Enthalpies of Formation, Combustion, and Vaporization of the 35 Nonanes and 75 Decanes

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Using an improved correlation procedure based on the trigonal or triatom additivity concept, the standard enthalpies of formation and combustion for the liquid and ideal gaseous states and the standard enthalpy of vaporization for the liquid state, at 298.15 K, are calculated for 35 isomeric nonanes (C_9H_{20}) and 75 isomeric decanes ($C_{10}H_{22}$).

The enthalpies of formation, $\Delta H_f°$, combustion, $\Delta H_c°$, and vaporization, $\Delta H_v°$, at 25 °C for the 35 nonanes and 75 decanes were calculated by Labbauf, Greenshields, and Rossini (*9*), using the empirical equations developed by Greenshields and Rossini (*6*). The coefficients of the molecular structural parameters for calculating $\Delta H_f°$ (liq, 298.15 K) were obtained from a least-squares fit of selected experimental values for 32 alkanes in the range C_5 to C_9. Those for computation of $\Delta H_v°$ (liq, 298.15 K) were derived based on the selected $\Delta H_v°$ values for 27 alkanes in the range C_5 to C_8.

Somayajulu and Zwolinski (*25, 26*) have proposed a new concept of trigonal or triatomic additivity for calculating the thermochemical and thermodynamic properties of polyatomic substances. Recently, they improved their previously developed triatomic additivity method by including the branching and buttressing effects in deriving the empirical equation (*27*). The aim of this work is the use of this improved correlation procedure, called the generalized trigonal additivity procedure, to reevaluate the values of $\Delta H_f°$ and $\Delta H_v°$ for the liquid isomeric nonanes, C_9H_{20}, and decanes, $C_{10}H_{22}$, at 298.15 K for which experimental data are currently not available. Based on these calculated results, the $\Delta H_f°$ (g, 298.15 K), $\Delta H_c°$ (liq, 298.15 K), and $\Delta H_c°$ (g, 298.15 K) for these isomers were also derived.

Calculation Method

The empirical equations employed for calculating the $\Delta H_f°$ (liq, 298.15 K) and $\Delta H_v°$ (liq, 298.15 K) for isomeric nonanes and decanes are given below in units of kilocalories per mole (1 cal = 4.1840 J):

$$\Delta H_f°\ (\text{liq, } 298.15\ \text{K}) = -13.1835 - 4.6157n - 2.0043W_2 + 0.4691W_3 + 0.0274W_4 + 0.6807Y_1 + 0.0217W_{34} - 0.0165W_{44} + 0.0432n_{23} + 0.1567n_{24} + 0.6501n_{33} + 1.1238n_{34} + 2.1332n_{44} + 0.0535Q_0 + 1.8871Q_2 + 4.6911Q_3 + 0.0174Q_{33} + 0.0793Q_{34} + 0.9301Q_{44}$$

$$\Delta H_v°\ (\text{liq, } 298.15\ \text{K}) = -2.3720 + 2.3720n - 0.8484W_2 - 0.2367W_3 - 0.1031W_4 + 0.2310Y_1 + 0.1217W_{34} - 0.0696W_{44} + 0.2301n_{23} + 0.5233n_{24} + 0.7363n_{33} + 1.3373n_{34} + 2.2684n_{44} + 0.0619Q_0 - 0.0838Q_2 - 0.2039Q_3 + 0.0529Q_{33} + 0.0866Q_{34} + 0.2808Q_{44}$$

These two equations were deduced from the generalized equation, i.e., eq 10 of ref 27, which contains 19 structural parameters. The numerical values of the structural parameters derived for each isomeric nonane and decane are summarized in Table I. In the above equations, the coefficients for the structural parameters were obtained by fitting the selected $\Delta H_f°$ (liq, 298.15 K) and $\Delta H_v°$ (liq, 298.15 K) values by multiple linear regression procedures. The sources and method of selection of these $\Delta H_f°$ and $\Delta H_v°$ have been described (*27*). The abbreviations used to represent the molecular formulas in Table I are: m = methyl, e = ethyl, ip = isopropyl; for example, 243mmip5 = 2,4-dimethyl-3-isopropylpentane.

The values of $\Delta H_f°$ (liq, 298.15 K) and $\Delta H_v°$ (liq, 298.15 K) calculated from the above two equations were employed in computing the $\Delta H_f°$ (g, 298.15 K), $\Delta H_c°$ (liq, 298.15 K), and $\Delta H_c°$ (g, 298.15 K) for each alkane with the following equations:

$$\Delta H_f°\ (\text{g, } 298.15\ \text{K}) = \Delta H_f°\ (\text{liq, } 298.15\ \text{K}) + \Delta H_v°\ (\text{liq, } 298.15\ \text{K})$$

$$\Delta H_c°\ (\text{liq, } 298.15\ \text{K}) = -68.315 - 162.366n - \Delta H_f°\ (\text{liq, } 298.15\ \text{K})$$

