

## A Group Additivity Approach for the Estimation of Vapor Pressures of Liquid Hydrocarbons from 298 to 500 K

James S. Chickos\* and Sarah Hosseini

Department of Chemistry, University of Missouri, St. Louis, Missouri 63121

Joel F. Liebman

Department of Chemistry and Biochemistry, University of Maryland—Baltimore County, Baltimore, Maryland 21228

Received March 2, 1993\*

A group additivity relationship is developed to estimate vapor pressures of hydrocarbons. These group values are able to reproduce experimental vapor pressures of the 326 compounds that comprise the dataset within a factor of 1.6. The vapor pressures range from about 1000 kPa (10 atm) to  $10^{-6}$  kPa, about 9 orders of magnitude. The temperature dependence of these group values are provided to cover the temperature range 298–500 K.

Vapor pressure is an important thermochemical property, and measurements of this property have been reported for many different compounds.<sup>1</sup> The success of numerous separation techniques depends on differences in the magnitude of this property. Evaluation of sublimation and vaporization enthalpies are often based on vapor pressure measurements. Theories designed to model transport rate data in the environment require vapor pressure information.<sup>2</sup> The evaluation of flash points, boiling points, and distillation conditions are other examples where some knowledge of the magnitude of this property can be very important. Vapor pressure information between the normal boiling point and the critical temperature is often of interest to process engineers.

A variety of equations for estimating vapor pressures are available in the literature. Over 50 have been reported.<sup>1-3</sup> Many evaluation techniques require the following properties: (1) the critical temperature and (2) pressure (3) and the vapor pressure at some reference temperature below the critical temperature. For many compounds, some of this information, notably the critical properties, is not available and must be also estimated.

The mathematical relationships that have frequently been used in these estimations include the integrated form of the Clausius Clapeyron equation (1), the Antoine (eq

$$\ln P = A - \Delta H_v/RT \quad (1)$$

$$\ln P = A - B/(T - C) \quad (2)$$

$$\Delta H_v = \Delta H_{vb} [(1 - T/T_c)/(1 - T_b/T_c)]^m \quad (3)$$

2) and Watson's equation (eq 3). The terms A, B, C, and the exponent m in eqs 1-3 are constants and P, T, T<sub>b</sub>, T<sub>c</sub>, ΔH<sub>v</sub>, and ΔH<sub>vb</sub> refer to vapor pressure, temperature, boiling

point, critical point, vaporization enthalpy at temperature T, and vaporization enthalpy at the boiling point, respectively.

Most estimation methods of vapor pressure have been developed by engineers and have been designed for greatest accuracy between the normal boiling point and the critical temperature. Application of these methods to determine vapor pressures at ambient temperature often require extensive extrapolations. The accuracy of the predictions when large extrapolations are necessary and when some of the input parameters themselves must be estimated is open to question.

We have had an interest in developing estimation techniques using the methods of group additivity. A major advantage of this method is that the only variable in the calculation is the molecular structure. If the property being correlated responds well to group methods, then it is possible to use parameters generated from the experimental data of available compounds to estimate the property in question for compounds that are less accessible or simply unavailable. In principle, group methods can provide a reasonable estimate of a property without the need to extrapolate. The major limitation to developing group methods is the need of a large reliable data base.

Group methods to estimate vapor pressures of hydrocarbons have been reported by Stein<sup>4</sup> and Macknick and Prausnitz.<sup>5</sup> The group method of Stein can be used to estimate the vapor pressure of the n-alkanes. The Gibbs energy of vaporization is estimated from which the vapor pressure of the n-alkane may be obtained. The group method of Macknick and Prausnitz gives parameters for a vapor pressure equation based on a kinetic theory of fluids. Good representation of the vapor pressure in the region of 1.3–265 kPa is obtained for the 67 liquid hydrocarbons used in the database.

We would like to report a group additivity scheme that has been developed to estimate the vapor pressures of liquid hydrocarbons. In contrast to most previous work which uses critical properties, this method focuses on the low vapor pressure end of the scale. This scheme is not designed for estimations close to the critical pressure. Experimental data available from 298 to 500 K have been

\* Abstract published in *Advance ACS Abstracts*, August 15, 1993.

