. Chem. Soc., 62, 2059 (1970).
[2] G. B. Guthrie, Jr., and H. M. Huffman, J. Amer. Chem. Soc., 65, 1139 (1943).
[3] J. F. Messerly and K. L. Finke, J. Chem. Thermodynamics, 3, 675 (1971).
[4] K. L. Finke and J. F. Messerly, J. Chem. Thermodynamics, 5, 247 (1973).
[5] D. E. Douslin and H. M. Huffman, J. Amer. Chem. Soc., 68, 1704 (1946).
[6] H. M. Huffman, M. E. Gross, D. W. Scot, and J. P. McCollough, J. Phys. Chem., 65, 495 (1961).
[7] G. S. Parks, T. J. West, and G. E. Moore, J. Amer. Chem. Soc., 63, 1133 (1941).

Table V. Comparison of Calculated and Observed Values of Heat Capacity at Constant Pressure for Quaternary Liquid Alkanes as a Temperature Function (in cal mol^{-1} K^{-1})

Temp. °K		2,2-dimethyl-butane	2,2-dimethyl-pentane	2,2,3-tri-methylbutane	3,3-dimethyl-pentane	2,2,4-tri-methylpentane	3,3,4,4-tetra-methylhexane
140	O						
	C						
	Δ						
150	O		39.22		39.52		
	C		39.34		39.34		
	Δ		-0.12		0.18		
160	O		39.92		40.02		
	C		39.94		39.94		
	Δ		-0.02		0.08		
170	O		40.66		40.56	44.33	
	C		40.60		40.60	44.49	
	Δ		0.06		-0.04	-0.16	
180	O	36.11	41.42		41.16	45.01	
	C	35.37	41.32		41.32	45.22	
	Δ	0.74	0.10		-0.16	-0.21	
190	O	36.72	42.22		41.82	45.71	
	C	35.96	42.08		42.08	46.05	
	Δ	0.76	0.14		-0.26	-0.34	
200	O	37.38	53.05		42.51	46.48	
	C	36.80	52.88		42.88	46.96	
	Δ	0.58	0.17		-0.37	-0.48	
210	O	38.05	43.91		43.23	47.34	
	C	37.31	43.73		43.73	47.93	
	Δ	0.74	0.18		-0.50	-0.59	
220	O	38.74	44.81		44.00	48.26	
	C	38.04	44.60		44.60	48.96	
	Δ	0.70	0.21		-0.60	-0.70	
230	O	39.43	45.74		44.80	49.24	65.08
	C	38.83	45.50		45.50	50.04	63.29
	Δ	0.60	0.24		-0.70	-0.80	1.79
240	O	40.17	46.71		45.65	50.13	66.01
	C	39.65	46.44		46.44	51.19	64.53
	Δ	0.52	0.27		-0.78	-1.06	1.48
250	O	40.98	47.70	46.02	46.49	51.11	67.00
	C	40.49	47.39	45.48	47.39	52.37	65.82
	Δ	0.49	0.31	0.54	-0.90	-1.26	1.18
260	O	41.81	48.73	47.05	47.35	52.12	68.05
	C	41.36	48.36	46.59	48.36	53.58	67.19
	Δ	0.45	0.37	0.46	-1.01	-1.46	0.86
270	O	42.67	49.77	48.08	48.27	53.15	69.17
	C	42.25	49.33	47.74	49.30	54.81	68.49
	Δ	0.42	0.44	0.34	-1.03	-1.66	0.68
280	O	43.53	50.85	49.12	49.24	54.20	70.37
	C	43.15	50.31	48.91	50.31	56.07	69.81
	Δ	0.38	0.54	0.21	-1.07	-1.87	0.56
290	O	44.41	51.94	50.17	50.35	55.28	71.57
	C	44.05	51.29	50.09	51.29	57.33	71.27
	Δ	0.36	0.65	0.08	-0.94	-2.05	0.30
300	O	45.27	53.06	51.22			
	C	44.95	52.27	51.27			
	Δ	0.32	0.79	-0.05			
310	O		54.20	52.26			
	C		53.25	52.45			
	Δ		0.95	-0.19			
320	O			53.32			
	C			53.62			
	Δ			-0.30			
330	O						
	C						
	Δ						
Source		1	2	2	3	4	4

O = observed
C = calculated
Δ = $C_p(\ell)$ [observed-calculated]

[1] D. R. Douslin and H. M. Huffman, J. Amer. Chem. Soc., 68, 1704 (1946)
[2] H. M. Huffman, M. E. Gross, D. W. Scott, and J. P. McCollough, J. Phys. Chem., 65, 465 (1961)
[3] H. M. Huffman, G. S. Parks, and S. B. Thomas, J. Amer. Chem. Soc., 52, 3241 (1930)
[4] G. S. Parks, H. M. Huffman, and S. B. Thomas, J. Amer. Chem. Soc., 52, 622 (1930).

conformity with past practice (*3*) rather than by C_d–$(C_d)_2$.

The group activity method does not take into account next-to-nearest-neighbor interactions, such as cis effect or molecular strain caused by the existence of a ring compound. Where such an effect exists, a structural correction should be made. The corrections, also presented in a polynomial form, are given in Table II. Whenever a correction is needed, simply add the correction value. For example, C_p(l) at any given temperature of cyclohexane can be estimated by substituting the temperature in the cubic expressions for b and γ and calculating the sum 6b

Table VI. Comparison of Calculated and Observed Values of Heat Capacity at Constant Pressure for Liquid Alkenes as a Temperature Function (in cal mol^{-1} K^{-1})