$$\Delta H_c°\ (\text{g, } 298.15\ \text{K}) = -68.315 - 162.366n - \Delta H_f°\ (\text{g, } 298.15\ \text{K})$$

where n is the number of carbon atoms in the given alkane (C_nH_{2n+2}) molecule. The enthalpy of combustion ($\Delta H_c°$, in kilocalories per mole) represents the heat evolved in the combustion of the given alkane hydrocarbon, in the state indicated, in gaseous oxygen to form gaseous carbon dioxide and liquid water, at 298.15 K and constant pressure, with all reactants and products in their appropriate standard reference states. For deriving the above equations for calculating $\Delta H_c°$, the values $\Delta H_f°$ (CO_2, g, 298.15 K) = −94.051 kcal mol^{-1} (*7, 14*) and $\Delta H_f°$ (H_2O, liq, 298.15 K) = −68.315 kcal mol^{-1} (*7, 20*) were used.

Results and Discussion

Based on the above five equations and the structural parameters given in Table I for the isomeric nonanes and decanes, the enthalpies of vaporization, formation, and combustion of the 35 nonanes and 75 decanes were calculated. The results are presented in Table II.

It is important to note that the values of the structural parameters listed in Table I can be used for calculating other physical and thermodynamic properties for these isomers. In such calculations, appropriate experimental data on the required property for these isomers are needed for evaluating the numerical coefficients, as shown in the equations for the computation of $\Delta H_f°$ (liq, 298.15 K) and $\Delta H_v°$ (liq, 298.15 K), by a multiple linear regression procedure.

The reliability of the derived results depends mainly on the accuracy of the experimental data selected for evaluation. In principle, the property values adopted for structural correlation study should be measured in the same laboratory for consistency. In reality, however, it is almost impossible to obtain such values.

The enthalpies of combustion of alkanes were measured by Thomsen, Berthelot, and others, in the European laboratories in the period from about 1850 to 1900. In the U.S. some data

Table I. Variables of the Generalized Trigonal Additivity Equation for 35 Nonanes and 75 Decanes

