ABSTRACT

Title of Thesis: Temperature Dependency of the Group Interaction Parameters in the AGSM and UNIFAC Models for the Prediction of Heats of Mixing

Ignatius Ojini, Master of Science, 1980

Thesis directed by: Dr. Dimitrios Tassios
Professor of Chemical Engineering

A four-parameter group-contribution model (UNIFAC) has been developed for the prediction of heats of mixing of non-electrolyte mixtures. Both the UNIFAC and AGSM models are evaluated over a wide range of temperature dependencies of the group interaction parameters. The UNIFAC model has been chosen over the AGSM model and an optimum parameter-temperature relationship has been established.

Adopting the optimum temperature dependency, group interaction parameters have been calculated using UNIFAC for the prediction of four types of mixtures: n-Alcohols/n-Alkanes; Benzene/n-Alkanes; Nitriles/n-Alkanes; Amines/n-Alkanes.

TEMPERATURE DEPENDENCY OF THE GROUP INTERACTION PARAMETERS IN THE AGSM AND UNIFAC MODELS FOR THE PREDICTION OF HEATS OF MIXING

by

Ignatius Okoronkwo Ojini

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Name of Candidate: Ignatius Okoronkwo Ojini
Master of Science, 1980

Thesis and Abstract Approved: ______________________________

Dr. Dimitrios Tassios
Professor
Department of Chemical Engineering
and Chemistry

____

Dr. Deran Hanesian
Professor
Chairman, Department of Chemical
Engineering and Chemistry

Dr. Mahmoud Abd-el-Bary
Assistant Professor
Department of Chemical Engineering
and Chemistry

Date Approved: ______________________________

VITA

Name:	Ignatius Okoronkwo Ojini
Permanent Address:	
Degree and Date to be Conferred:	M.Sc., 1980
Date of Birth:	
Place of Birth:	
Secondary Education:	St. Joseph's High School, 1969 Cameron College of Arts, Sci. & Tech., 1971

College Institutions Attended	Date	Degree	Date of Degree
New Jersey Institute of Technology	1974	B.Sc.	1977
New Jersey Institute of Technology	1978	M.Sc.	1980

Major: Chemical Engineering

Minor: Mathematics

Publications: Thesis to be published

Positions Held: Process Engineer, ARCO PETROLEUM PRODUCTS CO.
Harvey Technical Center, Harvey, Illinois 60426

DEDICATION

This work is being dedicated to my Mother, Virginia Akunna Ojini. All along, her advice and prayer constituted the great pillar beneath this endeavor. I share this sense of accomplishment, heart-to-heart, with her, for that special care and inspiration.

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I am very grateful to my advisor, Dr. Dimitrios Tassios. His views, all through the period of this work, were a constant source of motivation; his sustained interest, an invaluable asset.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

I. INTRODUCTION

In the chemical process industry several processes involve the separation of liquid mixtures. The design of separation equipment often requires knowledge of the heats of mixing of the liquid mixtures.

Often, it is very difficult to get data for the numerous liquid mixtures encountered in the chemical industry. It therefore becomes imperative to correlate available data to obtain parameters which could be used to predict heats of mixing for systems where no experimental data are available. Determination of these parameters could be done using the concept of functional group contributions. The idea here is to consider a molecule as being made up of functional groups such as aromatic, amino, nitro, keto, carbonyl, methylene, etc. Thus, for the calculation of the required data, it is the groups, not the molecules in the liquid mixtures, that are used.

This approach has the advantage that whereas there are several molecules which in turn make up thousands of mixtures used in chemical processes, the number of functional groups they contain are much smaller. A basic assumption of this approach is that a functional group appearing in one liquid mixture will have the same chemical effect in another mixture containing the same group but different molecules, the group contribution in the mixture being only a function of the group concentrations and temperature. A second assumption is that the group contributions to a thermodynamic property is considered as the sum of the individual contributions of the groups forming the molecule of the chemical compound.

For heats of mixing, parameters characterizing the energy of interaction among the groups in the mixture must be determined and related to temperature. As temperature increases, heats of mixing of liquid mixtures either increase or decrease. It therefore follows that a sound relationship between the group parameters and temperature could account for this reverse trends in liquid mixtures.

Group contribution, and other thermodynamic, models have been used considerably to correlate and predict heats of mixing and other thermodynamic properties of mixtures.

Nagata and Yamada(20) calculated heat-of-mixing data by using the Wilson, Heil and NRTL equations in which the binary parameters were made temperature dependent. When these parameters, calculated from either excess Gibbs energy or heat-of-mixing data, were used to estimate the other data, the results were not satisfactory. However, using the three (Wilson, Heil and NRTL) equations, they recalculated the parameters based on a simultaneous correlation of g^E and h^E data of 13 binary systems. Good heat-of-mixing data were obtained for five predicted ternary systems.

Abrams and Prausnitz(1) by inclusion of the Local Area Fraction Theory into Guggenheim's quasi-chemical theory, developed the UNIQUAC (Universal Quasi-Chemical) model, for the calculation of the excess Gibbs energy, and hence, vapor-liquid and liquid-liquid equilibria of both binary and multi-component liquid mixtures using two adjustable molecular parameters per binary. By using the model to reduce binary experimental data through non-linear regression, they obtained binary molecular parameters with reasonable goodness-of-fit. The parameters were then used to predict ternary vapor-liquid equilibria. The accuracy obtained was comparable to that attained by using the Wilson or the NRTL (Non-Random-Two-Liquid) equations.

Ratcliff and Chao(29) developed a modified group solution model for the prediction of thermodynamic properties of liquid mixtures. To characterize the effect of molecular size in a solution, they replaced the Flory-Huggins' relation earlier used by Wilson and Deal(4) with the Bronsted-Koefoed Congruence Principle. They attained reasonable predictions of vapor-liquid equilibria by representing mixtures containing n-alkanes, n-alcohols and water at 40°C and 90°C with the methylene and hydroxyl groups. Their work did not include predictions of heats of mixing of liquid mixtures.

The Group Contribution Method was also used in 1971 by Maripuri and Ratcliff(17) in which they extended the work of Ratcliff and Chao(29) on the prediction of excess free energies to mixtures containing alkanes and ketones. By considering the groups CH_2, CO, group interaction parameters were generated from experimental data on acetone/n-heptane mixtures at 65°C. They were used to predict excess free energies of binary and multi-component mixtures containing alkanes and ketones at 65°C. Good results were obtained.

In 1971, Nguyen and Ratcliff(22) applied their Analytic Group Solution Model (AGSM) to the prediction of excess enthalpy of normal alcohol and hydrocarbon mixtures. The model entailed the use of partial molar enthalpies which had to be determined by the differentiation of the experimental data, a procedure with high built-in errors. To reduce such errors, they applied the Spline-fit method of Van Ness,(36) a procedure which fits the function $\Delta H/X_1X_2$, as a function of composition. They also calculated group contributions due to group sizes and shapes by using data on the heats of mixing of higher alkanes. Using the fitted parameters to predict fourteen binary systems, an average prediction error of 10% was attained. Also, fairly good results were obtained for predictions of ternary alcohol/alkane systems but only at the same temperature range at which the parameters were fitted.

The authors also used the same model on mixtures containing aliphatic hydrocarbons and ketones. But, this time, group skeletal contribution was neglected because it was considered too small. Using the Forsythe method(21) to obtain polynormial expressions relating the group excess enthalpies to group composition, and splitting the group composition range into three parts for better fits, group parameters were determined.

Predictions of heats of mixing of other ketone/n-alkane systems gave fair results. Again, predictions were within the same temperature range used in the fitting.

In 1974, Nguyen and Ratcliff(23) developed an Analytical Group Solution Model (AGSM) for prediction of heats of mixing using the Wilson equation. Using experimental heats-of-mixing data between 15°C and 55°C from a wide range of n-alcohol/n-alkane mixtures, they calculated temperature-independent coefficients for the methylene/hydroxyl group energy interactions. These coefficients were used to predict heats of mixing of binary and ternary liquid mixtures containing the two structural groups (CH_2, OH). The results obtained were good for mixtures with components high in the homolgous series but poor for those in the lower series. For example, mixtures containing Ethanol showed poor results.

Siman and Vera,(32) extended the Analytical Group Solution Model (AGSM). By combining both the heat-of-mixing and vapor-liquid equilibrium, data of some n-alcohol/n-alkane mixtures between temperatures of 20°C and 40°C, and considering heat-of-mixing data alone for amylamine/n-alcohol mixtures, they calculated temperature-independent coefficients with the extended AGSM. They predicted some n-amine/n-alcohol and n-alcohol/n-alkane systems within the same temperature range; good results were obtained generally, but poor results were obtained for those mixtures whose alcohol components constitute first members of the homologous series. No predictions were done for mixtures at temperatures higher than those at which the fitting was done. Their work did not distinguish between those mixtures for which the heats of mixing increase or decrease with increasing temperature.

Using five types of binary mixtures, each containing a normal alkane, over a given range of temperature, and assuming the group energy interaction parameters to be linearly dependent on temperature in the UNIFAC model, Nagata and Ohta,(18) calculated binary parameters with which they predicted heat--of-mixing data for selected binary and ternary mixtures within the same temperature range with good accuracy.

By retaining two parameters per binary pair of molecules or groups in the original UNIQUAC and UNIFAC models, and letting the lattice coordination number (z) be dependent on temperature, Skjold-Jørgensen et al.,(33) developed an expression for Z(T) from simultaneous fitting of vapor-liquid equilibrium (VLE), and heat-of-mixing, data. This modification enabled the authors to predict VLE data from binary parameters based on heat-of-mixing data with high accuracy for systems with non-associating molecules. The reverse case also gave satisfactory results.

The present work is divided into two phases: the first phase involves the introduction of temperature dependent interaction parameters in the UNIFAC model, for the prediction of heats of mixing of liquid mixtures. Then, an extensive study of the temperature dependency of heat-of-mixing group energy interaction parameters is conducted using both the AGSM and the UNIFAC models; the purpose here being to compare the two models and select the one that gives the best predictions with the best parameter-temperature relationship.

The second phase would then entail the use of the chosen model to reduce experimental heat-of-mixing data in order to generate group energy interaction parameters to be subsequently utilized in the prediction of mixtures for which no experimental heat-of-mixing data exist, and at temperatures where most industrial separations occur. This work is concerned with the first phase.

II. THEORY

The heats of mixing (excess enthalpy) expression can be derived from Gibbs Energy functions. An excess property of a solution is that which is in excess of that of an ideal solution at the same conditions of temperature, pressure and composition. Hence, Gibbs excess free energy is represented by:

$$G^E = \underset{(\text{at } T,P,x)}{G_{(\text{real solution})}} - \underset{(\text{at } T,P,x)}{G_{(\text{ideal solution})}} \qquad (1)$$

The partial excess Gibbs energy is given by:

$$\left[\frac{\partial N_T g^E}{\partial N_j}\right]_{P,T,N_{i\neq j}} = \bar{g}_j^{\,E} \qquad (2)$$

where N_j = number of moles of species, j

$N_T = n_2 + n_2 + n_3 \ldots . n_M = \sum_{i=1}^{M} n_i$

M = number of components in the mixture.

From the definition of excess functions:

$$\bar{G}_i^E = \bar{G}_{i(\text{real})} - \bar{G}_{i(\text{ideal})} \qquad (3)$$

which is related to the fugacity of component i in a mixture.

$$\bar{G}_{i(\text{real})} - \bar{G}_{i(\text{ideal})} = RT(\ln\hat{f}_{i(\text{real})} - \ln\hat{f}_{i(\text{ideal})}) \ldots \qquad (4)$$

where $\hat{f}_i$ = fugacity of species i in solution

Thus,

$$\bar{G}_i^E = RT(\ln \hat{f}_{i(real)} - \ln \hat{f}_{i(ideal)}) \tag{5}$$

$$= RT \ln \frac{\hat{f}_{i(real)}}{\hat{f}_{i(ideal)}}$$

If $\hat{f}_{i(ideal)}$ is defined as

$$\hat{f}_{i(ideal)} = f_i^0 x_i \tag{6}$$

where

x_i = mole fraction of species i in solution

f_i^0 = standard state fugacity of pure liquid i at solution temperature and pressure.

then,

$$\bar{G}_i^E = RT \ln \frac{\hat{f}_{i(real)}}{f_i^0 x_i} \tag{7}$$

By definition, the activity coefficient of species i, γ_i, is

$$\gamma_i = \frac{\alpha_i}{x_i} \tag{8}$$

where α_i is the activity of species i in solution.

Thus,

$$\alpha_i = x_i \gamma_i \tag{9}$$

Also,

$$\alpha_i = \frac{\hat{f}_i}{f_i^0} \tag{10}$$

Therefore,

$$\alpha_i = x_i \gamma_i = \frac{f_i}{f_i^0} \qquad (11)$$

where

$$f_i = x_i \gamma_i f_i^0 \qquad (12)$$

substituting equation (11) into equation (7).

$$\bar{G}_i^E = RT \ln \gamma_i \qquad (13)$$

Following from Euler's Theorem,

$$M^E = \Sigma n_i \bar{m}_i^E, \qquad (14)$$

Thus,

$$G^E = \sum_i x_i \bar{G}_i^E = RT \Sigma x_i \ln \gamma_i \qquad (15)$$

At constant pressure and composition, a partial differential of the Gibbs equation with respect to temperature results in the Gibbs-Helmholtz expression for heats of mixing (excess enthalpy):

$$\left(\frac{\partial (G^E/T)}{\partial T}\right)_{P,x} = - \frac{H^E}{RT^2} \qquad (16)$$

Equation (15) describes how Gibbs free energy can be calculated by molecular approach. According to the functional group contribution method, the activity coefficient consists of two parts: the combinatorial part due to differences in sizes and shapes of the molecules, and the residual part due to the energy interactions of the functional groups contained in the mixture. Thus, equation (15) takes the form

$$G^E/RT = \sum_i x_i (\ln\gamma_i^R + \ln\gamma_i^C) \qquad (17)$$

III. GROUP CONTRIBUTION METHODS

Group contribution methods have been extensively used to determine thermodynamic properties of liquid mixtures. Langmuir(15) had pioneered work in the area, but little recognition was given to it then. However, Derr and co-workers(5) later utilized the idea to correlate heats of mixing of liquid mixtures. Wilson and Deal(4) then conceptualized the 'Solution-of-Groups' method for calculating activity coefficients. Ratcliff and co-workers(21) applied the Analytical Solution of Groups (ASOG) model to calculate heats of mixing. They later modified the Wilson equation and came up with a more accurate method, the Analytical Group Solution Model (AGSM) for correlating heat-of-mixing data.(23)

The basic assumptions of 'solution-of-groups' methods are:

1. The logarithm of the activity coefficient is divided into two parts: combinatorial and residual. The combinatorial part is characterized by differences in size and shape of the molecules in the mixture; the residual part is due to molecular energy interactions.