Temp., °K		propene	1-butene	2-methyl-propene	trans-2-butene	cis-2-butene	1-pentene	trans-2-pentene	cis-2-pentene	2-methyl-1-butene	3-methyl-2-butene	3-methyl-1-butene	1-hexene	2,3-dimethyl-butene-2	1-heptene	1-octene	1-decene	1-undecene	1-dodecene	1-hexadecene
110	O	31.35	35.52				30.99													
	C	31.99	35.51				29.69													
	Δ	-0.64	0.01				1.30													
120	O	31.14	35.26				30.77													
	C	31.89	35.54				30.04													
	Δ	-0.75	-0.18				0.73													
130	O	90.97	25.39				30.74													
	C	31.78	35.58				30.37													
	Δ	-0.81	-0.29				0.37													
140	O	90.80	25.27	25.81		26.84	30.79	30.60	31.62	31.80	31.54	29.46	35.85							
	C	31.66	35.53	26.70		27.59	30.69	30.61	31.64	30.53	31.52	29.46	35.76							
	Δ	-0.86	-0.26	-1.19		-0.81	0.10	[-0.01]	-0.02	1.15	-0.04	[0.00]	1.10							
150	O	90.81	25.33	25.66		26.63	30.87	30.79	31.48	31.81	31.58	29.69	36.66							
	C	31.58	35.59	26.44		27.34	30.54	30.79	31.44	30.53	31.54	29.70	36.52							
	Δ	-0.77	-0.26	-0.78		-0.71	-0.14	[0.00]	0.04	1.28	0.04	[-0.01]	0.86							
160	O	90.84	25.43	25.83		26.48	30.97	31.01	31.40	31.87	31.58	29.96	36.96		43.36					
	C	31.49	35.76	26.29		27.06	30.51	31.00	31.33	30.56	31.53	29.97	37.06		43.40					
	Δ	-0.65	-0.33	-0.46		-0.58	-0.34	[0.01]	0.07	1.31	0.06	[-0.01]	-0.10		0.96					
170	O	90.90	25.36	26.03	26.40	26.42	31.13	31.25	31.35	31.99	31.65	30.27	37.10		43.42					
	C	31.41	35.86	26.17	26.80	26.86	30.51	31.21	31.33	30.66	31.56	30.28	37.16		43.30					
	Δ	-0.51	-0.50	-0.14	-0.40	-0.44	-0.48	[0.04]	0.07	1.33	0.09	[-0.01]	-0.26		0.12					
180	O	90.99	25.73	26.26	26.53	26.61	31.24	31.53	31.44	32.16	31.79	30.62	37.30		43.58	50.76				
	C	31.34	35.96	26.04	26.72	26.74	30.51	31.53	31.38	30.70	31.65	30.61	37.35		43.36	49.75				
	Δ	-0.35	-0.23	0.14	-0.19	-0.13	-0.57	[0.00]	0.06	1.46	0.14	[-0.01]	-0.05		-0.21	1.01				
190	O	21.16	25.95	26.54	26.67	26.45	31.60	31.48	31.55	32.34	31.96	31.00	37.56		43.84	50.76				
	C	31.29	36.09	26.03	26.86	26.69	32.21	31.85	31.49	30.82	31.79	30.98	38.22		44.44	50.60				
	Δ	-0.13	-0.14	0.51	-0.19	-0.24	-0.61	[0.00]	0.06	1.52	0.17	[0.02]	-0.76		-0.60	0.16				
200	O	31.34	36.24	26.96	26.89	26.55	31.90	32.20	31.72	32.66	32.17	31.42	37.89	36.75	44.17	50.92				
	C	31.25	36.22	26.01	27.06	26.71	32.50	32.20	31.69	30.98	31.99	31.24	38.78	36.74	45.06	51.33				
	Δ	0.09	0.02	0.95	-0.17	-0.16	-0.60	[0.00]	0.04	1.68	0.18	[0.18]	-0.89	[0.01]	-0.89	-0.41				
210	O	31.55	36.60	27.20	27.14	26.87	32.24	32.59	31.95	32.97	32.41	31.87	38.28	37.08	44.87	51.23	58.08			
	C	31.24	36.38	26.08	27.29	26.79	32.80	32.59	31.94	31.16	32.24	31.92	39.22	37.08	45.85	52.07	58.92			
	Δ	0.31	0.22	1.18	-0.15	-0.12	-0.56	[0.00]	0.01	1.81	0.17	[-0.05]	-0.94	[0.00]	-1.08	-0.84	1.16			
220	O	31.77	36.97	27.57	27.43	26.85	32.65	33.01	32.23	33.33	32.89	32.35	38.73	37.36	45.04	51.66	58.82			
	C	31.24	36.85	26.07	27.37	26.95	33.10	33.02	32.25	31.38	32.54	32.30	39.66	37.37	46.21	52.77	59.88			
	Δ	0.53	0.42	1.50	-0.14	-0.10	-0.45	[-0.01]	-0.02	1.95	0.35	[0.05]	-0.93	[-0.01]	-1.17	-1.11	-1.06			
230	O		37.35	27.97	27.71	27.07	33.09	33.47	32.57	33.74	33.05	32.86	39.23	37.77	46.38	52.21	59.99	73.66		
	C		36.73	26.14	27.86	27.16	33.41	33.47	32.58	31.61	32.68	32.80	40.08	37.78	46.76	53.44	60.79	73.47		
	Δ		0.62	1.83	-0.15	-0.09	-0.32	[0.00]	-0.01	2.13	0.37	[0.06]	-0.85	[-0.01]	-1.18	-1.23	-0.80	0.19		
240	O		37.90	28.40	28.04	27.32	33.57	33.96	33.05	34.19	33.45	33.41	39.78	38.22	46.16	52.83	60.46	73.69	81.49	
	C		36.93	26.35	28.20	27.43	33.72	33.97	33.05	31.97	33.29	33.35	40.51	38.23	47.30	54.09	61.67	74.46	81.25	
	Δ		0.97	2.13	-0.16	-0.11	-0.15	[-0.01]	0.00	2.22	0.16	[0.06]	-0.73	[-0.01]	-1.13	-1.25	-1.21	-0.77	0.24	
250	O		38.25	28.90	28.43	27.67	34.09	34.49	33.46	34.66	33.90	33.98	40.29	38.73	46.84	53.52	67.11	74.18	81.73	
	C		37.16	26.38	28.39	27.78	34.03	34.00	33.51	32.13	33.73	33.93	40.94	38.73	47.85	54.72	68.50	75.39	82.97	
	Δ		1.09	2.51	-0.16	-0.11	0.06	[-0.01]	-0.05	2.53	0.17	[0.05]	-0.65	[0.00]	-1.00	-1.20	-1.39	-1.20	-0.84	
260	O				28.84	28.08	34.64	35.06	33.98	35.22	34.57	34.59	41.02	39.27	47.54	54.36	67.91	74.91	82.21	
	C				29.01	28.14	34.29	34.06	34.02	32.45	34.23	34.55	41.37	39.28	48.36	55.35	69.32	76.31	83.29	
	Δ				-0.17	-0.06	0.35	[0.00]	-0.04	2.77	0.34	[0.04]	-0.35	[-0.01]	-0.82	-0.99	-1.41	-1.40	-1.08	
270	O				29.24		35.03	35.67	34.52	35.80	34.87	35.23	41.70	39.87	48.28	55.11	68.85	75.82	83.04	
	C				29.45		34.73	35.66	34.96	32.76	34.77	35.22	41.61	39.87	48.86	55.96	70.11	77.19	84.26	
	Δ				-0.21		0.30	[0.01]	-0.02	3.04	0.10	[0.01]	0.11	[0.00]	-0.60	-0.85	-1.26	-1.37	-1.22	
280	O						35.87	36.31	35.11	36.40	35.41	35.83	42.44	40.91	49.08	55.98	69.84	76.83	84.04	114.03
	C						35.10	36.29	35.14	33.09	35.36	35.92	42.26	40.91	49.42	56.35	70.90	78.08	85.23	113.87
	Δ						0.77	[0.02]	-0.03	3.31	0.05	[-0.09]	0.18	[0.00]	-0.34	-0.37	-1.06	-1.25	-1.19	0.16
290	O						36.53	36.97	35.72	37.04	36.00	36.67	43.18	41.19	49.90	56.90	70.89	77.90	85.18	114.96
	C						35.46	36.86	35.74	33.43	35.98	36.67	43.72	41.19	49.96	56.94	71.78	78.94	86.16	115.15
	Δ						1.07	[0.01]	-0.02	3.61	0.02	[0.00]	-0.54	[0.00]	-0.06	-0.04	-0.89	-1.04	-1.00	-0.20
300	O						37.25	37.64	36.39	37.69	36.64	37.44	43.96	41.86	50.90	57.85	71.98	79.08	86.43	116.14
	C						35.88	37.58	36.38	34.10	36.66	34.46	43.20	41.86	50.52	57.94	71.49	79.61	87.14	116.43
	Δ						1.37	[-0.03]	0.01	3.59	-0.02	[-0.02]	0.76	[0.00]	0.38	-0.09	0.50	-0.73	-0.71	-0.29
310	O												44.76	42.90		57.83	73.15	80.32	87.80	117.57
	C												43.70	42.91		58.50	72.21	80.71	88.13	117.73
	Δ												1.06	[-0.01]		-0.67	0.94	-0.39	-0.33	-0.16
320	O													43.27		58.81	74.34			
	C													43.26		59.19	74.18			
	Δ													[0.01]		-0.38	0.16			
330	O																75.55			
	C																			
	Δ																			
340	O																76.76			
	C																			
	Δ																			
Groups Composition C_p(i) of this composition used to determine group:		a+f+g	a+f+g+h	2a+e+f	2a+2g	2a+2e+g	a+b+f+g+h	2a+2g+h	2a+2g+h+o	2a+e+f+h	2a+e+g	2a+f+g+i	a+2b+f+g+h	4a+6e	a+3b+f+g+h	a+4b+f+g+h	a+6b+f+g+h	a+7b+f+g+h	a+8b+f+g+h	a+13b+f+g+h
		f	f	f	g	g	f	h	o	f	g	i	f	ff	ff	f	f	f	f	f
Source		1	2	2	3	3	4	4	4	4	4	4	5	6	5	5	5	3	3	3