	n	W_2	W_3	W_4	W_5[a]	Y_1	Q_0	Q_2	Q_3	Q_{33}	Q_{34}	Q_{44}	W_{34}	W_{44}	n_{23}	n_{24}	n_{33}	n_{34}	n_{44}
9	9	7	6	5	4	0	0	0	0	0	0	0	0	0	0	0	0	0	0
2m8	9	8	6	5	4	1	0	0	0	0	0	0	0	0	1	0	0	0	0
3m8	9	8	7	5	4	1	0	0	0	0	0	0	0	0	2	0	0	0	0
4m8	9	8	7	6	4	1	0	0	0	0	0	0	0	0	2	0	0	0	0
3e7	9	8	8	6	4	1	1	0	0	0	0	0	0	0	3	0	0	0	0
4e7	9	8	8	7	4	1	1	0	0	0	0	0	0	0	3	0	0	0	0
22mm7	9	10	6	5	4	4	0	0	0	0	0	0	1	1	0	1	0	0	0
23mm7	9	9	8	5	4	2	0	0	0	1	0	0	0	0	1	0	1	0	0
24mm7	9	9	7	6	3	2	0	0	0	0	0	0	0	0	3	0	0	0	0
25mm7	9	9	7	5	5	2	0	0	0	0	0	0	0	0	3	0	0	0	0
26mm7	9	9	6	5	4	2	0	0	0	0	0	0	0	0	2	0	0	0	0
33mm7	9	10	8	5	4	4	0	0	0	0	0	0	1	1	0	2	0	0	0
34mm7	9	9	9	6	3	2	0	0	0	2	0	0	0	0	2	0	1	0	0
35mm7	9	9	8	6	4	2	0	0	0	0	0	0	0	0	4	0	0	0	0
44mm7	9	10	8	7	2	4	0	0	0	0	0	0	2	0	0	2	0	0	0
23me6	9	9	8	7	3	2	1	0	0	2	0	0	0	0	2	0	1	0	0
24me6	9	9	8	7	4	2	1	0	0	0	0	0	0	0	4	0	0	0	0
33me6	9	10	10	6	2	4	1	0	0	0	0	0	1	0	0	3	0	0	0
34em6	9	9	10	7	2	2	1	0	0	3	0	0	0	0	3	0	1	0	0
223mmm6	9	11	9	5	3	5	0	0	0	0	1	0	1	1	1	0	0	1	0
224mmm6	9	11	7	7	3	5	0	1	0	0	0	0	2	1	2	1	0	0	0
225mmm6	9	11	6	5	6	5	0	0	0	0	0	0	1	2	1	1	0	0	0
233mmm6	9	11	10	5	2	5	0	0	0	0	1	0	1	0	0	1	0	1	0
234mmm6	9	10	10	6	2	3	0	0	0	5	0	0	0	0	1	0	2	0	0
235mmm6	9	10	8	6	4	3	0	0	0	1	0	0	0	0	2	0	1	0	0
244mmm6	9	11	8	7	2	5	0	1	0	0	0	0	2	0	1	2	0	0	0
334mmm6	9	11	11	5	1	5	0	0	0	0	2	0	1	0	1	1	0	1	0
33ee5	9	10	12	6	0	4	2	0	0	0	0	0	0	0	0	4	0	0	0
223mme5	9	11	10	7	0	5	1	1	0	0	2	0	2	0	2	0	0	1	0
233mme5	9	11	12	5	0	5	1	0	0	0	2	0	0	0	0	2	0	1	0
234mem5	9	10	10	8	0	3	1	1	0	6	0	0	0	0	1	0	2	0	0
2233mmmm5	9	13	12	3	0	8	0	0	0	0	0	1	1	0	0	1	0	0	1
2234mmmm5	9	12	10	6	0	6	0	1	0	3	2	0	2	0	0	0	1	1	0
2244mmmm5	9	13	6	9	0	8	0	0	1	0	0	0	6	0	0	2	0	0	0
2334mmmm5	9	12	12	4	0	6	0	0	0	0	4	0	0	0	0	0	0	2	0
10	10	8	7	6	5	0	0	0	0	0	0	0	0	0	0	0	0	0	0
2m9	10	9	7	6	5	1	0	0	0	0	0	0	0	0	1	0	0	0	0
3m9	10	9	8	6	5	1	0	0	0	0	0	0	0	0	2	0	0	0	0
4m9	10	9	8	7	5	1	0	0	0	0	0	0	0	0	2	0	0	0	0
5m9	10	9	8	7	6	1	0	0	0	0	0	0	0	0	2	0	0	0	0
3e8	10	9	9	7	5	1	1	0	0	0	0	0	0	0	3	0	0	0	0
4e8	10	9	9	8	6	1	1	0	0	0	0	0	0	0	3	0	0	0	0
22mm8	10	11	7	6	5	4	0	0	0	0	0	0	1	1	0	1	0	0	0
23mm8	10	10	9	6	5	2	0	0	0	1	0	0	0	0	1	0	1	0	0
24mm8	10	10	8	8	5	2	0	0	0	0	0	0	0	0	3	0	0	0	0
25mm8	10	10	8	7	6	2	0	0	0	0	0	0	0	0	3	0	0	0	0
26mm8	10	10	8	6	5	2	0	0	0	0	0	0	0	0	3	0	0	0	0
27mm8	10	10	7	6	5	2	0	0	0	0	0	0	0	0	2	0	0	0	0
33mm8	10	11	9	6	5	4	0	0	0	0	0	0	1	1	0	2	0	0	0
34mm8	10	10	10	7	5	2	0	0	0	2	0	0	0	0	2	0	1	0	0
35mm8	10	10	9	8	5	2	0	0	0	0	0	0	0	0	4	0	0	0	0
36mm8	10	10	9	6	6	2	0	0	0	0	0	0	0	0	4	0	0	0	0
44mm8	10	11	9	8	5	4	0	0	0	0	0	0	2	1	0	2	0	0	0
45mm8	10	10	10	8	5	2	0	0	0	2	0	0	0	0	2	0	1	0	0
4np7	10	9	9	9	6	1	1	0	0	0	0	0	0	0	3	0	0	0	0
4ip7	10	10	10	9	6	2	1	0	0	2	0	0	0	2	0	1	0	0	0
23me7	10	10	10	8	5	2	1	0	0	2	0	0	0	0	2	0	1	0	0
24me7	10	10	9	9	6	2	1	0	0	0	0	0	0	0	4	0	0	0	0
25me7	10	10	9	7	6	2	1	0	0	0	0	0	0	0	4	0	0	0	0
33me7	10	11	11	7	5	4	1	0	0	0	0	0	1	1	0	3	0	0	0
34me7	10	10	11	9	5	2	1	0	0	3	0	0	0	0	3	0	1	0	0
35me7	10	10	10	8	6	2	1	0	0	0	0	0	0	0	5	0	0	J	0
43me7	10	10	11	9	4	2	1	0	0	3	0	0	0	0	3	0	1	0	0
44me7	10	11	11	9	4	4	1	0	0	0	0	0	2	0	0	3	0	0	0
223mmm7	10	12	10	6	5	5	0	0	0	0	1	0	1	1	1	0	0	1	0
224mmm7	10	12	8	9	4	5	0	1	0	0	0	0	2	1	2	1	0	0	0
225mmm7	10	12	8	6	7	5	0	0	0	0	0	0	1	2	2	1	0	0	0
226mmm7	10	12	7	6	5	5	0	0	0	0	0	0	1	1	1	1	0	0	0
233mmm7	10	12	11	6	5	5	0	0	0	0	1	0	1	1	0	1	0	1	0
234mmm7	10	11	11	8	4	3	0	0	0	5	0	0	0	0	1	0	2	0	0
235mmm7	10	11	10	7	6	3	0	0	0	1	0	0	0	0	3	0	1	0	0

