Table V. Acid *Vs.* Neutral Difference Spectra of Tyrosine, Tryptophan, and Phenylalanine

$M\mu$	Tyrosine	Tryptophan	Phenylalanine
230	...	... ...	46.7
232	576	421 ± 49	34.1
234	441	610 ± 37	23.3
236	346	590 ± 31	16.0
238	218	512 ± 29	10.8
240	108	432 ± 23	6.9
242	40	358 ± 19	3.9
244	4	305 ± 20	3.3
246	−13	263 ± 21	1.2
248	−18	240 ± 16	−0.3
250	−20	223 ± 14	2.5
252	−16	216 ± 17	−1.8
254	−12	219 ± 15	−1.9
256	−7	222 ± 11	4.0
258	−5	223 ± 14	−3.3
260	−3	225 ± 14	−4.3
262	0	232 ± 13	2.5
264	0	232 ± 18	−3.1
266	−4	224 ± 15	−3.4
268	−8	214 ± 7	−4.4
270	−11	190 ± 9	−2.0
272	−13	159 ± 12	−0.7
274	−20	127 ± 15	−0.3
276	−40	128 ± 16	0
278	−45	110 ± 10	
280	−34	71 ± 11	
282	−46	−23 ± 7	
284	−73	−92 ± 9	
286	−71	−3 ± 9	
288	−49	−26 ± 4	
290	−31	−250 ± 5	
292	−20	−317 ± 9	
294	−16	−276 ± 9	
296	−14	−227 ± 5	
298	−12	−177 ± 7	
300	−10	−131 ± 9	
302	−9	−88 ± 6	
304	−7	−59 ± 8	
306	−6	−40 ± 10	
308	−4	−24 ± 10	
310	−3	−13 ± 10	
312	−2	−7 ± 7	
314	−1	−4 ± 4	
316	−1	0	
318	0		

photometers demonstrated also the accuracy of this instrument. Apparently, with proper checking of the performance, the results with different instruments should agree to within 1% over most, but certainly at the upper half, of the absorbancy scale.

Difference spectra are becoming increasingly important. The alkaline-neutral difference spectrum of the three amino acids investigated can be calculated easily from the data presented. As a check on these, direct difference spectra were also recorded and the data are listed in Table IV. These figures are either from one single determination or are averages obtained from two individual runs. The calculated and the direct differences agree much better than the general 1% accuracy assumed for the spectral data.

More attention was paid in this work to neutral and alkaline solutions, because these are of general applicability to proteins. In acid solution, a large number of the latter are insoluble. Nevertheless, to have a complete set of data, difference spectra of acid-neutral solutions of the aromatic amino acids were also run and the data are presented in Table V. The tyrosine and phenylalanine data are from a single run, those for tryptophan are the averages of two runs. Apparently, the differences are much smaller than with the alkaline-neutral pairs. The spectra of the three amino acids in acid solution can be calculated from the neutral and the corresponding acid difference spectra.

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RECEIVED for review June 23, 1967. Accepted December 9, 1967.

Correlation Studies on Vapor Pressures and Critical Properties for Isomeric Alkanes

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IN SPITE of the great amount of effort that has been expended in developing correlation procedures for physical properties of branched alkanes, the authors still find the situation in a somewhat unsatisfactory state. Furthermore, recently additional, precise data have become available (*1, 12*), which serve as an incentive to re-examine the status of the problem on branched alkanes, with the further goal in mind that these hydrocarbons may serve as a framework for properties of alkyl derivatives. Thus, the authors have chosen to examine critically the vapor pressure and boiling point data and the values of the critical points of isomeric alkanes from the butanes (C_4) through the decanes (C_{10}).

Structural dependence of isomeric variations in physical and thermodynamic properties has been the subject of investigation by various authors (*5, 6, 11, 15, 18*). Greenshields and Rossini (*6*) have correlated the variation in physical and thermodynamic properties between an isomer and the normal compound with the structural param-

Since correlations based on constants B and C of the Antoine vapor pressure equation, $\log P$ (mm.) $= A - \{B/[C + t(°C.)]\}$, have proved successful in several studies, the isomeric variation procedure was applied to the difference in B and C for the isomer and the normal compound. Equations were developed to predict constants B_i and C_i of isomeric alkanes. With these values for the Antoine constants and a single experimental value of a boiling point—preferably at 1 atm.—for each isomer, boiling points were calculated over the range from 10 to 1500 mm. of Hg pressure. Experimental literature data on 36 API Research hydrocarbon alkanes, C_5 to C_9 (seven nonanes), were used for regression analysis giving the error sum of squares of 3.22 deg. ($\sigma = \pm 0.3$) in the boiling point at 60 mm. of Hg and of 0.40 deg. ($\sigma = \pm 0.1$) at 1500 mm. of Hg. This procedure was used to predict Antoine constants A, B, and C thereby improving vapor pressure–boiling point data for all 35 isomeric nonanes and obtaining new data for all 75 isomeric decanes. New correlations were also developed for the critical state predicting T_c, P_c, and d_c of isomeric alkanes which are modifications of the Riedel and the Greenshields and Rossini empirical procedures. The standard error of estimate, $[(\Sigma\delta^2)/N]^{1/2}$ where δ is the difference between calculated and the experimental value, for T_c, P_c, and d_c calculated using these relations were as follows: T_c, ± 0.52 deg.; P_c, ± 0.14 atm.; d_c, ± 0.005 gram per cc. These methods for critical state were compared with those of Riedel and of McMicking and Kay.