(1) Stephenson, R. M.; Malanowski, S. *Handbook of the Thermodynamics of Organic Compounds*; Elsevier: New York, 1987.

(2) Grain, C. F. In *Handbook of Chemical Property Estimation Methods*, Lyman, W. J., Reehl, W. F., Rosenblatt, D. H., Eds.; American Chemical Society: Washington D.C., 1990.

(3) Partington, J. R. *An Advanced Treatise on Physical Chemistry*; Longmans, Green and Co.: London, 1951; Vol. 2. See also Ambrose, D. *J. Chem. Thermodyn.* 1982, 14, 61. Ambrose, D.; Davies, R. H. *J. Chem. Thermodyn.* 1980, 12, 871. Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill: New York, 1987.

(4) Stein, S. E. *J. Chem. Soc. Faraday Trans. 1* 1981, 77, 1457.

(5) Macknick, A. B.; Prausnitz, J. M. *I&EC Fundam.* 1979, 18, 348.

Table I. Group Values for Estimating Vapor Pressures of Liquid Hydrocarbons

298 K	350 K	400 K	450 K	500 K		
Acyclic Components						
1.693	1.769	1.905	1.964	1.921	primary sp <sup>3</sup> carbon	A
-0.492	-0.363	-0.292	-0.227	-0.175	secondary sp <sup>3</sup> carbon	B
-2.575	-2.383	-2.399	-2.339	-2.166	tertiary sp <sup>3</sup> carbon	C
-4.589	-4.395	-4.48	-4.416	-4.159	quaternary sp <sup>3</sup> carbon	D
1.827	1.854	1.961	1.904	1.911	secondary sp <sup>2</sup> carbon	E
-0.563	-0.349	-0.285	-0.249	-0.165	tertiary sp <sup>2</sup> carbon	F
-2.759	-2.497	-2.475	-2.318	-2.142	quaternary sp <sup>2</sup> carbon	G
-0.711	-0.483	-0.388	-0.292	NA	quaternary sp carbon	H
1.824	1.956	2.122	NA	NA	tertiary sp carbon	I
Aromatic Components						
0.194	0.328	0.419	0.479	0.511	tertiary aromatic sp <sup>2</sup> carbon	J
-1.972	-1.848	-1.802	-1.726	-1.581	quaternary aromatic sp <sup>2</sup> carbon adjacent to an sp <sup>3</sup> carbon	K
-2.267	-2.045	-1.975	-1.782	-1.680	quaternary aromatic sp <sup>2</sup> carbon adjacent to an sp <sup>2</sup> carbon	L
[-2.024] <sup>b</sup>	-1.363	-1.235	-1.117	-1.092	bridging quaternary aromatic sp <sup>2</sup> ring carbon of a fused ring	M
Cyclic Components						
-0.515	-0.381	-0.310	-0.270	-0.208	slope (cyclic hydrocarbons)	N
2.627	3.073	3.451	3.759	3.813	intercept (cyclic hydrocarbons)	O
-2.056	-2.076	-2.154	-2.238	-2.210	cyclic tertiary sp <sup>3</sup> carbon	P
-3.975	-4.027	-4.220	-4.248	-4.289	cyclic quaternary sp <sup>3</sup> carbon	Q
0.0143	0.0013	-0.016	-0.019	0.005	cyclic tertiary sp <sup>2</sup> carbon	R
-2.142	-2.129	-2.219	-2.229	-2.438	cyclic quaternary sp <sup>2</sup> carbon	S
-1.498	-1.480	-1.541	-1.560	-1.476	cyclic quaternary aromatic sp <sup>2</sup> carbon common to an alicyclic ring	T

<sup>a</sup> NA = Not available. <sup>b</sup> Based on only two compounds.

used to derive a set of equations that can provide group additivity constants at any temperature in this range. These equations permit the evaluation of the vapor pressure of any liquid hydrocarbon exhibiting a vapor pressure between 10<sup>4</sup> and 10<sup>-6</sup> kPa between 298 and 500 K in our database within a factor of 1.6 (standard deviation) and within 1 order of magnitude for vapor pressures between 10<sup>-6</sup> and 10<sup>-10</sup> kPa.

