from eq 17 and of $\tilde{v}$ calculated from T^* or α according to eq 11 or 12. Error limits from values of α calculated on the basis of this scheme for a given temperature are $\pm 1.0\%$; for γ, $\pm 1.5\%$.

The results of compression measurements on n-$C_{16}H_{34}$ made by Boelhouwer[20] are compared with theoretical isotherms in Figure 8. At 1000 bars the calculated compressions underestimate the measured values by 6, 4, and 6% at 60, 90, and 120°, respectively.

Differentiation of eq 12 with respect to temperature at zero pressure and substitution of $\alpha = (1/\tilde{v})(\partial\tilde{v}/\partial T)_p$ yields[1]

$$(\partial\alpha/\partial T)_{p=0} = (7 + 4\alpha T)\alpha^2/3 \qquad (24)$$

The observed values of $(\partial\alpha/\partial T)_p$ for the alkanes listed in Table VI are 0.1×10^{-6} to 14×10^{-6} deg^{-2}. In most instances these are 0.5×10^{-6} to 2.5×10^{-6} deg^{-2} less than $(\partial\alpha/\partial T)_p$ calculated on the basis of eq 24. Thus, the theory correctly predicts a positive coefficient $(\partial\alpha/\partial T)_p$ but is quantitatively inaccurate in its estimate of the magnitude of this quantity. This is a further manifestation of the limitation of the treatment with respect to the dependence of properties on temperature.[1,4]

The temperature derivative of γ for $p = 0$ is given by

$$(T/\gamma)(\partial\gamma/\partial T)_{p=0} = (1 + 2\alpha T) \qquad (25)$$

Measured values of the dimensionless quantity $(T/\gamma)\cdot(\partial\gamma/\partial T))_{p=0}$ range from -4.6 to -1.5. Those calculated from α on the basis of eq 25 are also negative but are 0 to 30% smaller in magnitude.

The thermodynamic properties of binary mixtures of the n-alkanes are treated in the following paper with the aid of the results which have been presented here.

Acknowledgment. Support of the U. S. Air Force Office of Scientific Research under Contract No. AF49(638)-1341 is gratefully acknowledged. One of us (R. A. O.) thanks the National Science Foundation for an NSF Summer Fellowship. The authors also wish to thank Mr. R. D. Ireson for his assistance in performing the experiments, and the Phillips Petroleum Co. for making available a sample of Marlex-6050, specially prepared, fractionated, and characterized.

Thermodynamic Properties of Binary Mixtures of *n*-Alkanes

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Abstract: The excess thermodynamic properties of mixtures of normal paraffin hydrocarbons are interpreted according to statistical mechanical theory developed earlier. The comprehensive equation-of-state data of the preceding paper are used to characterize the pure components, as required by the theory referred to. Effects of intrinsic properties of the components, ignored in conventional treatments of solutions, are large for these systems. A single arbitrary parameter, reflecting the differences of the interactions involving terminal (methyl) as compared to internal (methylene) groups, suffices to reproduce the excess volumes, excess thermal expansion coefficients, excess compressibilities, and excess enthalpies, ΔH_M, for all mixtures of normal paraffins, C_nH_{2n+2}, $n > 5$, for which data are available. The decrease in ΔH_M with temperature and the reversal of its sign at elevated temperatures, observed for several systems, are predicted, but the magnitude of the change with temperature is underestimated. Precise agreement of calculated excess chemical potentials with those observed for the several systems investigated experimentally is achieved through introduction of an additional parameter to represent the entropy associated with interactions between terminal and midchain groups; the same value is assigned to this parameter for all systems and temperatures. The theoretical equations, in conjunction with the equation-of-state information and the two parameters cited, correctly predict the occurrence of lower critical miscibility for solutions of polymethylene in the n-alkanes. Calculated critical temperatures approximate those found by experiment for n-C_6H_{14}, n-C_7H_{16}, and n-C_8H_{18}.

In earlier papers[1-4] we have called attention to the contributions of the characteristic properties of the pure liquid components to the excess thermodynamic properties of liquid mixtures. The conventional formulation of the free energy of mixing from a combinatory entropy and an interaction energy (*e.g.*, of the van Laar form) attributable to contacts between neighboring molecules does not afford an adequate representation of the thermodynamic functions of typical solutions. For the express purpose of taking account of the effects of the liquid-state properties peculiar to the components, a simple statistical mechanical theory was developed which admits of application to mixtures as well as to pure liquids.[1-3] The properties of component i of the solution are represented by a characteristic molar volume v_i^*, a characteristic temperature T_i^*, and a characteristic pressure p_i^*. These parameters may be evaluated from the molar volume v_i, the thermal expansion coefficient α_i, and the thermal pressure coefficient γ_i in the manner set forth in the preceding paper.[5] One additional pa-

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(1) P. J. Flory, R. A. Orwoll, and A. Vrij, *J. Am. Chem. Soc.*, **86**, 3507 (1964).

(2) P. J. Flory, R. A. Orwoll, and A. Vrij, *ibid.*, **86**, 3515 (1964).

(3) P. J. Flory, *ibid.*, **87**, 1833 (1965).

(4) A. Abe and P. J. Flory, *ibid.*, **87**, 1838 (1965).

(5) R. A. Orwoll and P. J. Flory, *ibid.*, **89**, 6814 (1967).

rameter representing neighbor interactions is subject to arbitrary assignment.

Excess enthalpies, entropies, and volumes for solutions of 23 pairs of small, nonpolar molecules were examined[4] on the basis of this theory. The agreement between calculated and observed values was quite satisfactory, and the importance of equation-of-state contributions to the excess properties was demonstrated. The generally excellent account of the excess volumes, often ignored in treatments of solutions, was particularly noteworthy. A previous attempt[2] to interpret the thermodynamic properties of binary mixtures of *n*-alkanes was limited by a scarcity of reliable determinations of α and γ for the pure components.[1]

In the preceding paper[5] we have reported measurements of α and γ for six normal paraffins and have collated the published results of careful measurements of these coefficients for various hydrocarbons of this series. For homologs on which no accurate measurements have been made, α and γ were obtained by interpolation of these quantities on the basis of functions of chain length prescribed by the theory. In the present paper these equation-of-state data are applied to the interpretation of the excess thermodynamic properties of mixtures of normal paraffin hydrocarbons.

The effects of the characteristic properties of the component liquids on the properties of their mixtures are nowhere more clearly manifest than in mixtures of the homologous normal paraffins. The molar excess volume v^E for these mixtures is negative and its magnitude increases rapidly with temperature. The molar enthalpy of mixing ΔH_M, determined with unusual accuracy for a number of these systems, is positive at ordinary temperature but decreases markedly with temperature, becoming negative at sufficiently elevated temperatures. The excess chemical potentials $(\mu_1 - \mu_1^0)^E$ of these mixtures elude all possibility of interpretation according to conventional solution theories.