eters such as n, n_3, n_4, P, W, P_4', and P_4''. They expressed the variation in any specific property, G, of the liquid state by the following relation:

$$G_i - G_n = \alpha_1[n_3/(n)^{1/2}] + \alpha_2[n_4/(n)^{1/2}] + \alpha_3(P_i - P_n)/n^{1/2} + \alpha_4(W_i - W_n)/(n^2 - n) + \alpha_5 P_4' + \alpha_6 P_4'' \qquad (1)$$

The "Platt" number P is the total number of pairs of carbon atoms three bonds apart and is simply given by $(n - 3)$ for n-alkanes. For the branched alkanes, a procedure suggested by one of the authors (*18*) is used. The Platt number P_i of the isomer is the sum of the $P_{k,l}^i$'s characteristic of the C_k—C_l bonds in the molecule (k,l = 1, 2, 3, 4)—i.e.,

$$P_i \equiv \Sigma_{k,l} P_{k,l}^i = \Sigma(k - 1)(l - 1) \quad k,l = 1,2,3,4$$

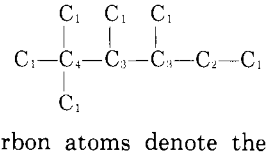
For the 10 C_k—C_l bonds, the following values for the $P_{k,l}$'s are:

$$\begin{array}{lll} P_{11} = P_{12} = P_{13} = P_{14} = 0 & & \\ P_{22} = 1 & & P_{33} = 4 \\ P_{23} = 2 & & P_{34} = 6 \\ P_{24} = 3 & & P_{44} = 9 \end{array}$$

The "Wiener" number W is the total number of bonds between all pairs of carbon atoms and is equal to $\{[(n - 1)(n)(n + 1)]/6\}$ for n-alkanes. A mathematical expression could not be derived for W for branched alkanes. A simplified method has been suggested by Wiener (*24*) for calculating W by multiplying the number of carbon atoms on one side of a bond by the number on the other side and summing the products for all bonds. Greenshields and Rossini (*6*) have given an example calculation for all structural parameters used in Equation 1. However, a sample calculation of P and W is as follows:

n-decane $C_1—C_2—C_2—C_2—C_2—C_2—C_2—C_2—C_2—C_1$

2,2,3,4-tetramethylhexane



$$C_1—C_4(C_1)_2—C_3(C_1)—C_3(C_1)—C_2—C_1$$

The subscripts on the carbon atoms denote the type of carbon atom in the molecule.

$$P_n = (n - 3) = 7$$

$$P_i = 1(P_{1-2}) + 2(P_{1-3}) + 3(P_{1-4}) + 1(P_{2-3}) + 1(P_{3-3}) + 1(P_{3-4})$$

$$P_i = 0 + 0 + 0 + 2 + 4 + 6 = 12$$

$$W_n = \frac{(n - 1)(n)(n + 1)}{6} = \frac{(9)(10)(11)}{6} = 165$$

$$W_i = (1 \times 9) + (4 \times 6) + (6 \times 4) + (8 \times 2) + (9 \times 1) + (1 \times 9) + (1 \times 9) + (1 \times 9) + (1 \times 9) = 118$$

This equation was applied to physical properties such as molal volume, molal refraction, boiling point at 10 mm. of Hg pressure, normal boiling point, standard enthalpy of formation of the liquid at 25°C., and the standard enthalpy of vaporization for alkanes and aliphatic alcohols. This procedure has been used in the preparation of American Petroleum Institute Research Project 44 Tables (*17*) for isomeric alkanes. Lydersen's group contribution method (*11*) was modified and improved upon by Riedel (*15*), who successfully correlated critical properties using an isomeric variation method with only three structural parameters n_3, n_4, and P. The Riedel equation takes the form:

$$G_i - G_n = an_3 + bn_4 + c(P_i - P_n) \qquad (2)$$

and was used to predict critical properties of C_9 and C_{10} paraffins, for which compound experimental data are still unavailable. Both the Lydersen's additivity group method and Greenshields and Rossini's and Riedel's isomeric correlation procedures have recently been justified, at least for hydrocarbons, in terms of the generalized treatment of nonbonded interactions and higher order steric terms by Somayajulu and Zwolinski (*18-20*). For example, Riedel's two parameters n_3 and n_4 define contributions from the tertiary ($HC_3 \equiv C$) and quaternary ($C_4 \equiv C$) groups, whereas the Platt number (P) defines the number of vicinal interactions between carbon-carbon bonds across a single carbon bond.