The general guidelines followed in developing this group additivity scheme were to provide the best possible correlation using the fewest parameters. We have also tried to maintain consistency with our previous work regarding definitions and conventions.<sup>6</sup> It should be noted that the terms primary, secondary, tertiary, and quaternary carbon described in Table I and elsewhere in this work, define a substitution pattern of carbon that is based solely on the number of attached hydrogens, 3, 2, 1, 0, respectively. Values in Table I based on limited experimental data are enclosed in brackets and should be considered as tentative assignments.

All experimental data was obtained from the compilations by Stephenson and Malanowski.<sup>1</sup> These workers list Antoine constants, the temperature range of applicability, and other data for over 6000 organic compounds. Vapor pressures for the hydrocarbons in this compendium were calculated from these constants for the temperature range of the correlation. In most cases, vapor pressures were calculated by interpolation. In those cases where some extrapolation was necessary, the temperature range of extrapolation was usually less than 20 K.

An examination of the integrated form of the Clausius-Clapeyron equation (eq 1) suggests a format for the generation of group constants. Group methods for the estimation of vaporization enthalpies are well known and

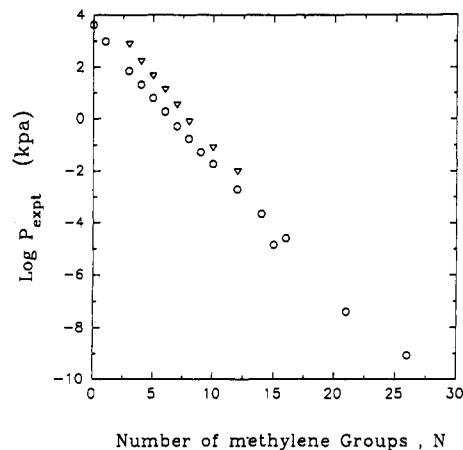


Figure 1. Log *P* as a function of the number of methylene groups in the molecule; (O) linear alkanes; Δ cycloalkanes.

simple additivity of group values affords good estimates of these quantities.<sup>7</sup> Since the relationship between vapor pressure and vaporization enthalpy is logarithmic, this equation suggests that group constants for estimating vapor pressure should translate into additivity of logarithms. Examination of the logarithm of vapor pressure of the *n*-alkanes (in kPa) as a function of the number of methylene groups quickly confirms that a linear correlation does exist. This is illustrated in Figure 1 (circles). Preliminary group values for a methyl and methylene group were obtained from the intercept (intercept/2) and slope of the line, respectively. These values were then used in subsequent correlations to obtain preliminary group values for tertiary and quaternary carbon centers

(6) Chickos, J. S.; Braton, C. M.; Hesse, D. G.; Liebman, J. F. *J. Org. Chem.* 1991, 56, 927. Chickos, J. S.; Hesse, D. G.; Liebman, J. F. *J. Org. Chem.* 1990, 55, 3833.

(7) DuCros, M.; Greison, J. F.; Sannier, H. *Thermochim. Acta* 1980, 36, 39. DuCros, M.; Greison, J. F.; Sannier, H.; Velasco, I. *Thermochim. Acta* 1981, 44, 134. Guthrie, J. P.; Taylor, K. F. *Can. J. Chem.* 1983, 61, 602. Chickos, J. S.; Hesse, D. G.; Liebman, J. F.; *J. Org. Chem.* 1989, 54, 5250.

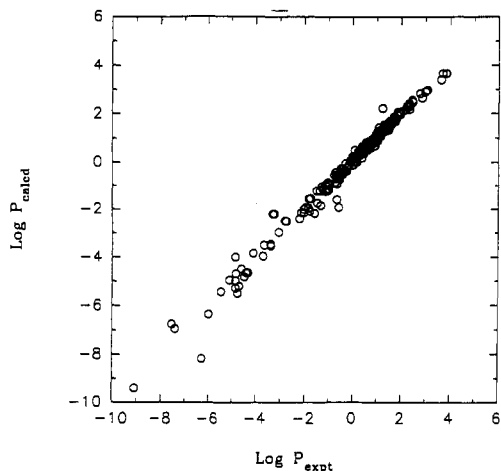


Figure 2. Calculated and experimental vapor pressures (kPa) of hydrocarbons at 298 K.

and then in turn for all the remaining acyclic and aromatic group values listed in Table I. Additional details concerning the sequence of evaluation, the compounds used to obtain these group values, the calculations involved, and a comparison of experimental and calculated log  $P$  values can be found in the tables in the supplementary material.