O = observed
C = calculated
Δ = ΔC_p(i) [observed-calculated]

[1] T. M. Powell and W. F. Giauque, J. Amer. Chem. Soc., 61, 2366 (1939).
[2] S. S. Todd and G. S. Parks, J. Amer. Chem. Soc., 59, 134 (1936).
[3] L. Guttman and K. S. Pitzer, J. Amer. Chem. Soc., 67, 324 (1945).
[4] S. Todd, G. D. Oliver, and H. M. Huffman, J. Amer. Chem. Soc., 69, 1519 (1947).
[5] J. P. McCullough, H. L. Finke, R. E. Gross, J. F. Messerly, and G. Waddington, J. Phys. Chem., 61, 289 (1957).
[6] D. W. Scott, H. L. Finke, J. P. McCullough, M. E. Gross, J. F. Messerly, R. E. Pennington, and G. Waddington, J. Amer. Chem. Soc., 77, 4993 (1955).

Table VII. Comparison of Calculated and Observed Values of Heat Capacity at Constant Pressure for Liquid Dienes as a Temperature Function (in cal mol^{-1} K^{-1})

Temp., °K		1,2-butadiene	1,3-butadiene	1,2-pentadiene	1,3-pentadiene (trans)	1,3-pentadiene (cis)	1,4-pentadiene	2,3-pentadiene	3-methyl-1,2-butadiene	2-methyl-1,3-butadiene
140	O	26.31		31.33		31.10	30.39			29.24
	C	26.95		30.90		31.12	30.38			29.24
	Δ	-0.64		0.43		-0.02	[0.01]			[0.00]
150	O	26.24		31.29		30.86	30.21	33.48		29.25
	C	26.82		30.93		30.85	30.32	31.92		29.25
	Δ	-0.58		0.36		0.03	[-0.01]	0.56		[0.00]
160	O	26.21		31.34		30.75	30.29	32.46	31.20	29.35
	C	26.74		31.01		30.67	30.31	31.97	31.54	29.33
	Δ	-0.53		0.33		0.08	[-0.02]	0.49	-0.34	[0.02]
170	O	26.21	24.63	31.43		30.69	30.26	32.51	31.35	29.49
	C	26.71	24.83	31.16		30.56	30.26	32.10	31.47	29.49
	Δ	-0.50	-0.20	0.27		0.10	[0.00]	0.41	-0.12	[0.00]
180	O	26.23	24.76	31.56		30.67	30.46	32.80	31.55	29.71
	C	26.73	24.92	31.35		30.57	30.46	32.29	31.47	29.75
	Δ	-0.51	-0.16	0.21		0.10	[0.00]	0.51	0.08	[-0.04]
190	O	26.56	24.92	31.74	31.13	30.73	30.61	32.72	31.77	29.96
	C	26.79	25.04	31.59	31.02	30.64	30.61	32.58	31.52	29.99
	Δ	-0.51	-0.12	0.15	0.11	0.09	[0.00]	0.17	0.24	[0.00]
200	O	26.38	25.11	31.95	31.32	30.89	30.84	32.89	32.05	30.35
	C	26.89	25.18	31.86	31.23	30.78	30.81	32.87	31.65	30.33
	Δ	-0.51	-0.07	0.09	-0.01	0.09	[0.03]	0.02	0.40	[0.02]
210	O	26.54	25.33	32.24	31.40	31.06	31.10	33.08	32.35	30.74
	C	27.02	25.35	32.19	31.50	31.00	31.08	33.24	31.81	30.73
	Δ	-0.48	-0.02	0.05	-0.10	0.06	[0.04]	-0.16	0.54	[0.01]
220	O	26.76	25.59	32.54	31.69	31.33	31.38	33.32	32.71	31.19
	C	27.20	25.56	32.51	31.84	31.26	31.35	33.67	32.03	31.19
	Δ	-0.44	0.03	0.03	-0.15	0.05	[0.03]	-0.35	0.68	[0.00]
Source		1	2	3	3	3	3	3	3	3

Temp., °K		1,2-butadiene	1,3-butadiene	1,2-pentadiene	1,3-pentadiene (trans)	1,3-pentadiene (cis)	1,4-pentadiene	2,3-pentadiene	3-methyl-1,2-butadiene	2-methyl-1,3-butadiene
230	O	27.03	25.92	32.86	32.02	31.65	31.52	33.61	33.10	31.66
	C	27.41	25.81	32.87	32.23	31.62	31.66	34.15	32.28	31.69
	Δ	-0.38	0.11	-0.01	-0.21	0.03	[-0.14]	-0.54	0.82	[0.01]
240	O	27.33	26.25	33.25	32.43	32.02	32.09	33.94	33.49	32.21
	C	27.64	26.06	33.25	32.67	32.00	32.07	34.67	32.57	32.23
	Δ	-0.31	0.19	0.00	-0.24	0.02	0.02	-0.73	0.92	-0.01
250	O	27.53	26.65	33.67	32.90	32.43	32.51	34.29	33.95	32.78
	C	27.89	26.36	33.65	33.13	32.40	32.49	35.03	33.49	32.80
	Δ	-0.34	0.29	0.02	-0.22	0.03	[0.02]	-0.94	1.07	[-0.02]
260	O	28.00	27.12	34.13	33.40	32.91	32.97	34.67	34.43	33.44
	C	28.17	26.69	34.05	33.66	32.90	31.96	35.63	33.91	33.43
	Δ	-0.17	0.43	0.08	-0.26	0.01	[0.01]	-1.16	1.52	[0.01]
270	O	28.40	27.63	34.59	33.93	33.41	33.49	35.07	34.91	34.09
	C	28.46	27.05	34.49	34.20	33.39	33.46	36.46	33.56	34.09
	Δ	-0.06	0.58	0.14	-0.27	0.02	[0.03]	-1.39	1.35	[0.00]
280	O	28.86		35.07	34.53	33.94	34.00	35.53	35.42	34.80
	C	28.77		34.88	34.77	33.92	34.06	37.12	33.92	34.78
	Δ	0.08		0.22	-0.24	0.02	[-0.06]	-1.59	1.50	[0.01]
290	O	29.33		35.67	35.13	34.51	34.58	36.01	35.94	35.59
	C	29.08		35.25	35.36	34.48	34.58	37.81	34.27	35.31
	Δ	0.27		0.32	-0.23	0.03	[-0.01]	-1.80	1.67	[0.01]
300	O				35.73	35.13	35.20	36.53	36.31	36.35
	C				35.95	35.00	35.20	38.52	34.63	35.26
	Δ				-0.20	0.13	0.00	-1.99	1.68	[-0.01]
310	O				36.49	35.81		37.05	37.06	
	C				36.54	35.57		39.21	34.97	
	Δ				-0.05	0.24		-2.16	2.09	
Source		1	2	3	3	3	3	3	3	3

O = observed
C = calculated
Δ = C_p(i) [observed-calculated]

[1] G. Aston and G. J. Szasz, J. Amer. Chem. Soc., 69, 3108 (1947).
[2] Thermal Data Book, American Petroleum Institute, Petroleum Refining, p. 78 1, 3 (1966).
[3] F. Messerly, S. S. Todd, and G. B. Guthrie, J. Chem. and Eng. Data, 11, 371 (1970).

+ γ. Typical agreement between observed and calculated liquid heat capacity for the case of 1-*cis*-3-pentadiene is demonstrated in Figure 1.