The analysis of properties of mixtures of *n*-alkanes presented here represents an elaboration and refinement of the earlier effort[2] to the same ends. This further study has been made possible by the much improved equation-of-state data for the pure hydrocarbons presented and correlated in the preceding paper.[5]

Treatment of Mixtures of Normal Alkanes

Adaptation of the partition function for pure liquids formulated in earlier papers[1,3] to binary liquid mixtures is straightforward.[2,3] The notation defined in the preceding paper[5] will be used here without repetition of definitions. Subscripts 1 and 2 appended to the various symbols will serve to distinguish the components of lower and higher molecular weight, respectively. Thus the segment fraction, mole fraction, and site fraction for component *i*, with $i = 1, 2$, are given respectively by

$$\varphi_i = N_i r_i/(N_1 r_1 + N_2 r_2) = x_i r_i/(x_1 r_1 + x_2 r_2) \quad (1)$$

$$x_i = N_i/(N_1 + N_2) \quad (2)$$

$$\theta_i = \varphi_i s_i/(\varphi_1 s_1 + \varphi_2 s_2) = \varphi_i s_i/s \quad (3)$$

where for the hydrocarbon $H(CH_2)_{n_i}H$ we take $r_i = n_i + 1$,[5] and *s* is specified by eq 5 below. Characters without subscripts will represent mean quantities for the mixture. The mean numbers of segments *r* per molecule, of sites *s* per segment, and of external degrees of freedom *c* per segment are given by

$$r = x_1 r_1 + x_2 r_2 = (\varphi_1/r_1 + \varphi_2/r_2)^{-1} \quad (4)$$

$$s = \varphi_1 s_1 + \varphi_2 s_2 = s_m + s_e/r \quad (5)$$

$$c = \varphi_1 c_1 + \varphi_2 c_2 = c_m + c_e/r \quad (6)$$

The lattermost expressions for *s* and *c* follow from eq 14* and 16* of the preceding paper.[5,6] The characteristic volume v* per mole of mixture is

$$v^* = (N_1 v_1^* + N_2 v_2^*)/(N_1 + N_2) \quad (7)$$

Since $v_i^* = v^* r_i$, where v^* is the same for all homologs

$$\varphi_i = N_i v_i^*/(N_1 v_1^* + N_2 v_2^*) \quad (8)$$

It is convenient to define a quantity X_{12} in such a way that the characteristic pressure p^* of a solution is given by[3,4,7]

$$p^* = \varphi_1 p_1^* + \varphi_2 p_2^* - \varphi_1 \theta_2 X_{12} \quad (9)$$

From eq 22*, 6, and 9 it follows that

$$T^* = (\varphi_1 p_1^* + \varphi_2 p_2^* - \varphi_1 \theta_2 X_{12})/(\varphi_1 p_1^*/T_1^* + \varphi_2 p_2^*/T_2^*) \quad (10)$$

The reduced volume $\tilde{v}$ of a solution is related to T^* through eq 11*. Equations 9 and 10 are appropriate for binary mixtures in general,[3,4] with the parameter X_{12} chosen to express the difference between interactions of neighboring pairs of like and unlike species. This interaction parameter has been evaluated from the excess thermodynamic properties of a number of binary systems consisting of small, nonpolar molecules.[4]

If we assume eq 14* and 17* to be applicable to the mixture with *r* and *s* defined by eq 4 and 5, then by substitution of these relationships in eq 9 and use of eq 3 we obtain eq 11. This equation for X_{12} is limited

$$X_{12} = \frac{p_\infty^*(1/r_1 - 1/r_2)^2(1 - 2\eta_{em}/\eta_m + \eta_e/\eta_m)(s_e/s_m)^2}{(1 + s_e/s_m r_1)(1 + s_e/s_m r_2)^2} \quad (11)$$

to mixtures of linear chain homologs exemplified by the *n*-alkanes. It appears to offer the prospect of evalua- of X_{12} from equation-of-state data for the pure homologs,[2] a prospect which cannot be realized in practice (*cf.* below).

The free-energy change accompanying mixing of N_1 moles of component 1 with N_2 moles of component 2 at nominal pressure is given by[2,3] eq 12, where, for these

$$\Delta G_M = RTN_1 \ln \varphi_1 + RTN_2 \ln \varphi_2 + \theta_2 N_1 v_1^* X_{12}/\tilde{v} + N_1 v_1^* p_1^* \{3\tilde{T}_1 \ln [(\tilde{v}_1^{1/3} - 1)/(\tilde{v}^{1/3} - 1)] + 1/\tilde{v}_1 - 1/\tilde{v}\} + N_2 v_2^* p_2^* \{3\tilde{T}_2 \ln [(\tilde{v}_2^{1/3} - 1)/(\tilde{v}^{1/3} - 1)] + 1/\tilde{v}_2 - 1/\tilde{v}\} \quad (12)$$

solutions of chain molecule liquids, the combinatorial contribution to ΔG_M, *viz.*, $RTN_1 \ln \varphi_1 + RTN_2 \ln \varphi_2$, has been taken from polymer solution theory. The molar heat of mixing is

$$\Delta H_M = \theta_2 x_1 v_1^* X_{12}/\tilde{v} + x_1 v_1^* p_1^*(1/\tilde{v}_1 - 1/\tilde{v}) + x_2 v_2^* p_2^*(1/\tilde{v}_2 - 1/\tilde{v}) \quad (13)$$

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(6) Numbers marked with an asterisk refer to equations or tables of the preceding paper.[5]

(7) The quantity X_{12} is related to p_{12}^* used in ref 2 according to $X_{12} = p_{12}^* \varphi_2/\theta_2$.

