Heat Capacity of Hydrocarbons in the Normal Liquid Range

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Stemming from a dimensionless equation for heat capacity, reliable empirical equations are presented for the C_p of pure liquid hydrocarbons up to the normal boiling point. The correlating equations are for members of specific homologous series. The homologous series covered are: *n*-alkanes, isoalkanes, 1-alkenes, alkylcyclohexanes, alkylcyclopentanes, and alkylbenzenes. A separate correlation is presented for the light alkanes from methane through *n*-butane. The hydrocarbons isobutane, ethene, propene, and 1-butene have individual equations. Using the concept of conformal solutions, the heat capacity of mixtures of *n*-alkanes can be calculated. The excess heat capacity of such mixtures can also be computed with reasonable accuracy.

INFORMATION on the heat capacity of substances is frequently required. A nomogram published in 1966 (*12*) presented the heat capacity of liquid hydrocarbons with five or more carbon atoms in the molecule. The nomogram was incorporated into the API "Technical Data Book Petroleum Refining" (*1*), which presents correlations primarily directed toward desk use. Since the nomogram was constructed, additional precision heat capacity data for liquid hydrocarbons have been published. It is now desirable to include these more recent data in correlations which cover a broader range of hydrocarbon types, including the lighter members, and to have computer-oriented methods.

The earlier correlation (*12*) depended on the empirical observation that a simple relation existed between the heat capacities of the successive members of a homologous series at equal reduced temperatures. A reduced temperature is used here to present, in so far as possible, general equations for several homologous series. The concept also gives a reasonable means for interpolating heat capacities for hydrocarbons that have no experimental data and extrapolating the temperature range on hydrocarbons with data for only part of the temperature range between freezing and boiling points.

Currently, the experimental heat capacity of liquid hydrocarbons at temperatures below their normal boiling points are usually presented as quadratic or cubic functions of temperature (*18*) for the individual hydrocarbons. The available experimental data are for different temperature ranges between freezing and boiling points for the successive hydrocarbons of a given type. As a result, the coefficients in the least squares heat capacity equations change erratically as the number of carbon atoms increases for the members of a homologous series. Consequently, the use of such equations is limited and should not be extrapolated beyond the temperature range on which they are based. Estimation methods for heat capacities primarily at temperatures above the normal boiling point have been reviewed by Reid and Sherwood (*27*). Thus, there is a need for a systematic correlation which covers the temperature range from the freezing point to the normal boiling point for hydrocarbons.

EXPERIMENTAL DATA

The literature sources for experimental data used in the correlation are shown in Tables I and II. The temperature range of the heat capacity information and the normal liquid range (freezing and normal boiling point temperatures) is given for comparison. Whenever possible, only heat capacity data more recent than 1945 have been used, because the best calorimetry work has been done since 1945. Prior to about 1930, calorimetry work was largely unsatisfactory by present standards. No pre-1930 data have been used. The data for the following hydrocarbons are in the 1930 to 1945 period: methane through butane, *n*-pentacosane, isobutane (2-methylpropane), isopentane (2-methylbutane), ethene, propene, 1-butene, and cyclohexane. With the exception of one data point for *n*-undecane and one for *n*-hexadecane, all of the data for each hydrocarbon were used in fitting the least squares equations. Timmermans' (*35*) valuable guide and listing of reliable physicochemical constants was a substantial aid in locating useful data. However, he includes some old heat capacity data, prior to 1930, which should not now be used.

More recent data for cyclopentane and cyclohexane are indicated in Table II. None of these later data were used. They confirm the older data's reliability for cyclopentane, but the later data for cyclohexane are higher and seem to be out of line with the homologous series data.

The most extensive studies on the heat capacity for any hydrocarbon have been made for *n*-heptane. Consequently, it was the base hydrocarbon used in deriving the correlation for pentane and heavier *n*-alkanes.

The literature indicated in Tables I and II presents the heat capacity at saturation pressure, C_s. Other than for *n*-heptane, virtually all C_s values are for circumstances below the normal boiling point. At pressures of 1 atm. or less, the values of C_s can be considered identical to C_p, and this has been done here.

