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NOTATION

A,B,C = concentrations of components as function of time
A_o,B_o,C_o = initial (or feed) concentrations of components
c_i = stoichiometric coefficients in reaction kinetics formulation
k_1,k_2 = reaction velocity constants
k = k_1
$K_{equil.}$ = equilibrium constant = k_1/k_2
K_A,K_B = equilibrium adsorption coefficients
L_i = generalized components in reaction kinetics formulation
P_i = powers in reaction kinetics formulation
r = rate of reaction
s = standard deviation of residuals
x = vector of independent variables
y = observations on dependent variable
α,β = powers in denominator of Langmuir-Hinshelwood rate expressions
η = dependent variable
ϕ = vector of parameters

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Interaction Model for Critical Temperatures of Multicomponent Mixtures of Methane-Free Aliphatic Hydrocarbons

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A mathematical treatment based on an interaction model has yielded an expression capable of establishing the critical temperatures of multicomponent aliphatic hydrocarbon mixtures. This model postulates an infinite-series expansion for the difference between the actual critical temperature and its corresponding pseudocritical value. For methane-free aliphatic hydrocarbon mixtures, this infinite series has been truncated beyond the third-order interactions. Explicit relationships are given for the second-order interaction coefficients A_{ij} and B_{ij} as a function of the binary-system parameter τ_{ij} and the third-order interaction coefficient β_{ijk} as a function of χ_{ijk}, the ternary-system parameter.

This interaction model has been applied to one hundred-sixteen different compositions of binary, ternary, quaternary, and quinary aliphatic hydrocarbon systems to produce an overall average deviation of 0.35%. Owing to the different interaction behavior of methane, systems containing methane have not been included in this study.

The prediction of the critical temperatures of binary and multicomponent hydrocarbon systems has been a subject of considerable speculation, treated for the most part from empirical approaches. These considerations utilize convenient parameters for the establishment of basic constants pertinent to each of these studies (*2, 3, 5–7, 13*). The present study attempts to employ a direct mathematical development which utilizes an interaction model as a basis to formulate the governing relationships for establishing the critical temperature of a multicomponent system.

MATHEMATICAL DEVELOPMENT

The model postulated in this study utilizes the results of the interactions of the different species to establish the critical temperature of an n component mixture. For this purpose, the following series expansion is proposed:

$$T_c = \sum_{i=1}^{n} \alpha_i n_i + \sum_{i,j}^{n} \alpha_{ij} n_i n_j + \sum_{i,j,k}^{n} \alpha_{ijk} n_i n_j n_k + \sum_{i,j,k,l}^{n} \alpha_{ijkl} n_i n_j n_k n_l + \dots \quad (1)$$

In Equation (1), α_i, α_{ij}, α_{ijk}, α_{ijkl} ... represent coefficients resulting from all the possible interactions of the species in the mixture. The subscripts i, j, k, l, ... denote the interacting species, and n_i, n_j, n_k, n_l ... are the mole fractions of components i, j, k, l, ... in the mixture.

If α_i is defined to represent the critical temperature of component i, then the quantity $\sum_{i=1}^{n} \alpha_i n_i$ becomes T_c', the pseudocritical temperature of the mixture. Thus, Equation (1) can be rearranged as follows:

$$T_c - T_c' = \sum_{i,j}^{n} \alpha_{ij} n_i n_j + \sum_{i,j,k}^{n} \alpha_{ijk} n_i n_j n_k + \sum_{i,j,k,l}^{n} \alpha_{ijkl} n_i n_j n_k n_l + \ldots \quad (2)$$

The sum of the series on the right-hand side of Equation (2) represents the deviation resulting from a linear approximation of the critical temperature of the mixture.

If it is assumed that the effect of an interaction is independent of its order, then it is possible to associate a symmetry property with the interaction coefficients of Equation (2), defined in accordance with

$$\alpha_{i,j,k,l \ldots s} = \alpha_{p(i,j,k,l \ldots s)} \quad (3)$$

where $p(i, j, k, l \ldots s)$ represents any permutation of the indexes $i, j, k, l \ldots s$.