The excess chemical potential of component 1, defined by

$$(\mu_1 - \mu_1{}^0)^{\mathrm{E}} = (\mu_1 - \mu_1{}^0) - RT \ln x_1 \qquad (14)$$

may be obtained by differentiation of eq 12, which gives eq 15.

$$\mu_1 - \mu_1{}^0 = RT \ln \varphi_1 + RT(1 - \mathrm{v}_1{}^*/\mathrm{v}_2{}^*)\varphi_2 + \theta_2{}^2\mathrm{v}_1{}^*X_{12}/\tilde{v} + \mathrm{v}_1{}^*p_1{}^*\{3\tilde{T}_1 \ln [(\tilde{v}_1{}^{1/3} - 1)/(\tilde{v}^{1/3} - 1)] + 1/\tilde{v}_1 - 1/\tilde{v}\} \qquad (15)$$

Adoption of the expressions for p^* and T^*, namely, eq 14*, 17*, and 18* (or more directly through use of eq 22*), derived in the preceding paper for the pure alkanes implies a correspondence between the properties of the mixtures and the pure components. In taking r to be given by eq 4 with $r_i = n_i + 1$, we specify this correspondence by asserting, in effect, that the properties of the mixture are those of the pure hydrocarbon having a number $n = r - 1$ of carbon atoms per molecule. (This number will in general be nonintegral, of course.) In other words, the partition function for the mixture, apart from combinatory contributions, is taken to be identical with that for the pure normal alkane having the same fraction of CH_3 groups per molecule. It follows that the equation of state for the mixture is required to match that for its pure analog having $n = r - 1$ carbon atoms per molecule. This correspondence comprehends the principle of congruence enunciated by Brønsted,[8,9] which asserts that a property of the mixture such as the molar volume or the molar enthalpy should equal that for the intermediate homolog for which $n = n_1x_1 + n_2x_2$. The present scheme goes beyond the principle of congruence, however, in prescribing explicitly the dependence of each such property on n (or r) and therefore on the composition. It also specifies this relationship for different temperatures, X_{12} being taken to be independent of temperature (*cf.* below). To the extent that the treatment of the preceding paper errs in its representation of characteristic properties (notably v*, T^*, and p^*) as functions of chain length, the adaptation to mixtures may of course depart from the principle of congruence. The theory is remarkably accurate in this respect, however, as we have pointed out.[5]

Comparison of Theory with Experiment

Values of the parameters $T_i{}^*$, $\mathrm{v}_i{}^*$, and $p_i{}^*$ characterizing the pure components and required by the foregoing equations for the thermodynamic properties of mixtures were calculated from the density ρ_i, the thermal expansion coefficient α_i, and the thermal pressure coefficient γ_i for those alkanes for which these quantities have been determined experimentally with sufficient accuracy, eq 10*–13* being used for this purpose. Thus, ρ_i and α_i for C_6, C_8, C_{16}, C_{22}, C_{36}, and C_∞ (polymethylene) were obtained at the desired temperatures from the least-squares polynomials given in Table I*. The corresponding expressions given in Table V* yielded ρ_i and α_i for C_7, C_9, C_{10}, and C_{12}. The characteristic parameters $T_i{}^*$ and $\mathrm{v}_i{}^*$ for these hydrocarbons at temperatures within the ranges of the measurements quoted in the tables were calculated from eq 10*–12* of the preceding paper. At temperatures beyond these ranges, they were estimated according to eq 18* and 19* with the aid of the coefficients tabulated in Table VI*. The same parameters $T_i{}^*$ and $\mathrm{v}_i{}^*$ for C_{24}, C_{32}, and C_{62} were estimated in like manner using coefficients in Table VI*. The parameter $p_i{}^*$ was calculated using eq 13* from values of γ_i given by the polynomial expressions in Table III* for C_6, C_8, C_{16}, C_{22}, C_{36}, and C_∞ within the ranges of temperature specified in Table III*. At other temperatures and for other alkanes, $p_i{}^*$ was estimated according to eq 17*. In order to suppress errors arising from the dependence of the characteristic parameters $\mathrm{v}_i{}^*$, $T_i{}^*$, and $p_i{}^*$ on temperature, these quantities were evaluated at the temperature of the experiments on the given mixture.

The remaining parameter, namely, the interaction parameter X_{12}, required for a given mixture by the foregoing equations, may be calculated according to eq 11 for any alkane pair if $p_\infty{}^*$, $\eta_{\mathrm{em}}/\eta_{\mathrm{m}}$, $\eta_{\mathrm{e}}/\eta_{\mathrm{m}}$, and $s_{\mathrm{e}}/s_{\mathrm{m}}$ are known. Values of these four quantities are available from the results compiled in Table VI* of the preceding paper; the first three were calculated from properties of the pure homologs, the lattermost, $s_{\mathrm{e}}/s_{\mathrm{m}}$, having been assigned[5] the value 0.60 on the basis of molecular dimensions. The ratios $\eta_{\mathrm{em}}/\eta_{\mathrm{m}}$ and $\eta_{\mathrm{e}}/\eta_{\mathrm{m}}$ could not be reliably determined[5] since they appeared as coefficients of small terms in the polynomials expressing p^* and T^* as functions of reciprocal powers of r (see eq 17* and 18*). Use of these ill-defined values of $\eta_{\mathrm{em}}/\eta_{\mathrm{m}}$ and $\eta_{\mathrm{e}}/\eta_{\mathrm{m}}$ in the calculation of X_{12} (eq 11) yields enthalpies of mixing which are lower than those observed. The discrepancies are of no significance except insofar as they serve to call attention to the inadequacy of equation-of-state data, at the level of accuracy attainable, for the specification of these parameters. Hence, we have chosen to introduce $(1 - 2\eta_{\mathrm{em}}/\eta_{\mathrm{m}} + \eta_{\mathrm{e}}/\eta_{\mathrm{m}})(s_{\mathrm{e}}/s_{\mathrm{m}})^2$ as an adjustable parameter which we call Γ. Equation 11 may then be written as

$$X_{12} = \Gamma p_\infty{}^*(1/r_1 - 1/r_2)^2/(1 + s_{\mathrm{e}}/s_{\mathrm{m}}r_1)(1 + s_{\mathrm{e}}/s_{\mathrm{m}}r_2)^2 \qquad (16)$$

The value $\Gamma = 1.40$ offers optimum agreement of calculated excess enthalpies with those observed (*cf.* below). It is to be noted that in adopting for mixtures the approximation represented by eq 16 we depart from strict conformity with the principle of congruence.

Excess Volumes

Observed[9–12] and calculated molar excess volumes defined by

$$\mathrm{v}^{\mathrm{E}} = \mathrm{v} - (x_1\mathrm{v}_1 + x_2\mathrm{v}_2) \qquad (17)$$

are compared in Table I. Sources of experimental data are indicated at the foot of the table. Values given in the last column were calculated as follows: X_{12} was obtained from eq 16 with $\Gamma = 1.40$ and with $p_\infty{}^*$ for the specified temperature taken from Table VI*. Substitution in eq 10 gave T^*, the composition-dependent quantities φ_1, φ_2, and θ_2 having been determined by eq 1–5. The reduced volume $\tilde{v}$ of the mixture

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(11) J. D. Gómez-Ibáñez and C.-T. Liu, *J. Phys. Chem.*, 67, 1388 (1963).