CORRELATION

It is desirable to have a dimensionless equation for the constant pressure heat capacity of the members of a homologous series of hydrocarbons. The following equation symbolizes such a relation

$$\frac{C_p}{R} = f(n, T_r) \tag{1}$$

Multiplying both sides of Equation 1 by R gives a relation for molar heat capacity. If each side of this

Table I. Heat Capacity Data for Liquid Acyclic Hydrocarbons

	n-Alkanes					2-Methylalkanes (Isoalkanes)					*n*-1-Alkenes				
No. of C Atoms	Ref.	Heat Capacity Temp. Range, ° K.		Liquid Range, ° K. (1)		Ref.	Heat Capacity Temp. Range, ° K.		Liquid Range, ° K. (1)		Ref.	Heat Capacity Temp. Range, ° K.		Liquid Range, ° K. (1)	
				T_f	T_b				T_f	T_b				T_f	T_b
1	(37)	98	111	90.67	111.66										
2	(38)	90	180	89.88	184.52						(28)	107	169	104.00	169.44
3	(15)	90	230	85.46	231.08						(26)	94	223	87.90	225.45
4	(3)	140	268	134.80	272.65	(2)	117	257	113.55	261.42	(31)	150	300	87.80	266.89
5	(18)	149	303	143.43	309.22	(11)	115	300	113.25	301.00	(36)	135	295	107.93	303.12
6	(7)	177	296	177.80	341.89	(7)	200	300	119.48	333.42	(16)	133	310	133.33	336.63
7	(5)	182	370[a]	182.54	371.58				154.87	363.20	(16)	150	300	154.27	366.79
	(22)	278	318												
	(17)[b]	183	367												
8	(8)	220	300	216.35	398.81	(22)	283	308	164.11	390.80	(16)	171	310	171.41	394.43
9	(8)	220	320	219.63	423.95				192.75	416.41				191.78	420.02
10	(8)	250	320	243.49	447.27	(25)	200	290	198.50	440.15	(16)	207	360	206.84	443.72
11	(8)	250	300	247.56	469.04						(16)	224	310	223.97	465.82
12	(8)	270	320	263.56	489.43						(16)	247	310	237.92	486.51
13	(8)	270	310	267.76	508.58									250.08	505.93
14	(8)	280	300	279.01	526.67									260.30	524.25
15	(8)	290	310	283.08	543.77									269.42	541.54
16	(8)	290	320	291.32	559.94						(16)	278	310	277.27	558.00
17	(18)	302	384	295.13	575.30										
18	(18)	304	379	301.33	589.86										
19				305.05	603.76										
20				309.6	616.9										
21				313.6	629.6										
22				317.5	641.8										
23				320.8	653.4										
24				324.0	664.4										
25	(33)	333	373	326.9	675.0										

[a] Experimental data for saturated liquid extended to critical temperature.

[b] Data from 5 separate studies reported. All sets included in least square fit.

Table II. Heat Capacity Data for Liquid Alkyl Cyclic Hydrocarbons

	n-Alkylcyclopentanes					*n*-Alkylcyclohexanes					*n*-Alkylbenzenes				
No. of C Atoms	Ref.	Heat Capacity Temp. Range, ° K.		Liquid Range, ° K. (1)		Ref.	Heat Capacity Temp. Range, ° K.		Liquid Range, ° K. (1)		Ref.	Heat Capacity Temp. Range, ° K.		Liquid Range, ° K. (1)	
				T_f	T_b				T_f	T_b				T_f	T_b
5	(6)(34)[a]	180	300	179.28	322.41										
6	(6)	150	300	130.69	344.96	(23)(4,29)[a]	280	295	279.70	353.89	(21)	279	353	278.68	353.25
7	(10)	140	302	134.70	376.62	(6)	155	286	146.56	374.08	(32)	160	371	178.16	383.77
8	(19)	162	365	155.79	404.10	(14)	170	310	161.83	404.93	(30)	178	300	178.17	409.34
9	(19)	168	368	165.18	429.75	(9)	186	373	178.25	429.87	(20)	181	371	173.65	432.37
10				190.2	453.6	(9)	208	365	198.43	454.10	(20)	194	370	185.18	456.42
11				200.4	476.0				215.6	476.82					
12				220.4	497.0				230.0	497.9					
13				229.3	516.7	(24)	240	300	242.6	518.0					
14				244.3	535.2				253.5	536.8					
15	(19)	258	321	251.02	552.53				263.0	554.6					
16						(9)	274	300	271.41	570.74					
17									278.90	586.4					
18						(24)	290	300	285.6	601.0					

[a] Auxiliary data on heat capacity, not used in obtaining correlation.

relation is divided by the molecular weight of the hydrocarbon with n carbon atoms, the heat capacity, c_p, in cal./(g. ° K.) is obtained. In the following, both relations are used.