Preliminary group values for monocyclic and polycyclic materials were obtained by a procedure similar to the one recently reported for estimating fusion entropies.<sup>6</sup> A plot of log  $P$  against the number of methylene groups in the cycloalkane ring,  $n$ , is given by the triangles in Figure 1 and resulted in the following relationship between volatility and ring size:

monocyclic hydrocarbons

$$\log P_{(298)} = 2.626 - 0.5228(n-3) \quad (4)$$

polycyclic hydrocarbons

$$\log P_{(298)} = 2.626N - 0.5228(R - 3N) + \sum n_i G_i \quad (5)$$

The equation for parent polycyclic hydrocarbons can be derived from eq 4 by correcting for the number of rings,  $N$ , in the molecule and by taking into account the atoms common to both rings so that they are not counted twice. The  $R$  in eq 5 refers to the total number of ring atoms and the  $(R - 3N)$  term corrects for this possible redundancy. Depending on structure, this term can make either a positive or negative contribution to the calculation. For parent polycyclic hydrocarbons, the final term in eq 5 corrects for the bridgehead carbons which are no longer methylene groups.

Group values for these more highly substituted ring carbons were obtained from the difference between the experimental log  $P$  values and the predictions of eq 4 or 5 to estimate the contributions of the parent ring. The contributions of any acyclic or aromatic substituents were also subtracted from the experimental log  $P$  values in arriving at the group values for the substituted carbon atoms listed under the heading "cyclic components" in Table I.

The group values cited in Table I were obtained by a weighted least-squares procedure similar to those reported previously. The parameters were varied in order to

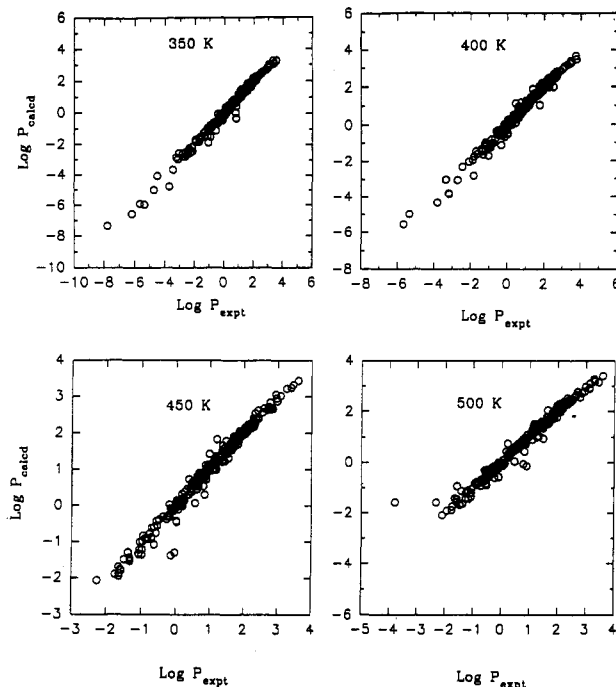


Figure 3. Calculated and experimental vapor pressures of hydrocarbons at 350, 400, 450, and 500 K; note the differences in range of each plot.