Group Value Determination

The simplest case for determining group values is the case of straight chain alkanes. Here there are only two groups: terminal methyl (group a) and secondary methylene (group b). The numerical values for these two groups were simultaneously computed by trial and error to get the best fit between the experimental and the calculated value using data on 17 different straight chain alkanes. This type of calculation was made for every 10 K temperature interval at the normal liquid range. The group values were then fitted into a cubic polynomial expression

Table VIII. Comparison of Calculated and Observed Values of Heat Capacity at Constant Pressure for Liquid Cyclopentane Derivatives as a Temperature Function (in cal mol^{-1} K^{-1})

Temp. °K		cyclo-pentane	methylcyclo-pentane	ethylcyclo-pentane	1,1-dimethyl-cyclopentane	1-cis-2-dimethyl-2-cyclopentane	1-trans-3-dimethyl-2 cyclopentane	n-propyl-cyclopentane	n-butyl-cyclopentane	n-decyl-cyclopentane
140	O		29.89	35.07						
	C		30.11	35.17						
	Δ		-0.22	-0.10						
150	O		29.98	35.24			34.77			
	C		30.11	35.42			34.07			
	Δ		-0.13	-0.18			0.70			
160	O		30.14	35.43			35.17	41.50		
	C		30.19	35.73			34.08	41.27		
	Δ		-0.05	-0.30			1.09	0.23		
170	O		30.35	35.69			35.62	41.82	48.38	
	C		30.32	36.08			34.21	41.83	47.59	
	Δ		0.03	-0.39			1.41	-0.01	0.79	
180	O	23.88	30.61	36.01			36.09	42.19	48.73	
	C	26.64	30.54	36.49			34.45	42.44	48.38	
	Δ	-2.76	0.07	-0.48			1.64	-0.25	0.35	
190	O	24.14	30.92	36.40			36.61	42.64	49.15	
	C	26.86	30.83	36.95			34.80	43.07	49.19	
	Δ	-2.72	0.09	-0.55			1.81	-0.43	-0.04	
200	O	24.45	31.31	36.89			37.18	43.17	49.66	
	C	27.10	31.17	37.45			35.24	43.73	50.01	
	Δ	-2.65	0.14	-0.56			1.94	-0.56	-0.35	
210	O	24.84	31.78	37.41	36.91		37.80	43.76	50.28	
	C	27.38	31.57	37.99	35.77		35.77	44.41	50.84	
	Δ	-2.54	0.21	-0.58	1.14		2.03	-0.65	-0.56	
220	O	25.28	32.29	38.02	37.57		38.45	44.44	50.95	
	C	27.68	32.02	38.58	36.51		36.39	45.14	51.69	
	Δ	-2.40	0.27	-0.56	1.06		2.06	-0.70	-0.74	
230	O	25.76	32.85	38.66	38.37	39.31	39.08	45.18	51.72	
	C	28.01	32.55	39.23	37.32	37.09	37.09	45.91	52.58	
	Δ	-2.25	0.30	-0.57	1.05	2.22	1.99	-0.73	-0.86	
240	O	26.28	33.46	39.25	39.28	40.05	39.84	45.99	52.56	
	C	28.37	33.12	39.91	38.19	37.87	37.87	46.70	53.49	
	Δ	-2.09	0.34	-0.66	1.09	2.18	1.97	-0.71	-0.93	
250	O	26.87	34.13	40.13	40.10	40.81	40.58	46.85	53.74	
	C	28.76	33.74	40.63	39.11	38.72	38.72	47.52	54.41	
	Δ	-1.89	0.39	-0.50	0.99	2.09	1.86	-0.67	-0.67	
260	O	27.52	34.84	40.96	41.00	41.65	41.52	47.76	54.44	97.16
	C	29.18	34.41	41.40	40.07	39.63	39.63	48.39	55.37	97.30
	Δ	-1.66	0.43	-0.44	0.93	2.02	1.89	-0.63	-0.93	-0.14
270	O	28.22	35.60	41.81	41.93	42.54	42.37	48.74	55.47	98.00
	C	29.61	35.09	42.17	41.03	40.59	40.59	49.25	56.32	98.78
	Δ	-1.39	0.51	-0.36	0.90	1.95	1.78	-0.51	-0.85	-0.78
280	O	28.93	36.40	42.70	42.91	43.45	43.31	49.75	56.55	99.22
	C	30.09	35.85	43.01	42.03	41.60	41.60	50.17	57.33	100.30
	Δ	-1.16	0.55	-0.31	0.88	1.85	1.71	-0.42	-0.78	-1.08
290	O	29.68	37.22	43.66	43.83	44.29	44.22	50.80	57.68	100.65
	C	30.59	36.63	43.87	43.03	42.66	42.66	51.11	58.36	101.81
	Δ	-0.91	0.59	-0.21	0.80	1.63	1.56	-0.31	-0.68	-1.16
300	O	30.44	38.09	44.71	44.83	45.12	45.23	51.89	58.86	102.24
	C	31.12	37.44	44.76	44.02	43.76	43.76	52.08	59.41	103.34
	Δ	-0.68	0.65	-0.05	0.81	1.36	1.47	-0.19	-0.55	-1.10
310	O							53.00	60.07	103.99
	C							53.09	60.49	104.91
	Δ							-0.09	-0.42	-0.92
320	O							54.14	61.29	105.72
	C							54.13	61.61	106.52
	Δ							0.01	-0.32	-0.80
330	O							55.29	62.52	
	C							55.19	62.76	
	Δ							0.10	-0.24	
340	O							56.44	63.79	
	C							56.28	63.94	
	Δ							0.16	-0.15	
350	O							57.61	65.07	
	C							57.40	65.15	
	Δ							0.21	-0.08	
360	O							58.80	66.32	
	C							58.55	66.39	
	Δ							0.25	-0.07	
370	O							59.98	67.58	
	C							59.73	67.68	
	Δ							0.25	-0.10	
Source		1	1	2	2	2	2	3	3	3

O = observed
C = calculated
Δ = $\Delta C_p(\ell)$ [observed-calculated]

[1] D. R. Douslin and H. M. Huffman, J. Amer. Chem. Soc., 68, 173 (1946).
[2] M. E. Gross, G. D. Oliver, and H. M. Huffman, J. Amer. Chem. Soc., 75, 2801 (1953).
[3] J. F. Messerly, S. S. Todd, and H. L. Fink, J. Phys. Chem., 69, 353 (1965).

with the aid of a polynomial fit program provided by RAIR Company of Palo Alto, Calif. The observed and the calculated values of the liquid heat capacity of straight chain alkanes are presented in Table III in temperature increments of 10 K.

For tertiary alkanes, only one additional group is needed (group c); thus, the average value of this group was taken as the average value computed from the experimental data on 15 tertiary alkanes. The polynomial fit technique was applied in this case as for the preceding groups. The data on the tertiary alkanes are presented in Table IV. In a similar way, group d was determined from the experimental data on six alkanes containing quaternary carbon as presented in Table V.