For molecule i in a solution:

$$\ln\gamma_i = \underset{\text{combinatorial}}{\ln\gamma_i^C} + \underset{\text{residual}}{\ln\gamma_i^R} \tag{1}$$

The distinction between the two kinds of contribution to the logarithm of the activity coefficient is necessary since the liquid phase non-idealities caused by size and shape effects cannot be associated with group energy interactions.

2. The residual part, which is due to group energy interactions, is assumed to be the sum of the individual contributions of each solute group in the solution less the sum of the individual contributions in the pure-component environment:

$$\ln\gamma_i^R = \sum_{i=1} V_k^{(i)} [\ln\Gamma_k - \ln\Gamma_k^{(i)}] \qquad (2)$$

$k = 1, 2 \ldots N$

$\Gamma_k^{(i)}$ = the residual group activity coefficient of group k in a reference solution containing only molecules of type i. It is used to normalize the activity coefficient, that is, γ_i becomes unity as $x_i \rightarrow 1$.

Γ_k = the residual group activity coefficient of group k in a solution

$V_k^{(i)}$ = the number of groups of kind k in molecule i.

3. Individual group contribution to a 'solution of groups' is only a function of group concentrations and temperature of mixture:

$$\left.\begin{matrix}\Gamma_k \\ \Gamma_k^{(i)}\end{matrix}\right\} = f(x_1, x_2 \ldots\ldots x_n, T) \ldots \qquad (3)$$

The two major group contribution methods: AGSM and UNIFAC, are discussed next.

A. The Analytical Group Solution Model (AGSM)

The Analytical Group Solution Model (AGSM) was developed by Ratcliff and co-workers.(17) Like all other group contribution methods, it attempts to characterize heats of mixing of liquid mixtures by a consideration not of the molecules in the mixture but of the functional groups making up the mixture. Also, its basic assumption is that the contribution of each functional group to the residual thermodynamic properties of a mixture is independent of other structural groups forming the molecule. And, that the contribution to heats of mixing of a given component of a mixture is accounted for by summing the contributions of the separate functional groups making up the molecule of the chemical compound, thus,

$$\Delta\bar{H}_i = \sum_k N_k^{(i)} (H_k - H_k^{(i)}) \tag{4}$$

Where the heat of mixing is given by

$$\Delta H = \sum_i X_i \Delta\bar{H}_i \quad \ldots. \tag{5}$$

The group heat of mixing (H_k) is given by

$$\frac{H_k}{RT^2} = \frac{\sum_j X_j b_{kj}}{\sum_j X_j a_{kj}} + \sum_j \frac{x_j b_{jk}}{\sum_m X_m a_{jm}} - \sum_j \frac{X_j a_{jk}}{(\sum_m X_m a_{jm})^2} \sum_m X_m b_{jm} \ldots. \tag{6}$$

The standard state heats of mixing of group k in pure component i, $H_k^{(i)}$, i

$$\frac{H_k^{(i)}}{RT^2} = \frac{\sum_j X_j^{(i)} b_{kj}}{\sum_j X_j^{(i)} a_{kj}} + \sum_j \frac{X_j^{(i)} b_{jk}}{\sum_m X_m^{(i)} a_{jm}} - \sum_j \frac{X_j^{(i)} a_{jk}}{(\sum_m X_m^{(i)} a_{jm})^2} \sum_m X_m^{(i)} b_{jm} \ldots \tag{7}$$

where

$$X_m = \frac{\sum_{i=j}^{J} X_i N_j^{(i)}}{\sum_{i}\sum_{m} X_i N_m^{(i)}} \quad . \; . \; . \qquad (8)$$

and

$$X_j^{(i)} = N_j^{(i)} / \sum_m N_m^{(i)} \qquad (9)$$

The group temperature dependent parameters a_{jk}, a_{kj}, b_{jk}, b_{kj} are related to each other as

$$b_{jk} = \frac{\partial a_{jk}}{\partial T} \qquad (10)$$

And, in order to increase the analytical flexibility of the AGSM model, a temperature dependence of the parameters of the following type has been considered

$$a_{jk} = \mathrm{EXP}(A_{jk} + B_{jk}/T) \qquad (11)$$

and

$$b_{jk} = \mathrm{EXP}(A_{jk} + B_{jk}/T)(-B_{jk}/T^2) \qquad (12)$$

The AGSM model as presented above can be used to correlate heat of mixing of liquid mixtures by using available heat-of-mixing data to determine the temperature independent parameters (coefficients), A_{jk}, A_{kj}, B_{jk}, B_{kj}, and then applying them in the prediction of heats of mixing of mixtures containing the same groups, j, k.

The group energy interaction parameters are determined by heat-of-mixing data reduction using a non-linear regression subroutine(26) with the AGSM model.

They are then used to predict heats of mixing of mixtures having the same groups, j, k but may not have experimental data available. The quality of prediction depends on how accurate the parameters are. This accuracy depends in turn on the accuracy of the experimental heat-of-mixing data used in the parameter calculations and, of course, the accuracy of the model.

AGSM does not differentiate between normal chemical compounds and isomeric ones. For example, it will use the same parameters to predict heats of mixing of, say, n-octanol/n-heptane and 3-octanol/n-heptane.

The determination of AGSM parameters id done using binary group mixtures. For example, in using the mixture n-octanol/n-heptane, chosen groups may be CH_3, CH_2, OH (where the interactions involving groups CH_3, CH_2 are considered the same).

The group temperature independent interaction parameters then become $A(CH_2,OH)$, $A(OH,CH_2)$; $B(CH_2,OH)$, $B(OH,CH_2)$ where ($A(CH_3,OH) = A(CH_2,OH)$; $B(CH_3,OH) = B(CH_2,OH)$). To calculate these, the AGSM is fitted to heat-of-mixing data; the final values are obtained at the point of minimum error of regression.

But determination of some group interaction parameters requires, often, the use of more than one binary group mixture; for example, in characterizing group interactions for the mixture type, say, n-alcohol-n-amine, chosen groups could be $CH_2(CH_3)$, OH, NH_2. Hence, 12 coefficients will have to be calculated from the three binary group pairs, CH_2/OH, CH_2/NH_2, NH_2/OH (for each binary group pair there are four coefficients). That number of coefficients is too large to be computed at one time considering the limited amount of data available for any one system type; it also calls into question the ability of the regression program to handle massive amounts of data even when these are available.

It becomes imperative, then, to calculate the twelve parameters, four at a time. Firstly, the four coefficients of the group pair, CH_2/OH, are calculated with data for an n-alcohol-n-alkane system; the next four coefficients for the pair, CH_2/NH_2, are calculated using an n-amine-n-alkane system, bringing the total to eight coefficients. These are called primary coefficients because their computation does not involve coefficients calculated elsewhere. Finally, for the group pair, NH_2/OH, the eight primary coefficients are used together with data for a normal alcohol-n-amine system to compute the four temperature independent coefficients, namely:

$$A(NH_2,OH),\ A(OH,NH_2);\quad B(NH_2,OH),\quad B(OH,NH_2)$$

These are called secondary coefficients because in their determination the eight primary coefficients computed earlier are used.

B. The UNIFAC Method

The UNIQUAC equation, as developed by Abrams and Prausnitz,(1) has been shown to provide good representation of both vapor-liquid and liquid-liquid equilibria for binary and multicomponent mixtures containing non-electrolytes such as water, hydrocarbons, ketones, esters, amines, alcohols, nitriles, etc. The UNIQUAC equation for calculating the molecular component (i) activity coefficient is:

$$\ln\gamma_i = \ln\gamma_i^C + \ln\gamma_i^R \tag{13}$$

where

$$\ln\gamma_i^C = \ln\frac{\Phi_i}{X_i} + \frac{z}{2}\, q_i \ln\frac{\theta_i}{\Phi_i} + L_i - \frac{\Phi_i}{X_j}\sum_j X_j L_j \tag{14}$$

$$\ln\gamma_i^R = q_i[1 - \ln(\Sigma_j \theta_j J_{ji}) - \Sigma_j(\theta_j J_{ij}/\Sigma_k \theta_k J_{kj})] \tag{15}$$

$$L_i = \frac{z}{2}(r_i - q_i) - (r_i - 1);\; z = 10 \tag{16}$$

$$\theta_i = \frac{q_i X_i}{\sum_{j=1}^{M} q_j X_j} \tag{17}$$

$$\Phi_i = \frac{r_i X_i}{\sum_{j=1}^{M} r_j X_j} \tag{18}$$

$$\tau_{ji} = \mathrm{EXP}-[\frac{U_{ji} - U_{ii}}{RT}] \tag{19}$$

The combinatorial part of the group activity coefficient is independent of temperature. Also, its contribution to activity coefficient is small as compared to that of the residual part. However, when the molecules of the mixture differ markedly in size and shape, the combinatorial share becomes significant.

For the UNIFAC model, only the combinatorial part of the UNIQUAC activity coefficient, (equation 14) is used directly. Only pure-component properties calculated from molecular structure data enter into this equation. The pure-component volume and area parameters, r and q, respectively are calculated as the sum of the group volume and area parameters, R_k, Q_k.

$$r_i = \sum_{k=1}^{N} V_k^{(i)} R_k \quad ; \quad q_i = \sum_{k=1}^{N} V_k^{(i)} Q_k \qquad (20)$$

where N is the number of groups in molecule i.

$V_k^{(i)}$, an integer, is the number of type k group in component i.

$$R_k = V_{wk}/15{\cdot}17 \quad ; \quad Q_k = A_{wk}/(2.5 \cdot 10^9) \qquad (21)$$

where R_k and Q_k are group volume and area parameters obtained from Van der Waals group volumes and surface areas, V_{wk}, and A_{wk} given by Bondi.(2) The normalization factors 15.17 and $2.5.10^9$ are given by Abrams and Prausnitz.(1)

Unlike the ASOG method in which "size counts" are determined arbitrarily and used to signify group sizes and surface areas, the UNIFAC method uses well-established, rational procedures; once a group has been established, it retains that structure and its assigned volume and surface area throughout its use.

The residual part of UNIQUAC (equation 15) is replaced in the UNIFAC model by the solution-of-groups concept

$$\ln\gamma_i^R = \sum_{k=1}^{N} V_k^{(i)} [\ln\Gamma_k - \ln\Gamma_k^{(i)}] \qquad (22)$$

where N is the number of groups in molecule i.

$$\Gamma_k = Q_k [1 - \ln(\sum_m \theta_m \psi_{mk}) - \sum_m (\theta_m \psi_{km} / \sum_n \theta_n \psi_{nm}) \qquad (23)$$

$$\Gamma_k^{(i)} = Q_k [1 - \ln(\sum_m \theta_m^{(i)} \psi_{mk}) - \sum_m (\theta_m^{(i)} \psi_{km} / \sum_n \theta_n^{(i)} \psi_{nm}) \qquad (24)$$

$$\theta_m = \frac{Q_m X_m}{\sum_{n=1}^{N} Q_n X_n} \quad ; \quad \theta_m^{(i)} = \frac{Q_m X_m^{(i)}}{\sum_{n=1}^{N} Q_n X_n^{(i)}} \qquad (25)$$

$$X_m = \frac{\sum_{j=1} V_m^{(j)} X_j}{\sum\sum^{jn} V_n^{(j)} X_j} \quad ; \quad X_m^{(i)} = \frac{V_m^{(i)}}{\sum^{n} V_n^{(j)}} \qquad (26)$$

m and n = 1, 2 .... N (all groups)

Substituting equation (22) into equation (17) of Chapter 2, gives $G^E/RT = \sum_i X_i (\sum_k V_k^{(i)} ([\ln\Gamma_k - \ln\Gamma_k^{(i)}] + \ln\gamma_i^C))$ (27)

Complete derivation of equation (27) is presented in the appendix.

The activity coefficient of group k in molecule i depends on the molecule in which k is situated. For example, $\Gamma_k^{(i)}$ for the CCOH group in n-pentanol refers to a solution containing twenty-five group percent CCOH, fifty group percent CH_2, and twenty-five group percent CH_3.

In equations (23) and (24), the parameter ψ_{nm}, is temperature dependent:

$$\psi_{nm} = \text{EXP}[-\frac{a_{nm}}{T}] \qquad (28)$$

where a_{nm} characterize the energy interactions between a group n and a group m. $a_{nm} \neq a_{mn}$ and each is assumed temperature-independent. Thus, there are two group interaction parameters for each pair of groups. As in the UNIQUAC case, no ternary or higher parameters are needed; and the parameters must be evaluated from phase equilibrium data. They have the units of degrees Kelvin.

The combinatorial contribution to the activity coefficient (equation 14) depends only on the sizes and shapes of the molecules present. For large chain molecules, $q_i/r_i \rightarrow 1$, and in that limit equation (14) reduces to the Flory-Huggins equation used in the ASOG method.

The residual contribution to the activity coefficient (equations 22, 23, 24) depends on group areas and group interactions. When all groups are equal, equations (22), (23), and (24) are similar to those used in the ASOG method.

From a main group of, say, CH_2, (in a hydrocarbon) subgroups CH_3, CH_2, CH, are formed. While each group has its own calculated values of R and Q, the subgroups within the same main group are assumed to have identical group energy interaction parameters. Also, by the use of subgroups of the same main group, the UNIFAC method can predict systems containing isomeric components. For example, by using group interaction parameters ($A(CH_2,CH_2CH_2OH$, $A(CH_2CH_2OH,CH_2))$ determined from a n-alcohol/n-alkane system, an isomeric system containing the groups CH_3, CH_2, CH_2CHOH, can be predicted by only accounting for the new values of R_{CH_2CHOH} and Q_{CH_2CHOH} since $a_{CH_2,CH_2CH_2OH} = a_{CH_2,CH_2CHOH}$. Certain advantages have been attributed to the UNIFAC method:

1. Flexibility, because UNIFAC has a well-founded basis for establishing group sizes and shapes.

2. Simplicity, because UNIFAC parameters can be considered nearly independent of temperature for reasonable temperature ranges and for vapor-liquid equilibrium calculations.