(12) M. Díaz Peña and M. Benítez de Soto, *Anales Real Soc. Espan. Fis. Quim.* (Madrid), *Ser. B.*, 61, 1163 (1965).

Table I. Observed and Calculated Excess Volumes of Equimolar Mixtures

Component 1	Component 2	Temp, °C	v^E, cm³ mole⁻¹ Obsd	Calcd
n-C_6H_{14}	n-$C_{12}H_{26}$	20	-0.31^a	-0.34
		25	-0.35^b	-0.37
		35	-0.38^b	-0.44
n-C_6H_{14}	n-$C_{16}H_{34}$	20	$-0.49,^a$ -0.48^c	-0.56
		25	$-0.58,^a$ -0.53^b	-0.61
		30	-0.58^c	-0.65
		35	-0.62^b	-0.70
		40	-0.69^c	-0.76
		50	-0.82^c	-0.89
		51	-0.82^d	-0.90
		60	-0.97^c	-1.05
n-C_6H_{14}	n-$C_{24}H_{50}$	51	-1.19^d	-1.34
n-C_7H_{16}	n-$C_{12}H_{26}$	25	-0.17^b	-0.23
		35	-0.20^b	-0.26
n-C_7H_{16}	n-$C_{16}H_{34}$	20	-0.31^a	-0.40
		25	-0.34^a	-0.42
		40	-0.45^a	-0.50
		76	-0.77^d	-0.74
n-C_7H_{16}	n-$C_{24}H_{50}$	76	-1.22^d	-1.24
n-C_7H_{16}	n-$C_{36}H_{74}$	76	-1.56^d	-1.77
n-C_8H_{18}	n-$C_{16}H_{34}$	20	-0.19^a	-0.24
		30	-0.21^a	-0.27
		50	-0.33^a	-0.36
		51	-0.32^d	-0.36
		76	-0.48^d	-0.52
		106	-0.74^d	-0.82
n-C_8H_{18}	n-$C_{24}H_{50}$	106	-1.33^d	-1.46
n-C_8H_{18}	n-$C_{32}H_{66}$	96	-1.49^d	-1.61
		106	-1.70^d	-1.86
n-C_8H_{18}	n-$C_{36}H_{74}$	96	-1.62^d	-1.83
		106	-1.85^d	-2.07
n-C_9H_{20}	n-$C_{16}H_{34}$	126	-0.61^d	-0.70
n-C_9H_{20}	n-$C_{24}H_{50}$	51	-0.43^d	-0.42
		76	-0.63^d	-0.62
		96	-0.84^d	-0.89
		106	-0.96^d	-1.05
		126	-1.28^d	-1.38
n-C_9H_{20}	n-$C_{32}H_{66}$	96	-1.14^d	-1.19
n-C_9H_{20}	n-$C_{36}H_{74}$	96	-1.25^d	-1.39
		106	-1.41^d	-1.59
		126	-1.89^d	-2.05
n-C_9H_{20}	n-$C_{62}H_{126}$	126	-2.51^d	-2.62
n-$C_{10}H_{22}$	n-$C_{16}H_{34}$	20	-0.07^a	-0.10
		30	-0.09^a	-0.10

[a] Reference 10. [b] Reference 11. [c] Reference 12. [d] Reference 9.

was calculated from eq 11*; its molar volume was given by $v = \tilde{v}(x_1v_1^* + x_2v_2^*)$. Equation 17 then yielded the excess molar volume. Observed and calculated molar excess volumes for the system n-C_6H_{14} + n-$C_{16}H_{34}$ are displayed in Figure 1 for temperatures between 20 and 60°.

Contraction of the volume upon mixing occurs for all combinations of n-alkanes, *i.e.*, $v^E < 0$ in all cases. The calculated excess volumes, given in the last column of Table I, conform to this rule but are slightly more negative than those observed. The average difference and standard deviation are 0.09 and 0.11 cm³ mole⁻¹, respectively. The excess volume is comparatively insensitive to X_{12}. An increase of Γ by a factor of *ca.* 1.7 would be required to suppress the discrepancy for the C_6 + C_{16} system; such an increase would markedly affect the calculated enthalpies of mixing. Straightforward application of the principle of congruence leads to calculated excess volumes which

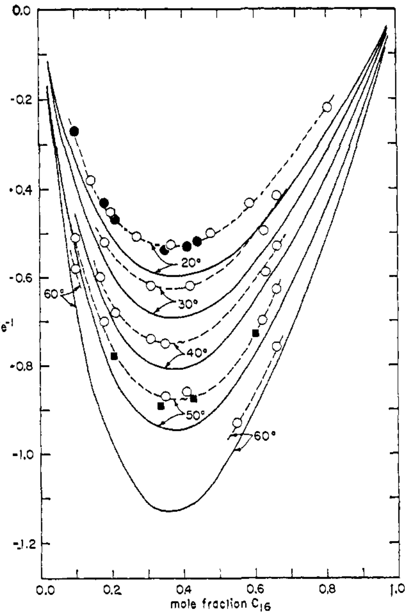

Figure 1. Molar excess volumes for n-hexane + n-hexadecane. Filled circles represent data of Desymter and van der Waals;[10] open circles, data of Díaz Peña and Benítez de Soto;[12] and squares, data of Holleman[9] at 51°. Calculated excess volumes are given by the solid lines.

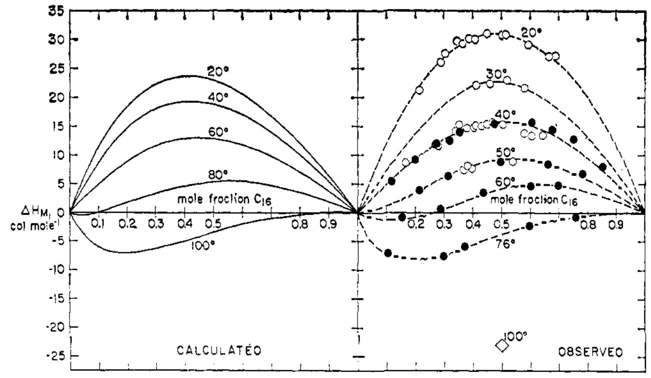

Figure 2. Molar enthalpies of mixing for n-hexane + n-hexadecane. The open circles represent data of McGlashan and Morcom (footnote *d*, Table II); filled circles represent those of Holleman;[13] and the diamond represents the datum of Friend, *et al.*[14]

similarly exceed, in magnitude, the values observed.[10,11] Discrepancies between observed and calculated excess volumes appear to be attributable to limitations inherent in the formal scheme of interpretation, rather than to the particular values chosen for the parameters which are involved in the calculations. These discrepancies are small.