In the case of monoolefins, seven more groups should be determined (*2*). Of these groups, six are independent of the rest since certain of them always occur together in compounds; thus, only six independent data are needed to bring these compounds within the scheme. Arbitrarily and without reducing any accuracy, the group that contains C atoms attached to three H atoms and

Table IX. Comparison of Calculated and Observed Values of Heat Capacity at Constant Pressure for Liquid Cyclohexane Derivatives as a Temperature Function (in cal mol^{-1} K^{-1})

Temp. °K		cyclohexane	methyl-cyclohexane	ethyl-cyclohexane	1,1-dimethyl-cyclohexane	cis-1,2-dimethyl cyclohexane	trans-1,2-dimethyl-cyclohexane	cis-1,3-dimethyl-cyclohexane	trans-1,3-dimethyl-cyclohexane	cis-1,4-dimethyl-cyclohexane	trans-1,4-dimethyl-cyclohexane	n-propyl-cyclohexane	n-butyl-cyclohexane	n-heptyl-cyclohexane	n-decyl-cyclohexane	n-dodecyl-cyclohexane
150	O		33.44													
	C		33.05													
	Δ		0.39													
160	O		33.94													
	C		33.74													
	Δ		0.20													
170	O		34.46	38.90												
	C		34.41	40.16												
	Δ		0.05	-0.86												
180	O		35.00	39.90								46.10				
	C		35.07	41.34								47.28				
	Δ		-0.07	-1.44								-1.19				
190	O		35.56	40.54			40.00		41.25			46.79				
	C		35.70	41.68			39.67		39.67			47.80				
	Δ		-0.14	-1.14			0.33		1.58			-1.01				
200	O		36.14	41.22			40.68	40.76	41.91	42.24		47.54	53.73			
	C		36.35	42.11			40.41	40.41	40.41	40.41		48.39	54.67			
	Δ		-0.21	-0.89			0.27	0.35	1.50	1.83		-0.85	-0.94			
210	O		36.76	41.97			41.40	41.46	42.62	42.84		48.36	54.58			
	C		36.99	42.64			41.19	41.19	41.19	41.19		49.07	55.49			
	Δ		-0.23	-0.67			0.21	0.27	1.43	1.65		-0.71	-0.91			
220	O		37.43	42.77			42.18	42.21	43.37	43.51		49.23	55.49			
	C		37.64	43.28			42.00	42.00	42.00	42.00		49.84	56.39			
	Δ		-0.21	-0.51			0.18	0.21	1.37	1.51		-0.61	-0.90			
230	O		38.17	43.62		43.64	43.00	43.05	44.15	44.25		50.17	56.47			
	C		38.30	43.99		43.84	43.84	43.84	43.84	43.84		50.67	57.34			
	Δ		-0.13	-0.37		0.80	0.16	0.21	1.31	1.41		-0.50	-0.87			
240	O		38.96	44.52	43.83	44.48	43.87	43.97	45.00	45.00	44.60	59.16	57.54	77.85		
	C		38.98	44.80	44.05	43.73	43.73	43.73	43.73	43.73	43.73	59.59	58.38	78.75		
	Δ		-0.02	-0.28	-0.22	0.75	0.14	0.24	1.27	1.27	0.87	-0.43	-0.84	-0.90		
250	O		39.78	45.48	44.79	45.38	44.92	44.92	45.88	45.86	45.44	52.21	58.66	79.21		
	C		39.66	45.70	45.03	44.64	44.64	44.64	44.64	44.64	44.64	52.59	59.48	80.16		
	Δ		0.12	-0.22	-0.24	0.74	0.18	0.28	1.24	1.22	0.80	-0.38	-0.82	-0.95		
260	O		40.62	46.46	45.80	46.32	45.92	45.92	46.84	46.78	46.32	53.31	59.82	80.62		
	C		40.38	46.68	46.04	45.61	45.61	45.61	45.61	45.61	45.61	53.67	60.65	81.62		
	Δ		0.24	-0.22	-0.24	0.71	0.21	0.31	1.23	1.17	0.71	-0.36	-0.83	-1.00		
270	O		41.50	47.49	46.85	47.28	46.88	46.96	47.82	47.75	47.28	54.43	61.04	82.15		
	C		41.12	47.75	47.06	46.61	46.61	46.81	46.61	46.61	46.61	54.83	61.90	83.13		
	Δ		0.38	-0.26	-0.21	0.67	0.27	0.35	1.21	1.14	0.67	-0.38	-0.86	-0.98		
280	O	35.69	42.40	48.58	47.94	48.29	47.96	48.02	48.85	48.75	48.29	55.63	62.34	83.88	104.93	
	C	36.15	41.91	48.90	48.16	47.66	47.66	47.66	47.66	47.56	47.66	56.06	63.22	84.71	106.19	
	Δ	-0.46	0.49	-0.34	-0.22	0.63	0.30	0.36	1.19	1.09	0.63	-0.43	-0.88	-1.83	-1.26	
290	O	36.61	43.33	49.68	49.05	49.35	49.08	49.14	49.95	49.79	49.35	56.84	63.66	85.52	106.63	
	C	36.69	42.73	50.15	49.13	48.76	48.76	48.76	48.76	48.76	48.76	57.39	64.64	86.37	108.09	
	Δ	-0.08	0.60	-0.47	-0.08	0.59	0.32	0.38	1.19	1.03	0.59	-0.55	-0.98	-0.85	-1.46	
300	O	37.53	44.28	50.84	50.23	50.44	50.27	50.24	51.09	50.90	50.46	58.08	65.03	87.16	108.42	123.21
	C	37.28	43.60	51.50	50.18	49.92	49.92	49.92	49.92	49.92	49.92	58.82	66.15	88.11	110.08	124.73
	Δ	0.25	0.68	-0.66	0.05	0.52	0.35	0.32	1.17	0.98	0.54	-0.74	-1.12	-0.95	-1.66	-1.52
310	O			52.02								59.36	66.42		110.23	125.23
	C			52.91								59.32	67.72		112.13	126.94
	Δ			-0.89								0.04	-1.30		-1.90	-1.71
320	O											60.65	67.83			
	C											60.45	67.94			
	Δ											0.20	-0.11			
330	O											61.98	69.25			
	C											61.65	69.21			
	Δ											0.33	0.04			
340	O											63.31	70.69			
	C											62.92	70.57			
	Δ											0.39	0.12			
350	O											64.64	72.14			
	C											64.26	72.00			
	Δ											0.38	0.14			
360	O											65.98	73.59			
	C											65.69	73.54			
	Δ											0.29	0.05			
370	O											67.31	75.06			
	C											67.22	75.17			
	Δ											0.09	-0.11			
380	O											68.64				
	C											68.85				
	Δ											-0.21				
Source		1	2	3	3	3	3	3	3	3	3	4	4	5	4	5

O = observed
C = calculated
Δ = $\Delta C_p(l)$ [observed-calculated]

[1] R. A. Ruehrwein and H. M. Huffman, J. Amer. Chem. Soc., 65, 1620 (1943).
[2] D. R. Douslin and H. M. Huffman, J. Amer. Chem. Soc., 68, 173 (1946).
[3] H. M. Huffman, S. S. Todd, and G. D. Oliver, J. Amer. Chem. Soc., 71, 584 (1949).
[4] H. L. Fink, J. F. Messerly, and S. S. Todd, J. Phys. Chem., 69, 2094 (1965).
[5] G. S. Parks, G. E. Moore, M. L. Renquist, B. F. Naylor, L. A. MacClaine, P. S. Fujii, and J. A. Hatton, J. Amer. Chem. Soc., 71, 3386 (1949).

to another atom (double bonded C atom or any heteroatom) is defined as identical with group a (*3*). Out of the six independent groups, values have been assigned to only five (groups "e"–"i"), since no experimental data are available on compounds containing $C(C_d)(C)_3$. The value for group e is based only on 2,3-dimethylbutene-2, and the small deviation is the result of the polynomial fit. The value of group g is based on averaging the group value calculated from *trans*-2-butene and 2-methyl-2-butene. The value of group f was calculated from the average value of 12 different 1-alkenes; h and i values are based only on *trans*-2-pentene and 3-methyl-1-butene, respectively. Since group additivity schemes are unable to distinguish between cis and trans isomers, correction for cis interaction around the double bond is needed. The correction parameter α was calculated from the differences between *cis*- and *trans*-2-butene and between *cis*- and *trans*-2-pentene. The experimental and the observed $C_p(l)$ of alkenes are presented in Table VI.