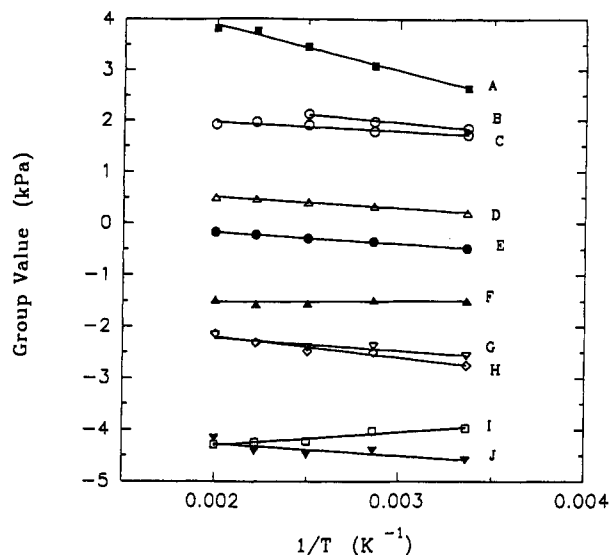
Table II. A Summary of the Parameters Generated from a Linear Regression Analysis Using the Parameters of Table I To Estimate Experimental Vapor Pressures from 298–500 K

temperature (K)	298	350	400	450	500
intercept	-0.0022	0.0029	-0.0061	-0.0301	0.0408
slope	1.026	1.003	1.010	1.029	0.970
correl coeff	0.9902	0.9940	0.9927	0.9902	0.9871
no. of data points	325	405	463	331	313
std dev	0.257	0.161	0.156	0.163	0.203

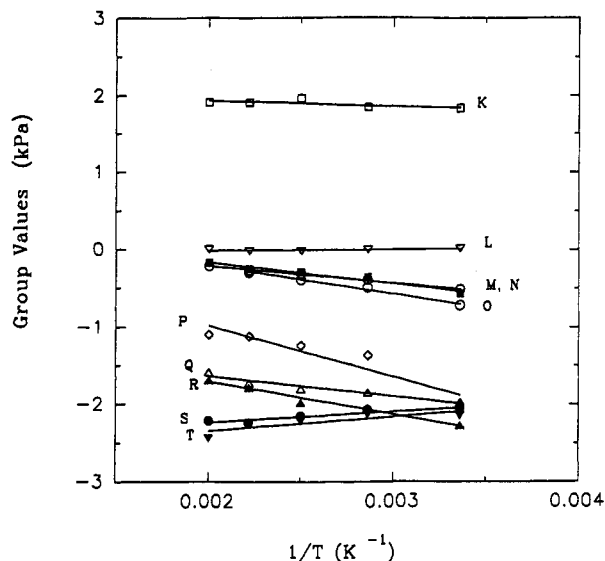
Table III. The Temperature Dependence of the Group Values from 298–500 K

intercept A	slope B	correl coeff	
2.370	-200.69	0.941	primary sp <sup>3</sup> carbon
0.288	-231.14	0.999	secondary sp <sup>3</sup> carbon
-1.720	-252.05	0.924	tertiary sp <sup>3</sup> carbon
-3.795	-236.90	0.803	quaternary sp <sup>3</sup> carbon
0.241	-223.84	0.994	cyclic hydrocarbons carbon
5.733	-923.46	0.994	cyclic hydrocarbons carbon
-2.513	141.84	0.937	cyclic tertiary sp <sup>3</sup> carbon
-4.783	242.70	0.956	cyclic quaternary sp <sup>3</sup> carbon
-0.050	18.57	0.617	cyclic tertiary sp <sup>2</sup> carbon
-2.726	191.73	0.823	cyclic quaternary sp <sup>2</sup> carbon
2.077	-71.83	0.732	secondary sp <sup>2</sup> carbon
0.388	-274.42	0.977	tertiary sp <sup>2</sup> carbon
-1.387	-405.08	0.970	quaternary sp <sup>2</sup> carbon
1.002	-237.92	0.996	tertiary aromatic sp <sup>2</sup> carbon
-1.109	-261.56	0.966	quaternary aromatic sp <sup>2</sup> carbon
			adjacent to an sp <sup>3</sup> carbon
-0.854	-423.76	0.988	quaternary aromatic sp <sup>2</sup> carbon
			adjacent to an sp <sup>2</sup> carbon
-1.552	15.93	0.227	cyclic quaternary aromatic sp <sup>2</sup> carbon common to an alicyclic ring
			bridging quaternary aromatic sp <sup>2</sup> carbon of a fused ring
0.363	-668.41	0.935	quaternary sp carbon
0.527	-364.33	0.993	quaternary sp carbon
2.963	-342.94	0.987	tertiary sp carbon

minimize the sum of the squared fractional difference between experiment and calculation,  $[(\log P_{\text{expt}} - \log P_{\text{calcd}}) / \log P_{\text{expt}}]^2$ . Since both positive and negative log  $P_{\text{expt}}$  values are generated, it was necessary to add an arbitrary