Enthalpies of Mixing

Observed values of ΔH_M are compared in Table II with those calculated for 13 pairs of normal paraffins at selected compositions near the middle of the range. Sources of these results are indicated at the foot of the table. Experimental results for the system n-C_6H_{14} + n-$C_{16}H_{34}$ are shown as a function of the mole fraction at several temperatures in the right-hand part of Figure 2.

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(13) Th. Holleman, *Physica*, 31, 49 (1965); see also Thesis, University of Amsterdam, 1964.

(14) J. A. Friend, J. A. Larkin, A. Maroudas, and M. L. McGlashan, *Nature*, 198, 683 (1963).

Table II. Observed and Calculated Excess Enthalpies

Component 1	Component 2	Temp, °C	x_2	ΔH_M, cal mole^{-1} Obsd	ΔH_M, cal mole^{-1} Calcd
n-C_6H_{14}	n-$C_{10}H_{22}$	20	0.50	4[a]	7
n-C_6H_{14}	n-$C_{12}H_{26}$	20	0.50	11[b,c]	12
n-C_6H_{14}	n-$C_{16}H_{34}$	20	0.50	31,[d] 30[c,e]	23
		25	0.50	27[f]	22
		30	0.50	23[d]	21
		40	0.50	16,[g] 15[d]	19
		50	0.50	8[d]	16
		51	0.50	9[g]	16
		60	0.50	4[g]	13
		76	0.50	−4[g]	7
		100	0.50	−23[h]	−3
n-C_6H_{14}	n-$C_{24}H_{50}$	51	0.50	33[g]	31
		60	0.50	22[g]	27
		76	0.50	6[g]	19
n-C_6H_{14}	n-$C_{36}H_{74}$	76	0.50	28[g]	33
n-C_7H_{16}	n-$C_{16}H_{34}$	20	0.50	26,[a] 25[e]	16
		25	0.50	23[i]	16
		25	0.33	21[e]	16
		50	0.50	10[i]	13
n-C_7H_{16}	n-$C_{36}H_{74}$	76	0.50	31[g]	35
n-C_8H_{18}	n-$C_{16}H_{34}$	20	0.50	21[a]	12
		20	0.36	18[e]	12
		30	0.36	13[e]	11
		50	0.36	8[e]	9
n-C_8H_{18}	n-$C_{24}H_{50}$	51	0.50	28[g]	21
		76	0.50	10[g]	16
		96	0.50	−1[g]	11
		106	0.50	−6[g]	8
n-C_8H_{18}	n-$C_{32}H_{66}$	76	0.50	23[g]	24
n-C_9H_{20}	n-$C_{36}H_{74}$	76	0.50	29[g]	26
n-$C_{10}H_{22}$	n-$C_{16}H_{34}$	20	0.50	12,[a] 10[e]	5
		30	0.40	8[e]	5
		73	0.40	4[e]	4
n-$C_{16}H_{34}$	n-$C_{36}H_{74}$	76	0.50	14[g]	9

[a] M. L. McGlashan and K. W. Morcom, *Trans. Faraday Soc.*, **57**, 907 (1961). [b] J. H. van der Waals, *Rec. Trav. Chim.*, **70**, 101 (1951). [c] H. F. Stoeckli, J. G. Fernández-García, and C. G. Boissonnas, *Trans. Faraday Soc.*, **62**, 3044 (1966). [d] M. L. McGlashan and K. W. Morcom, *ibid.*, **57**, 581 (1961). [e] J. H. van der Waals and J. J. Hermans, *Rec. Trav. Chim.*, **69**, 949 (1950). [f] J. A. Larkin, D. V. Fenby, T. S. Gilman, and R. L. Scott, *J. Phys. Chem.*, **70**, 1959 (1966). [g] Reference 13. [h] Reference 14. [i] G. W. Lundberg, *J. Chem. Eng. Data*, **9**, 193 (1964).

Calculated curves are shown on the left half of the diagram. All calculations were carried out with X_{12} given by eq 16 with $\Gamma = 1.40$, the same value used for the calculation of excess volumes. The reduced volume $\tilde{v}$ for the mixture was first calculated as indicated above. The enthalpy of mixing was then obtained according to eq 13. All calculations were confined to temperatures which are integral multiples of 10°. Values of ΔH_M for temperatures within the intervals thus defined were obtained by interpolation.

The observed enthalpies of mixing are generally small and positive. Their temperature coefficients are negative and surprisingly large in contrast to the small magnitudes of ΔH_M. The enthalpy has been observed to become negative at higher temperatures for several binary n-alkane systems;[13,14] a reversal of sign with composition has been observed for $C_6 + C_{16}$ at 60° (see Figure 2) and for several other mixtures as well.[13] All of these qualitative features are reproduced in the calculated enthalpies. The dependence on temperature is underestimated, however. This deficiency of the calculated results is apparent in Figure 2; the curves calculated for 80 and 100° approximate observations at 60 and 76°, respectively. The asymmetry implied by the change of sign of ΔH_M with composition at intermediate temperatures is reproduced, however. The mean of the absolute difference between observed and calculated excess enthalpies in Table II is 5 cal mole^{-1}.

Since the reduced excess volume $\tilde{v}^E = v^E/rv^*$ is small compared to the reduced volume $\tilde{v}$, the reciprocal of $\tilde{v}$ may be approximated by

$$1/\tilde{v} = 1/\tilde{v}^0 - \tilde{v}^E/(\tilde{v}^0)^2 \tag{18}$$

where $\tilde{v}^0$, defined by $\tilde{v}^0 = \varphi_1\tilde{v}_1 + \varphi_2\tilde{v}_2$, is the reduced volume which would obtain for mixing without volume change. The result of substitution of eq 18 into 13 can, by rearrangement, be expressed as a sum of three terms as

$$\Delta H_M = x_1 v_1^* \theta_2 X_{12}/\tilde{v} + x_1 v_1^* \varphi_2[(\tilde{v}_1 - \tilde{v}_2)/\tilde{v}^0] \times (p_2^*/\tilde{v}_2 - p_1^*/\tilde{v}_1) + [v^E/(\tilde{v}^0)^2](\varphi_1 p_1^* + \varphi_2 p_2^*) \tag{19}$$

as we have shown previously.[2] The first term represents the contact interaction energy; the second term depends on the difference between the reduced volumes for the two pure components and is zero for $\tilde{v}_1 = \tilde{v}_2$; the third term depends directly on the excess volume. Taking the equimolar $C_6 + C_{16}$ mixture at 20° for illustration, we find for these terms 27.5, 34.5, and −39 cal mole^{-1}, respectively. The algebraic sum of the latter two terms is small and negative. The interaction term thus dominates these equation-of-state terms in this instance. As the temperature is raised, $-v^E$ increases, causing the enthalpy of mixing to decrease and ultimately to become negative. The main features of ΔH_M are thus readily interpreted.