3. Large range of applicability, because UNIFAC parameters are now available for a considerable number of different functional groups.

The UNIFAC model may be applied to non-electrolyte binary and multi-component mixtures at conditions where the UNIQUAC model applies, that is, removed from the critical region. Furthermore, all components must be condensable. The temperature range considered is typically 30-125°C.

C. Temperature Dependency of the Group Interaction Parameters in the AGSM and UNIFAC Models

Fredenslund et al. applies the two-parameter version of UNIFAC (equation 5, Appendix 1) for correlation and prediction of heat-of-mixing data. The two parameters, a_{ij}, a_{ji}, are independent of temperature.

Initially, in this work, the application of this version and the four-parameter version with linear temperature dependency of the parameter, a_{ij}, ($a = AT + B$), proved unsatisfactoty (Section IV). Further complication to the heat-of-mixing picture is caused by the occurrence of two types of mixtures; while, on the one hand, the heats of mixing of some mixtures, for example, alcohol mixtures, increase with increasing temperature, those of other mixtures, like benzene systems, on the other hand, decrease with increasing temperature. Here, the former type will be called 'TYPE I' and the latter, 'TYPE II.'

In the light of this phenomenon therefore it becomes necessary to develop a model in which the parameters assume a temperature dependency capable of, not only improving the poor results encountered with the linear dependency, but, also, of predicting the heats of mixing of the two types of mixtures, within a reasonable degree of accuracy.

To achieve this aim, the group energy interaction parameters in both the AGSM and UNIFAC models were assumed to vary according to the relation:

$$a_{ij} = A_{ij}T_n + B_{ij} \qquad (29)$$

where A_{ij} and B_{ij} are the temperature independent parameters and n is the temperature exponent.

Our preliminary work indicated (Section IV) that when positive values were assumed for n, better results were obtained for Type I mixtures than for Type II mixtures. However, the above results were reversed for negative values of n. In order to account for these tendencies, eight values of n (+1/2, +1, +1 1/2, +2, -1/2, -1, -1 1/2, -2), two Type I and two Type II, systems, were selected. The systems were: n-Octanol-n-Heptane(24) (Type I), Nitroethane/2,2-dimethylbutane(12) (Type I), Benzene-n-Octane(8) (Type II) and Butylamine-n-Heptane(14) (Type II), at 303, 293, 298, 308 degrees Kelvin, respectively. The purpose, here, was to use both the AGSM and UNIFAC models with heat-of-mixing data of the selected systems to calculate the temperature independent group interaction parameters (equation 29) for each of the selected values of the n. Then, the parameters calculated for each system were used to predict its heat-of-mixing data at a temperature higher than that at which the parameters were determined. Thus, the best exponent would be that for which the lowest prediction error was attained.

In selecting the four systems, certain criteria were followed. Each system should contain an alkane so that only primary, and no secondary parameters should appear in their computations; this was necessary in order to avoid complications usually encountered with secondary parameters. Each of the two systems representing each mixture type should be different from the other so as to adequately spread the representation of that type; for example, on selecting the system, n-Octanol-n-Heptane (Type I), it was necessary to choose a second system that did not contain an alcohol. Thus, the system Nitroethane/2,2-Dimethylbutane (Type I).

It was also important that each selected system must have its data reported for at least two temperatures. This would ensure that group interaction parameters for each system are calculated at low temperature where most of the literature data are available, and, then, be used to predict the same system at the higher temperature where most of the practical needs occur.

After selecting the values of n and the four systems for the study, the following procedure was used to determine the group model and the exponent which would achieve the best performance in the prediction of heat-of-mixing data for both Type I and Type II mixtures:

First, for each exponent and system, and using each of the two group models (AGSM and UNIFAC), the group energy interaction parameters were calculated by regression analysis. The heat-of-mixing data used for each system were those reported at the respective temperatures 303, 293, 298, 308, degrees Kelvin, for the four systems as mentioned earlier. Then, for each group model and value of n, the calculated parameters were used to predict the heat-of-mixing data of the systems at higher temperatures. The percentage prediction errors were computed as follows:

$$\text{ERROR (\%)} = \frac{1}{P} \sum_{i=1}^{i=P} \left| \frac{(\Delta H_{EXP})_i - (\Delta H_{CAL})_i}{(\Delta H_{EXP})_i} \right| (100) \qquad (30)$$

where P = number of experimental data points for each system.

Average prediction errors were calculated for each mixture Type as:

$$\text{AVERAGE ERROR (\%)} = \frac{1}{2} \sum_{1}^{m} \frac{1}{P} \sum_{i=1}^{i=P} \left| \frac{(\Delta H_{EXP})_i - (\Delta H_{CAL})_i}{(\Delta H_{EXP})_i} \right| (100) \qquad (31)$$

where m = 2 since there are two systems for each type of mixture and P = number of experimental data points for each of the two systems.

The average error is necessary in order to prepare plots of Average Prediction Error (%) versus n. Such plots should indicate how satisfactorily the positive and negative values of n affected the predicted results of the Type I and Type II mixtures, respectively.

The overall prediction error was calculated for each value of n as follows:

$$\text{OVERALL ERROR (\%)} = \frac{1}{4} \sum_{1}^{m} \frac{1}{P} \sum_{i=1}^{i=P} \left| \frac{(\Delta H_{EXP})_i - (\Delta H_{CAL})_i}{(\Delta H_{EXP})_i} \right| (100) \qquad (32)$$

Here, m = 4 and P = number of experimental data points for each of the four selected systems.

In this case, the prediction errors calculated from Equation 30 for all four systems were added together for each value of n. Thus, since there are eight values of n, there will be eight overall errors. These were to be used in the plot of Overall Prediction Error (%) versus n. This plot is called the "Overall Plot" or "Grand Plot" because it lumps all four systems together for each value of n. From it, the exponent that corresponds to the minimum prediction error for each model is determined. Since there are two models (AGSM and UNIFAC) being used, there will be two of such exponents, one for each model. Thus, the preferred model is that for which the minimum prediction error is lower, and the exponent corresponding to that minimum prediction error is called the optimum exponent. The minimum prediction error (%) and the optimum exponent yield the optimum minimum point on the "Grand Plot" (Section IV).

IV. RESULTS AND DISCUSSION

In our preliminary work, both the two and four-parameter versions of the UNIFAC model were fitted to the data for n-propanol-n-heptane at 30°C; the final parameters were used to predict other alcohol-alkane mixtures at different temperatures. On comparing results, the four-parameter version achieved better results than the two-parameter version (figure 1). But, while on the one hand, the four-parameter program proves superior to the two-parameter one, on the other hand, it does not always predict other mixtures within reasonable accuracy. For example, using the final parameters mentioned above to predict the system, n-butanol-n-heptane, a large average error of 19.0% was obtained (figure 2).

Our preliminary work also indicated that the value of n that gave good results for mixtures for which heats of mixing increase with temperature (Type I) failed to give good results with Type II mixtures. For example, when the UNIFAC model was used to predict heats of mixing of n-octanol/n-heptane mixture at 55° (from parameters obtained from data at 30°C) using a value of $n = +2.0$, the average prediction error was 1.2%. But, when the group parameters for the benzene-n-octane mixture (Type II) were calculated at 25°C by similarly assuming $n = +2.0$, prediction of heat-of-mixing data at 50°C resulted in an average percentage error of 17.6% (figure 3).

On the other hand, when n = -1.0 for the same two systems above, the respective average prediction errors were 24% for Type I and 6% for Type II (figure 4).

The above results reflect some tendencies general to either Type I or Type II mixtures. That is, as the exponent involves more positive values, (+1/2, +1, +1 1/2, +2) for Type I mixtures, and more negative values, (-1/2, -1, -1 1/2, -2), for Type II mixtures, better results are attained for the respective mixtures. This implies that exponents involving more positive values for Type II mixtures, will attain poor results for those mixtures.

Detailed results for UNIFAC are presented in Table I and plotted in figure (5). The results for the AGSM are presented in Table II, with an overall plot in figure (6). Minimum prediction errors of 7.7% and 13.0%, occurred at the exponent values of n = +1/2 and n = -2, for the UNIFAC and AGSM, models, respectively; hence UNIFAC was preferred over AGSM since it has the lower prediction error.

Heat-of-mixing group energy interaction parameters, determined, using UNIFAC, for the n-alcohol/n-alkane, benzene/n-alkane, nitrile/n-alkane, and n-amine/n-alkane, mixtures, with n = +0.5, are presented in Table III. References for the data used for calculating these parameters are presented in Table IV. Groups chosen to represent the above mixtures were, respectively: CH_2CH_2OH, CH_2, CH_3; ACH, CH_2, CH_3; CH_2NO_2, CH_2CH_3; CH_2NH_2, CH_2CH_3.

The nonlinear regression subroutine, "REG,"$^{(26)}$ was used in the data-reduction calculations.

All computer programs and data used in the study are presented in the Appendix.

A look at the results reveal certain trends; in the positive region of figure (5), plots (D) and (F) follow the expected pattern of results: better predictions are obtained for Type I mixtures as the exponent, n, takes values in the order, +1/2, +1, +1 1/2, +2; except for the +1 exponent where results show an unusually high error. Type II mixture results improved with the exponent order, +2, +1 1/2, +1, +1/2. Addition of both plots yielded plot (E), the "Overall Plot," so called because it lumps all four mixtures together. The minimum-error point of plot (E), 7.5% at n = +1/2, compares favorably with the minimum-error point of plot (C), 8.6% at n = -1 1/2.

In the negative region of AGSMs' figure 6, Type II mixtures performed well with good results in the exponent order, -1/2, -1, -1 1/2, -2. Type I mixtures, (plot H), performed poorly as expected in this region. A minimum error of 13.0% at n = -2.0 was obtained for the "Overall Plot," (plot G). Some points in the positive region (particularly at n = +1/2) were not determined. This was due to the program's inability to converge to final parameters. Overall performance of UNIFAC as shown on figure (5) is better than AGSM's performance on figure (6).

Heats of mixing of mixtures containing isomeric compounds differ from those of normal systems. In some cases the differences are small while in other cases they are substantially high. For example, while on the one hand the heats of mixing of the mixtures, chloroalkane-alkane and 2-chloroalkane-alkane differ very little, on the other hand, those between, say, n-propanol/n-heptane and 2-propanol/n-heptane differ substantially in excess of about 25% (figure 7).

By using group surface area parameters, the UNIFAC model has the flexibility to account for both isomeric and normal mixtures.

However, the degree of this accountability is questioned in the light of the results obtained with the model on isomeric systems; for example, the system, 2-propanol-n-heptane, with parameters calculated using n-propanol-n-heptane data at 30°C and with group surface area parameter values (Q) of 1.664 and 1.660 for the groups CH_2CH_2OH and $CHOHCH_3$, respectively, was predicted at 30°C.

Results (figure 8) indicated, that similar to the AGSM, UNIFAC's surface area parameter value ($Q_{CHOHCH_3} = 1.660$), computed from pure component molecular structure data, did not account for the change in heats of mixing between the normal and isomeric mixtures.

There is a possibility, that by calculating the surface area parameters by another method, for example, by correlation of heat-of-mixing data, results might be improved. But such parameters will not correctly reflect the structural (physical) nature of the groups they are meant to define. Another approach could be, namely, to determine separate parameters for isomeric group interactions. The shortfall here is that it will be quite cumbersome to calculate such large numbers of parameters for the numerous isomeric groups which exist in many different kinds of mixtures.

However, further work in this area is vital as that would underline more concretely the ability of UNIFAC to adequately represent those systems containing isomers.

Another area of significant interest in the calculation of heat-of-mixing data is the family of mixtures appearing in the lower homologous series, for example, low alcohol mixtures. Poor results have, consistently, been reported for ethanol mixtures. Ratcliff et al.,(23) using the AGSM, and, reporting heat-of-mixing data predicted for the systems, ethanol-n-hexane and ethanol-n-nonane, at 45°C, obtained average errors of 11% and 22% respectively. Fredensland et al.,(10) using UNIFAC in their work on vapor-liquid equilibria (VLE) of low alcohol mixtures, reported substantial prediction errors for ethanol mixtures. They considered ethanol as a group by itself with a surface area value of 1.972, calculated from pure molecular structural data. But by correlating VLE data of several ethanol-alkane mixtures, they recalculated an optimum value for the group surface area parameter, $Q_{CH_3CH_2OH}$ to be 1.50. On predicting VLE data of ethanol systems not included in the correlation data base, much improved results were obtained.(10)

For this research, the latter optimum value for the ethanol group surface area was used together with UNIFAC's heat-of-mixing program to predict data for the same systems predicted by Ratcliff. Results are compared in figure (9); it is evident that UNIFAC has produced better results than AGSM, this being attributable to the former's additional ability to improve performance by adaption of the group surface area parameter.

The energy interaction parameters used in figure (9) were made linearly dependent on temperature; those of AGSM were computed by correlating data from several alcohol systems at different temperatures while those of UNIFAC were calculated from only n-propanol-n-heptane data at 30°C.

A couple of problems were encountered in this work. There was the problem of the number of data points needed for accurate calculation of the group parameters.

The n-octanol/n-heptane and the benzene/n-octane mixtures had 18 and 20 data points, respectively.(32,8) These were fairly more adequate for the parameter determinations than the 10 and 8 data points for the butylamine/n-heptane and the nitroethane/2,2-dimethylbutane systems, respectively.(14,12)

The latter points were hardly sufficient for use in the group parameter calculations. However, they were the only available number of data points for those systems.

The magnitude of the prediction error attributable to inadequacy of data points, can be improved by including data points obtained at other temperatures. This approach was not adopted at this stage of the study because the main purpose here was to investigate group parameter variations with temperature. Since most heat-of-mixing data are reported at only one or two temperatures, the object of these investigations can only be achieved by calculating the group parameters using data at one temperature and then predicting the heats of mixing data at the second temperature.