Table I (*Continued*)

	n	W_2	W_3	W_4	W_5[a]	Y_1	Q_0	Q_2	Q_3	Q_{33}	Q_{34}	Q_{44}	W_{34}	W_{44}	n_{23}	n_{24}	n_{33}	n_{34}	n_{44}
236mmm7	10	11	9	6	6	3	0	0	0	1	0	0	0	0	2	0	1	0	0
244mmm7	10	12	9	10	3	5	0	1	0	0	0	0	3	0	1	2	0	0	0
245mmm7	10	11	10	8	5	3	0	0	0	2	0	0	0	0	3	0	1	0	0
246mmm7	10	11	8	9	4	3	0	0	0	0	0	0	0	0	4	0	0	0	0
255mmm7	10	12	9	6	7	5	0	0	0	0	0	0	1	2	1	2	0	0	0
334mmm7	10	12	12	7	4	5	0	0	0	0	2	0	1	1	1	1	0	1	0
335mmm7	10	12	10	8	5	5	0	1	0	0	0	0	2	1	2	2	0	0	0
344mmm7	10	12	12	8	3	5	0	0	0	0	2	0	2	0	1	1	0	1	0
345mmm7	10	11	12	8	4	3	0	0	0	6	0	0	0	0	2	0	2	0	0
23mip6	10	11	11	10	4	3	1	1	0	6	0	0	0	0	1	0	2	0	0
33ee6	10	11	13	9	3	4	2	0	0	0	0	0	1	0	0	4	0	0	0
34ee6	10	10	12	10	4	2	2	0	0	4	0	0	0	0	4	0	1	0	0
223mme6	10	12	11	9	4	5	1	1	0	0	2	0	2	1	2	0	0	1	0
224mme6	10	12	9	9	6	5	1	1	0	0	0	0	2	2	3	1	0	0	0
233mme6	10	12	13	8	3	5	1	0	0	0	2	0	1	0	0	2	0	1	0
234mme6	10	11	12	9	4	3	1	0	0	6	0	0	0	0	2	0	2	0	0
243mme6	10	11	12	10	3	3	1	1	0	7	0	0	0	0	2	0	2	0	0
244mme6	10	12	11	9	4	5	1	1	0	0	0	0	2	0	1	3	0	0	0
253mme6	10	11	10	9	6	3	1	0	0	2	0	0	0	0	3	0	1	0	0
334mme6	10	12	13	9	2	5	1	1	0	0	3	0	2	0	2	1	0	1	0
343mme6	10	12	14	8	2	5	1	0	0	0	3	0	1	0	1	2	0	1	0
2233mmmm6	10	14	13	6	3	8	0	0	0	0	0	1	2	1	0	1	0	0	1
2234mmmm6	10	13	12	8	3	6	0	1	0	4	2	0	2	1	1	0	1	1	0
2235mmmm6	10	13	10	7	6	6	0	0	0	0	1	0	1	2	2	0	0	1	0
2244mmmm6	10	14	9	10	3	8	0	0	1	0	0	0	6	1	0	3	0	0	0
2245mmmm6	10	13	9	8	6	6	0	1	0	1	0	0	2	2	1	1	1	0	0
2255mmmm6	10	14	7	6	9	8	0	0	0	0	0	0	2	6	0	2	0	0	0
2334mmmm6	10	13	14	7	2	6	0	0	0	0	5	0	1	0	1	0	0	2	0
2335mmmm6	10	13	11	8	4	6	0	1	0	0	1	0	2	0	1	1	0	1	0
2344mmmm6	10	13	13	8	2	6	0	1	0	3	3	0	2	0	0	1	1	1	0
2345mmmm6	10	12	12	8	4	4	0	0	0	8	0	0	0	0	0	0	3	0	0
3344mmmm6	10	14	15	6	1	8	0	0	0	0	0	2	2	0	0	2	0	0	1
243mmip5	10	12	12	12	0	4	1	0	1	12	0	0	0	0	0	0	3	0	0
233mee5	10	12	15	9	0	5	2	1	0	0	3	0	0	0	0	3	0	1	0
2233mmme5	10	14	15	7	0	8	1	1	0	0	0	2	2	0	0	2	0	0	1
22334mmmmm5	10	15	15	6	0	9	0	1	0	0	3	2	2	0	0	0	0	1	1

[a] Note that W_5 does not appear as one of the parameters of the new generalized trigonal additivity equation. It was used in the earlier equation and hence is reported in this table along with other parameters.

were obtained by Richards and his co-workers from about 1905 to 1915. The results published by these early workers in the field were critically reviewed by Rossini (*21, 22*). Due to the lack of high purity samples and the use of inadequate experimental equipment, their reported $\Delta H_c°$ values are only of historical interest at the present time.