The enthalpies of mixing of the n-alkanes, though small, depend strongly on X_{12}, this being in contrast to the excess volumes. Inasmuch as the formulation of X_{12} through eq 16 may not necessarily conform to the principle of congruence, the calculated enthalpies may depart from those deduced on the basis of this principle.[13] Our treatment is much more specific in its stipulations than this principle would allow, for we have chosen the parameter Γ which determines X_{12} (see eq 16) to be the same for all temperatures. Choice of an arbitrary value of Γ, and hence of X_{12}, for each temperature would afford a freedom of adjustment comparable to that permitted within the scope of the principle of congruence. If mere matching of the experimental data were the object, doubtless very close agreement with experiment could be arranged by this device. It could be argued, of course, that X_{12} should be expected to depend on temperature. However, treatment of X_{12} as variable with temperature would introduce a degree of arbitrariness which we prefer to avoid.

Excess Chemical Potentials

Results of carefully executed measurements of vapor pressures of various n-alkane mixtures investigated by Brønsted and Koefoed,[8] van der Waals and Hermans,[15] and McGlashan and Williamson[16] are summarized in the second column of Table III. The data here presented have been obtained by interpolation to the mole fractions chosen for this tabulation. Actual experi-

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[15] J. H. van der Waals and J. J. Hermans, *Rec. Trav. Chim.*, **69**, 971 (1950).

[16] M. L. McGlashan and A. G. Williamson, *Trans. Faraday Soc.*, **57**, 588 (1961).

Table III. Observed and Calculated Excess Chemical Potentials

	$(\mu_1 - \mu_1^0)^E/RT$		
x_2	Obsd	Calcd (eq 15)	Calcd (eq 20, 21) with $\Gamma_S = 0.10$
	$C_6 + C_{12}$, 20°		
0.2	−0.002[a]	0.003	0.000
0.4	−0.006[a]	0.007	−0.004
0.6	−0.014[a]	0.007	−0.012
0.8	−0.026[a]	0.004	−0.024
	$C_6 + C_{16}$, 20°		
0.2	−0.005,[b] −0.004[a]	0.005	−0.003
0.4	−0.019,[b] −0.018[a]	0.005	−0.017
0.6	−0.040,[b] −0.040[a]	−0.005	−0.041
0.8	−0.068,[b] −0.071[a]	−0.022	−0.071
	$C_6 + C_{16}$, 40°		
0.2	−0.005[b]	0.005	−0.003
0.4	−0.021[b]	0.005	−0.017
0.6	−0.044[b]	−0.005	−0.042
0.8	−0.074[b]	−0.023	−0.073
	$C_6 + C_{16}$, 60°		
0.2	−0.006[b]	0.006	−0.002
0.4	−0.021[b]	0.006	−0.016
0.6	−0.045[b]	−0.003	−0.040
0.8	−0.076[b]	−0.021	−0.071
	$C_7 + C_{16}$, 20°		
0.2	−0.004[a]	0.001	−0.003
0.4	−0.015[a]	−0.001	−0.016
0.6	−0.033[a]	−0.011	−0.035
0.8	−0.059[a]	−0.026	−0.060
	$C_7 + C_{32}$, 73°		
0.2	−0.031[c]	−0.014	−0.036
0.4	−0.113[c]	−0.070	−0.118
0.6	−0.202[c]	−0.145	−0.212
0.8	−0.286[c]	−0.226	−0.307

[a] Reference 8. [b] Reference 16. [c] Reference 15.

mental determinations are represented by the points in Figure 3 for the system $C_6 + C_{16}$ at 20°. McGlashan and Williamson[16] claim an accuracy of ±0.001 in $(\mu_1 - \mu_1^0)/RT$; error limits in the experiments of Brønsted and Koefoed[8] and of van der Waals and Hermans[15] are probably two or three times greater.

The partial molal entropy of dilution for chain molecules of disparate size is, of course, greater than the ideal entropy $-R \ln x_1$ (see eq 14 and 15), and on this account we expect the excess chemical potentials for these solutions to be negative. This expectation is borne out by the experimental results. However, the magnitude of $(\mu_1 - \mu_1^0)^E/RT$ is much smaller than would be predicted on this basis alone. The difference could in principle be ascribed to a positive contribution of the enthalpy of dilution. This explanation would require enthalpies of mixing exceeding those observed. Moreover, as we pointed out previously,[2] the decrease in ΔH_M with temperature and the ultimate reversal of the sign of ΔH_M are not reflected in commensurate changes in the excess chemical potential. The observed values and their dependence on temperature can in no way be reconciled with the conventional procedure of joining the combinatorial entropy with an enthalpy of mixing dependent solely upon contact interactions. Equation-of-state contributions, represented by the last term in eq 15, must be taken into account, as inspection of the results of calculations presented in the last two columns of Table III will show.[2]

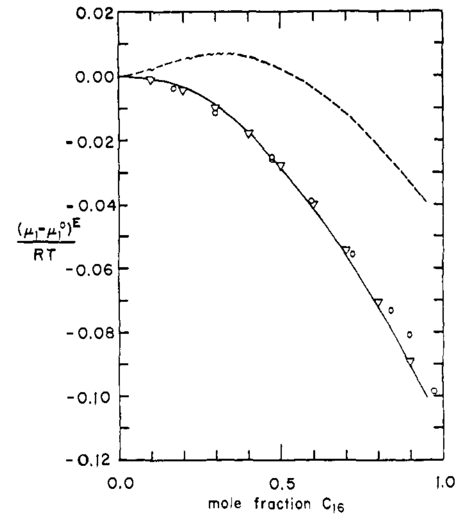

Figure 3. Excess chemical potentials for *n*-hexane + *n*-hexadecane at 20°. Experimental results of McGlashan and Williamson[16] are represented by circles, those of Brønsted and Koefoed[8] by triangles. The dashed line has been calculated according to eq 14–16 with $X_{12} = 1.40$. The solid line, calculated according to eq 14, 16, 20, and 21 with $\Gamma = 1.40$ and $\Gamma_S = 0.20$, includes the empirical interaction entropy contribution.

Excess chemical potentials calculated on the basis of eq 14, 15, and 16 with $\Gamma = 1.40$ in accordance with the treatment of excess volumes and enthalpies are given in the third column of Table III and by the dashed curve in Figure 3. Without exception they exceed the values observed, being positive over the lower range of composition. The differences are small, however; they correspond to only 2–6% of the combinatorial contribution, *viz.*, $\ln \varphi_1 + (1 - v_1^*/v_2^*)\varphi_2$. It might indeed be questioned whether the combinatorial entropy can be reproduced, by this expression or any other, within closer limits.