In this model the state of the pure substance is defined as the limit when all the interacting species approach each other in identity. For this limiting case the sum of the series of Equation (2) must vanish. To satisfy this limiting condition, another property of the interaction coefficients is postulated:

$$\alpha_{ii} = \alpha_{iii} = \alpha_{iiii} = \ldots = 0 \quad (4)$$

For this study, the frequency of interactions, from a probability point of view, is assumed to become insignificant beyond the third-order interactions. Thus, Equation (2) becomes

$$T_c - T_c' = \sum_{i,j}^{n} \alpha_{ij} n_i n_j + \sum_{i,j,k}^{n} \alpha_{ijk} n_i n_j n_k \quad (5)$$

Utilizing the symmetry property of the interaction coefficients represented by Equation (3) in conjunction with Equation (4) makes it possible for Equation (5) to be expressed as follows:

$$T_c - T_c' = 2\sum_{\substack{i,j \\ i<j}}^{n} \alpha_{ij} n_i n_j + 3\left[\sum_{\substack{j,k \\ l \leq j<k \\ i \equiv j}}^{n} \alpha_{jjk} n_j^2 n_k + \sum_{\substack{i,k \\ l \leq i<k \\ j \equiv k}}^{n} \alpha_{ikk} n_i n_k^2\right] + 6\sum_{\substack{i,j,k \\ i<j<k}}^{n} \alpha_{ijk} n_i n_j n_k \text{ for } n \geq 3 \quad (6)$$

The interaction coefficients α_{jjk} and α_{ikk} denote three-molecule interactions in which two of the species are identical; whereas α_{ijk} represents a three-molecule interaction in which each of the interacting species is different. When expanded, each of the first three summations of Equation (6) produces $\binom{n}{2}$ terms, and the last summation gives rise to $\binom{n}{3}$ terms.

For a binary system, Equation (6) reduces to

$$T_c - T_c' = n_i n_j [A_{ij} + B_{ij} n_i] \quad (7)$$

where $A_{ij} = 2\alpha_{ij} + 3\alpha_{ijj}$ and $B_{ij} = 3(\alpha_{iij} - \alpha_{ijj})$.

Solving for α_{iij} and α_{ijj} in terms of A_{ij}, B_{ij}, and α_{ij} and substituting into Equation (6), one can show that

$$T_c - T_c' = 2\sum_{\substack{i,j \\ i<j}}^{n} \alpha_{ij} n_i n_j (1 - n_i - n_j) + \sum_{\substack{i,k \\ i<k}}^{n} n_i n_k [A_{ik}(n_i + n_k) + B_{ik} n_i] + 6\sum_{\substack{i,j,k \\ i<j<k}}^{n} \alpha_{ijk} n_i n_j n_k \text{ for } n \geq 3 \quad (8)$$

To simplify Equation (8), we combined the first and third terms of this equation by utilizing Equations (3) and (4) to produce the following expression for their sum:

$$2\sum_{\substack{i,j \\ i<j}}^{n} \alpha_{ij} n_i n_j (1 - n_i - n_j) + 6\sum_{\substack{i,j,k \\ i<j<k}}^{n} \alpha_{ijk} n_i n_j n_k = \sum_{i,j,k}^{n} (\alpha_{ij} + \alpha_{ijk})(1 - \delta_{ij})(1 - \delta_{ik})(1 - \delta_{jk}) n_i n_j n_k \quad (9)$$

where δ_{ij} is the Kronecker delta function. Again, taking advantage of the postulated properties of the interaction coefficients expressed by Equations (3) and (4) permits Equation (9) to be further manipulated and combined with Equation (8) to yield

$$T_c - T_c' = \sum_{\substack{i,j \\ i<j}}^{n} n_i n_j [A_{ij}(n_i + n_j) + B_{ij} n_i] + \sum_{\substack{i,j,k \\ i<j<k}}^{n} \beta_{ijk} n_i n_j n_k \text{ for } n \geq 3 \quad (10)$$

where $\beta_{ijk} = 2(\alpha_{ij} + \alpha_{ik} + \alpha_{jk} + 3\alpha_{ijk})$. The intermediate steps leading to the development of Equation (10), which have not been included in this presentation, can be found in detail elsewhere (*4*).