Employing specially purified hydrocarbon samples and high precision experimental equipment, Rossini and his co-workers (*19*) have measured the $\Delta H_c°$ for eight gaseous alkanes, C_1 to C_5, and nine liquid normal alkanes, C_5 to C_{12} and C_{16}. For evaluation of $\Delta H_f°$ (liq, 298.15 K) for isomeric alkanes, they also determined the enthalpies of isomerization at 298.15 K for 5 hexanes (*16*), 9 heptanes (*17*), 18 octanes (*18*), and 5 nonanes (*8*). Incorporating the above data with appropriate $\Delta H_v°$ (*19*) and $\Delta H_f°$ (298.15 K) for CO_2(g) and H_2O(liq), the authors obtained the best values for the $\Delta H_c°$ (liq and g, 298.15 K) and $\Delta H_f°$ (liq and g, 298.15 K) of the 52 alkane hydrocarbons, C_1 to C_8 and *n*-C_9 to *n*-C_{20}. These reported values were adopted for the American Petroleum Institute Research Project 44 Tables (*23, 28*).

Additional combustion calorimetric measurements were made for the following compounds: 5 gaseous alkanes C_1 to C_4 (*13*), 2 gaseous butanes (*15*), 3 gaseous pentanes (*12*), 3 liquid pentanes (*4*); and 9 heptanes (*1*), 2 octanes (*5*), 12 nonanes (*2, 3*), 3 decanes (*2*), 1 undecane (*2*), 2 dodecanes (*2*), and 1 hexadecane (*2*), all in the liquid state. Additional data on $\Delta H_v°$ (298.15 K) for 6 liquid *n*-alkanes C_{12} to C_{17} (*10*), 3 solid *n*-alkanes C_{18} to C_{20} (*10*), and 35 isomeric liquid alkanes C_5 to C_{10} (*11*) were also reported.

In this work the numerical coefficients in the equations for calculating $\Delta H_f°$ (liq, 298.15 K) and $\Delta H_v°$ (liq, 298.15 K) were obtained by multiple linear regression of 84 selected $\Delta H_f°$ (298.15 K) and 48 $\Delta H_v°$ (298.15 K) values, respectively (*27*). The calculated enthalpies of formation and isomerization were reported to be in good agreement with the available experimental data (*27*).

The calculated $\Delta H_v°$ and $\Delta H_f°$ at 298.15 K for liquid nonanes and decanes are compared with the available experimental data in Table III. It should be emphasized that there were two $\Delta H_f°$ (*n*-nonane, liq, 298.15 K) values reported in the literature. The difference between these two values is 0.16 ± 0.25 kcal mol^{-1}, which is within the assigned experimental uncertainty of each set of measurements. Our results are consistent with the experimental data shown in Table III. All of the calculated values are within the experimental uncertainties of the measured ones except for 2,2,3,4-tetramethylpentane for which the calculated value is more positive than the Johnson, Prosen, and Rossini experimental value of −66.37 ± 0.28 kcal mol^{-1} (*8*) by 0.45 kcal mol^{-1}. A correlation procedure recently developed by Scott (*24*) also gives a value more positive than the experimental value by 0.47 kcal mol^{-1}. The large difference for this single compound may call for a refinment in the procedure for the estimation of steric energies involving 1,5 H···H interactions.

Also listed in Table III are the calculated values of Labbauf, Greenshields, and Rossini (*9*), for comparison. In general, the differences between the two sets of values for $\Delta H_f°$(liq) are as follows: less than 0.20 kcal mol^{-1} for 23 isomeric nonanes, 0.20–0.42 kcal mol^{-1} for eight other nonanes, and 0.48–1.83

Table II. Standard Enthalpies of Vaporization, Formation, and Combustion for the 35 Nonanes and 75 Decanes in kcal mol^{-1} at 298.15 K [a]