The contact interaction between neighbors has been assumed in the foregoing treatment to contribute only to the enthalpy; X_{12} has been treated as an enthalpy parameter and it has been construed to represent these interactions in their entirety. In general, interactions between neighboring species may reasonably be expected to affect the entropy also, as Guggenheim[17] has pointed out and as his quasi-chemical method makes clear. Such an entropy contribution involving contacts of terminal (methyl) with midchain (methylene) segments must depend on the composition of the mixture in the same manner as the interaction energy term. Arguments supporting an (approximate) inverse dependence of the intermolecular energy on volume, however, do not apply to the interaction entropy. If, as seems plausible, these interactions are comparatively insensitive to the volume within the liquid range, then the term in question may be formulated as independent of the volume. On this basis eq 12 for the free energy of mixing should be revised by adding a term for the interaction entropy which, by analogy to the term in X_{12}, takes the form $-\theta_2 N_1 v_1^* T Q_{12}$ where

$$Q_{12} = \Gamma_S(1/r_1 - 1/r_2)^2/(1 + s_e/s_m r_1)(1 + s_e/s_m r_2)^2 \quad (20)$$

and Γ_S is a parameter for the entropy expressed in cal

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[17] E. A. Guggenheim, "Mixtures," Oxford University Press, London, 1952, pp 78–80; see also E. A. Guggenheim, *Trans. Faraday Soc.*, **44**, 1007 (1948).

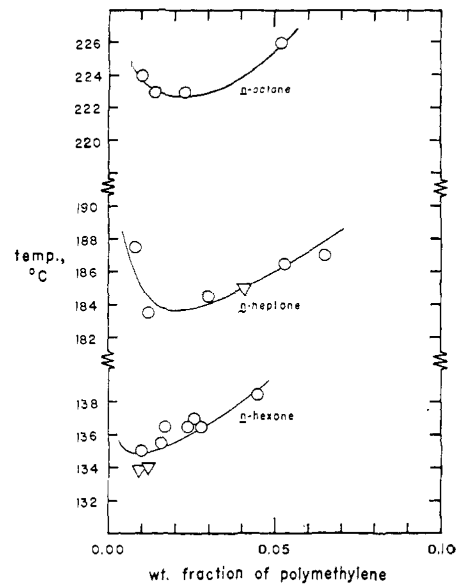

Figure 4. Phase boundary curves for polymethylene in *n*-hexane, *n*-heptane, and *n*-octane. Circles represent measurements on Marlex-50 polymethylene having a number-average molecular weight of 10^4; triangles, Marlex-6050 having a molecular weight of 1.8×10^5.

cm^{-3} deg^{-1}. It is analogous to Γ for the interaction enthalpy but, unlike the latter, is not dimensionless. The assumed independence of volume eliminates a contribution from this term to the equation of state; obviously, this term does not contribute to the enthalpy. Equation 15 for the chemical potential is accordingly to be replaced by

$$\mu_1 - \mu_1^0 = RT \ln \varphi_1 + RT(1 - \mathrm{v}_1^*/\mathrm{v}_2^*)\varphi_2 + \theta_2^2 \mathrm{v}_1^*(X_{12}\tilde{v}^{-1} - TQ_{12}) + \mathrm{v}_1^* p_1^* \{3\tilde{T}_1 \ln [(\tilde{v}_1^{1/3} - 1)/(\tilde{v}^{1/3} - 1)] + 1/\tilde{v}_1 - 1/\tilde{v}\} \quad (21)$$

The calculated results given in the last column of Table III and represented by the solid curve in Figure 3 were obtained by taking $\Gamma_S = 0.20$ in eq 20 and substituting values of Q_{12} calculated on this basis into eq 21. The agreement with observed results is almost within the limits of experimental errors. Only at lower concentrations (x_2) does the difference between calculated and observed values display a definite trend; the differences are very small, however. While the close agreement achieved in Table III has entailed introduction of a second arbitrary parameter Γ_S (in addition to Γ), it is to be noted that the same assignments for Γ and Γ_S are retained for all compositions and temperatures, and for alkanes of different chain lengths as well. The experimental results on the effects of variations of r_1 and r_2 are somewhat limited, to be sure.

The magnitude of TQ_{12} in eq 21 is slightly less than half of $X_{12}/\tilde{v}$. Obviously, very nearly equivalent excess chemical potentials would have been calculated if X_{12} had been reduced correspondingly through choice of a lower value of Γ. While the calculated excess volumes would have been lowered only minutely by this alteration, the excess enthalpies would have been seriously underestimated.

Lower Critical Solution Temperatures

Lower critical miscibility for the system n-C_6H_{14} + polymethylene occurs near 130° according to measurements reported by Freeman and Rowlinson[18] and by Nakajima and Hamada.[19] The former authors[18] found *n*-pentane and polymethylene to be incompletely miscible at all temperatures above 110°, the temperature at which the crystalline form of the polymer vanishes in the presence of the solvent. We have measured the lower critical solution temperatures (LCST's) of mixtures of polymethylene with n-C_6H_{14}, with n-C_7H_{16}, and with n-C_8H_{18} by the procedure described briefly below.

The two samples of polymethylene described in the preceding paper[5] were used. Chromatoquality n-C_6H_{14}, n-C_7H_{16}, and n-C_8H_{18} (Matheson Coleman and Bell) served as solvents for the polymethylene in the measurements of the lower critical solution temperatures. The n-C_6H_{14} contained 0.6 mole % impurity;[5] impurities comprising 0.3 mole % were present in the samples of the other two hydrocarbons.

Solvent and polymethylene were placed in 4-mm Pyrex glass tubes sealed at one end. In the experiments on Marlex-50 polymethylene, a trace of the antioxidant N-phenyl-β-naphthylamine was added, and/or nitrogen was bubbled through the mixture. After the air had been evacuated, the tube was sealed. The length of the sealed tube was about 6 cm. It was positioned horizontally in an oil bath and slowly heated. A bubble moving inside the tube as it was tilted served to mix its contents. The temperature at which the solution, on heating, first appeared turbid was measured at several concentrations of polymethylene (Figure 4). The turbidity disappeared on cooling. The cloud point was easily reproducible.