A second source of problem could be due to the presence of multiple roots. It was observed that with different starting values for the parameters, different final values were obtained (Table V). Thus, since the minimized objective functions, (FMIN), for each set of starting values were adequately low, (Tables VI-XIII), it became quite difficult to select the set of final parameters (roots) which best fitted the systems. However, those parameters obtained at the lowest error of regression were chosen. All data used in this study are presented in Table XIV.

V. CONCLUSIONS

With optimum exponents of, $n = +1/2$, $n = -2$, overall average prediction errors of, 7.7% and 13.0%, were obtained for the UNIFAC and AGSM models, respectively. Hence UNIFAC achieves better accuracy than AGSM.

Also, by using the group surface-area concept, UNIFAC retains an additional flexibility which allows it some means of accommodating the significant differences that exist between heats of mixing of normal and isomeric mixtures.

Group energy interaction parameters, based on the UNIFAC optimum exponent of $n = +1/2$, have been determined by data correlation (Table I).

TABLE I

Effect of the value of n on the performance of the UNIFAC model for the four systems: n-Octanol-n-Heptane; Benzene-n-Octane; Nitroethane/2,2-Dimethylbutane; Butylamine-n-Heptane

Types	Systems	Regression Temperature (°C)	Prediction Temperature (°C)	Temperature Exponents							
				+2.0	+1.5	+1.0	+0.5	-2.0	-1.5	-1.0	-0.5
				Average Absolute Prediction Error (%)							
I	n-Octanol-n-Heptane	30	55	1.2	4.5	18.0	12.1	21.1	22.0	24.0	43.0
II	Benzene-n-Octane	25	50	17.6	13.6	9.3	9.6	7.2	5.6	5.9	7.8
II	Butylamine-n-Heptane	35	45	10.2	8.1	6.2	5.0	8.6	5.0	2.4	1.7
I	Nitroethane/2,2-Dimethylbutane	20	40	10.6	7.0	12.5	4.0	3.0	3.0	3.0	2.17
				Overall Average Absolute Prediction Error (%)							
				10.0	8.3	11.5	7.7	9.99	8.9	8.8	13.7

TABLE II

Effect of the value of n on the performance of the AGSM model for the four systems: n-Octanol-n-Heptane; Benzene-n-Octane; Nitroethane/2,2-Dimethylbutane; Butylamine-n-Heptane

Types	Systems	Regression Temperature (°C)	Prediction Temperature (°C)	Temperature Exponents							
				+2.0	+1.5	+1.0	+0.5	-2.0	-1.5	-1.0	-0.5
				Average Absolute Prediction Error (%)							
I	n-Octanol-n-Heptane	30	55	13.94	NA	5.52	NA*	31.73	30.84	53.0	31.90
II	Benzene-n-Octane	25	50	NA	78.55	13.46	NA	NA	24.29	17.53	14.20
II	Butylamine-n-Heptane	35	45	59.61	24.80	57.46	NA	6.30	4.98	26.80	1.83
I	Nitroethane/2,2-Dimethylbutane	20	40	14.38	10.94	8.23	NA	1.02	NA	2.57	23.94
				Overall Average Absolute Prediction Error (%)							
				29.31	38.10	21.14	NA	13.02	20.04	24.98	17.97

*NA = not available; program did not converge for any of the different starting parameter values used.

TABLE III

Group interaction parameters for the UNIFAC model with n = 1/2

Systems	Groups	Group Surface Area (Q)	Group Interaction Parameters			
			A_{CH_2,CH_2CH_2OH}	$A_{CH_2CH_2OH,CH_2}$	B_{CH_2,CH_2CH_2OH}	$B_{CH_2CH_2OH,CH_2}$
n-Alcohol / n-Alkanes	CH_2	0.540				
	CH_3	0.848	158.852	32.755	-4540.016	-384.138
	CH_2CH_2OH	1.664				
			A_{CH_2,CH_2NO_2}	$A_{CH_2NO_2,CH_2}$	B_{CH_2,CH_2NO_2}	$B_{CH_2NO_2,CH_2}$
Nitroalkane / Alkanes	CH_2	0.540				
	CH_3	0.848	0.389888	55.271698	-1176.1895	-962.5103
	CH_2NO_2	1.560				
			$A_{CH_2,ACH}$	A_{ACH,CH_2}	$B_{CH_2,ACH}$	B_{ACH,CH_2}
Benzene / n-Alkanes	CH_2	0.540				
	CH_3	0.848	.003068	0.101509	-82.5032	-66.6500
	ACH	0.400				

TABLE III (Cont'd.)

Systems	Groups	Group Surface Area (Q)	Group Interaction Parameters			
			A_{CH_2,CH_2NH_2}	$A_{CH_2NH_2,CH_2}$	B_{CH_2,CH_2NH_2}	$B_{CH_2NH_2,CH_2}$
Alkyl-Amines / n-Alkanes	CH_2	0.540	79.777	12.928	-1770.376	-13.441
	CH_3	0.848				
	CH_2NH_2	1.236				

TABLE IV

Systems used in generating final group interaction parameters for n = +1/2

Systems	T(K)	Number of Data Points	Ref.
N-Alcohols-N-Alkanes			
Iso-Pentanol/2,2-Dimethylbutane	298	5	25
n-Propanol-n-Heptane	298	5	28
	303	5	32
	318	5	32
Octanol-n-Heptane	288	5	25
	328	4	25
n-Pentanol-n-Hexane	318	4	32
n-Butanol-n-Heptane	328	3	25
n-Butanol-n-Octane	328	4	25
Nitroalkane-N-Alkanes			
Nitroethane/2,2-Dimethylbutane	303	10	12
	313	4	12
Nitroethane/3-Pentane	303	7	12
	313	3	12
Benzene-N-Alkanes			
Benzene-n-Heptane	298	3	14
	318	3	14
Benzene-n-Hexadecane	298	4	16
	323	4	16
Benzene-n-Octane	298	4	8
	323	6	8
Benzene-Iso-Octane	298	4	16
Alkylamine-N-Alkanes			
Butylamine-n-Heptane	298	8	14
	318	6	14

TABLE V

Multiplicity of roots for the systems, nitroethane/2,2-Dimethylbutane at 20°C and n-Propanol-n-Heptane at 30°C with exponents, n = +1.5, n = -1, respectively

	Initial Parameters	Final Parameters	% Regression Error
System: Nitroethane/2,2-Dimethylbutane at 20°C n = +1.5			
$^{A}\mathrm{CH_2,CH_2NO_2}$	.002930	.120228	6.000%
$^{A}\mathrm{CH_2NO_2,CH_2}$	.000285	.068700	
$^{B}\mathrm{CH_2,CH_2NO_2}$	.999999	99.272800	
$^{B}\mathrm{CH_2NO_2,CH_2}$	1.89000	-77.594000	
$^{A}\mathrm{CH_2,CH_2NO_2}$	.002930	.048138	6.000%
$^{A}\mathrm{CH_2NO_2,CH_2}$	.000285	-.006764	
$^{B}\mathrm{CH_2,CH_2NO_2}$	-733.06396	-535.95920	
$^{B}\mathrm{CH_2NO_2,CH_2}$	-778.00000	-325.35000	
System: n-Propanol-n-Heptane at 30°C n = -1			
$^{A}\mathrm{CH_2,CH_2NO_2}$	-1409.00000	-1410.073	0.600%
$^{A}\mathrm{CH_2NO_2,CH_2}$	421.500	421.907	
$^{B}\mathrm{CH_2,CH_2NO_2}$	87764.850	87805.000	
$^{B}\mathrm{CH_2NO_2,CH_2}$	-73087.400	-73159.750	
$^{A}\mathrm{CH_2,CH_2NO_2}$	-196.000	-1133.854	0.700%
$^{A}\mathrm{CH_2NO_2,CH_2}$	45.750	257.382	
$^{B}\mathrm{CH_2,CH_2NO_2}$	-187000.000	18835.289	
$^{B}\mathrm{CH_2NO_2,CH_2}$	10700.000	-160511.938	

TABLES VI to XIII

UNIFAC and AGSM interaction parameters determined for the mixtures:

(1) n-octanol-n-Heptane;
(2) Nitroethane/2,2-Dimethylbutane;
(3) Benzene-n-octane;
(4) n-Butylamine-n-Heptane,

at 30°, 20°, 25°, and 35°C, respectively.

TABLE VI

Parameters for n-Octanol-n-Heptane at 30°C (UNIFAC)

	Temperature Exponent ($a_{jk} = A_{jk}T^n + B_{jk}$)							
	n = +2.0	n = +1.5	n = +1.0	n = +0.5	n = -2.0	n = -1.5	n = -1.0	n = -0.5
Regression Error (%)	1.1	1.5	1.1	3.0	3.7	5.4	7.7	1.08
FMIN	0.00402	0.00607	0.00406	0.0263	0.0342	0.06921	0.00253	0.00402
A_{CH_2,CH_2CH_2OH}	0.00277	0.08918	1.5186	35.793	-0.107508 $*10^8$	-0.514011 $*10^6$	-218207.9	-17681.36
$A_{CH_2CH_2OH,CH_2}$	0.00220	0.05878	1.316	48.153	-0.16252377 $*10^8$	-.9739313 $*10^6$	-131051.44	-14080.85
B_{CH_2,CH_2CH_2OH}	-1873.198	-2155.83	-2089.816	-2106.508	-.1322092 $*10^4$	-.1281318 $*10^4$	-951.631	-602.326
$B_{CH_2CH_2OH,CH_2}$	127.684	92.391	-75.760	-1018.116	-.215146 $*10^1$	-.1389 $*10^1$	795.963	1138.464

TABLE VII

Parameters for Nitroethane/2,2-Dimethylbutane at 20°C (UNIFAC)

	Temperature Exponent ($a_{jk} = A_{jk}T^{n} + B_{jk}$)							
	n = +2.0	n = +1.5	n = +1.0	n = +0.5	n = -2.0	n = -1.5	n = -1.0	n = -0.5
Regression Error (%)	1.5	1.4	1.7	0.7	7.4	4.7	5.8	3.0
FMIN	.0032218	.003295	.00437	.00007145	.070096	NA	.042213	.013690
A_{CH_2,CH_2NO_2}	.000008	.096161	.13122	-1.311705	-.21304272 10^{8}	-.5892306 10^{6}	-98108.5	-5380.645
$A_{CH_2NO_2,CH_2}$	.005022	.101562	4.17142	64.6028	-.56439631 10^{6}	-.161941 10^{7}	-154896.44	-4586.699
B_{CH_2,CH_2NO_2}	-733.064	-185.53	-733.75	-1018.817	.1347435 10^{2}	-.342759 10^{3}	2.081	2.940
$B_{CH_2NO_2,CH_2}$	-778.249	202.961	-1657.216	-1236.074	-.721125	-.144826 10^{2}	9.711	12.013

TABLE VIII

Parameters for Benzene-n-Octane at 25°C (UNIFAC)

	Temperature Exponent ($a_{jk} = A_{jk}T^n + B_{jk}$)							
	n = +2.0	n = +1.5	n = +1.0	n = +0.5	n = -2.0	n = -1.5	n = -1.0	n = -0.5
Regression Error (%)	.32	.33	.33	.65	.34	.54	.52	.57
FMIN	.000390	.000395	.00039	.00109	.000416	.000821	.000762	.000866
$A_{CH_2,ACH}$	.000628	.000710	.02640	.002854	-.46088570 10^7	.65513844 10^5	124.429	7.715
A_{ACH,CH_2}	-.063721	.015134	.38333	.094427	-.15390825 10^6	-.14911681 10^6	-9622.766	-725.448
$B_{CH_2,ACH}$	-95.229	-55.204	-59.348	-103.129	.92996 10^1	-.11591974 10^3	-95.192	-98.407
B_{ACH,CH_2}	18.1401	-45.3967	-82.410	-62.056	-.87364 10^{-1}	-282951	-0.246	-.304

TABLE IX

Parameters for n-Butylamine-n-Heptane at 35°C (UNIFAC)

	Temperature Exponent ($a_{jk} = A_{jk}T^n + B_{jk}$)							
	n = +2.0	n = +1.5	n = +1.0	n = +0.5	n = -2.0	n = -1.5	n = 1.0	n = -0.5
Regression Error (%)	1.3	1.4	1.4	1.4	1.2	1.3	1.5	1.3
FMIN	.0027126	.0029421	.00293	.003063	.00243	.00257	.00346	.00243
A_{CH_2,CH_2NH_2}	.002968	.060483	1.59388	50.37349	-.46148272 10^8	-.24989370 10^7	-40237788 10^6	-32355.6
$A_{CH_2NH_2,CH_2}$	-.003767	.000321	-.3066	-5.7966	.9448488 10^7	.37638181 10^6	-.398639 10^5	7109.016
B_{CH_2,NH_2CH_2}	-684.03345	-758.718	-918.6565	-1329.245	.1784157 10^3	.10556863 10^3	-161.421	1523.993
$B_{CH_2NH_2,CH_2}$	-5.98369	-6.947	0.31772	-27.83107	.258232 10^2	.578939 10^{+1}	-10.579	-305.900

TABLE X

Parameters for n-Octanol-n-Heptane at 30°C (AGSM)

	Temperature Exponent ($a_{jk} = A_{jk}T^n + B_{jk}$)							
	n = +2.0	n = +1.5	n = +1.0	n = +0.5	n = -2.0	n = -1.5	n = -1.0	n = -0.5
Regression Error (%)	1.72	2.44	0.99	NA	15.72	15.30	1.51	1.07
FMIN	.01097	.01792	.00447	NA	.823	.7727	.00553	.00411
A_{CH_2,CH_2CH_2OH}	.003847	2.575	1.904	NA	1050.00	-.093	-191378.4	-20892.97
$A_{CH_2CH_2OH,CH_2}$	.007731	0.162	5.203	NA	1710.00	.383	-435731.1	-54987.2
B_{CH_2,CH_2CH_2OH}	-206.186	-14042.48	-123.657	NA	-3260.0	-160.373	1179.365	1697.072
$B_{CH_2CH_2OH,CH_2}$	-2549.67	-2657.07	-3469.864	NA	-1200.00	-1216.006	-451.15	1258.854