Compound	$\Delta H_v°$(liq)	$\Delta H_f°$(liq)	$\Delta H_f°$(gas)	$\Delta H_c°$(liq)	$\Delta H_c°$(gas)
9	11.10	−65.80	−54.70	−1463.81	−1474.91
2m8	10.71	−67.08	−56.37	−1462.53	−1473.24
3m8	10.71	−66.57	−55.86	−1463.04	−1473.75
4m8	10.60	−66.82	−56.22	−1462.79	−1473.39
3e7	10.66	−65.98	−55.32	−1463.63	−1474.29
4e7	10.56	−65.95	−55.39	−1463.66	−1474.22
22mm7	10.06	−68.88	−58.82	−1460.73	−1470.79
23mm7	10.41	−66.80	−56.39	−1462.81	−1473.22
24mm7	10.22	−67.82	−57.60	−1461.79	−1472.01
25mm7	10.32	−67.85	−57.53	−1461.76	−1472.08
26mm7	10.33	−68.36	−58.03	−1461.25	−1471.58
33mm7	10.11	−67.84	−57.73	−1461.77	−1471.88
34mm7	10.36	−66.24	−55.88	−1463.37	−1473.73
35mm7	10.21	−67.31	−57.10	−1462.30	−1472.51
44mm7	10.09	−67.74	−57.65	−1461.87	−1471.96
23me6	10.55	−66.63	−56.08	−1462.98	−1473.53
24me6	10.17	−67.23	−57.06	−1462.38	−1472.55
33me6	10.18	−66.64	−56.46	−1462.97	−1473.15
34em6	10.36	−65.63	−55.27	−1463.98	−1474.34
223mmm6	9.87	−67.57	−57.70	−1462.04	−1471.91
224mmm6	9.48	−67.60	−58.12	−1462.01	−1471.49
225mmm6	9.58	−70.11	−60.53	−1459.50	−1469.08
233mmm6	9.99	−67.18	−57.19	−1462.43	−1472.42
234mmm6	10.17	−66.44	−56.27	−1463.17	−1473.34
235mmm6	9.91	−67.88	−57.97	−1461.73	−1471.64
244mmm6	9.62	−66.97	−57.35	−1462.64	−1472.26
334mmm6	10.07	−66.33	−56.26	−1463.28	−1473.35
33ee5	10.17	−65.82	−55.65	−1463.79	−1473.96
223mme5	9.90	−65.18	−55.28	−1464.43	−1474.33
233mme5	10.06	−65.95	−55.89	−1463.66	−1473.72
234mem5	9.99	−64.47	−54.48	−1465.14	−1475.13
2233mmmm5	9.84	−66.51	−56.67	−1463.10	−1472.94
2234mmmm5	9.76	−65.92	−56.16	−1463.69	−1473.45
2244mmmm5	9.02	−66.92	−57.90	−1462.69	−1471.71
2334mmmm5	9.95	−66.43	−56.48	−1463.18	−1473.13
10	12.28	−71.92	−59.64	−1620.05	−1632.33
2m9	11.90	−73.21	−61.31	−1618.76	−1630.66
3m9	11.89	−72.69	−60.80	−1619.28	−1631.17
4m9	11.79	−72.67	−60.88	−1619.30	−1631.09
5m9	11.79	−72.67	−60.88	−1619.30	−1631.09
3e8	11.84	−72.10	−60.26	−1619.87	−1631.71
4e8	11.74	−72.07	−60.33	−1619.90	−1631.64
22mm8	11.24	−75.05	−63.81	−1616.92	−1628.16
23mm8	11.60	−72.92	−61.32	−1619.05	−1630.65
24mm8	11.30	−73.92	−62.62	−1618.05	−1629.35
25mm8	11.40	−73.95	−62.55	−1618.02	−1629.42
26mm8	11.50	−73.97	−62.47	−1618.00	−1629.50
27mm8	11.51	−74.49	−62.98	−1617.48	−1628.99
33mm8	11.29	−73.96	−62.67	−1618.01	−1629.30
34mm8	11.54	−72.37	−60.83	−1619.60	−1631.14
35mm8	11.29	−73.41	−62.12	−1618.56	−1629.85
36mm8	11.50	−73.46	−61.96	−1618.51	−1630.01
44mm8	11.21	−73.88	−62.67	−1618.09	−1629.30
45mm8	11.44	−72.34	−60.90	−1619.63	−1631.07
4np7	11.64	−72.05	−60.41	−1619.92	−1631.56
4ip7	11.40	−72.26	−60.86	−1619.71	−1631.11
23me7	11.50	−72.29	−60.79	−1619.68	−1631.18
24me7	11.25	−73.33	−62.08	−1618.64	−1629.89
25me7	11.46	−73.38	−61.92	−1618.59	−1630.05
33me7	11.30	−72.78	−61.48	−1619.19	−1630.49
34me7	11.44	−71.73	−60.29	−1620.24	−1631.68
35me7	11.35	−72.84	−61.49	−1619.13	−1630.48
43me7	11.44	−71.73	−60.29	−1620.24	−1631.68
44me7	11.28	−72.69	−61.41	−1619.28	−1630.56
223mmm7	11.04	−73.88	−62.84	−1618.09	−1629.13
224mmm7	10.57	−73.83	−63.26	−1618.14	−1628.71
225mmm7	10.78	−75.84	−65.06	−1616.13	−1626.91
226mmm7	10.85	−76.33	−65.48	−1615.64	−1626.49
233mmm7	11.10	−73.30	−62.20	−1618.67	−1629.77
234mmm7	11.25	−72.54	−61.29	−1619.43	−1630.68
235mmm7	11.10	−73.67	−62.57	−1618.30	−1629.40
236mmm7	11.21	−74.20	−62.99	−1617 77	−1628.98

Table II (*Continued*)