Results are presented in Figure 4, where the lowest temperatures at which incomplete miscibility was observed are plotted as functions of the polymethylene concentration. The minima in these curves are recorded as the LCST's listed in Table IV, together with the results of Freeman and Rowlinson[18] and of Nakajima and Hamada.[19]

At the LCST

$$[\partial(\mu_1 - \mu_1^0)/\partial\varphi_2]_{T,p} = [\partial^2(\mu_1 - \mu_1^0)/\partial\varphi_2^2]_{T,p} = 0$$

The first derivative vanishes at $\varphi_2 = 0$ for a polymer of infinite molecular weight ($r_2 = \infty$). Differentiation of eq 21 and substitution using eq 4, 5, 16, 20, 11*, and 12* lead to[2,3,20] eq 22. Critical temperatures calculated from this expression equated to zero are given in the last column of Table IV. The equation-of-state parameters required for these calculations have been taken from the tabulations in the preceding paper.[5] The parameters Γ and Γ_S were assigned the same values 1.40 and 0.20, respectively, as above.

$$\left[\frac{\partial^2(\mu_1 - \mu_1^0)}{\partial\varphi_2^2}\right]_{T,p,\varphi_2=0} = -RT + \frac{\alpha_1 T \mathrm{v}_1^* p_\infty^{*2}}{\tilde{v}_1 p_1^*} \times \left[1 - \frac{T_1^*}{T_\infty^*} - \frac{\Gamma}{(r_1 + s_e/s_m)^2}\right]^2 + 2\mathrm{v}_1^*(\Gamma p_\infty^* \tilde{v}_1^{-1} - \Gamma_S T) r_1 (r_1 + s_e/s_m)^{-3} \quad (22)$$

The theory predicts lower critical miscibility for each of the hydrocarbons n-C_6H_{14} and above. The calculated LCST's are somewhat lower than those ob-

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[18] P. I. Freeman and J. S. Rowlinson, *Polymer*, 1, 20 (1960).

[19] A. Nakajima and F. Hamada, *Kolloid-Z.*, 205, 55 (1965); also, their paper presented at the Annual Meeting of the Society of Polymer Science, Nagoya, Japan, 1966.

[20] A. Abe and P. J. Flory, *J. Am. Chem. Soc.*, **88**, 2887 (1966).

Table IV. LCST's for *n*-Alkanes and Polymethylene

n-Alkane	LCST, °C Obsd	LCST, °C Calcd (eq 22)
n-C_6H_{14}	127,[a] 133,[b] 135[c]	70
n-C_7H_{16}	184[c]	120
n-C_8H_{18}	223[c]	150

[a] Reference 18. The molecular weight of the polymethylene was 10^6. [b] Reference 19. This value has been extrapolated to infinite molecular weight. [c] This work.

served. The calculations, however, are sensitive to the precise values of the parameters, and doubtless also to minor aberrations of the theory itself inasmuch as the LCST is located through a second derivative of the chemical potential. Moreover, the densities of the solvents are low in the range of the LCST's; they are in fact not very much greater than the critical densities for the pure liquids. At low liquid densities some of the assumptions underlying the treatment become questionable.[1,3] In view of these considerations, the measure of agreement between observed and calculated LCST's is gratifying. It is achieved without additional parameters beyond those assigned earlier on the basis of other measurements.

Inclusion of the term Γ_S improves the representation of lower critical miscibility. Calculations carried out without it predict limited miscibility for polymethylene (liquid) in *n*-C_6H_{14} and in *n*-C_7H_{16} at all temperatures above 20°; the LCST calculated on this basis for *n*-C_8H_{18} is about 80°.

Excess Coefficients of Expansion and Compressibility

Díaz Peña and Benítez de Soto[12] have measured the coefficients of expansion α and compressibility κ of solutions of *n*-C_6H_{14} and *n*-$C_{16}H_{34}$. Excess expansions

$$\alpha^E = (1/v)(\partial v^E/\partial T)_p = \alpha - (x_1v_1\alpha_1 + x_2v_2\alpha_2)/v \quad (23)$$

and excess compressibilities

$$\kappa^E = -(1/v)(\partial v^E/\partial p)_T = \kappa - (x_1v_1\kappa_1 + x_2v_2\kappa_2)/v \quad (24)$$

calculated from the results of their experiments are presented in Table V.

The values of α^E and κ^E given in the third and sixth columns of Table V have been computed from the thermal expansion coefficients, thermal pressure coefficients, and molar volumes of the components, and from α and $\kappa = \alpha/\gamma$ calculated for the mixture from T^* and p^* using eq 11*–13*. The agreement is excellent.

Table V. Excess Coefficients of Expansion and Compressibility for the Equimolar Mixture of *n*-Hexane and *n*-Hexadecane

Temp, °C	$10^3\alpha$, deg^{-1} Calcd	$10^3\alpha^E$, deg^{-1} Calcd	$10^3\alpha^E$, deg^{-1} Obsd[a]	$10^3\kappa$, cm^3 cal^{-1} Calcd	$10^3\kappa^E$, cm^3 cal^{-1} Calcd	$10^3\kappa^E$, cm^3 cal^{-1} Obsd[a]
30	1.024	−0.039	−0.049	4.56	−0.37	−0.37
40	1.038	−0.045	−0.057	4.90	−0.45	−0.47
50	1.054	−0.053	−0.064	5.27	−0.55	−0.57
60	1.072	−0.063	−0.071	5.67	−0.69	−0.66

[a] Reference 12.

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Interpretation of Random-Coil Configurations of *trans*-1,4-Polybutadiene and *trans*-1,4-Polyisoprene

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Abstract: Results of calculations based on a rotational isomeric state model with neighbor dependence are used to interpret experimental values of the chain dimensions and their temperature coefficient for *trans*-1,4-polybutadiene and *trans*-1,4-polyisoprene. Similarities and differences in conformational and configurational properties between these polymers and *cis*-1,4-polybutadiene and *cis*-1,4-polyisoprene are elucidated. The interpretation of the properties of the *trans*-diene polymers is found to be consistent with that reported previously for the corresponding *cis*-diene chains.

In a recent investigation[2] a rotational isomeric state model treated by Ising lattice methods was successfully used to interpret the chain dimensions and their temperature coefficient for the *cis* forms of 1,4-polybutadiene (PBD), $\left[CH_2CH{=}CHCH_2\right]_x$, and 1,4-polyisoprene (PIP), $\left[CH_2C(CH_3){=}CHCH_2\right]_x$, in the limit of high degree of polymerization *x*. Such calculations can readily be extended to include the *trans* forms of these polymers, for which some experimental results are available.

In this approach, correlation of experimental and theoretical results yields estimates of the energies associated with various conformations of the chain backbone. Since some intramolecular interactions occurring in the *trans*-diene chains are very similar to

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[2] J. E. Mark, *J. Am. Chem. Soc.*, **88**, 4354 (1966).