TABLE XI

Parameters for Nitroethane/2,2-Dimethylbutane at 20°C (AGSM)

	Temperature Exponent ($a_{jk} = A_{jk}T^n + B_{jk}$)							
	n = +2.0	n = +1.5	n = +1.0	n = +0.5	n = -2.0	n = -1.5	n = -1.0	n = -0.5
Regression Error (%)	7.14	7.83	8.43	NA	4.94	NA	7.54	7.23
FMIN	.066	.0748	NA	NA	.0291	NA	NA	NA
A_{CH_2,CH_2NO_2}	.003952	.0939	-9.911	NA	-3.1249 10^7	NA	.69976375 10^5	-26232.7
$A_{CH_2NO_2,CH_2}$	.004745	-.325	2.7879	NA	2.009 10^6	NA	-.256043 10^5	-13081.34
B_{CH_2,CH_2NO_2}	84.912	-48.33	-1279.007	NA	468.239	NA	-3261.364	2185.9
$B_{CH_2NO_2,CH_2}$	108.948	-368.089	-1347.51	NA	-894.995	NA	-3261.364	440.871

TABLE XII

Parameters for Benzene-n-Octane at 25°C (AGSM)

	Temperature Exponent $(a_{jk} + A_{jk}T^n + B_{jk})$							
	n = +2.0	n = +1.5	n = +1.0	n = +0.5	n = -2.0	n = -1.5	n = -1.0	n = -0.5
Regression Error (%)	.32	1.16	0.33	1.54	.4000	.3000	0.34	1.00
FMIN	.000249	.00337	.00039	.0049	.00043	.000237	.00039	.0025
$A_{CH_2,ACH}$	.005154	.092	-13.068	15.302	2.14683 10^7	-2.34926 10^5	8227.8	-82.069
A_{ACH,CH_2}	-.010693	-.135	-.274	-15.651	-1.13821 10^8	-3.3573 10^6	24430.74	-4.313
$B_{CH_2,ACH}$	-84.33	-169.89	-747.49	-.0349	96.831	409.719	-3897.900	38.665
B_{ACH,CH_2}	591.34	436.504	-362.294	.0907	930.784	268.541	-526.238	-384.53

TABLE XIII

Parameters for n-Butylamine-n-Heptane at 35°C (AGSM)

	Temperature Exponent ($a_{jk} = A_{jk}T^n + B_{jk}$)							
	n = +2.0	n = +1.5	n = +1.0	n = +0.5	n = -2.0	n = -1.5	n = -1.0	n = -0.5
Regression Error (%)	1.250	1.460	1.76	2.13	1.410	1.380	1.38	1.38
FMIN	.00245	.00315	.0044	NA	.00292	.00292	NA	NA
A_{CH_2,CH_2NH_2}	.005	.1012	8.102	-15.925	-1.22859 10^8	2.2372 10^6	-.1475773 10^6	8770.105
$A_{CH_2NH_2,CH_2}$	-.010	.0392	.795	6.389	-2.92557 10^7	-2.27713 10^6	-.16868863 10^6	-.2277155 10^5
B_{CH_2,CH_2NH_2}	269.471	122.223	-2623.50	-.31496	-837.775	-957.957	974.07	-.153155 105
$B_{CH_2NH_2,CH_2}$	-283.995	-121.020	-1038.433	.1322	-284.422	-166.134	-55.061	707.823

TABLE XIV

Data used in the study

System: n-Propanol-n-Heptane(32) at 30°C, 45°C

Mole Fraction Alcohol (X)	Heats of Mixing (Joule/C mole) at 30°	at 45°C
0.0100	189.0000	206.0000
0.0200	282.0000	347.0000
0.0300	338.0000	439.0000
0.0400	378.0000	506.0000
0.0500	411.0000	553.0000
0.0750	479.0000	646.0000
0.1000	529.0000	720.0000
0.1250	570.0000	778.0000
0.1500	603.0000	824.0000
0.1750	631.0000	859.0000
0.2000	654.0000	890.0000
0.3000	708.0000	958.0000
0.4000	708.0000	958.0000
0.5000	668.0000	900.0000
0.6000	590.0000	797.0000
0.7000	485.0000	657.0000
0.8000	353.0000	477.0000
0.9000	194.0000	258.0000

TABLE XIV (Cont'd.)

System: 2-Propanol-N-Heptane at 30°,(16) 45°C

Mole Fraction Alcohol (X)	ΔH_{mix} J/G mole 30°C	ΔH_{mix} J/G mole 45°C
0.0019	47.0000	52.0000
0.0061	134.0000	111.0000
0.0121	224.0000	157.0000
0.0188	292.0000	448.0000
0.0250	339.0000	566.0000
0.0400	420.0000	739.0000
0.0642	511.0000	852.0000
0.1157	643.0000	1008.0000
0.1931	777.0000	1097.0000
0.2614	855.0000	1155.0000
0.3126	893.0000	1186.0000
0.3676	915.0000	1185.0000
0.4195	918.0000	1160.0000
0.5086	887.0000	1122.0000
0.5744	834.0000	1080.0000
0.6140	793.0000	1029.0000
0.6425	761.0000	978.0000
0.6666	729.0000	890.0000
0.7122	660.0000	845.0000
0.7590	580.0000	735.0000
0.7938	514.0000	642.0000
0.8466	403.0000	572.0000

TABLE XIV (Cont'd.)

System: 2-Propanol-N-Heptane at 30°,(16) 45°C (Cont'd.)

Mole Fraction Alcohol (X)	ΔH_{mix} J/G mole 30°C	ΔH_{mix} J/G mole 45°C
0.8928	296.0000	440.0000
0.9114	249.0000	329.0000
0.9492	147.0000	154.0000

System: n-Octanol-n-Heptane(32) at 30°, 45°C

Mole Fraction Alcohol (X)	Heats of Mixing (Joule/C mole)	
	at 30°	at 45°C
0.0100	177.0000	196.0000
0.0200	259.0000	322.0000
0.0300	306.0000	400.0000
0.0400	338.0000	452.0000
0.0500	362.0000	491.0000
0.0750	409.0000	563.0000
0.1000	442.0000	610.0000
0.1250	468.0000	643.0000
0.1500	487.0000	867.0000
0.1750	501.0000	686.0000
0.2000	512.0000	699.0000
0.3000	538.0000	718.0000
0.4000	530.0000	698.0000
0.5000	495.0000	643.0000
0.6000	432.0000	554.0000

TABLE XIV (Cont'd.)

System: n-Octanol-n-Heptane(32) at 30°, 45°C (Cont'd.)

Mole Fraction Alcohol (X)	Heats of Mixing (Joule/C Mole) at 30°	at 45°C
0.7000	342.0000	443.0000
0.8000	237.0000	307.0000
0.9000	119.0000	157.0000

System: n-Octanol-n-Heptane(25) at 15°, 55°C

Mole Fraction Alcohol (X)	Heats of Mixing (Joule/C Mole) at 15°	at 55°C
0.0500	244.0000	522.0000
0.1500	337.0000	788.0000
0.2500	377.0000	855.0000
0.3500	392.0000	853.0000
0.4500	382.0000	802.0000
0.5500	350.0000	715.0000
0.6500	291.0000	596.0000
0.7500	209.0000	450.0000
0.8500	117.0000	281.0000
0.9500	36.0000	95.0000

TABLE XIV (Cont'd.)

System	Mole Fraction Alcohol (X)	ΔH_{mix} J/G mole	T	Ref.
Iso-Pentanol/2,2-Dimethylbutane	0.5500	455.0000	298°	25
	0.6500	366.0000	298°	25
	0.7500	266.0000	298°	25
	0.8500	158.0000	298°	25
	0.9500	52.0000	298°	25
n-Propanol-n-Heptane	0.0703	371.0000	298°	28
	0.1309	465.0000	298°	28
	0.2314	552.0000	298°	28
	0.3754	585.0000	298°	28
	0.5124	545.0000	298°	28
	0.6096	577.0000	303°	32
	0.7089	473.0000	303°	32
	0.7519	419.0000	303°	32
	0.8580	265.0000	303°	32
	0.9171	163.0000	303°	32
	0.0500	553.0000	318°	32
	0.1000	720.0000	318°	32
	0.2000	890.0000	318°	32
	0.3000	958.0000	318°	32
	0.4000	958.0000	318°	32
Octanol-n-Heptane	0.0500	244.0000	288°	25
	0.1500	337.0000	288°	25
	0.2500	377.0000	288°	25

TABLE XIV (Cont'd)

System	Mole Fraction Alcohol (X)	ΔH_{mix} J/G mole	T	Ref.
Octanol-n-Heptane	0.3500	392.0000	288°	25
	0.4500	382.0000	288°	25
n-Octanol-n-Heptane	0.5500	715.0000	328°	25
	0.6500	596.0000	328°	25
	0.7500	450.0000	328°	25
	0.8500	281.0000	328°	25
n-Pentanol-n-Hexane	0.5000	720.0000	318°	32
	0.6000	619.0000	318°	32
	0.7000	487.0000	318°	32
	0.9000	168.0000	318°	32
n-Butanol-n-Heptane	0.1500	957.0000	328°	25
	0.2500	1074.0000	328°	25
	0.3500	1107.0000	328°	25
n-Butanol-n-Octane	0.5500	1069.0000	328°	25
	0.6500	910.0000	328°	25
	0.7500	700.0000	328°	25
	0.9500	160.0000	328°	25
Benzene-n-Heptane	0.6868	939.0000	298°	14
	0.7602	836.0000	298°	14
	0.8216	690.0000	298°	14
	0.3550	773.0000	318°	14
	0.6020	946.0000	318°	14
	0.6100	955.0000	318°	14

TABLE XIV (Cont'd)

System	Mole Fraction Alcohol (X)	ΔH_{mix} J/G mole	T	Ref.
Benzene-n-Hexadecane	0.6670	797.0000	298°	16
	0.6890	809.0000	298°	16
	0.6950	752.0000	298°	16
	0.7950	620.0000	298°	16
	0.1454	476.0000	32°	16
	0.2689	816.0000	323°	16
	0.3499	1013.0000	323°	16
	0.4289	1145.0000	323°	16
Benzene-n-Octane	0.7142	1135.0000	298°	8
	0.8049	986.0000	298°	8
	0.8744	766.0000	298°	8
	0.9721	244.0000	298°	8
	0.4744	955.0000	323°	8
	0.5636	991.0000	323°	8
	0.6469	968.0000	323°	8
	0.7438	858.0000	323°	8
	0.8224	697.0000	323°	8
	0.9531	231.0000	323°	8
Benzene-120-Octane	0.0600	160.0000	298°	16
	0.1607	413.0000	298°	16
	0.2546	591.0000	298°	16
	0.3483	763.0000	298°	16

TABLE XIV (Cont'd)

System	Mole Fraction Alcohol (X)	ΔH_{mix} J/G mole	T	Ref.
Nitroethane-3-Penatane	0.1707	1199.0000	303°	12
	0.3218	1553.0000	303°	12
	0.3946	1618.0000	303°	12
	0.04425	1651.0000	303°	12
	0.4945	1653.0000	303°	12
	0.6128	1608.0000	303°	12
	0.7494	1365.0000	303°	12
	0.3908	1700.0000	313°	12
	0.5050	1739.0000	313°	12
	0.6164	1663.0000	313°	12
Nitroethane-2,2-Dimethylbutane	0.1674	1147.0000	303°	12
	0.1796	1180.0000	303°	12
	0.3242	1504.0000	303°	12
	0.4051	1579.0000	303°	12
	0.5057	1610.0000	303°	12
	0.6151	1533.0000	303°	12
	0.7109	1406.0000	303°	12
	0.7889	1176.0000	303°	12
	0.9282	503.0000	303°	12
	0.9703	223.0000	303°	12
	0.3202	1563.0000	313°	12
	0.3902	1645.0000	313°	12
	0.5108	1696.0000	313°	12
	0.6195	1592.0000	313°	12

TABLE XIV (Cont'd)

System	Mole Fraction Alcohol (X)	ΔH_{mix} J/G mole	T	Ref.
Butylamine-n-Heptane	0.3350	1254.0000	298°	14
	0.3740	1296.0000	298°	14
	0.4020	1305.0000	298°	14
	0.5520	1311.0000	298°	14
	0.6210	1151.0000	298°	14
	0.6280	1156.0000	298°	14
	0.7320	907.0000	298°	14
	0.7410	868.0000	298°	14
Butylamine-n-Heptane	0.3250	1200.0000	318°	14
	0.4420	1281.0000	318°	14
	0.4840	1275.0000	318°	14
	0.5160	1241.0000	318°	14
	0.5490	1225.0000	318°	14
	0.6880	1003.0000	318°	14

System: n-Butanol-n-Heptane(32) at 30°, 45°C

Mole Fraction Alcohol (X)	Heats of Mixing (Joule/C Mole) at 15°	at 55°C
0.0100	182.0000	203.0000
0.0200	274.0000	341.0000
0.300	331.0000	430.0000
0.0400	373.0000	498.0000
0.0500	407.0000	547.0000

TABLE XIV (Cont'd.)

System: n-Butanol-n-Heptane$^{(32)}$ at 30°, 45°C (Cont'd.)

Mole Fraction Alcohol (X)	Heats of Mixing (Joule/C Mole) at 15°	at 55°C
0.0750	468.0000	645.0000
0.1000	515.0000	701.0000
0.1250	552.0000	747.0000
0.1500	584.0000	788.0000
0.1750	611.0000	822.0000
0.2000	632.0000	854.0000
0.3000	687.0000	922.0000
0.4000	686.0000	922.0000
0.5000	643.0000	865.0000
0.6000	560.0000	761.0000
0.7000	447.0000	611.0000
0.8000	314.0000	430.0000
0.9000	163.0000	225.0000

System: Ethanol-n-Hexane at 30°, 45°C

Mole Fraction Alcohol (X)	Heats of Mixing (Joule/C Mole) at 15°	at 55°C
0.0100	178.0000	201.0000
0.0200	256.0000	323.0000
0.0300	303.0000	398.0000
0.0400	339.0000	452.0000
0.0500	369.0000	495.0000
0.0750	427.0000	577.0000
0.1000	470.0000	637.0000

TABLE XIV (Cont'd.)