Equation (10) represents the final form of the postulated interaction model for an n component system. The validity of this equation will be tested by experimental critical temperatures not only for binary hydrocarbon systems but also for systems containing three, four, and more components. This analysis will require the establishment of coefficients A_{ij}, B_{ij}, and β_{ijk} and their relationships to parameters associated with each system. The nature of Equation (10) presupposes that the interaction coefficients A_{ij}, B_{ij}, and β_{ijk} should be independent of composition.

TREATMENT OF EXPERIMENTAL DATA

Experimental critical temperatures reported in the literature for binary and ternary hydrocarbon systems have been utilized to develop the relationships necessary to establish the second-order interaction coefficients A_{ij} and B_{ij} and the third-order interaction coefficient β_{ijk} respectively. The validity of the resulting expressions, and of Equation (10), has been tested with available experimental critical temperatures on other binary and ternary systems and, in addition, on quaternary and quinary mixtures. With the values of the interaction coefficients A_{ij}, B_{ij}, and β_{ijk} established, the interaction model permits

the prediction of the critical temperature of a system containing an unlimited number of components.

Constituent j is defined as heavier than the constituent i if $(T_{cj}/M_j) < (T_{ci}/M_i)$, where T_c represents the critical temperature of the pure component and M its corresponding molecular weight. In this study the indexes $i, j, k, l \ldots$ represent the species in the order of decreasing T_c/M_c ratios. A critical temperature parameter for a binary system is defined as

$$\tau_{ij} = \frac{T_{ci}/M_i}{T_{cj}/M_j} \qquad \tau_{ij} = \begin{cases} 1, i = j \\ > 1, i \neq j \end{cases} \tag{11}$$

where the indexes i and j indicate the light and heavy components of the binary system, respectively.

It is essential that a proposed parameter should vary monotonically with the deviation resulting from the actual value and its corresponding pseudovalue for the entire range of composition. The parameter τ_{ij} was found to satisfy this requirement.

When the quantity $(T_c - T_c')/n_i n_j$ of Equation (7) was plotted against n_i, linear relationships resulted for methane-free binary hydrocarbon systems. In accordance with the asumption of truncating the series beyond the third-order interactions, the resulting expression for a binary system represented by Equation (7) is consistent with the behavior of methane-free binary hydrocarbon systems. However, binary systems containing methane indicated a different behavior, apparently due to the nonconforming interaction associated with methane. Consequently, methane-containing systems have not been included in this study. Also, due to the lack of sufficient experimental critical temperatures for aromatic- and naphthenic-containing binary hydrocarbon systems, these classes of hydrocarbons were not included in this study.

Equation (7) was applied to the following binary methane-free aliphatic hydrocarbon systems:

	τ_{ij}
Ethane-propylene (*15*)	1.171
n-Pentane-*n*-heptane (*1*)	1.208
Ethane-propane (*14*)	1.211
Propane-*n*-pentane (*16*)	1.288
Propane-*i*-pentane (*17*)	1.314
n-Butane-*n*-heptane (*11*)	1.357
Ethane-*n*-butane (*10*)	1.388
Ethane-*n*-pentane (*4*)	1.559
Ethylene-*n*-heptane (*12*)	1.872
Ethane-*n*-heptane (*4*)	1.883

The quantities $T_c - T_c'$ resulting from these methane-free binary hydrocarbon systems were plotted against n_i to produce a family of curves, each parametrized with a τ value. Each of these curves exhibited a maximum in the vicinity of $0.50 < n_i < 0.60$ and terminated at $n_i = 0$ and $n_i = 1.00$, the pure component compositions. These curves can be described analytically by Equation (7) once the constants A_{ij} and B_{ij} are established. When expanded, Equation (7) becomes

$$T_c - T_c' = A_{ij}n_i + (B_{ij} - A_{ij})\, n_i^2 - B_{ij}n_i^3 \tag{12}$$

The method of least squares was applied to a number of points obtained from the $T_c - T_c'$ vs. n_i relationships to establish the corresponding A_{ij} and B_{ij} values for each binary system. The resulting A_{ij} and B_{ij} values of each system were related to their corresponding parameter τ_{ij} and curve-fitted to an exponential form to produce the following relationships, which are consistent with the property of the interaction coefficients represented by Equation (4):

$$A_{ij} = e^{6.048(\tau_{ij} - 1)^{1/3}} - 1 \tag{13}$$

and

$$B_{ij} = e^{6.356(\tau_{ij} - 1)^{1/4}} - 1 \tag{14}$$

All these computations were performed on an IBM-709 digital computer.