A linear relation between heat capacity, c_p, and the number of carbon atoms in the molecule at a constant reduced temperature was found earlier (12) for members of several homologous series. These relations were for a unit weight of the hydrocarbons with five or more carbon atoms in the molecule and with the reduced temperature calculated with respect to the normal boiling point temperature, $T_r = T/T_b$. The present study largely confirms the earlier one. However, the more recent data now available result in modifications for some homologous series as described below. A correlation is given for the light *n*-alkanes, as well as equations for other individual light hydrocarbons with less than five carbon atoms per molecule.

The heat capacity of a liquid hydrocarbon can be represented reliably in a limited temperature range by a quadratic or cubic equation in temperature. The choice for the temperature scale is usually arbitrary. For present purposes, the choice is a reduced temperature for each hydrocarbon as defined above. Thus, the heat capacity per unit weight is represented by

$$c_p = a + bT_r + cT_r^2 + dT_r^3 \qquad (2)$$

where a, b, c, and d are constants and T_r is reduced temperature.

For some homologous series, the constants in Equation 2 vary linearly with the number of carbon atoms in the molecule. For normal alkanes with general formula C_nH_{2n+2} with $n \geqslant 5$, the heat capacity as a function of n and T_r is given by

$$c_p = a + bT_r + cT_r^2 + dT_r^3 + n(\Delta a + \Delta bT_r + \Delta cT_r^2 + \Delta dT_r^3) \qquad (3)$$

where Δa, etc., are the changes in the constant per carbon atom.

A linear least squares computer program was used to determine the constants in Equation 3 for the homologous series n-alkanes, isoalkanes (2-methylalkanes), 1-alkenes, and the n-alkylcyclohexanes. The results given for the constants in Table III are the least square fits, using the experimental data from the sources listed in Tables I and II.

The heat capacities of the two homologous series, n-alkylcyclopentanes and n-alkylbenzenes, are not adequately represented by Equation 3. For each hydrocarbon of these two series, c_p can be represented by a cubic relation, as in Equation 2. However, the heat capacity changes systematically with the number of carbon atoms in the molecule at constant reduced temperature, and the number of carbon atoms is represented by

$$c_p = (a_1 + b_1T_r + c_1T_r^2 + d_1T_r^3)^{\left(\frac{n_2 - n}{n_2 - n_1}\right)} \times (a_2 + b_2T_r + c_2T^2{}_r + d_2T^3{}_r)^{\left(\frac{n - n_1}{n_2 - n_1}\right)} \qquad (4)$$

where a_i, etc., are constants; n = number of carbon atoms in the hydrocarbon for which c_p is to be calculated; n_1 and n_2 = number of carbon atoms in first and second reference hydrocarbons. The molar heat capacity, C_p, of light n-alkanes, methane through n-butane, is also represented by Equation 4.

For the n-alkylcyclopentanes, the relation of reduced temperature and the number of carbon atoms is represented by

$$c_p = (a_1 + b_1T_r + c_1T_r^2 + d_1T_r^3)^{\left(\frac{\ln n/8}{\ln 5/8}\right)} \times (a_2 + b_2T_r + c_2T_r^2 + d_2T_r^3)^{\left(\frac{\ln 5/n}{\ln 5/8}\right)} \qquad (5)$$

where a ratio of logarithms in the exponents is involved.

A nonlinear least squares computer program was used to determine the constants in Equations 4 and 5 for the indicated hydrocarbon series. The results given for the constants in Table IV are the least square fits, using the experimental data from the sources listed in Tables I and II.

The light hydrocarbons not covered in the preceding correlations for the homologous series included here are ethene, propene, 1-butene, and isobutane. The experimental data from the sources indicated in Table I were used to determine the coefficients in Equation 2 for quadratic or cubic equations giving the best fit, as presented in Table V.