System: Ethanol-n-Hexane at 30°, 45°C

Mole Fraction Alcohol (X)	Heats of Mixing (Joule/C Mole) at 30°	at 45°C
0.1250	505.0000	684.0000
0.1500	534.0000	723.0000
0.1750	557.0000	754.0000
0.2000	578.0000	779.0000
0.3000	622.0000	832.0000
0.4000	629.0000	830.0000
0.5000	603.0000	790.0000
0.6000	554.0000	713.0000
0.7000	477.0000	605.0000
0.8000	368.0000	459.0000
0.9000	219.0000	264.0000

System: Ethanol-n-Nonane at 30°, 45°C

Mole Fraction Alcohol (X)	Heats of Mixing (Joule/C Mole) at 30°	at 45°C
0.0100	194.0000	208.0000
0.0200	291.0000	356.0000
0.0300	349.0000	451.0000
0.0400	394.0000	519.0000
0.0500	431.0000	574.0000
0.0750	498.0000	674.0000
0.1000	544.0000	745.0000
0.1250	583.0000	800.0000
0.1500	617.0000	847.0000
0.1750	754.0000	882.0000

TABLE XIV (Cont'd)

System: Ethanol-n-Nonane at 30°, 45°C

Mole Fraction Alcohol (X)	Heats of Mixing (Joule/C Mole)	
	at 30°	at 45°C
0.2000	670.0000	912.0000
0.3000	731.0000	981.0000
0.4000	746.0000	991.0000
0.5000	730.0000	955.0000
0.6000	684.0000	881.0000
0.7000	607.0000	767.0000
0.8000	491.0000	602.0000
0.9000	311.0000	368.0000
System: n-Octanol-n-Nonane at 30°, 35°C		
0.0100	184.0000	200.0000
0.0200	282.0000	346.0000
0.0300	338.0000	440.0000
0.0400	398.0000	500.0000
0.0500	411.0000	544.0000
0.0150	467.0000	629.0000
0.1000	506.0000	688.0000
0.1250	536.0000	730.0000
0.1500	559.0000	760.0000
0.1750	578.0000	784.0000
0.2000	592.0000	802.0000
0.3000	624.0000	832.0000

TABLE XIV (Cont'd)

System: n-Octanol-n-Nonane at 30°, 35°C

Mole Fraction Alcohol (X)	Heats of Mixing (Joule/C Mole)	
	at 30°	at 45°C
0.4000	622.0000	816.0000
0.5000	588.000o	763.0000
0.6000	511.0000	677.0000
0.7000	414.0000	552.0000
0.8000	291.0000	392.0000
0.9000	150.0000	205.0000

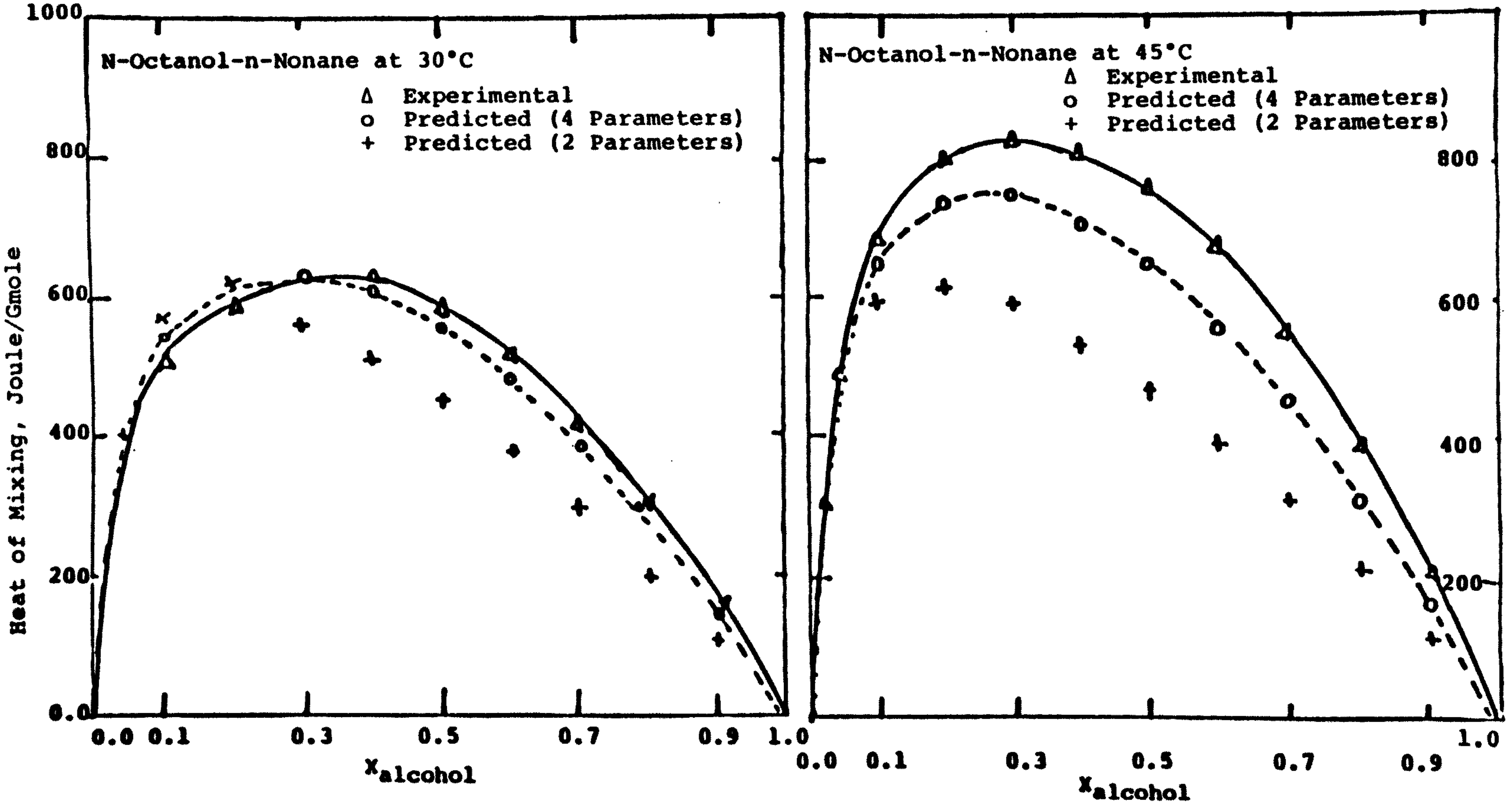

FIGURE 1: Comparison of predicted and experimental heat-of-mixing data for the system, Octanol-n-Nonane at 30° and 45°C, using UNIFAC's Two and Four-Parameter versions. Parameters were obtained from n-Propanol-n-Heptane data at 30°C.

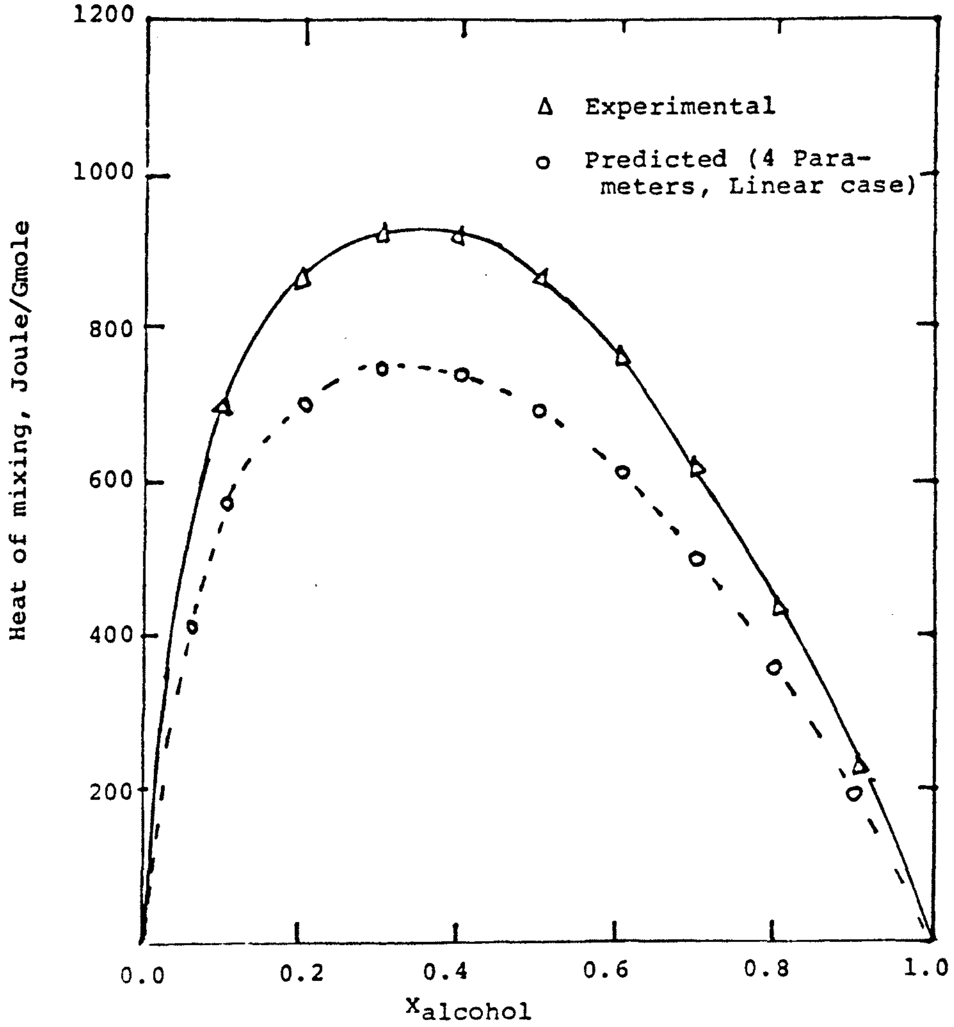

FIGURE 2: Prediction of n-Butanol-n-Heptane data using linear temperature dependency for UNIFAC Parameters. Parameters were obtained from n-propanol-n-heptane data at 30°C.

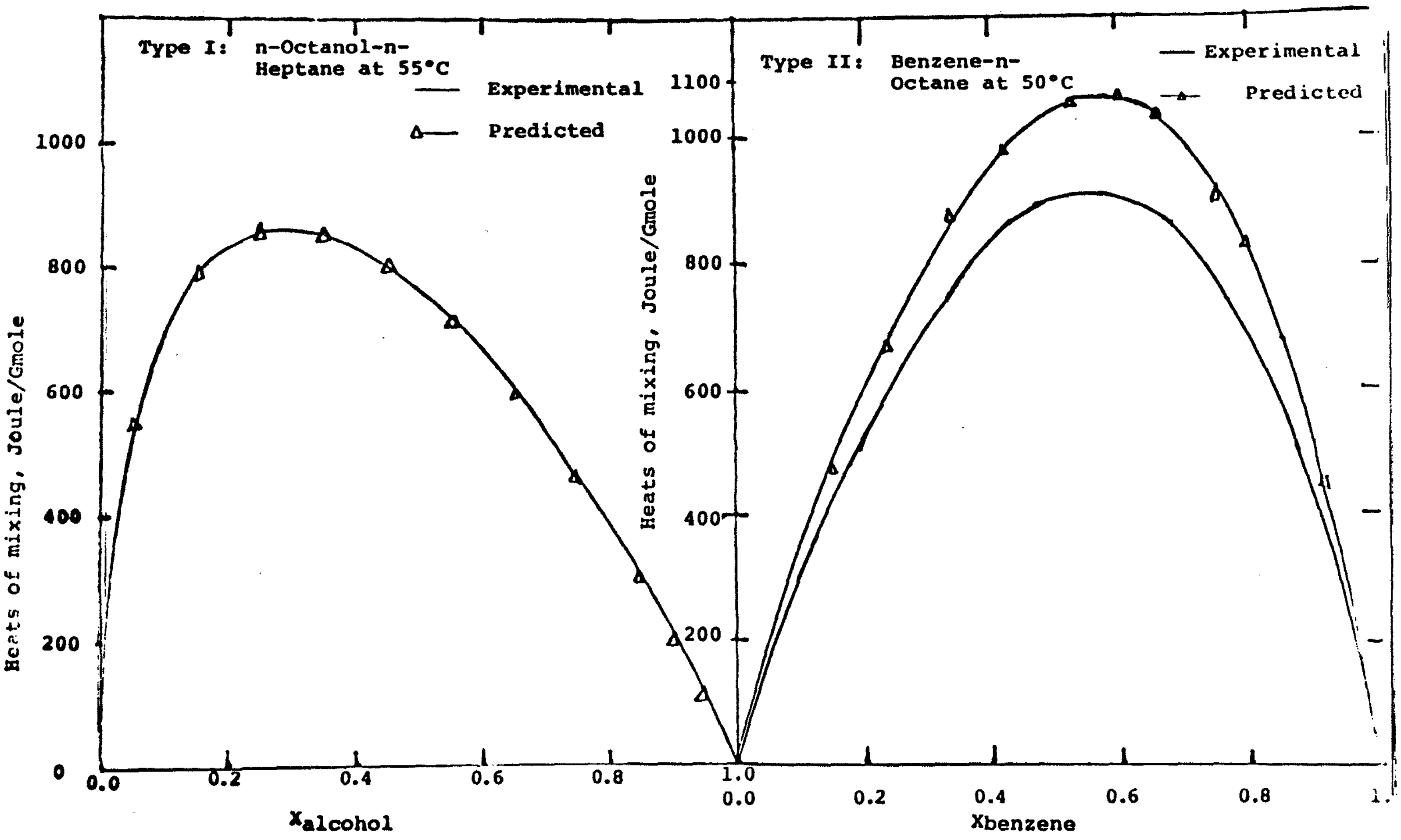

FIGURE 3: Predicted heats of mixing data for n-Octanol-n-Heptane at 55°C and Benzene-n-Octane at 50°C for n = +2.0 (UNIFAC). (Parameters were obtained from n-Octanol-n-Heptane data at 30°C, and Benzene-n-octane data at 25°C, respectively.)