Sondak and Thodos (*21*) correlated the constants of the Frost-Kalkwarf vapor pressure equation with molecular structure, and the predicted parameters were used to calculate vapor pressure data for all 34 isomeric nonanes. Thodos and coworkers (*5, 22*) also developed a group contribution procedure to predict van der Waals' constants a and b from structural parameters, which in turn were used to calculate critical properties of hydrocarbons. McMicking and Kay (*12*) recently determined vapor pressure–boiling point data, saturated liquid and vapor densities, and critical properties of C_7 and C_8 alkanes (API Research hydrocarbons). They also developed correlations for the prediction of critical properties as a function of certain structural variables. Complete references to the older literature on correlation of physical properties of liquid isomeric alkanes are given by Reid and Sherwood (*14*) and Greenshields and Rossini (*6*).

The purpose of this study was to critically examine all currently acceptable, empirical procedures for interpolation of physical properties of isomeric alkanes to develop a more precise and general correlation method for predicting vapor pressures and defined boiling points and properties of the critical point.

VAPOR PRESSURE OF ISOMERIC ALKANES

For the prediction of the vapor pressure–boiling point data, the Antoine equation

$$\log P(\text{mm.}) = A - B/[C + t(^\circ\text{C.})] \tag{3}$$

has been particularly useful for hydrocarbons and certain related compounds (*8, 17, 23*). Since the Antoine equation is relatively insensitive to the value of C, various authors (*3, 8, 16, 23*) have developed simple relations for C as a function of normal boiling point. Camin (*3*) chose a single value of C based on experimental data for each group of monoolefinic isomers. Using the relation $B = 3.42\ T_b$ to estimate B, he predicted vapor pressure data of C_7 and C_8 monoolefins. For the C_9 isomeric alkanes, adjusted values of C in the range of 207 to 214 were used to predict vapor pressures in the API Research Project 44 Tables. For the prediction of the vapor pressures for the n-alkanes ($n > 20$), the authors have used the Antoine constants B and C as functions of the normal boiling point (*9*). This procedure, however, is not suitable for the isomeric hydrocarbons.

Since correlations based on the Antoine constants have proved successful in several other studies (*8, 9, 20*), it seemed logical to adapt the equally effective Greenshields and Rossini isomeric variation procedure for predicting the Antoine constants B and C of the isomeric alkanes.

Since Greenshields and Rossini chose ΔH_v and T_b as their dependent variables, it appeared appropriate to correlate B and C with the structural parameters used by both Riedel and Greenshields and Rossini. Besides B and C, several reduced expressions of the Antoine constants $B(^\circ\text{C.}^{-1})$ and $C(^\circ\text{C.}^{-1})$ were used as dependent variables such as B/T_b, $T_b/(B - T_b)$, $B/(B - T_b)$ with similar expressions for the constant C. These, however, did not improve the relations for either B or C. In all, 11 different functional relations were investigated with a variation of the pertinent structural parameters including the Riedel three-parameter model—Equation 2—and the Greenshields and Rossini four-parameter model—Equation 1 without the P'_4 and P''_4 terms. The accurate and precise experimental vapor pressure data on 36 isomeric alkanes (API Research hydrocarbons), C_5 through C_9 (only seven nonanes), served as a basis for testing the reliability of these proposed vapor pressure correlations, using regression techniques on the Texas A & M Data Processing Center IBM 7094. The following equations which result from this critical analysis of several correlation procedures are recommended for Antoine constants B and C.

$$B_i - B_n = -4.436\, n_3 + 25.774\,(P_i - \text{P}_n) + 313.971\,\frac{(\text{W}_i - \text{W}_n)}{n^2 - n} \tag{4}$$

$$C_i - C_n = 1.684\, n_4 - 24.374\,\frac{(W_i - W_n)}{n^2 - n} \tag{5}$$

Once the B_i and C_i values are determined, the constant A_i is evaluated for each isomer using Equation 3, providing one experimental vapor pressure or boiling point value is available for this substance. The Antoine constants B and C for the normal compound and the experimental normal boiling points for all compounds were taken from the American Petroleum Institute Research Project 44 Tables (*17*). The predicted constants were used to calculate the boiling points at the widest range of available vapor pressure measurements—namely, 60 and 1500 mm. of mercury. In general, the correlation procedures or models containing the Wiener number term gave lower errors for the boiling points suggesting that the Wiener term $(\text{W}_i - \text{W}_n)/(n^2 - n)$, which may be considered as the degree of compactness of the molecule, makes a realistic contribution in improving the correlation. The "best" correlation, Equations 4 and 5, with the error sum of squares of 3.22 ($\sigma = \pm 0.3$) in the boiling point at 60 mm. of Hg and of 0.40 ($\sigma = \pm 0.01$) at 1500 mm. of Hg, based on the use of the following four structural parameters, n_3, n_4, P, and W, is the one recommended for use in predicting vapor pressure data for isomeric alkanes.