In the lower portion of Tables III, IV, and V, statistical information is presented about the data and fit of the equations. The first item is the mean of the heat capacity data used. The second item is the root mean square deviation of the data about that mean. The third item is the standard deviation of the experimental data about the regression equation. The fourth item gives the ratio (expressed in per cent) of the standard deviation to the mean. In all the tables, this ratio reflects several things. One is the reliability of the selected equation to represent the data. Another may be the quality of the data that are being fitted. The fifth and sixth items give the maximum deviation between computed and experimental values and the number of data points used.

ACCURACY OF CORRELATIONS

The heat capacity correlation equations presented for the homologous series represent the experimental data

Table III. Constants in Equation 3 for Heat Capacity of Liquid Hydrocarbons with Five or More Carbon Atoms per Molecule

	Homologous Series			
Constant	n-Alkanes	Isoalkanes	1-Alkenes	n-Alkylcyclohexanes
a	0.84167	−0.03083	0.14510	0.26796
b	−1.47040	1.77589	1.26233	0.04311
c	1.67165	−2.50661	−2.03775	−0.06164
d	−0.59198	1.20202	1.06953	0.0
Δa	−0.003826	0.079670	0.067176	0.004331
Δb	−0.000747	−0.335664	−0.304272	−0.003439
Δc	0.041126	0.499756	0.478026	+0.039338
Δd	−0.013950	−0.221740	0.221610	0.0
Statistical Information				
1. Mean c_p	0.5184	0.4752	0.4844	0.4309
2. RMS dev. of c_p	0.0304	0.0394	0.0289	0.0522
3. Std. dev. of exp. c_p about Eq. 3	0.0012	0.0015	0.0021	0.0026
4. Mean percentage std. dev. of c_p (100% × item 3/item 1)	0.24	0.31	0.43	0.60
5. Max. dev. of c_p from Eq. 2	0.0051	0.0044	0.0065	0.0075
6. No. of exptl. pts.	289	76	127	98

Table IV. Constants in Equations 4 and 5 for Heat Capacity of Liquid Hydrocarbons

	Homologous Series		
	Eq. 4		Eq. 5
Constant	Light alkanes	*n*-Alkyl-benezenes	*n*-Alkyl cyclopentanes
a_1	14.7486	0.55158	0.32010
b_1	− 9.8198	−1.12912	−0.01800
c_1	12.9505	2.00806	+0.03292
d_1	− 4.8349	−0.91821	0.12834
a_2	13.1830	0.53865	0.44974
b_2	54.3924	−1.11510	−0.53041
c_2	−72.8410	2.12851	0.96861
d_2	37.1562	−1.01959	−0.31487
n_1	1	9	...
n_2	4	10	...
Statistical Information			
1. Mean c_p	20.835	0.4071	0.4203
2. RMS dev. of c_p	5.788	0.0378	0.0510
3. Std. dev. of exptl. c_p about eq.	0.178	0.0024	0.0027
4. Mean % std. dev. of c_p (100% × item 3/item 1)	0.85	0.59	0.64
5. Max. dev. of c_p from eq.	−0.403	0.0072	0.0096
6. No. of exptl. pts.	58	90	116

very reliably. Only for the light alkanes is the mean percentage standard deviation greater than 0.67%. As a group, the light alkane data (methane through butane) are the oldest data used. Consequently, their accuracy and consistency are suspect. The correlation equations reproduce the minimum in heat capacity, which is strongly exhibited in the alkenes. The *n*-alkanes have a slight minimum in their heat capacity curves. Table VI shows how this character is represented by the general equation for *n*-alkanes by comparing its values for *n*-heptane with "selected" values tabulated in the Bureau of Mines report (*17*) on *n*-heptane. In evaluating the constants of the general equation, the "selected values" were not used.

For the temperature range 240° to 370° K., an equation is given (*17*) for the "selected values" of an *n*-heptane, which has a maximum deviation of 0.04 cal./(g.-mole ° K.). The deviations of the general equation given in Table VI are about the same, except at one temperature in the same range.