To utilize the experimental critical temperatures of methane-free ternary hydrocarbon systems for the establishment of a relationship for the third-order interaction coefficient β_{ijk}, we had to define a ternary-system critical-temperature parameter. For this purpose, the following parameter was proposed:

$$\chi_{ijk} = \frac{(T_{ck}C_k - T_{ci}C_i) + (T_{ck}C_k - T_{cj}C_j) + (T_{cj}C_j - T_{ci}C_i)}{T_{ci}C_i + T_{cj}C_j + T_{ck}C_k} = \frac{2(T_{ck}C_k - T_{ci}C_i)}{T_{ci}C_i + T_{cj}C_j + T_{ck}C_k} \tag{15}$$

where T_{ci} and C_i indicate respectively the critical temperature and the number of carbon atoms of the i^{th} constituent of the ternary system consisting of the species i, j, and k. For a pure substance, χ_{ijk} vanishes.

Equation (10) produces a single third-order interaction coefficient β_{ijk}, with the critical temperature of a ternary hydrocarbon mixture and the three sets of values of binary interaction coefficients A_{ij} and B_{ij} comprising the ternary. Experimental critical temperatures for the following methane-free ternary hydrocarbon systems were used to establish the β_{ijk} values corresponding to these systems:

	χ_{ijk}
Ethane-*n*-butane-*n*-heptane (*4*)	1.041
Ethane-*n*-pentane-*n*-heptane (*4*)	0.941
Ethane-propane-*n*-pentane (*5*)	0.854
Ethane-propane-*n*-butane (*8*)	0.637
Propane-*n*-butane-*n*-pentane (*5*)	0.480

The resulting β_{ijk} values were found essentially constant for a particular ternary system. These values were then related to χ_{ijk} and were curve-fitted to an exponential form to yield the following expression:

$$\beta_{ijk} = e^{6.801\,\chi_{ijk}^{2/3}} - 1 \tag{16}$$

Equation (16) is also consistent with the property of the interaction coefficients represented by Equation (4).

APPLICATION OF INTERACTION MODEL

Equations (13), (14), and (16) generate the necessary interaction coefficients, which, when substituted into Equation (10), permit the prediction of the critical temperature of a methane-free aliphatic hydrocarbon mixture containing an unlimited number of components. To illustrate the application of Equation (10), the following example is presented.

Example

Calculate the critical temperature of the ternary hydrocarbon mixture having the following composition:

			Mole fraction
Ethane:	n_1	=	0.221
Propane:	n_2	=	0.354
n-Butane:	n_3	=	0.425
			1.000

For this mixture the pseudocritical temperature is

$$T_c' = 549.8(0.221) + 665.9(0.354) + 765.3(0.425) = 682.5°\text{R}.$$

For a ternary system, Equation (10) reduces to the expression

$$T_c - T_c' = n_1n_2[A_{12}(1 - n_3) + B_{12}n_1] + n_1n_3[A_{13}(1 - n_2) + B_{13}n_1]$$

$$+ n_2n_3[A_{23}(1 - n_1) + B_{23}n_2] + \beta_{123}n_1n_2n_3$$

The critical temperature parameter τ_{ij} for the three binary systems of this ternary mixture are calculated to be

$$\tau_{12} = 1.211, \quad \tau_{13} = 1.388, \quad \text{and} \quad \tau_{23} = 1.147$$

From these τ values, A_{ij} and B_{ij} are calculated with Equations (13) and (14) to be as follows:

$A_{12} = 35.571$	$A_{13} = 81.553$	$A_{23} = 23.312$
$B_{12} = 26.929$	$B_{13} = 69.305$	$B_{23} = 16.854$

Equation (16) is then used to calculate β_{123}. For this system

$$\chi_{123} = 0.637$$

Therefore

$$\beta_{123} = e^{6.801(0.637)^{2/3}} - 1 = 121.5$$

These values are substituted into the expanded form of Equation (10) to yield

$$T_c - 682.5 = 2.85 + 6.39 + 3.63 + 4.04 = 16.91$$

$$T_c = 699.4°\text{R.}(239.7°\text{F.})$$

For this hydrocarbon mixture Grieves and Thodos (8) report an experimental value of 238.8°F. as the critical temperature of this mixture.

Critical temperatures were calculated not only for the binary systems used to obtain the interaction coefficient relationships of Equations (13) and (14), but also for the olefinic system ethylene-propylene (9). For each of these eleven binaries, nine different compositions covering the entire composition range of each system were considered. Thus, ninety-nine different binary compositions were examined, and critical temperatures were calculated for each of them from Equations (13) and (14) and Equation (7). These calculated critical temperatures were compared with values obtained from experimental relationships to produce an overall deviation for these binary systems of 0.33%. A maximum deviation of 0.92% was noted for the ethylene-propylene system. Critical temperatures for the ternary systems used to develop Equation (16) and the mixture of the *n*-butane–*n*-pentane–*n*-hexane (5) were calculated with Equation (10) to produce an overall average deviation of 0.45% for thirteen different ternary mixtures. In addition, the following quaternary and quinary systems were considered:

Quaternary systems	Compositions	Critical temperature, °R. exptl.	calc'd.
Ethane-propane-*n*-butane-*n*-pentane (5)	1	730.6	734.1
Ethane-*n*-butane-*n*-pentane-*n*-heptane (4)	1	761.7	766.9
Propane-*n*-butane-*n*-pentane-*n*-hexane (5)	1	752.3	750.8
Quinary system			
Ethane-propane-*n*-butane-*n*-pentane-*n*-hexane (5)	1	693.8	694.1

Altogether one hundred and sixteen different multicomponent compositions were considered; the calculated critical temperatures were compared with experimental values and in the case of binaries with the values obtained from experimental relationships, to produce an overall average deviation of 0.35%, with a maximum value encountered with an ethane–propane–*n*-pentane mixture (5).

CONCLUSIONS

The interaction model postulated in this investigation for the establishment of the critical temperatures of methane-free aliphatic hydrocarbon mixtures has been successfully applied to binary, ternary, quaternary, and quinary systems. The comparison between calculated and experimental values produced critical temperature differences of no more than 9.9°R. The average critical temperature difference for the thirteen ternary and four higher-order systems was found to be 3.2°R.

The method outlined in this study is not yet applicable to methane-containing systems. Furthermore, since experimental information of naphthenic- and/or aromatic-containing systems is rather limited, the procedure outlined in this study should be restricted to methane-free aliphatic hydrocarbons.

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NOTATION

A_{ij} = binary interaction coefficient, Equation (8)
B_{ij} = binary interaction coefficient, Equation (8)
C_i = number of carbon atoms of component i
M_i = molecular weight of component i
$\binom{n}{i} = \dfrac{n!}{i!(n-i)!}$, binomial coefficient
n_i = mole fraction of component i
T_c = critical temperature of mixture, °R.
T_c' = pseudocritical temperature of mixture, °R.
T_{ci} = critical temperature of ith component, °R.

Greek Letters

α_i = T_{ci}, critical temperature of i^{th} component, °R.
$\alpha_{ijk}\ldots$ = coefficient resulting from the interaction of species $i, j, k \ldots$
β_{ijk} = third-order interaction coefficient, Equation (16)
δ_{ij} = Kronecker delta $\delta_{ij} = \begin{cases} 1 & i = j \\ 0 & i \neq j \end{cases}$
τ_{ij} = critical temperature parameter for binary systems, Equation (17)
χ_{ijk} = critical temperature parameter for ternary systems, Equation (15)

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