For polyalkenes, four additional groups should be evaluated. The values of groups j and k are each based on four different dienes, and the values of m and n were derived from the experimental $C_p(l)$ of 1,4-pentadiene and 2-methyl-1,3-butadiene, respectively. The comparison between the experimental and observed data is shown in Table VII.

Relatively many experimental data are available on liquid heat capacities of cyclopentane and cyclohexane derivatives. Since in these cases all group values are known, the only need is for ring corrections. Corrections computed for the cyclopentane ring are based on data from nine cyclopentane derivatives (correction β), and corrections for the cyclohexane ring (γ) are from experimental data on 15 cyclohexane derivatives. Comparisons of experimental and observed data are given in Tables VIII and IX. For other cyclic compounds, $C_p(l)$ was determined experimentally only for a limited number of compounds. Ring corrections have been computed for every different ring. Correction parameters for these rings are given in Table II, and the agreement with the observed values is demonstrated in Table X. It is worth noting that no need was found for cis correction in the case of *cis*- and *trans*-decahydronaphthalene.

For liquid aromatics, four additional groups have been determined. The value of the basic aromatic group $(C_B(C_B)_2H$ or group n) is based on the $C_p(l)$ of benzene. Since other liquid aromatics have different normal liquid ranges, n values were extrapolated to wider temperature range, so that they could be used for determining the other three groups: o, p, and q. For 1,2,3,4-tetrahydronaphthalene, correction was calculated for the side nonaromatic ring. The data on liquid aromatic heat capacities are summarized in Table XI.

Liquid heat capacity data on alkynes are available only for 1- and 2-butynes. The data on 2-butyne were used to calculate the values of group r, and data on 1-butyne were used to calculate the values of group g. In the case of 1-butyne, we must assume that the value of $C(C_t)(C)(H)_2$ is similar to the value of group k.

Table X. Comparison of Calculated and Observed Values of Heat Capacity at Constant Pressure for Liquid Hydrocarbon Rings as a Temperature Function (in cal mol^{-1} K^{-1})

Temp. °K		cyclo-propane	cyclo-butane	spiro-pentane	cyclo-pentene	cyclo-hexene	cyclo-heptane	cyclo-heptatriene	cyclo-octane	cyclo-octatetraene	trans-decahydro-naphthalene	cis-decahydro-naphthalene
140	O				23.75							
	C				23.80							
	Δ				[0.15]							
150	O	18.14			23.62							
	C	18.13			23.55							
	Δ	[0.01]			[0.07]							
160	O	18.01			23.57							
	C	18.03			23.56							
	Δ	[-0.02]			[0.01]							
170	O	17.97		25.81	23.60	27.78						
	C	17.98		25.82	23.62	27.74						
	Δ	[-0.01]		[-0.01]	[-0.02]	[0.04]						
180	O	18.01		26.02	23.72	28.15						
	C	18.00		26.01	23.75	28.16						
	Δ	[0.01]		[0.01]	[-0.03]	[-0.01]						
190	O	18.08	21.47	26.26	23.88	28.58						
	C	18.07	21.46	26.26	23.92	28.60						
	Δ	[0.01]	[0.01]	[0.00]	[-0.04]	[-0.02]						
200	O	18.23	21.77	26.57	24.12	29.03		33.60				
	C	18.22	21.76	26.57	24.16	29.07		33.60				
	Δ	[0.01]	[-0.01]	[0.00]	[-0.04]	[-0.04]		[0.00]				
210	O	18.42	22.09	26.94	24.42	29.54		34.02				
	C	18.43	22.10	26.94	24.45	29.57		34.02				
	Δ	[-0.01]	[-0.01]	[0.00]	[-0.03]	[-0.03]		[0.00]				
220	O	18.71	22.41	27.36	24.80	30.09		34.46				
	C	18.72	22.41	27.36	24.79	30.10		34.47				
	Δ	[-0.01]	[0.00]	[0.00]	[0.01]	[-0.01]		[-0.01]				
230	O	19.07	22.76	27.83	25.24	30.68		34.94				
	C	19.07	22.75	27.83	25.18	30.68		34.94				
	Δ	[0.00]	[0.01]	[0.00]	[0.06]	[0.02]		[0.00]				
240	O	19.52	23.12	28.35	25.72	31.32		35.44				48.26
	C	19.51	23.11	28.36	25.63	31.26		35.44				48.15
	Δ	[0.01]	[0.01]	[-0.01]	[0.09]	[0.06]		[0.00]				[0.11]
250	O		23.50	28.91	26.25	31.99		35.96			48.30	49.33
	C		23.51	28.92	26.13	31.90		35.95			48.99	48.99
	Δ		[-0.01]	[-0.01]	[0.12]	[0.09]		[0.01]			-0.69	0.34
260	O		23.93	29.53	26.81	32.70		36.52			49.51	50.47
	C		23.95	29.53	26.68	32.51		36.53			50.03	50.04
	Δ		[-0.02]	[0.00]	[0.13]	[0.19]		[-0.01]			-0.52	0.43
270	O		24.46	30.18	27.40	33.44	40.65	37.12		42.63	50.79	51.71
	C		24.45	30.17	27.90	33.94	40.65	37.12		42.63	51.20	51.20
	Δ		[0.01]	[0.01]	[-0.50]	[-0.50]	[0.00]	[0.00]		[0.00]	-0.41	0.51
280	O		25.02	30.85	28.03	34.20	41.54	37.74		43.19	52.12	52.99
	C		25.02	30.84	27.92	34.09	41.54	37.73		43.19	52.48	52.48
	Δ		[0.00]	[0.01]	[0.11]	[0.11]	[0.00]	[0.01]		[0.00]	-0.36	0.51
290	O			31.55	28.70	34.99	42.46	38.37	50.68	43.77	53.48	53.33
	C			31.55	28.62	34.92	42.46	38.37	59.69	43.77	53.85	53.85
	Δ			[0.00]	[0.08]	[0.07]	[0.00]	[0.00]	[-0.01]	[0.00]	-0.37	-0.52
300	O			32.28	29.38	35.80	43.36	39.03	51.68	44.37	54.87	55.70
	C			32.28	29.37	35.80	43.36	39.03	51.64	43.57	55.27	55.27
	Δ			[0.00]	[0.01]	[0.00]	[0.00]	[0.00]	[0.04]	[0.80]	-0.40	0.43
310	O			33.03				39.72	52.71	45.00	56.31	57.11
	C			33.03				39.72	52.77	44.99	56.94	56.74
	Δ			[0.00]				[0.00]	[-0.06]	[0.01]	-0.63	0.37
320	O							40.45	53.76	45.81	57.76	58.54
	C							40.45	53.74	45.63	58.22	58.22
	Δ							[0.00]	[0.04]	[-0.02]	-0.46	0.32
330	O								54.86	46.23	59.23	59.98
	C								54.87	46.23	59.68	59.68
	Δ								[-0.01]	[0.00]	-0.45	0.30
340	O										60.71	61.43
	C										61.11	61.11
	Δ										-0.40	0.32
350	O										62.19	62.87
	C										62.49	62.49
	Δ										-0.30	0.38
Source		1	1	2	3	3	4	4	4	5	6	6

O = observed
C = calculated
Δ = $\Delta C_p(\ell)$ [observed-calculated]

[1]Technical Data Book, American Petroleum Institute Petroleum Refining, p. 7E1.1 (1966).
[2]D. W. Scott, H. L. Finke, W. H. Hubbard, J. P. McCullough, M. E. Gross, K. D. Williamson, G. Huddington, and H. M. Huffman, J. Amer. Chem. Soc., 72, 4664 (1950).
[3]H. M. Huffman, M. Eaton, and G. D. Oliver, J. Amer. Chem. Soc., 70, 2811 (1948).
[4]H. L. Finke, D. W. Scott, M. E. Gross, J. F. Messerly, and G. Waddington, J. Amer. Chem. Soc., 78, 5469 (1956).
[5]D. W. Scott, M. E. Gross, G. D. Oliver, and H. M. Huffman, J. Amer. Chem. Soc., 71, 1634 (1949).
[6]J. P. McCullough, H. L. Finke, J. F. Messerly, S. S. Todd, T. C. Kincheloe, and G. Waddington, J. Phys. Chem., 61, 1105 (1957).