The differences between the calculated and the experimental values in the boiling points at 60 and 1500 mm. of Hg for 31 compounds (*12, 17*) are shown in Table I and compared with the differences calculated by the Camin procedure (*3*). The agreement with the experimental values is very satisfactory over a wide vapor pressure range and over the carbon range of C_5 to C_9. The new procedure was also compared with the Greenshields-Rossini procedure (*6*) for boiling points calculated at 10 mm. of Hg for C_5 to C_9 alkanes and was superior.

With this procedure, the Antoine constants A, B, and C can be predicted, thereby improving vapor pressure–boiling point data for all 35 isomeric nonanes and also obtaining new data for all 75 isomeric decanes (*17*). Reliable experimental vapor pressure data exist for only seven C_9 alkanes and one C_{10}, the normal decane. Less reliable data for one additional C_{10} hydrocarbon—namely, 4-n-propylheptane—was reported by API Research Project 42 (*2*), giving boiling points at 20, 30, 40, 60, and 100 mm. of Hg. With the new procedure, analysis of the data on this one compound predicts a revised value of 161.8° C. for the normal boiling point instead of the 157.5° C. value reported in the API Research Project 44 Tables (*17*). A practical advantage of this new method is that a single experimental value of a boiling point, preferably at 1 atm. pressure, enables one to predict the boiling points over the range from 10 to 1500 mm. of Hg pressure as permitted by the Antoine equation.

CRITICAL PROPERTIES OF ISOMERIC ALKANES

Reliable experimental values of properties of the critical state are now available for 31 isomeric alkanes, carbon range C_5 to C_8. It is not likely that experimental values for the critical properties of all the C_9 and C_{10} alkanes will ever become available owing to the experimental difficulties of purification and measurement of these properties. Although additional experimental data on selected "key" nonanes and decanes may become available in the future, at the present time, semiempirical or empirical procedures must be used for estimating realistic values of T_c, P_c, and d_c for all the nonanes and decanes. The usual correlation procedure will be followed to find acceptable relations for the critical properties of the lower isomeric alkanes (C_5 to C_8) where reliable data exist, and then be extrapolated into the higher isomeric carbon range, C_9 to C_{10}.

New Correlation Procedures For Critical Temperature. From the studies of other properties of alkanes such as boiling point, refractive index, enthalpy of formation, enthalpy of vaporization, etc., the contribution of the "Wiener Number" term in improving the fit of isomeric variation

Table I. Comparison of Calculated and Experimental Boiling Points at 60 and 1500 Mm. of Hg Pressure for 8 Heptanes, 16 Octanes, and 7 Nonanes

	60 Mm. of Hg			1500 Mm. of Hg		
		% Dev.[a]			% Dev.	
Compound	T_{expt}, ° K.	New procedure	Camin-Rossini (*3*)	T_{expt}, ° K.	New procedure	Camin-Rossini (*3*)
n-Heptane						
2-Methylhexane	296.199	+0.01	+0.26	387.82	+0.03	+0.12
3-Methylhexane	297.605	−0.09	+0.27	389.59	+0.10	+0.17
3-Ethylpentane	298.840	−0.16	+0.27	391.70	+0.04	+0.08
2,2-Dimethylpentane	286.122	−0.10	−0.38	379.92	+0.02	−0.14
2,3-Dimethylpentane	295.239	−0.14	0.00	387.71	+0.11	+0.07
2,4-Dimethylpentane	287.654	+0.12	−0.19	377.81	+0.03	0.00
3,3-Dimethylpentane	291.205	−0.13	−0.40	384.49	−0.02	−0.17
2,2,3-Trimethylbutane	286.535	+0.06	−0.68	379.04	−0.02	−0.21
n--Octane						
2-Methylheptane	319.705	+0.05	+0.44	416.86	+0.02	+0.18
3-Methylheptane	320.735	−0.07	+0.46	418.43	0.00	+0.14
4-Methylheptane	319.764	−0.13	+0.45	417.13	+0.02	+0.13
3-Ethylhexane	320.271	−0.16	+0.41	417.94	+0.06	+0.15
2,2-Dimethylhexane	309.826	−0.10	−0.09	406.04	0.00	−0.06
2,3-Dimethylhexane	317.346	−0.13	+0.19	415.05	+0.06	+0.08
2,4-Dimethylhexane	312.134	+0.11	+0.03	408.64	−0.05	0.00
2,5-Dimethylhexane	312.054	+0.11	+0.08	408.10	−0.02	+0.04
3,3-Dimethylhexane	313.520	−0.10	−0.14	411.57	+0.03	−0.04
3,4-Dimethylhexane	318.991	−0.14	+0.20	417.48	+0.02	+0.05
2-Methyl-3-ethylpentane	317.039	−0.06	+0.09	415.29	+0.01	+0.03
3-Methyl-3-ethylpentane	318.187	−0.04	−0.17	418.49	0.00	−0.05
2,2,3-Trimethylpentane	311.278	−0.03	−0.35	409.61	−0.02	−0.13
2,2,4-Trimethylpentane	302.297	+0.10	−0.67	397.85	−0.11	−0.09
2,3,3-Trimethylpentane	314.950	−0.17	−0.36	414.69	+0.05	−0.06
2,3,4-Trimethylpentane	314.713	−0.66	−0.13	413.23	+0.01	−0.05
n-Nonane						
2,2,5-Trimethylhexane	324.230	+0.06	−0.15	424.2	−0.02	−0.07
2,4,4-Trimethylhexane	328.883	−0.05	−0.24	431.4	+0.05	−0.07
3,3-Diethylpentane	341.328	+0.07	−0.04	448.0	−0.02	0.00
2,2,3,3-Tetramethylpentane	336.143	−0.22	−0.25	442.0	+0.05	−0.09
2,2,3,4-Tetramethylpentane	330.283	0.00	−0.36	434.2	0.00	−0.12
2,2,4,4-Tetramethylpentane	321.093	−0.15	−0.69	423.0	+0.19	−0.26
2,3,3,4-Tetramethylpentane	337.395	−0.09	−0.16	443.2	+0.02	−0.05