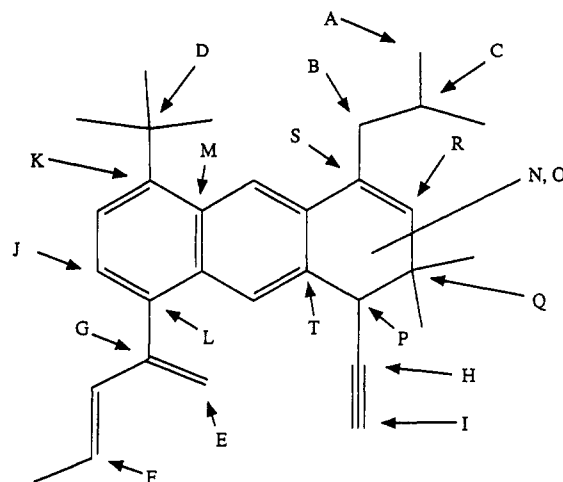
**Figure 4.** Group values as a function of temperature; (A) intercept (cyclic hydrocarbons); (B) tertiary  $sp^3$  carbon; (C) primary  $sp^3$  carbon; (D) tertiary aromatic  $sp^2$  carbon; (E) secondary  $sp^3$  carbon; (F) aromatic  $sp^2$  carbon common to an alicyclic ring; (G) tertiary  $sp^3$  carbon; (H) quaternary  $sp^2$  carbon; (I) cyclic quaternary  $sp^3$  carbon; (J) quaternary  $sp^3$  carbon.



**Figure 5.** Group values as a function of temperature; (K) secondary  $sp^2$  carbon; (L) cyclic tertiary  $sp^2$  carbon; (M) cyclic hydrocarbon (slope); (N) tertiary  $sp^3$  carbon; (O) quaternary  $sp$  carbon; (P) bridging quaternary aromatic  $sp^2$  carbon of a fused ring; (Q) quaternary  $sp^2$  carbon adjacent to an  $sp^3$  carbon; (R) quaternary  $sp^2$  carbon adjacent to an  $sp^2$  carbon; (S) cyclic tertiary  $sp^3$  carbon; (T) cyclic tertiary  $sp^2$  carbon.

number to both  $\log P_{\text{expt}}$  and  $\log P_{\text{calcd}}$  to prevent sign changes and keep this function well behaved. A value of  $-5$  was chosen and served two purposes. First, it prevented sign changes by converting all  $\log P$  values to negative numbers. It also had the effect of weighing the larger numbers (in the positive sense) more heavily than the smaller more-negative numbers. Vapor pressures at or slightly below atmospheric pressure are far easier to measure and are more accurately known than those at lower pressures, particularly at the lowest pressure ranges of this correlation.

Once preliminary group values were obtained for each carbon type listed in Table I, all of the values were allowed



**Figure 6.** A hypothetical molecule illustrating all the group values of Table I. Estimated  $\log P_{\text{calcd}}$  (298 K) for this molecule:  $O + 3N + P + Q + R + S + 2T + 8A + B + C + D + E + 2F + G + H + I + 4J + K + L + 2M = -12.6$ .

**Table IV.** Summary of the Parameters from a Linear Regression Analysis Using the Parameters of Table III To Estimate Experimental Vapor Pressures from 298–500 K

temperature (K)	298	350	400	450	500
intercept	0.064	-0.082	-0.081	-0.0407	0.1678
slope	1.016	1.040	1.014	1.016	0.945
correl coeff	0.9899	0.9929	0.9923	0.9897	0.9772
no. of data points	325	405	463	331	313
std dev	0.277	0.190	0.162	0.163	0.270

to vary in the least-squares minimization process. Our procedure varied parameters in groups of three. The process was continued until the changes in each successive iteration had little effect on the sum of the squared fractional difference. The initial value of most groups was not significantly affected by this iteration procedure.