Compound	$\Delta H_v°$(liq)	$\Delta H_f°$(liq)	$\Delta H_f°$(gas)	$\Delta H_c°$(liq)	$\Delta H_c°$(gas)
244mmm7	10.72	−73.18	−62.46	−1618.79	−1629.51
245mmm7	11.05	−73.62	−62.57	−1618.35	−1629.40
246mmm7	10.81	−75.17	−64.36	−1616.80	−1627.61
255mmm7	10.83	−75.26	−64.43	−1616.71	−1627.54
334mmm7	11.08	−72.68	−61.60	−1619.29	−1630.37
335mmm7	10.73	−72.84	−62.11	−1619.13	−1629.86
344mmm7	11.16	−72.61	−61.45	−1619.36	−1630.52
345mmm7	11.29	−72.01	−60.72	−1619.96	−1631.25
23mip6	11.07	−70.52	−59.45	−1621.45	−1632.52
33ee6	11.27	−71.56	−60.29	−1620.41	−1631.68
34ee6	11.45	−71.12	−59.67	−1620.85	−1632.30
223mme6	10.91	−71.25	−60.34	−1620.72	−1631.63
224mme6	10.56	−73.28	−62.72	−1618.69	−1629.25
233mme6	11.16	−72.00	−60.84	−1619.97	−1631.13
234mme6	11.25	−71.93	−60.68	−1620.04	−1631.29
243mme6	11.12	−69.99	−58.87	−1621.98	−1633.10
244mme6	10.81	−72.08	−61.27	−1619.89	−1630.70
253mme6	11.01	−73.54	−62.53	−1618.43	−1629.44
334mme6	11.12	−70.05	−58.93	−1621.92	−1633.04
343mme6	11.24	−71.41	−60.17	−1620.56	−1631.80
2233mmmm6	10.87	−72.53	−61.66	−1619.44	−1630.31
2234mmmm6	10.82	−71.50	−60.68	−1620.47	−1631.29
2235mmmm6	10.48	−75.15	−64.67	−1616.82	−1627.30
2244mmmm6	10.18	−72.18	−62.00	−1619.79	−1629.97
2245mmmm6	10.31	−74.11	−63.80	−1617.86	−1628.17
2255mmmm6	9.92	−78.25	−68.33	−1613.72	−1623.64
2334mmmm6	11.13	−71.84	−60.71	−1620.13	−1631.26
2335mmmm6	10.61	−72.60	−61.99	−1619.37	−1629.98
2344mmmm6	10.98	−70.84	−59.86	−1621.13	−1632.11
2345mmmm6	11.06	−72.73	−61.67	−1619.24	−1630.30
3344mmmm6	11.27	−70.40	−59.13	−1621.57	−1632.84
243mmip5	10.72	−67.81	−57.09	−1624.16	−1634.88
233mee5	11.05	−68.88	−57.83	−1623.09	−1634.14
2233mmme5	11.4	−68.44	−57.30	−1623.53	−1634.67
2243mmme5	10.73	−68.45	−57.72	−1623.52	−1634.25
2343mmme5	11.03	−69.24	−58.21	−1622.73	−1633.76
22334mmmmm5	11.12	−68.79	−57.67	−1623.18	−1634.30
22344mmmmm5	10.65	−69.86	−59.21	−1622.11	−1632.76

[a] 1 kcal = 4.184 kJ.

Table III. Comparison of Calculated Standard Enthalpies of Vaporization and Formation for Liquid Nonanes and Decanes with Experimental Data in kcal mol^{-1} at 298.15 K [a]

		Calcd values				Calcd values	
Compound	Exptl data	Labbauf et al.[b]	This work	Compound	Exptl data	Labbauf et al.[b]	This work
			Standard Enthalpy of Vaporization				
9	11.10[c]	11.10	11.10	225mmm6	9.58[d]	9.73	9.58
223mmm6	9.87[d]	9.97	9.87	235mmm6	9.91[e]	10.05	9.91
224mmm6	9.48[d]	9.73	9.48	10	12.28[c]	12.28	12.28
			Standard Enthalpy of Formation (liq)				
9	−65.65;[f] −65.81[h]	−65.84	−65.80	223mme5	−65.18;[f] −65.33[i]	−66.92	−65.18
4m8	−66.82[g]	−66.40	−66.82	234mem5	−64.47;[f] −64.62[i]	−66.30	−64.47
22mm7	−68.88;[f] −69.03[i]	−69.11	−68.88	2233mmmm5	−66.51[i]	−66.54	−66.51
223mmm6	−67.57;[f] −67.72[i]	−67.62	−67.57	2234mmmm5	−66.37[i]	−66.40	−65.92
224mmm6	−67.60;[f] −67.76[i]	−67.86	−67.60	2244mmmm5	−66.92[i]	−66.95	−66.92
225mmm6	−70.11;[f] −70.27[i]	−70.44	−70.11	2334mmmm5	−66.43[i]	−66.46	−66.43
233mmm6	−67.18;[f] −67.34[i]	−67.13	−67.18	10	−71.92[h]	−71.95	−71.92
235mmm6	−67.88;[f] −68.04[i]	−68.08	−67.88	335mmm7	−72.85[g]	−72.81	−72.84
244mmm6	−66.97;[f] −67.14[i]	−67.37	66.97	2233mmmm6	−72.54[g]	−72.57	−72.53
334mmm6	−66.33;[f] −66.49[i]	−66.52	−66.33	2255mmmm6	−77.33[g]	−78.54	−78.25
33ee5	−65.82[i]	−65.85	−65.82				