[a] % Deviation = $\dfrac{(G_{\text{calcd}} - G_{\text{expt}})}{G_{\text{expt}}} \times 100$

correlations has been well demonstrated by the authors (*18–20*) and by Forman and Thodos (*5*). Furthermore, the vapor pressure–boiling point studies in the previous section have again shown, in general, that equations with the W term, such as Equations 1, 4, and 5, give much closer agreement with the observed values, particularly for higher molecular weight isomers, such as the seven nonanes. On this basis, independent molecular structural parameters n_3, n_4, P, and W were chosen. For the dependent variable, T_i/T_c was initially chosen through a corresponding states treatment. An approximate application of the law of corresponding states for the prediction of T_c is the Guldberg rule, T_b(1 atm.)/$T_c \approx 2/3$. Lorenz and Herz (*10*) found better agreement with the Guldberg rule by using boiling points at corresponding pressures as given by $P_i/P_c = 1/33$ or $P_i/P_c = 1/50$, which is the correct application of the law of corresponding states. In the present study, the isomeric variation method was applied to the difference in (T_i/T_c) of the isomer to that of the normal compound, where T_i is the absolute boiling point temperature at P_i, and P_i was calculated using $P_i/P_c = 0.03$ (exactly). Various models primarily differing in the form of the independent variable were tried and the "best" model with the lowest error sum of squares was

$$\left(\frac{T_i}{T_c}\right)_i - \left(\frac{T_i}{T_c}\right)_n = -0.0083\,\frac{n_3}{[n]^{1/2}} - 0.0262\,\frac{n_4}{[n]^{1/2}} - 0.0028\,\frac{(P_i - P_n)}{[n]^{1/2}} + 0.0040\,\frac{(\text{W}_i - \text{W}_n)}{n^2 - n} - 0.0029\,P_4'' \qquad (6)$$

The application of this recommended Equation 6 for the prediction of T_c is limited at present owing to the nonavailability of reliable experimental P_c values and the vapor pressure–boiling point data. However, for a good number of these higher alkanes, the experimental normal boiling point, T_b, is available; thus, it proved convenient to use the new dependent variable T_b (1 atm.)/T_c. Carrying out a regression analysis using experimental data on 31 American Petroleum Institute Research hydrocarbon alkanes in the carbon range C_5 to C_8 (*17*), a modified equation—namely, Equation 7—was determined and used to predict critical constants of the higher isomeric alkanes.

$$\left(\frac{T_b}{T_c}\right)_i - \left(\frac{T_b}{T_c}\right)_n = -0.0102\,\frac{n_3}{[n]^{1/2}} - 0.0327\,\frac{n_4}{[n]^{1/2}} - 0.0081\,\frac{(P_i - P_n)}{[n]^{1/2}} - 0.0034\,\frac{(\text{W}_i - \text{W}_n)}{n^2 - n} - 0.0024\,P_4'' \qquad (7)$$

Initially 2,2,4-trimethylpentane was included in the analysis, but a deviation of −1.56 degrees was obtained for this compound with Equation 7 without the P_4'' term. Greenshields and Rossini (*6*) and also Somayajulu and Zwolinski (*18*) have reported that additional correction for steric interactions is necessary for compounds containing the C_4—C—C_3 angle (the apex carbon atom C being secondary, tertiary, or quaternary). Therefore, an additional molecular structural parameter, P_4'', was included in the recommended modified Equation 7 to take care of such specific isomeric compounds.