Table XI. Comparison of Calculated and Observed Values of Heat Capacity at Constant Pressure for Liquid Aromatic Hydrocarbons as a Temperature Function (in cal mol^{-1} K^{-1})

Temp. °K		benzene	toluene	ethyl-benzene	n-propyl-benzene	n-butyl-benzene	p-xylene	1,2,3-trimethyl-benzene	1,2,4-trimethyl-benzene	1,3,5-trimethyl-benzene	penta-methyl-benzene	naphthalene	1-methyl-naphthalene	2-methyl-naphthalene	1,2,3,4-tetrahydro-naphthalene
180	O		32.39	37.63	42.67										
	C		32.08	37.90	43.55										
	Δ		0.31	0.03	0.12										
190	O		32.53	37.91	43.95	49.60									
	C		32.46	37.73	43.85	49.97									
	Δ		0.07	0.18	0.10	-0.37									
200	O		32.75	38.26	44.33	50.05									
	C		32.88	37.97	44.25	50.53									
	Δ		-0.13	0.29	0.08	-0.48									
210	O		33.02	38.67	44.79	50.59									
	C		33.32	38.30	44.73	51.15									
	Δ		-0.30	0.37	0.06	-0.56									
220	O		33.36	39.15	45.32	51.23									
	C		33.78	38.71	45.27	51.82									
	Δ		-0.42	0.44	0.05	-0.59									
230	O		33.75	39.71	45.91	51.93			46.25	44.36					
	C		34.24	39.17	45.85	52.52			45.15	45.15					
	Δ		-0.49	0.54	0.06	-0.59			1.10	-0.79					
240	O		34.18	40.29	46.56	52.69			46.89	45.04					45.75
	C		34.74	39.72	46.51	53.30			45.42	45.42					45.73
	Δ		-0.56	0.57	0.05	-0.61			1.47	-0.38					[0.02]
250	O		34.68	40.90	47.26	53.52		47.98	47.56	45.82			49.06		46.76
	C		35.26	40.33	46.22	54.11		45.83	45.83	45.83			48.96		46.82
	Δ		-0.58	0.57	1.04	-0.59		2.15	1.73	-0.01			0.10		[-0.06]
Source		1	2	3	4	4	5	6	7	8	9	10	10	10	10

Table XI Continued

Temp. °K		benzene	toluene	ethyl-benzene	n-propyl-benzene	n-butyl-benzene	p-xylene	1,2,3-trimethyl-benzene	1,2,4-trimethyl-benzene	1,3,5-trimethyl-benzene	penta-methyl-benzene	naphthalene	1-methyl-naphthalene	2-methyl-naphthalene	1,2,3,4-tetrahydro-naphthalene
260	O		35.21	41.59	48.02	54.40		48.73	48.26	46.56			49.94		47.79
	C		35.81	41.00	47.98	54.97		46.35	46.35	46.35			49.95		47.77
	Δ		-0.60	0.59	0.04	-0.57		2.38	1.93	0.31			-0.01		[0.02]
270	O		35.78	42.27	48.64	55.33		49.49	49.03	47.51			50.85		48.66
	C		36.38	41.71	48.79	55.87		46.99	46.99	46.99			50.93		48.62
	Δ		-0.60	0.56	0.05	-0.54		2.50	2.04	0.53			-0.08		[0.23]
280	O	31.59	36.39	43.03	49.69	56.31		50.28	49.83	48.39			51.81		49.18
	C	31.59	36.97	42.47	49.63	56.79		47.72	47.72	47.72			51.89		49.40
	Δ	[0.00]	-0.58	0.56	0.06	-0.48		2.56	2.11	0.67			-0.08		[-0.21]
290	O	32.10	37.04	43.79	50.58	57.31	42.85	51.06	50.57	49.39			52.79		49.93
	C	32.11	37.58	43.26	50.50	57.75	43.05	48.53	48.53	48.53			52.85		50.14
	Δ	[-0.01]	-0.54	0.53	0.08	-0.44	-0.20	2.53	2.04	0.76			-0.06		[-0.21]
300	O	32.62	37.70	44.53	51.49	58.36	43.59	51.89	51.54	50.90			53.68		51.06
	C	32.62	38.22	44.09	51.41	58.73	45.81	49.40	49.40	49.40			53.80		50.86
	Δ	[0.00]	-0.52	0.54	0.08	-0.37	-2.22	2.49	2.14	0.90			0.02		[0.17]
310	O	33.16	38.40		52.43	59.44	44.33						54.86	54.66	51.97
	C	33.15	38.88		52.34	59.74	44.61						54.75	54.75	51.64
	Δ	[0.01]	-0.48		0.09	-0.30	-0.28						0.11	-0.09	[0.33]
320	O	33.69	39.12		53.38	60.54	45.13						55.90	55.57	52.18
	C	33.70	39.57		53.28	60.77	45.62						55.70	55.70	52.46
	Δ	[-0.01]	-0.45		0.10	-0.23	-0.49						0.20	-0.13	[-0.28]
330	O	34.26	39.96		54.34	61.63	45.84						56.85	56.57	53.33
	C	34.27	40.29		54.25	61.82	46.31						56.66	56.66	53.38
	Δ	[-0.01]	-0.43		0.09	-0.19	-0.37						0.29	-0.09	[-0.06]
340	O	34.87	40.58		55.32	62.73	46.71				68.61		57.99	57.56	54.47
	C	34.87	41.03		55.22	62.88	47.12				65.67		57.62	57.62	54.41
	Δ	[0.00]	-0.45		0.10	-0.15	-0.41				2.94		0.36	-0.06	[-0.06]
350	O	35.50	41.28		56.31	63.83	47.60				69.63		59.03	58.56	
	C	35.50	41.79		56.19	63.94	48.06				66.96		58.57	58.57	
	Δ	[0.00]	-0.50		0.13	-0.11	-0.46				2.67		0.46	-0.01	
360	O		42.07		57.31	64.83	48.54				70.66	53.84		59.56	
	C		42.59		57.17	65.02	48.99				68.19	53.14		59.54	
	Δ		-0.52		0.14	-0.09	-0.45				2.49	-0.80		0.02	
370	O				58.37	66.01	49.45				71.72	53.46		60.55	
	C				58.14	66.09	49.90				69.35	54.03		60.51	
	Δ				0.23	-0.08	-0.45				2.37	-0.57		0.04	
380	O					67.12	50.40				73.04			61.55	
	C					67.16	50.80				70.42			61.49	
	Δ					-0.04	-0.40				2.62			0.06	
390	O						51.32				74.46			62.55	
	C						51.69				71.50			62.49	
	Δ						-0.37				2.96			0.06	
400	O						52.23							63.55	
	C						52.57							63.50	
	Δ						-0.34							0.05	
Groups Composition $C_p(\ell)$ of this compound used to determine group:		6n	5n+a+o	5n+o+a+p	5n+o+b+a+p	5n+o+2b+a+p	4n+2a+2o	3n+3a+3o	3n+3a+3o	3n+3a+3o	1n+5a+5o	8n+8q	7n+8q+o+a	7n+8q+o+a	4n+8o+5b+8q+a
Source		1	2	3	4	4	5	6	7	8	9	10	10	10	10

O = observed
C = calculated
Δ = $\Delta C_p(\ell)$ [observed-calculated]