[a] 1 kcal = 4.184 kJ. [b] Reference 9. [c] Reference 19. [d] Private communication, ERDA Energy Research Center, Bartlesville, Okla. [e] References 19 and 28. [f] Reference 3. [g] Reference 2. [h] Reference 19, corrected for slight change in $\Delta H_f°$ for CO_2(g) and H_2O(liq) due to changes in atomic weights. [i] Calculated value based on $\Delta H_f°$ (*n*-nonane, liq, 298.15 K) = −65.81 kcal mol^{-1} (ref 19) and enthalpy of isomerization (ref 8); uncertainty ±0.25 kcal mol^{-1}. [j] Calculated values based on $\Delta H_f°$ (*n*-nonane, liq, 298.15 K) = −65.81 kcal mol^{-1} (ref 19) and enthalpy of isomerization (ref 3); uncertainty ±0.25 kcal mol^{-1}.

kcal mol^{-1} for four other isomers. The magnitude of the differences for the 75 liquid decanes is as follows: less than 0.20 kcal mol^{-1} for 44 isomeric decanes, 0.2–0.4 kcal mol^{-1} for 16 decanes, 0.4–1.0 kcal mol^{-1} for 4 isomers, and 1.2–4.9 kcal mol^{-1} for 11 other isomers. Since the experimental uncertainty in any one of these values is at least ±0.2 kcal mol^{-1}, the calculated property values for nonanes and decanes are considered as reliable as the experimental and are recommended for general use. It is also important to note that the generalized trigonal additivity procedure is the most accurate of all procedures developed thus far for the correlation of the thermodynamic properties of the alkanes.

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Activity and Osmotic Coefficients in Dilute Aqueous Solutions of Bi-Univalent Electrolytes at 25 °C

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In nonassociative dilute aqueous electrolyte solutions, the Stokes and Robinson equation reduces to a simpler form, $\log \gamma_{\pm} = \log f_{\pm,DH} + 0.0156(h - \nu/2)m$, where $f_{\pm,DH}$ is the mean rational activity coefficient calculated from the Debye–Hückel equation. Thus the mean molal activity coefficients of an electrolyte in dilute regions can be calculated from the equation if suitable values of $\mathring{a}$ and h are available. The molal osmotic coefficients of a solution are related to the activity coefficients by means of the Gibbs–Duhem relation. A simple equation for calculating osmotic coefficients is derived; it takes the form $\phi = \phi_{DH} + 0.018hm$ where ϕ_{DH} is the molal osmotic coefficient of the solution calculated from the Debye–Hückel equation by use of the Gibbs–Duhem relation. These equations are applied to calculate the activity and osmotic coefficients in dilute aqueous solutions of some bi-univalent electrolytes, including chlorides, bromides, and perchlorates, concentration up to 0.1 m.

Hamer and Wu (*2*) have recently compiled numerous data of osmotic and activity coefficients in dilute solutions of 1–1 electrolytes. However, these coefficients for other types of electrolytes in dilute regions are lacking in general. When the experimental data in more dilute regions are not available, they can be derived directly from equations containing parameters which are obtained experimentally at higher concentration regions. A method based on the Stokes–Robinson hydration model (*4, 6*) is proposed to solve this problem. Activity and osmotic coefficients in solutions of some 2–1 electrolytes are calculated and compiled in this communication.

In nonassociated dilute electrolyte solutions the Stokes–Robinson two-parameter equation reduces to a simpler form (*4*), i.e.

$$\log \gamma_{\pm} = \log f_{\pm,DH} + 0.0156(h - \nu/2)m \quad (1)$$

or

$$\ln \gamma_{\pm} = \ln f_{\pm,DH} + 0.036(h - \nu/2)m \quad (2)$$

in which $\gamma_{\pm}$ is the mean molal activity coefficient, $f_{\pm,DH}$ is the mean rational activity coefficient calculated from the Debye-Hückel equation, h is the hydration number, ν is the stoichiometric ion number of the electrolyte, and m is the molality of the solution. The Debye–Hückel equation (*5*) is

$$\log f_{\pm,DH} = -\frac{A|z_+z_-|(I^{1/2})}{1 + B\mathring{a}(I^{1/2})} \quad (3)$$