To compare the proposed Equation 7 with Riedel's equation in an internally consistent manner, the P_4'' steric parameter term was included and a regression analysis carried out using exactly the same experimental data for the isomeric paraffins. This "modified Riedel" equation given as Equation 8 follows.

$$\left(\frac{T_b}{T_c - T_b}\right)_i - \left(\frac{T_b}{T_c - T_b}\right)_n = -0.0358n_3 - 0.1129n_4 - 0.0287(P_i - P_n) - 0.0279\,P_4'' \qquad (8)$$

New Correlation Procedures for Critical Pressure (P_c) and Critical Density (d_c). The isomeric variation procedure developed for the critical temperature T_c was extended to the remaining two critical properties P_c and d_c. In terms of the same four structural parameter terms used for T_c in Equation 7, the analysis revealed that $1/[P_c]^{1/2}$ and $1/[d_c]^{1/2}$ are the appropriate dependent variables. The P_4'' term made a negligible correction and was eliminated. These dependent variables yield the lowest error sum of squares in P_c and d_c. The following Equations 9 and 10 for P_c and d_c, respectively, are recommended.

$$(1/[P_c]^{1/2})_i - (1/[P_c]^{1/2})_n = -0.00105\,\frac{n_3}{[n]^{1/2}} - 0.00639\,\frac{n_4}{[n]^{1/2}} - 0.00751\,\frac{(P_i - P_n)}{[n]^{1/2}} - 0.00280\,\frac{(W_i - W_n)}{n^2 - n} \qquad (9)$$

$$(1/[d_c]^{1/2})_i - (1/[d_c]^{1/2})_n = 0.0564\,\frac{n_3}{[n]^{1/2}} + 0.1243\,\frac{n_4}{[n]^{1/2}} + 0.0104\,\frac{(P_i - P_n)}{[n]^{1/2}} + 0.3761\,\frac{(W_i - W_n)}{n^2 - n} \qquad (10)$$

Riedel's equations in which the regression constants were redetermined using the newer data are given as Equations 11 and 12.

$$(M/P_c)_i^{1/2} - (M/P_c)_n^{1/2} = -0.00157\,n_3 - 0.0181\,n_4 - 0.0273\,(P_i - P_n) \qquad (11)$$

$$(V_c)_i - (V_c)_n = -6.360\,n_3 - 15.415\,n_4 - 7.298\,(P_i - P_n) \qquad (12)$$

DISCUSSION

Table II gives statistical deviations in the values of properties for isomeric alkanes obtained with the new correlation procedures, Equations 7, 9, and 10. For comparison, the deviations obtained with the modified Riedel Equations 8, 11, and 12, and the equations developed by McMicking and Kay [Equations 3, 4, and 5 of reference (*12*)] are included in the same table. The actual deviations for each isomer and each critical property, T_c, P_c, and d_c, respectively, are shown in Table III. These three isomeric variation procedures for prediction of critical properties give values much closer to measured values than the group contribution methods mentioned earlier. Isomeric variation procedures, as developed here, are limited at present to treatment of alkanes. Applicability of these procedures to alkyl derivatives needs to be re-examined. While group contribution methods have a wider application to diversified classes of organic compounds, they do so at the cost of precision and accuracy. The four-parameter equations developed in this study and the Riedel three-parameter equations yield almost the same standard deviations for T_c, P_c, and d_c (Table II). Only when experimental critical constants for the higher carbon range alkanes become available can it be determined whether Equations 7, 9, and 10 should be preferred to Riedel's equations for extrapolating into the higher carbon range—for example, in predicting the critical constants of C_9 and C_{10} alkanes.

Erroneous literature values of T_c and P_c for the branched octane, 2,2,3,3-tetramethylbutane, reported by Felsing, Cuellar, and Newton (*4*), are actually experimental values for 2,5-dimethyloctane as established by Kobe and Lynn

Table II. Summary of Deviations in the Values of the Properties for Isomeric Alkanes

Range	No. of Compounds	Property	Av. Dev.	Std. Error of Estimate[a]	Max. Dev.
C_5–C_9	36	Antoine constant *B* (Equation 4)	±5.92	±8.50	+19.52
C_5–C_9	36	Antoine constant *C* (Equation 5)	±0.95	±1.32	−3.56
C_7–C_9	31	Boiling point at 60 mm.	±0.28	±0.32	−0.74 deg.
C_7–C_8	24	Boiling point at 1500 mm.	±0.11	±0.13	+0.20 deg.
C_4–C_8	31	T_c, Equation 6	±0.35	±0.45	−0.96 deg.
C_4–C_8	31	T_c, Equation 7	±0.36	±0.42	−0.81 deg.
C_4–C_8	31	T_c, Equation 8	±0.36	±0.42	−0.83 deg.
C_4–C_8	28	T_c, Equation 3 of McMicking and Kay	±0.54	±0.75	−2.17 deg.
C_4–C_8	31	P_c, Equation 9	±0.10	±0.14	+0.38 atm.
C_4–C_8	31	P_c, Equation 11	±0.10	±0.14	+0.38 atm.
C_6–C_8	28	P_c, Equation 4 of McMicking and Kay	±0.09	±0.12	−0.31 atm.
C_4–C_8	31	d_c, Equation 10	±0.004	±0.005	−0.010 g./cc.
C_4–C_8	31	d_c, Equation 12	±0.004	±0.006	−0.013 g./cc.
C_6–C_8	28	d_c, Equations 5, 6, 7 of McMicking and Kay	±0.004	±0.005	−0.014 g./cc.