Table VI. Comparison of Molar Heat Capacity Values for *n*-Heptane

Temp., ° K.	Computed from Eq. 3 and Table III	Bur. Mines Selected Values (*17*)	Deviation, Cal./(G-Mole ° K.)
182.55	48.21	48.52	−0.31
190	48.14	48.27	−0.13
200	48.17	48.15	+0.02
210	48.33	48.23	0.10
230	48.97	48.88	0.09
250	50.00	49.98	0.02
270	51.37	51.39	−0.02
290	53.00	53.04	−0.04
310	54.83	54.85	−0.02
330	56.80	56.75	+0.05
350	58.83	58.79	0.04
370	60.88	61.04	−0.16

There has been a definite improvement in calorimetry in recent years. But, of necessity, data as far back as 1930 have had to be used. The discrepancies of "good" data prior to 1930 with modern heat capacity information can be large—*i.e.*, over 15%. Some evaluation of the improvement in calorimetry since 1930 can be seen by examining the bias between experimental and correlation values *vs.* the year of publication of the data for the individual hydrocarbons used in the correlations. The bias, *B*, for each hydrocarbon used in deriving an equation is defined as

$$B = \frac{1}{m} \Sigma \left(C_{pc} - C_{pe}\right) \qquad (6)$$

where C_{pe} = experimental heat capacity, C_{pc} = computed heat capacity, and m = number of points for the hydrocarbon.

To put the data for the different correlations on a common basis, the bias has been divided by the standard deviation of the points about the correlation (Tables III and IV) and is tabulated with the year of publication in Tables VII and VIII. Ignoring sign, larger numerical values occur up to 1946; thereafter there is a marked decrease in the magnitude of the largest values.

In addition to the age of the data, there seems to be some influence of the number of carbon atoms on the bias ratio. This can be seen in the ratios for *n*-octane through *n*-hexadecane, based on the data from one group of experimenters (*8*). For other hydrocarbons, there is a confounding of age with number of carbon atoms

Table V. Constants in Equation 2 for Heat Capacity of Some Individual Liquid Hydrocarbons

Hydrocarbon	Ethene	Propene	1-Butene	Isobutane
a	0.71418	0.64766	0.63192	0.32575
b	−0.29525	−0.43638	−0.46311	0.22823
c	0.15407	0.31228	0.33869	−0.14714
d	...	...	...	0.12786
Statistical Information				
1. Mean c_p	0.5788	0.5059	0.4967	0.4655
2. RMS dev. of c_p	0.0063	0.0092	0.0240	0.0355
3. Std dev. of exp. c_p about eq.	0.0007	0.0020	0.0004	0.0015
4. Mean % std. dev. of c_p (100% × item 3/item 1)	0.01	0.04	0.07	0.32
5. Max. dev. of c_p from Eq. 2	0.0011	0.0039	0.0010	0.0026
6. No. of exptl. pts.	12	18	18	25

Table VII. Bias Ratio for Heat Capacities of Liquid Hydrocarbons from Equation 3

	n-Alkanes		Isoalkanes		1-Alkenes		*n*-Alkylcyclohexanes	
No. of C Atoms	$\frac{B}{\text{std. dev.}}$	Year of publication	$\frac{B}{\text{std. dev.}}$	Year of publication	$\frac{B}{\text{std. dev.}}$	Year of publication	$\frac{B}{\text{std. dev.}}$	Year of publication
5	−0.13	1967	−0.15	1943	−0.97	1937		
6	+0.77	1946	+0.70	1946	−0.41	1939	−0.09	1930
7	0.10	1954 to 1961			+1.21	1944	+0.28	1946
8	0.44	1954	+0.41	1947	0.40	1947	+1.09	1949
9	−0.38	1954					−0.44	1965
10	−0.44	1954	−0.30	1941	−0.33	1957	−0.51	1965
11	−0.73	1954			−0.39	1957		
12	−0.88	1954						
13	−0.90	1954					(Excluded only 3 points)	
14	−0.78	1954						
15	−0.86	1954						
16	−0.73	1954					+0.80	1965
17	−0.06	1967						
18	+0.25	1967					+0.18	1949
25	−1.90	1932						

Table VIII. Bias Ratio for Heat Capacities of Liquid Hydrocarbons from Equation 4 or 5

	Equation 4				Equation 5	
	Light Alkanes		*n*-Alkylbenzenes		*n*-Alkylcyclopentanes	
No. of C Atoms	$\frac{B}{\text{std. dev.}}$	Year of publication	$\frac{B}{\text{std. dev.}}$	Year of publication	$\frac{B}{\text{std. dev.}}$	Year of publication
1	−0.51	1930				
2	−0.38	1937				
3	+1.21	1938				
4	−0.49	1940				
5					+0.89	1946
6			−1.23	1948	−1.58	1946
7			+0.82	1946	+0.23	1953
8			+0.19	1945	+0.07	1965
9			−0.41	1965	+0.43	1965
10			−0.11	1965		
15					−0.29	1965