The results in Figure 2 illustrate the quality of the correlation obtained from the treatment just described. Calculated  $\log P$  values are plotted against the corresponding experimental ones. Perhaps the most noteworthy feature of this correlation is that the correlation appears applicable over a range of pressure that covers 9 orders of magnitude.

The availability of data at elevated temperatures encouraged us to repeat the protocol just described at 350, 400, 450, and 500 K. Although Antoine constants for a particular compound may have been available for many of these temperatures, the database changed substantially as the temperature increased. Despite this change, the trends observed with temperature generally continued in a consistent fashion. The results obtained from this treatment are summarized in columns 2–5 of Table I and illustrated in Figure 3. A summary of the quality of the correlation obtained at each temperature in Figures 2 and 3 is given in Table II.

The correlations observed in Table II above ambient temperature are quite similar in quality. Although the largest standard deviation is observed at room temperature, it can be noted that only the room temperature correlation contains data down to  $10^{-10}$  kPa. If data down to  $10^{-6}$  is considered, the standard deviation in  $\log P_{\text{calcd}}$  (298) is  $\pm 0.2$  kPa, much more in line with the standard deviations observed at the other temperatures over a similar pressure range.

## Chart I. Examples of Some Sampler Vapor Pressure Estimations (kPa)

Examples of Some Sample Vapor Pressure Estimations (kPa)	
$C_7H_{14}$	<i>trans</i> 4-methyl-2-hexene (1) <i>cis</i> 4-methyl-2-hexene (2)
	prim $sp^3$ carb: 3(1.693) sec $sp^3$ carb: 1(-0.492) tert $sp^3$ carb: 1(-2.575) tert $sp^2$ carb: 2(-0.563)
	log $P_{calcd}(298)$ : 0.89 log $P_{expt}(298)$ (1): 0.99 log $P_{expt}(298)$ (2): 1.0
$C_{10}H_{12}$	2,4-dimethylstyrene(3) 2,5-dimethylstyrene(4)
	prim $sp^3$ carb: 2(1.693) quat arom $sp^2$ carb adj to an $sp^3$ carb: 2(-1.972) quat arom $sp^2$ carb adj to an $sp^2$ carb: 2(-2.267) tert $sp^2$ carb: 1(-0.563) sec $sp^2$ carb: 1(1.827) tert arom $sp^2$ carb: 3(0.194)
	log $P_{calcd}(298)$ : -0.98 log $P_{expt}(3)$ (298): -1.16 log $P_{expt}(4)$ (298): -0.96
$C_{10}H_{16}$	<i>d</i> -limonene(5) <i>l</i> -limonene(6) <i>dl</i> -limonene(7)
	ring contribution: 2.627-3(0.515) cyc tert $sp^2$ carb: 0.0143 cyc quat $sp^2$ carb: -2.142 prim $sp^3$ carb: 2(1.693) cyc tert $sp^3$ carb: -2.056 quat $sp^2$ carbon: -2.759 sec $sp^2$ carb: 1.827
	log $P_{calcd}(298)$ : -0.65 log $P_{expt}(5)$ (298): -0.56 log $P_{expt}(6)$ (298): -0.60 log $P_{expt}(7)$ (298): -0.59
$C_{11}H_{10}$	1-methylnaphthalene
	prim $sp^3$ carb: 1(1.693) tert arom $sp^2$ carb: 7(0.194) quat arom $sp^2$ carb adj to an $sp^3$ carb: 1(-1.972) bridg quat arom $sp^2$ carb of a fused ring: 2(-2.024)
	log $P_{calcd}(298)$ : -2.97 log $P_{expt}(298)$ : -3.05
$C_9H_8$	indene
	ring contribution: 2.627-2(0.515) cyc quat arom $sp^2$ carb common to an alicyclic ring: 2(-1.498) cyc tert $sp^2$ carb: 2(0.0143) tert arom $sp^2$ carb: 4(0.194)
	log $P_{calcd}(298)$ : -0.59 log $P_{expt}(298)$ : -0.66
$C_{10}H_{16}$	tetrahydrodicyclopentadiene
	ring contributions: [2.626]3-[0.523] tert cyc $sp^3$ carb: 4(-2.056)
	log $P_{calcd}(298)$ : -0.86 log $P_{expt}(298)$ : -0.72