[a] Standard error of estimate = $\dfrac{(G_{\text{calcd}} - G_{\text{obsd}})^2}{\text{No. of compounds}}$

Table III. Comparison of Calculated and Experimental Critical Constants T_c, P_c, and d_c for 2 Pentanes, 4 Hexanes, 8 Heptanes, and 16 Octanes

	T_c, ° K.	% Dev. Eqn. 7	P_c, atm.	% Dev. Eqn. 9	d_c, G./Cc.	% Dev. Eqn. 10
n-Pentane	469.49		33.16		0.245	
2-Methylbutane	460.39	−0.10	33.66	−0.83	0.236	+0.34
2,2-Dimethylpropane	433.75	−0.04	31.57	+0.32	0.238	−1.54
n-Hexane	507.30		29.71		0.233	
2-Methylpentane	497.45	+0.02	29.71	+0.88	0.235	+0.99
3-Methylpentane	504.4	+0.01	30.83	+0.45	0.235	+2.67
2,2-Dimethylbutane	488.73	−0.11	30.40	−0.56	0.240	+1.09
2,3-Dimethylbutane	499.93	−0.09	30.86	+0.62	0.241	+0.31
n-Heptane	540.14		27.05		0.232	
2-Methylhexane	530.31	+0.09	26.98	+0.26	0.238	−1.15
3-Methylhexane	535.19	+0.11	27.77	+0.18	0.248	−3.09
3-Ethylpentane	540.52	−0.03	28.53	+0.35	0.241	+1.90
2,2-Dimethylpentane	520.44	+0.12	27.37	+0.47	0.241	+0.34
2,3-Dimethylpentane	537.29	+0.12	28.70	+0.03	0.255	−4.02
2,4-Dimethylpentane	519.73	−0.04	27.01	+0.26	0.240	−0.57
3,3,-Dimethylpentane	536.34	−0.07	29.07	+0.34	0.242	+2.51
2,2,3-Trimethylbutane	531.11	0.00	29.15	+0.34	0.252	+1.89
n-Octane	568.69		24.54		0.232	
2-Methylheptane	559.57	+0.04	24.52	+0.20	0.234	+0.46
3-Methylheptane	563.60	+0.04	25.13	+0.24	0.246	−2.19
4-Methylheptane	561.67	+0.05	25.09	+0.36	0.240	+0.92
3-Ethylhexane	565.42	−0.02	25.74	+0.31	0.251	−1.20
2,2-Dimethylhexane	549.80	+0.06	24.96	−0.12	0.239	+1.26
2,3-Dimethylhexane	563.42	+0.09	25.94	−0.23	0.244	+0.98
2,4-Dimethylhexane	553.45	−0.13	25.23	−0.04	0.242	+0.77
2,5-Dimethylhexane	549.99	+0.03	24.54	+0.24	0.237	+0.52
3,3-Dimethylhexane	561.95	+0.02	26.19	+0.27	0.258	−2.96
3,4-Dimethylhexane	568.78	+0.09	26.57	+0.04	0.245	+2.30
2-Methyl-3-ethylpentane	567.02	−0.14	26.65	−0.30	0.258	−2.20
3-Methyl-3-ethylpentane	576.51	−0.11	27.71	−0.04	0.251	+2.55
2,2,3-Trimethylpentane	563.43	+0.12	26.94	+0.33	0.262	−3.42
2,2,4-Trimethylpentane	543.75	0.00	25.34	−1.50	0.244	+0.53
2,3,3-Trimethylpentane	573.49	+0.04	27.83	−0.18	0.251	+1.88
2,3,4-Trimethylpentane	566.34	−0.07	26.94	−1.11	0.248	+1.08

(*7*). Using recommended Equations 7 and 9, the following values are predicted for this tetramethylbutane: T_c = 568° K. and P_c = 28.3 atm. These values are in good agreement with Riedel's predicted values of 568.6° K. and 28 atm. The following new values were selected for 2,2,3,3-tetramethylbutane: $T_c = 568 \pm 1$° K., $P_c = 28 \pm 0.5$ atm., and $d_c = 0.248 \pm 0.010$ gram per cc. (*17*).

The internal consistency of Equations 7, 9, and 10 was checked by comparing the calculated Kammerlingh-Onnes ratio, $Z_c = P_cV_c/RT_c$, with the experimental values for 30 isomeric alkanes, C_5 to C_8. The absolute average deviation between the calculated and the McMicking and Kay's and Ambrose, Cox, and Townsend's observed values (*1*, *12*) was ± 0.0042 in Z_c. The maximum deviation of 0.010 was obtained for 2,3-dimethylpentane and 2,2,3-trimethylpentane. For comparison, the Z_c was also calculated from the Pitzer *et al.* procedure (*13*)—namely:

$$Z_c = Z_0(T_r, P_r) + \omega Z(T_r, P_r)$$

where the acentricity factor, ω, was equal to $-\log P_r - 1$ at $T_r = 0.7$. The maximum deviations between 0.010 to 0.013 were found for seven C_7 and C_8 isomers, with an absolute average deviation of ± 0.0047. Thus, this procedure is slightly more consistent and reliable than Pitzer's.