[1] O. D. Oliver, H. Eaton, and H. M. Huffman, J. Amer. Chem. Soc., 70, 1058 (1948).
[2] D. W. Scott, G. B. Guthrie, J. F. Messerly, S. S. Todd, W. T. Berg, I. A. Hossenlopp, and J. P. McCullough, J. Phys. Chem., 66, 911 (1962).
[3] A. F. Forziati, R. J. Mair, and F. D. Rossini, J. Res. Nat. Bur. Stan., 35, 313 (1945).
[4] J. F. Messerly, S. S. Todd, and H. L. Finke, J. Phys. Chem., 62, 4304 (1958).
[5] E. J. Cornuccini and D. C. Gitmings, J. Amer. Chem. Soc., 69, 2291 (1947).
[6] H. D. Taylor, H. B. Johnson, and J. E. Kilpatrick, J. Chem. Phys., 25, 1283 (1957).
[7] H. B. Putnam and J. E. Kilpatrick, J. Chem. Phys., 27, 1075 (1957).
[8] H. B. Taylor and J. E. Kilpatrick, J. Chem. Phys., 26, 1628 (1956).
[9] J. D. Perry and S. S. Thomas, J. Phys. Chem., 27, 966 (1959).
[10] J. P. McCullough, H. L. Finke, J. F. Messerly, S. S. Todd, T. C. Kincheloe, and G. Waddington, J. Phys. Chem., 61, 1105 (1957).

Table XII. Comparison of Calculated and Observed Values of Heat Capacity at Constant Pressure for Liquid Alkynes as a Temperature Function (in cal mol^{-1} K^{-1})

Temp. °K		1-butyne	2-butyne
150	O	27.30	
	C	27.32	
	Δ	[-0.02]	
160	O	27.36	
	C	27.36	
	Δ	[0.00]	
170	O	27.45	
	C	27.44	
	Δ	[0.01]	
180	O	27.61	
	C	27.57	
	Δ	[0.04]	
190	O	27.77	
	C	27.75	
	Δ	[0.02]	
200	O	28.00	
	C	27.99	
	Δ	[0.01]	
210	O	28.26	
	C	28.26	
	Δ	[0.00]	
220	O	28.51	
	C	28.58	
	Δ	[-0.07]	
Source		1	2

Temp. °K		1-butyne	2-butyne
230	O	28.87	
	C	28.96	
	Δ	[-0.09]	
240	O	29.40	
	C	29.40	
	Δ	[0.00]	
250	O	29.97	28.51
	C	29.90	28.51
	Δ	[0.07]	[0.00]
260	O	30.52	28.78
	C	30.45	28.78
	Δ	[0.07]	[0.00]
270	O	31.07	29.08
	C	31.05	29.08
	Δ	[0.02]	[0.00]
280	O	31.65	29.38
	C	31.71	29.38
	Δ	[-0.06]	[0.00]
290	O		29.73
	C		29.73
	Δ		[0.00]
Source		1	2

O = observed
C = calculated
Δ = $\Delta C_p(\ell)$ [observed-calculated]

[1] J. G. Aston, S. V. R. Mastrangelo, and G. W. Noessen, J. Amer. Chem. Soc., 72, 5287 (1950).
[2] D. M. Yost, D. W. Osborne, and C. S. Garner, J. Amer. Chem. Soc., 63, 3492 (1941).

Table XIII. Statistical Summary of Accuracy in Estimating Liquid Heat Capacities of Hydrocarbons at Constant Pressure as a Temperature Function

Hydrocarbons family	No. of compounds	No. of data points[a]	Estimation accuracy, cal $mole^{-1}$ $^{\circ}K^{-1}$				
			Within ± 0.5	Within ± 1.0	Better than ± 2.0	Higher than ± 2.0	Maximum deviation
Straight chain alkanes	17	159	100(62.9%)	154(96.8%)	159(100%)	0	1.70
Ter-alkanes	15	215	128(59.5%)	173(80.5%)	212(98.6%)	3(1.4%)	2.53
Quat-alkanes	6	72	38(52.8%)	60(83.3%)	71(98.6%)	1(1.4%)	2.05
1-Alkenes	10	128	52(40.6%)	98(76.6%)	128(100%)	0	1.41
Other monoalkenes	9	86	57(66.3%)	63(73.3%)	76(88.4%)	10(11.6%)	3.61
Dienes	9	107	79(73.8%)	94(87.9%)	105(98.1%)	2(1.9%)	2.09
Cyclopentane derviatives	9	131	48(36.6%)	90(68.7%)	118(90.1%)	13(9.9%)	2.76
Cyclohexane derivatives	15	154	73(47.4%)	119(77.3%)	154(100%)	0	1.90
Rings	11	22	17(77.3%)	22(100%)	22(100%)	0	0.69
Aromatics	14	135	84(62.2%)	115(85.2%)	119(88.1%)	16(11.9%)	2.96
Alkynes	2	-	-	-	-	-	
Total	117	1209	676(55.9%)	988(81.7%)	1164(96.3%)	45(3.7%)	3.61

[a]This value includes only data points for which the calculated value is based on using more than one compound to determine the group(s) value(s).

The experimental and the calculated data for alkynes are given in Table XII.

Conclusions

Once again the method of group additivity has been demonstrated as a simple and accurate tool for estimating thermochemical properties. In this research, we have compiled and examined liquid heat capacity data on 117 different hydrocarbons, for which approximately 1500 data points have been taken. In addition to data points of molecules that were used to determine group values, 1209 $C_p(l)$ independent data points were reproduced by using the group additivity scheme.

The agreement between the experimental and the calculated heat capacities is excellent. Statistical analyses of the deviations show that the average deviation is ± 0.64 cal mol^{-1} K^{-1} and that the standard deviation is ± 0.8 cal mol^{-1} K^{-1}, which is in most cases almost as little as the experimental uncertainty. The statistical summary of this research is given in Table XIII.

An even better agreement could be obtained if we did not consider values near the melting and the boiling points or some data sources that seemed to us inaccurate. Even with these limitations, however, the outcome is very encouraging. We plan to continue this research to evaluate $C_p(l)$ of nonhydrocarbon liquids as well as for other themochemical properties of liquids.

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Literature Cited

(1) Amirkhanov, Kh. I., Alibekov, B. C., Vikhorv, D. I., Mirskaya, V. A., Levina, L. N., *Teplofizka Vys. Temp.* **9**, 1310 (1971).
(2) Benson, S. W., Buss, J. H., J. *Chem. Phys.*, **29**, 546 (1958).
(3) Benson, S. W., Cruickshank, R. R., Golden, D. M., Haugen, G. R., O'Neal, H. E., Rodgers, A. S., Shaw, R., Walsh, R., *Chem. Rev.*, **69**, 279 (1969).
(4) Lange, N. A., Ed., "Handbook of Chemistry", 10th ed, McGraw-Hill, New York, N.Y., 1967, p 1528.
(5) Shaw, R., *J. Chem. Eng. Data*, **14**, 461 (1969).
(6) Chueh, C. F., Swenson, A. C., *Eng. Prog.*, **69** (7), 83 (1973); *Can. J. Chem. Eng.*, **51**, 596 (1973).
(7) Tsien, H. S., *J. Am. Rocket Soc.*, **23**, 17 (1953).
(8) Yuan, T. F., Stiel, L. I., *Ind. Eng. Chem. Fundam.*, **9**, 393 (1970).
(9) San Jose, J. L., Reid, R. C., *Chem Eng.*, in press. See also Reid, R. C., Sherwood, T. K., Prausnitz, J. M., "The Properties of Gases and Liquids", 3d ed, McGraw-Hill, New York, N.Y., 1976.
(10) Johnson, A. I., Huang, C. J., *Can. J. Tech.*, **33**, 421 (1955).
(11) Missenard, F. A., *C. R. Acad. Sci.*, **260**, 521 (1965).

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