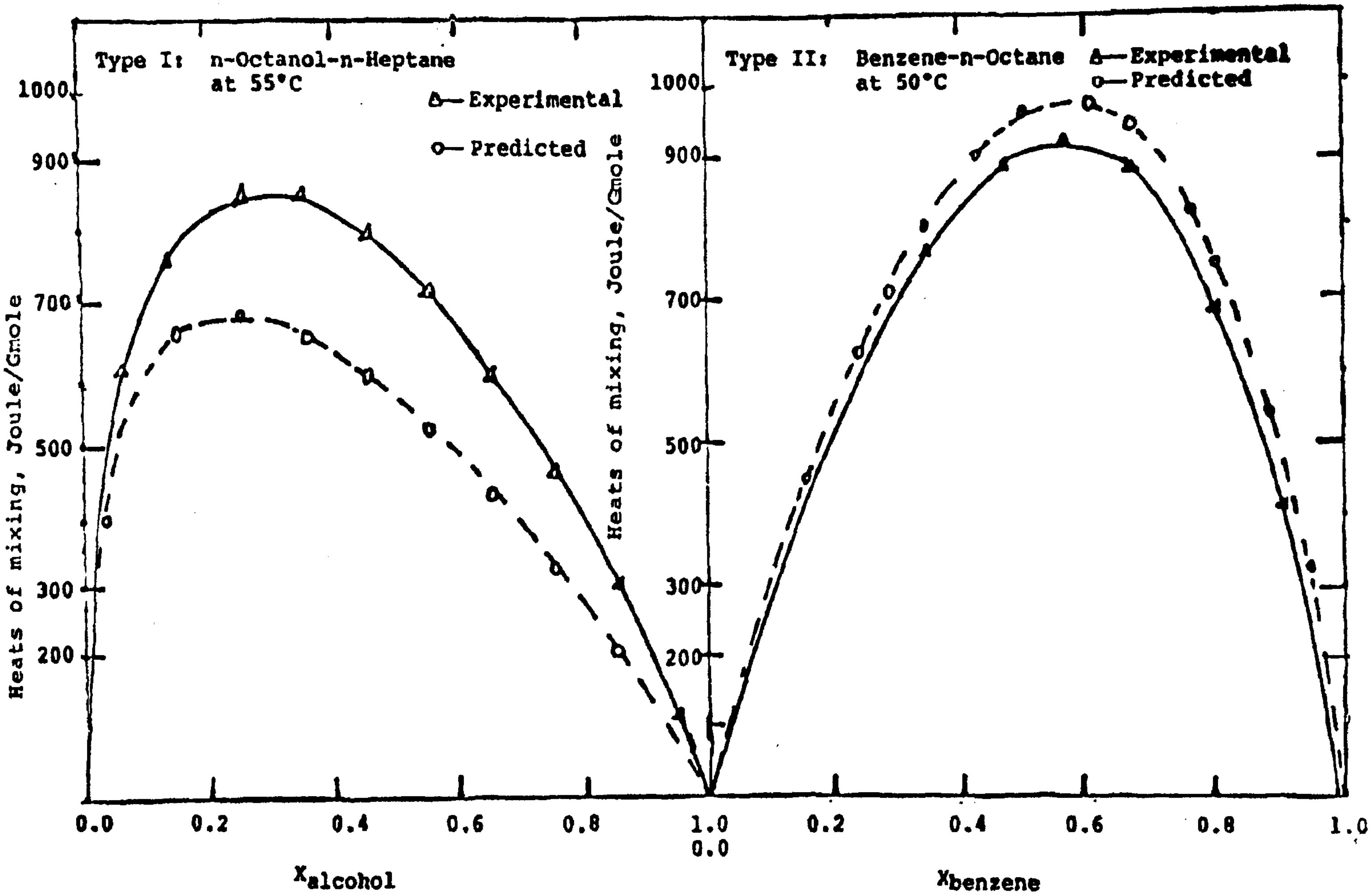

FIGURE 4: Predicted heats of mixing data for n-Octanol-n-Heptane at 55°C and Benzene-n-Octane at 50°C with $n = -1.0$ (UNIFAC). (Parameters were obtained from n-Octanol-n-Heptane data at 30°C, and Benzene-n-octane data at 25°C, respectively.)

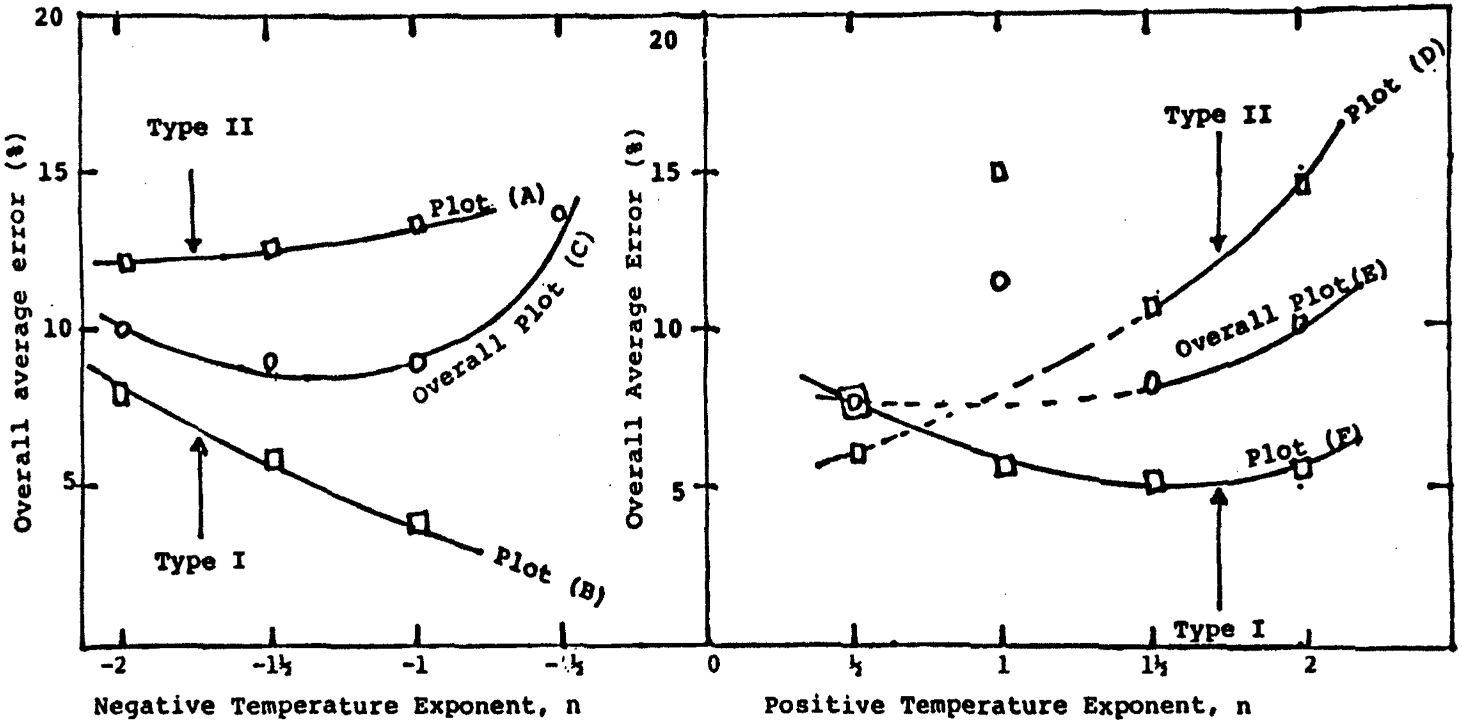

FIGURE 5. Plot of Overall Average Error (%) versus Temperature Exponent, n, (UNIFAC)

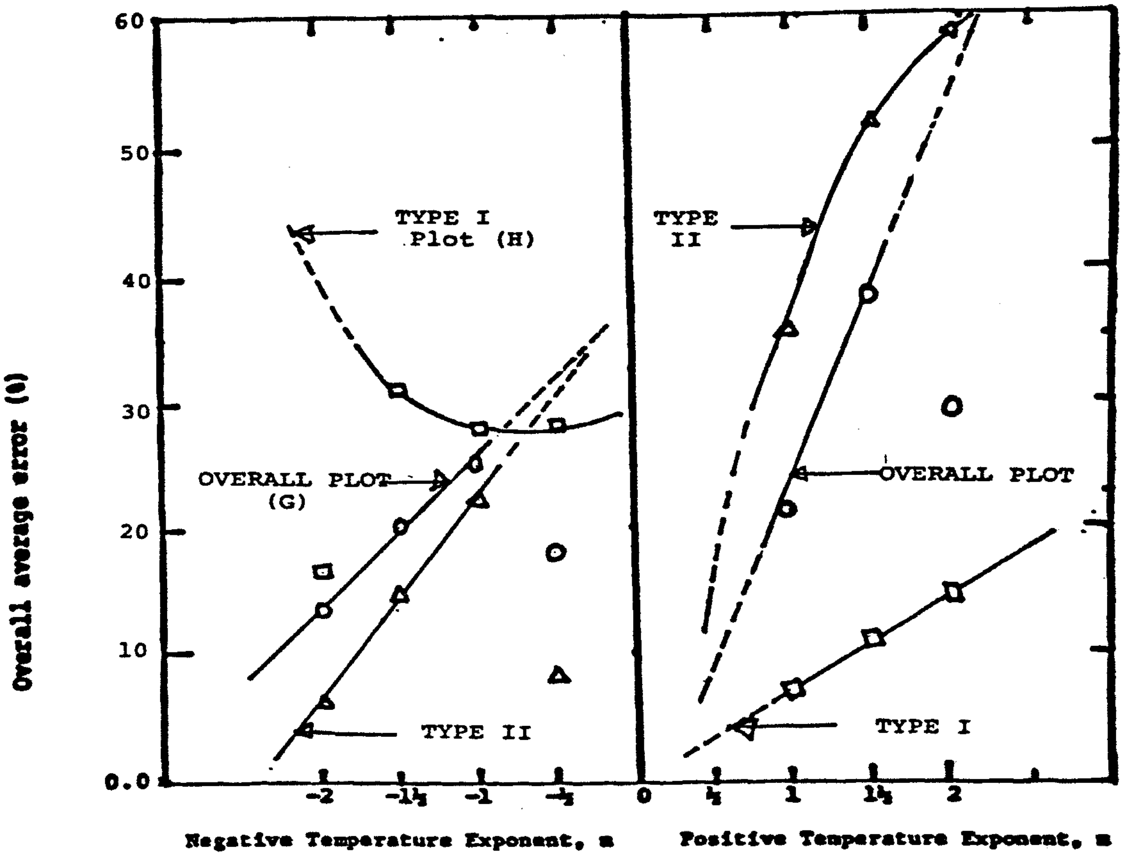

FIGURE 6: Plot of Overall Average Error (%) versus Temperature Exponent, m, (AGSM)

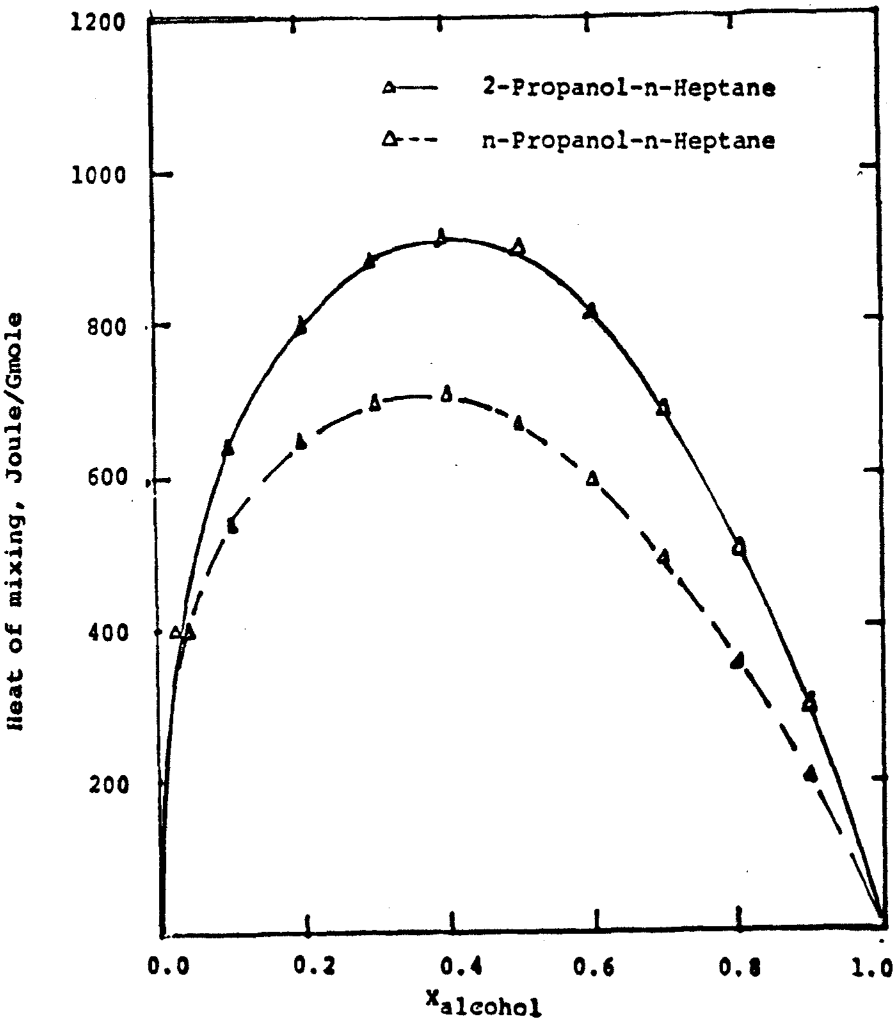

FIGURE 7: Difference in experimental heats of mixing for 2-Propanol-n-Heptane and n-Propanol-n-Heptane, at 30°C.