The availability of the parameters listed in Table II above ambient temperature prompted us to examine whether each group value could be expressed analytically as a function of temperature. Plotting each group value in Table I against the corresponding  $1/T$  gave the results listed in Table III and in Figures 4 and 5. Reasonable straight lines are obtained for most of the 20 group values listed in Table III. An examination of the correlation coefficients, column 3 of Table III, suggests that most parameters are successfully correlated by such a treatment. Only one parameter appears poorly correlated by such a treatment, line P in Figure 5 defined by the diamonds.

To see how much of an error in  $\log P_{calcd}$  would be introduced by using group values generated from the parameters of Table III instead of Table I, we repeated these calculations. The constants of Table III were used to generate new group values at 298, 350, 400, and 500 K. These values were then substituted for the values in Table I for each compound in the database at each respective temperature. This resulted in new correlations of  $\log P_{expt}$  and  $\log P_{calcd}$  which are summarized by the parameters in Table IV. Comparison of the correlation coefficients and standard deviations reported in Tables II and IV suggests that the correlations are not significantly affected by using group values generated from the equations of Table III. This suggests that these equations can be used to calculate new group parameters for any temperature between 298 and 500 K with equal success.

The group values in Table I may be used to predict the vapor pressure of a liquid phase at a temperature at which the hydrocarbon exists as a solid. Since data for subcooled liquids were not available for use in the correlation,<sup>1</sup> it is not clear how well the vapor pressures of subcooled liquids will be simulated by the group values in Table I. Estimation of vapor pressure of the liquid should remain reasonably accurate down to the melting point of the liquid. Below the melting point, the vapor pressure of the solid is expected to decrease more rapidly than predicted by the parameters in Table II.

The application of the group values of Table I to estimate vapor pressures is quite simple. The hypothetical molecule illustrated in Figure 6 was designed to illustrate a molecular structure that contains an example of all of the group values defined in Table I. The examples in Chart I provide some guide to the use of most of these parameters in estimating vapor pressure. Although estimation of vapor pressure is very similar to previous estimations of fusion entropies,<sup>6</sup> some differences do exist.

The estimation for acyclic and aromatic hydrocarbons is illustrated by the calculations for *trans*-4-methyl-2-hexene, 1-methylnaphthalene, and dimethylstyrene. Our procedure does not distinguish between geometric isomers in cyclic and olefinic compounds, substitution isomers in aromatic systems, or chiral molecules. Molecules containing non-benzenoid rings are estimated as a derivative of the corresponding cycloalkane. In nonaromatic ring

systems the contribution of the ring atoms is obtained by using the appropriate ring equation and the groups listed under "cyclic components" in Table I. Contributions of the remaining acyclic or aromatic portions of the molecule complete the calculation. Indene illustrates the estimation of a molecule that contains both a cycloalkane and aromatic ring. Contributions of the cyclopentane ring are corrected for the tertiary cyclic  $sp^2$  and quaternary cyclic aromatic  $sp^2$  carbons. The remaining groups, in this instance four tertiary aromatic  $sp^2$  carbons, complete the estimation. Limonene and tetrahydrocyclopentadiene in Chart I illustrate the calculations for a cyclic chiral molecule and the use of the ring equation for polycyclic molecules. For

additional examples the reader is referred to the tables in the supplementary material.

**Acknowledgment.** We are grateful to the Weldon Spring Fund of the University of Missouri and the USEPA, Office of Exploratory Research (Grant No.# R81-9067-010) for support of this work.

**Supplementary Material Available:** Tables containing the names, vaporization enthalpies, calculated and experimental vapor pressures, and estimations of the 326 hydrocarbons used in this correlation (22 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.