Table IX. Calculated Results[a] for Excess Heat Capacity in Binary *n*-Alkane Systems at $x_1 = x_2 = 0.5$

	Calculated C_p, using Eq. 3 and Table III			$C_p{}^E$	
Temp., ° C.	$n_1 = 6$	$n_2 = 16$	$n = 11$	From Eq. 8	H^M data (*13*) in Eq. 10
45	48.515	122.448	84.599	−0.88	−0.55[b]
60	49.801	124.875	86.562	−0.78	
68.74	50.545	126.421	87.785	−0.70	
	$n_1 = 6$	$n_2 = 24$	$n = 15$		
55.5	49.417	186.930	116.376	−1.80	−1.12[b]
68.74	50.545	190.214	118.582	−1.80	
	$n_1 = 8$	$n_2 = 24$	$n = 16$		
63.5	64.787	188.874	125.482	−1.35	−0.73[c]
86	67.412	194.990	129.743	−1.46	−0.57
101	69.208	199.572	132.897	−1.49	−0.48

[a] Molecular weights based on atomic weights for C = 12.010 and H = 1.008.

[b] Mean value over temperature range.

[c] Linearly interpolated values.

which cannot be separated without making questionable assumptions.

COMMENTS

The correlation equations give reliable heat capacities between the freezing and normal boiling points for liquid hydrocarbons if the reduced temperature is calculated using the boiling points listed in Tables I and II. The hydrocarbons are members of commonly occurring homologous series. Excepting the light alkanes, the heat capacities are expressed in cal./(g. ° K.). For computer applications these units can be converted to molar heat capacities by multiplying the equation by molecular weight expressed as a function of *n*.

A test for the soundness of the statistical method of correlating the data over a broad range of molecular weights is as follows. The temperature derivative of experimental heats of mixing—*i.e.*, identical with excess enthalpy of mixtures—is the excess heat capacity of the mixture. The excess heat capacity of a mixture can be calculated using the concept of conformal solutions. For this concept, the heat capacity of a mixture of components from a homologous series would be the same as the heat capacity of a member of the series with the number of carbon atoms per molecule the same as the molar average number for the constituents. This can be symbolized by

$$n = n_1x_1 + n_2x_2 \tag{7}$$

The molar excess heat capacity of the mixture is then

$$C_p{}^E = C_p{}^m - x_1C_{p_1} - x_2C_{p_2} \tag{8}$$

where $C_p{}^m$ = the molar heat capacity of the mixture and x_1 = mole fraction of component i.

Equation 8 is the temperature derivative of the relation for the heat of mixing, H^M,

$$H^M = H^E = H^m - x_1H_1 - x_2H_2 \tag{9}$$

where H = enthalpy per mole, M indicates mixing, E indicates excess, and m indicates mixture.

Heats of mixing for the binary mixtures *n*-hexane–*n*-hexadecane, *n*-hexane–*n*-tetracosane, and *n*-octane–*n*-tetracosane at three or more temperatures were determined by Holleman (*13*). The mean excess heat capacity over a temperature range from t_1 to t_2 is given by

$$\overline{C_p{}^E} = \frac{H_2{}^M - H_1{}^M}{t_2 - t_1} \tag{10}$$

As $C_p{}^E$ is a small difference between numbers of comparable size whether calculated by Equation 8 or 10, its accuracy is not particularly good in either case. The maximum absolute value of $C_p{}^E$ for a binary system might be expected to occur in an equal-molar mixture. With that in mind, calculations were made with the heat capacity relations to compare with the results calculated using Holleman's data for such mixtures. An approximation to the error arising from calculations implied by Equation 8 can be ascertained from the statistical data in Table III. For the *n*-hexane–*n*-hexadecane system the error in $C_p{}^E$ could be larger than ±0.12 cal./(g.-mole ° K.). In view of the unevenness of the mean values of dH^M/dT for successive temperature ranges in Holleman's results, it would seem that the errors in his smoothed H^M values are larger than his estimated errors.