ACKNOWLEDGMENT

The authors express appreciation to G. R. Somayajulu for fruitful discussions and to the Texas A & M Data Processing Center for use of IBM 7094 computer facilities.

NOMENCLATURE

a = pressure van der Waals' constant (cc./g. -mole)^2 atm.
b = volume van der Waals' constant, cc./g. -mole
a,b,c = constants in the Riedel equation
A,B,C = constants of the Antoine vapor pressure equation
C = carbon atom
C_1 = primary carbon atom
C_2 = secondary carbon atom
C_3 = tertiary carbon atom
C_4 = quaternary carbon atom
d_c = critical density, g./cc.
G = any specific property of the liquid state
H = hydrogen atom
ΔH_v = enthalpy of vaporization, kcal./mole
k,l = type of carbon-carbon bond, primary, secondary, tertiary, or quaternary
M = molecular weight, g./mole
n = total number of carbon atoms in the molecule
n_3 = number of tertiary carbon atoms in the molecule
n_4 = number of quaternary carbon atoms in the molecule
P = pressure, mm. of mercury
P = Platt number
P_c = critical pressure, atm.
P_t = pressure, mm. of Hg at T_t, ° K.
P_r = reduced pressure, P/P_c
P_4' = number of quaternary carbon pairs separated by one carbon atom in the isomer
P_4'' = number of pairs consisting of one quaternary and one tertiary carbon atom separated by one other carbon atom
R = gas constant, 1.98717 cal./deg. mole
t = temperature, ° C.
T_b = normal boiling point, ° K. at 760 mm. of Hg (° C. + 273.15)
T_c = critical temperature, ° K.
T_t = temperature, ° K. at pressure P_t, mm. of Hg
T_r = reduced temperature, T/T_c
V_c = critical volume, liter/mole
W = Wiener number
Z_0 = compressibility factor of simple fluid
Z_c = critical compressibility factor

Greek Letters

$\alpha_1,\alpha_2,\alpha_3,\alpha_4,$
α_5,α_6 = constants
ω = acentric factor
σ = standard deviation $[(G_{\text{calcd}} - G_{\text{obsd}})^2/(\text{No. of Points} - 1)]^{1/2}$

Subscripts

i = isomer
n = normal

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RECEIVED for review June 30, 1967. Accepted January 8, 1968. Work supported in part by the program of the American Petroleum Institute Research Project 44. Paper presented at A.I.Ch.E. Salt Lake City Meeting, May 1967.

Vapor-Liquid Equilibria of Binary Systems of Methanol with Anisole, Chlorobenzene, Nitromethane, and Pyridine

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Vapor-liquid equilibrium data are reported for binary systems of methanol with anisole (PhOMe), chlorobenzene (PhCl), nitromethane ($MeNO_2$), and pyridine at 730 mm. of Hg. Of the four systems studied, only methanol–$MeNO_2$ forms a minimum azeotrope—at 64.4° C., near 95.0 mole % of methanol. The other three systems are nonazeotropic. Limiting values of the activity coefficients of each component in an excess of methanol have been evaluated.

AS PART of a continuing study of phase equilibria involving alcohols, vapor-liquid equilibrium data have been measured for four binary systems of methanol with anisole (PhOMe), chlorobenzene (PhCl), nitromethane ($MeNO_2$), and pyridine, at 730 mm. of Hg. These systems were chosen to obtain additional information on the azeotropic behavior of the solutions of various organic liquids with alcohols and to make a rough estimate of the limiting values of the activity coefficients of these liquids in excess methanol.

EXPERIMENTAL

The sample liquids used in this study were purified by repeated distillations through a 30-plate column. The final purified samples gave no trace of impurity peaks with gas chromatography with silicone DC 500 column and hydrogen carrier gas. Table I lists some physical properties of the final purified liquids as well as the Antoine constants used for vapor pressure calculation.

A modified Colburn still (*11, 12, 14*) was used for vapor-liquid equilibrium measurements. A thermistor was calibrated against a standard thermometer and used to measure equilibrium temperatures to within ± 0.05° C. The barometric pressure varied between 720 and 735 mm. of Hg during the measurements. The observed boiling points were corrected to 760 mm. of Hg.

Analysis of the equilibrium compositions was made by density measurement at 25.0° C. Densities were determined using a 10-ml. pycnometer and were reproducible to within ± 0.0001 gram per cc.

RESULTS AND DISCUSSION

Table II lists the experimental t-x-y data for the four binary systems studied. Temperature-composition and x-y

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