The results of some calculations for $C_p{}^E$ are summarized in Table IX. In the hexane-hexadecane and hexane-tetracosane systems, Holleman's data do not lead to a well-defined relation of $C_p{}^E$ with temperature; consequently, only a mean value for the temperature range is given in Table IX. A reasonable value for the error in $C_p{}^E$ from Holleman's data for the hexane-hexadecane system might be greater than ±0.32 cal./(mole ° K.). The maximum difference between the two values for $C_p{}^E$ in this system is 0.33 cal./(mole ° K.).

This value approximates the error for a difference with the cited errors—*i.e.*, $[(0.12)^2 + (0.32)^2]^{1/2} = 0.34$. In the two systems containing tetracosane, the differences are larger than might be expected. The source of the larger differences may be a slight systematic overestimation of the C_p for tetracosane, as well as larger statistical errors.

The reasonableness of using the conformal solution concept can only be tested for the excess heat capacity of mixtures of the heavier *n*-alkanes. It seems plausible that conformal solution theory can be applied (Table III) when the heat capacity of members of a homologous series is represented by Equation 3.

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NOMENCLATURE

a, b, c, d = constants in Equations 2, 3, 4, and 5, cal./(g. ° K.)
$\Delta a, \Delta b, \Delta c, \Delta d$ = constants in Equations 3, increment in a, etc., per carbon atom in a molecule
c_p = heat capacity at constant pressure per unit weight, cal./(g. ° K.)
C_p = molal heat capacity at constant pressure cal./(g.-mole ° K.)
C_s = molal heat capacity at saturation pressure
f = symbol for a function of unspecified form
H = enthalpy, cal./g.-mole
m = number of points
n = number of C atoms per molecule, or molal average in a mixture
n_i = number of C atoms in *i*th hydrocarbon
R = ideal gas constant, cal./(g.-mole ° K.)
t = temperature, ° C.
T = t + 273.15, absolute temperature, ° K.
T_b = absolute temperature at boiling point of a hydrocarbon with n C atoms, ° K.
T_f = absolute temperature at freezing point, ° K.
T_r = T/T_b, reduced temperature
x_i = mole fraction of *i*th component in a mixture

SUPERSCRIPTS

E = excess
m = mixture
M = mixing

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Experimental Data and Procedures for Predicting Thermal Conductivity of Multicomponent Mixtures of Nonpolar Gases

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A hot-wire cell is used to determine the thermal conductivity of Ne, Ar, Kr, Xe, N_2, O_2, H_2, and D_2 gases at 40°, 65°, and 93° C. At these temperatures, the thermal conductivity is also measured as a function of composition for the systems H_2–N_2, H_2–O_2, N_2–O_2, D_2–N_2, H_2–O_2–Ne, H_2–N_2–O_2, H_2–Ar–Kr–Xe, and H_2–D_2–N_2–Ar. These data are compared with the predictions of the theory due to Hirschfelder, procedures due to Mason and Saxena, Lindsay and Bromley, Mathur and Saxena, and Ulybin, Bugrov, and Il'in, and a few simple methods. These detailed calculations and their interpretation in the light of experimental data lend valuable information concerning the status of the art of predicting thermal conductivity of multicomponent mixtures. The thermal conductivity data on binary systems are employed in conjunction with kinetic theory to obtain diffusion and viscosity coefficients.

A NUMBER OF METHODS have been developed for measuring the thermal conductivity of gases and gaseous mixtures [Saxena (*29*), Saxena and Gandhi (*32*)]. The choice of a particular method depends primarily upon environmental conditions (temperature and pressure) of the test gas, and the accuracy desired in the measurement. There is a considerable engineering interest in the thermal conductivity of multicomponent mixtures involving monatomic and polyatomic gases. Further, because it is impossible to have data for all possible choices, it is useful to have a scheme to achieve this goal. We have consequently measured the thermal conductivity of the binary systems H_2–N_2, H_2–O_2, N_2–O_2, and D_2–N_2; the ternary systems H_2–O_2–Ne and H_2–N_2–O_2; and the quaternary systems H_2–Ar–Kr–Xe and H_2–D_2–N_2–Ar. The thermal conductivity of the related eight pure gases was also measured. The measurements were made at 40°, 65°, and 93° C., at a pressure less than 1 atm., and in the case of mixtures as a function of composition. Several almost equally good methods can be adopted for measurement under these conditions.

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