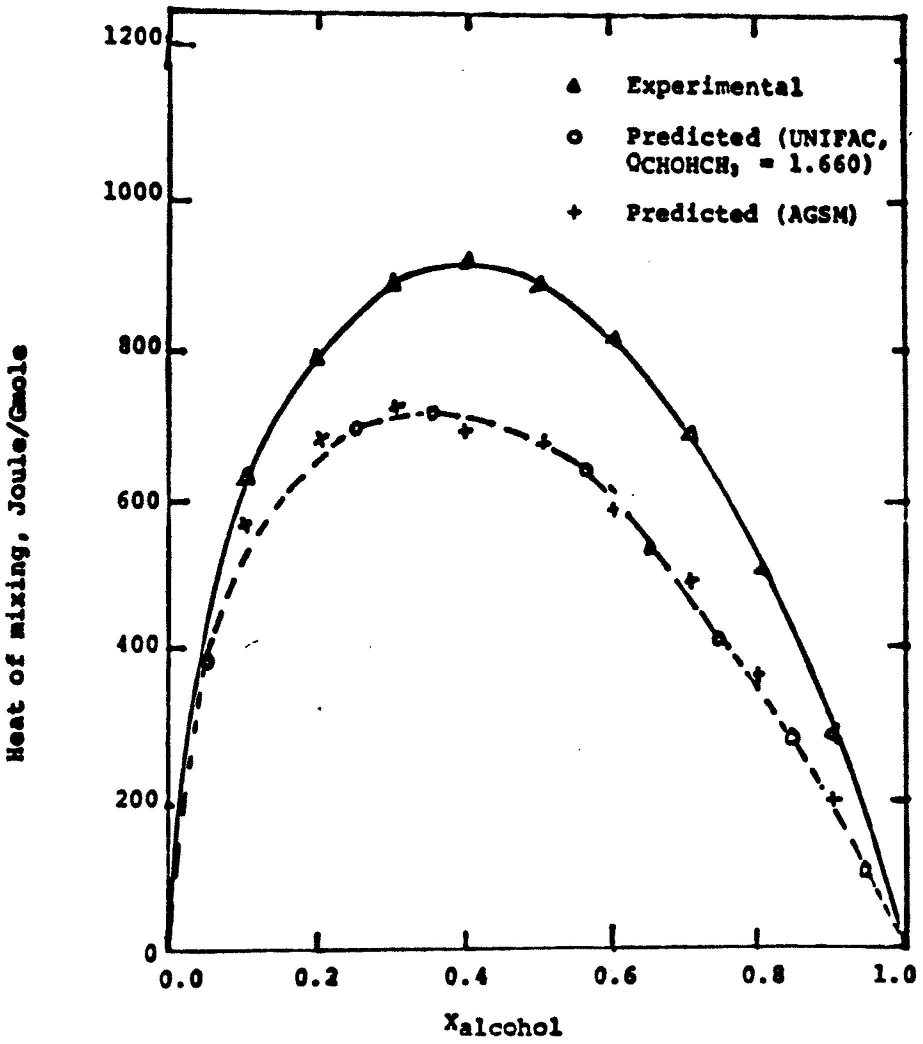

FIGURE 8: Comparison of predicted and experimental heat-of-mixing data for the system, 2-Propanol-n-Heptane at 30°C by AGSM and UNIFAC (Q_{CHOHCH_3} = 1.660)

Parameters were obtained from n-Propanol-n-heptane data at 30°C.

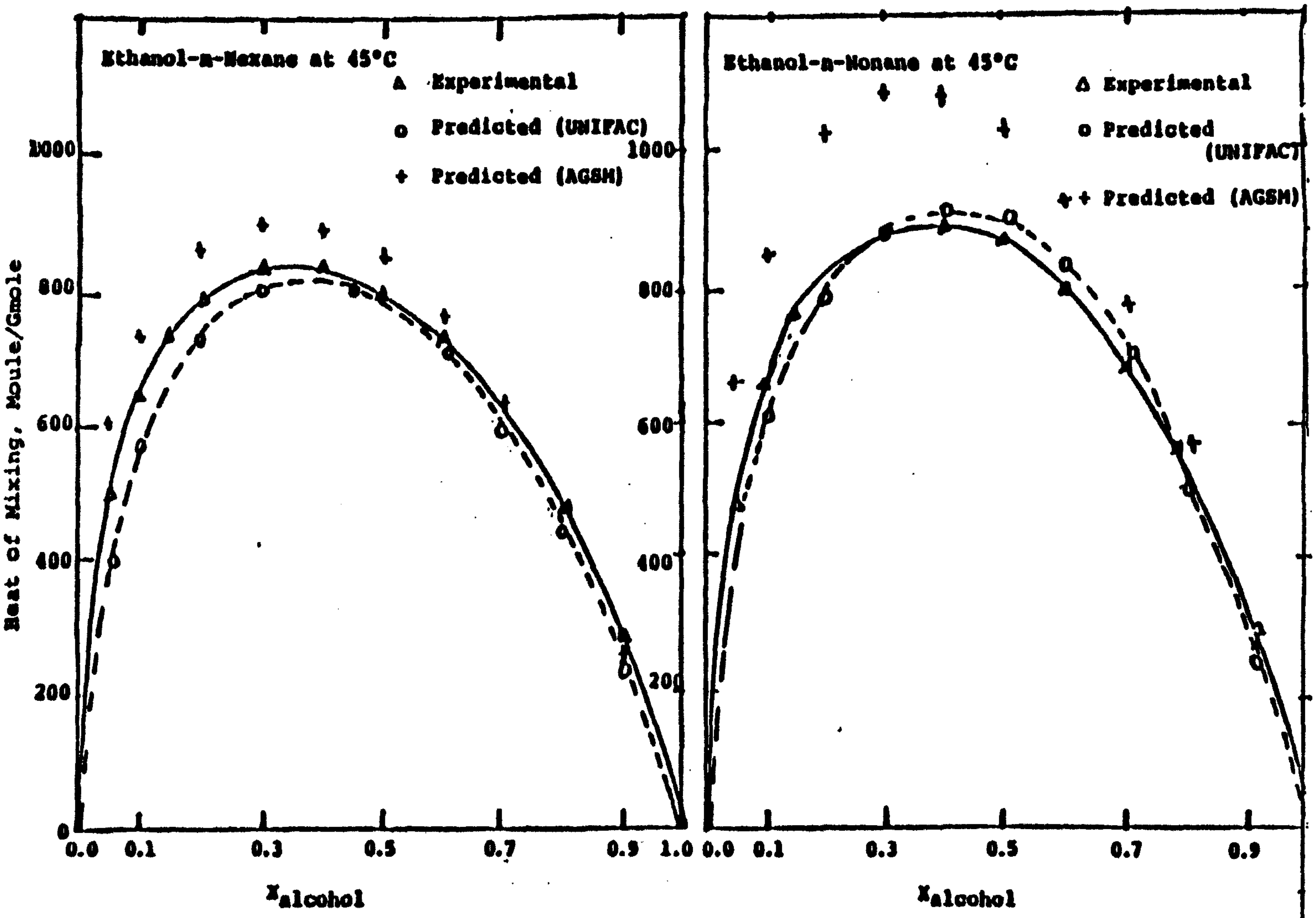

FIGURE 9: Comparison of predicted and experimental heat-of-mixing data for the systems, Ethanol-n-Hexane and Ethanol-n-Nonane at 45°C by UNIFAC $(O_{CH_3/CH_2OH} = 1.5)$ and AGSM. UNIFAC's parameters were obtained from n-Propanol-n-heptane data at 30°C; AGSM's parameters were obtained from several alcohol systems at different temperatures.

APPENDIX 1

DERIVATION OF THE HEAT-OF-MIXING EQUATION FOR THE UNIFAC MODEL

In chapter III, the relationship between Gibbs Excess Free Energy and the group activity coefficient is expressed in equation (27). Here, the essential steps are presented for the derivation of the UNIFAC model used for heat-of-mixing work.

Applying the Gibbs-Helmholtz relation to equation (27) of chapter III,

$$\left(\frac{\delta(G^E/RT)}{\partial T}\right)_{p,x} = \left(\frac{\partial \overset{i}{\Sigma} x_i (\overset{k}{\Sigma} V_k^{(i)} [\ln\Gamma_k - \ln\Gamma_k^{(i)}] + \ln\gamma_i^{c})}{\partial T}\right)_{p,x} \qquad (1)$$

$$\left(\frac{\partial(G^E/RT)}{\partial T}\right)_{p,x} = \left(\frac{\delta \overset{i}{\Sigma} x_i (\overset{k}{\Sigma} V_k^{(i)} [\ln\Gamma_k - \ln\Gamma_k^{(i)}])}{\partial T}\right)_{p,x} + \left(\frac{\partial \ln\gamma_i^{c}}{\partial T}\right)_{p,x} \qquad (2)$$

Since the combinatorial part of the group activity coefficient is independent of temperature, and therefore has little or no significant effect on heats of mixing, it is only the residual contribution that enters into heat-of-mixing calculations. Thus, equation (2) becomes

$$\left(\frac{\partial(G^E/RT)}{\partial T}\right)_{p,x} = \left(\frac{\partial \overset{i}{\Sigma} x_i (\overset{k}{\Sigma} V_k^{(i)} [\ln\Gamma_k - \ln\Gamma_k^{(i)}])}{\partial T}\right)_{p,x} \qquad (3)$$

or

$$\left(\frac{\delta (\overset{ik}{\Sigma\Sigma} x_i V_k^{(i)} [\ln\Gamma_k - \ln\Gamma_k^{(i)}])}{\partial T}\right)_{p,x} = -\frac{H^E}{RT^2} \qquad (4)$$

Therefore,

$$H^E = -RT\sum^{ik}\sum x_i V_k^{(i)} [T(\frac{\partial \ln\Gamma_k}{\partial T})_{p,x} - T(\frac{\partial \ln\Gamma_k^{(i)}}{\partial T})_{p,x}] \qquad (5)$$

where

$$\ln\Gamma_k = Q_k[1 - \ln(\sum^{m}\theta_m\psi_{mk}) - (\sum^{m}\theta_m\psi_{km}/\sum^{n}\theta_n\psi_{nm})]$$

From equation (28) of Chapter III,

$$-\ln\psi_{mn} = \frac{a_{mn}}{T} \qquad (6)$$

$$\frac{d\psi_{mn}}{dt} = \exp(-\frac{a_{mn}}{T})[\frac{a_{mn}}{T^2}] \qquad (7)$$

$$= -\frac{\psi_{mn}\ln\psi_{mn}}{T} \qquad (8)$$

Therefore,

$$T(\frac{\partial \ln\Gamma_k}{\partial T})_{p,x} = Q_k T(\frac{\partial[1 - \ln(\sum^{m}\theta_m\psi_{mk}) - \sum^{m}\theta_m\psi_{km}/\sum^{n}\theta_n\psi_{nm})]}{\partial T}_{p,x} \qquad (9)$$

$$= Q_k T(\frac{\partial(-\ln(\sum^{m}\theta_m\psi_{mk})_{p,x}}{\partial T} - \frac{\partial(\sum^{m}\theta_m\psi_{km}/\sum^{n}\theta_n\psi_{nm})}{\partial T})_{p,x} \qquad (10)$$

$$= Q_k T(-\frac{1}{\sum_{m}\theta m\psi mk}\ \frac{\sum^{m}\theta_m\psi_{mk}\ln\psi_{mk}}{T}$$

$$-\frac{(\sum^{m}\theta_m - \psi_{km}\ln\psi_{km}(\sum^{n}\theta_n\psi_{nm})}{T}$$

$$-\frac{\sum^{n}\theta_n - \psi_{nm}\ln\psi_{nm}(\sum^{n}\theta_m\psi_{km})}{T(\sum^{n}\theta_n\psi_{nm})^2})) \qquad (11)$$

$$T\left(\frac{\partial \ln \Gamma_k}{\partial T}\right)_{p,x} = Q_k [\frac{\sum^{m}\theta_m\psi_{mk}\ln\psi_{mk}}{\sum^{n}\theta_m\psi_{mk}} + \frac{\sum^{m}\theta_m\psi_{km}\ln\psi_{km}(\sum^{n}\theta_n\psi_{nm}) - \sum^{n}\theta_n\psi_{nm}\ln\psi_{nm}(\sum^{m}\theta_m\psi_{km}}{(\sum^{n}\theta_n\psi_{nm})^2} \tag{12}$$

$$T\left(\frac{\partial \ln \Gamma_k}{\partial T}\right)_{p,x} = Q_k\sum^{m}\theta_m [\frac{\psi_{mk}\ln\psi_{mk}}{\sum^{m}\theta_m\psi_{mk}} + \frac{\psi_{km}[\sum^{n}\theta_n\psi_{nm}(\ln\psi_{km} - \ln\psi_{nm})]}{[\sum^{n}\theta_n\psi_{nm}]^2}] \tag{13}$$

$$T\left(\frac{\partial \ln \Gamma_k}{\partial T}\right)_{p,x} = Q_k\sum^{m}\theta_m [\frac{\psi_{mk}\ln\psi_{mk}}{\sum^{m}\theta_m\psi_{mk}} + \frac{\psi_{km}\sum^{n}\theta_n\psi_{nm}(\ln(\psi_{km}/\psi_{nm}))}{(\sum^{n}\theta_n\psi_{nm})^2}] \tag{14}$$

Similarly,

$$T\left(\frac{\partial \ln \Gamma_k^{(i)}}{\partial T}\right)_{p,x} = Q_k\sum^{m}\theta_m^{(i)} [\frac{\psi_{mk}\ln\psi_{mk}}{\sum^{m}\theta_m^{(i)}\psi_{mk}} + \frac{\psi_{km}\sum^{m}\theta_n^{(i)}\psi_{nm}\ln(\psi_{km}/\psi_{nm})}{(\sum^{n}\theta_n^{(i)}\psi_{nm})^2}] \tag{15}$$

Substitution of equations (14), (15) into (5) gives the 2-parameter version of the heat-of-mixing expression for UNIFAC where ψ_{mn}, ψ_{mn} take the expressions in equation (28) of chapter III.

In the derivation of equations (14) and (15) ψ_{nm}, ψ_{mn} are the temperature dependent group energy interaction parameters for the pair of groups m and n; a_{nm}, a_{mn}, are assumed to be independent of temperature. Thus, equations (14) and (15) are based on the two-parameter version of the UNIFAC model in which ψ_{nm}, ψ_{mn}, are exponentially related to a_{mn}, a_{nm}.

In order to enhance the flexibility and, hence, the accuracy of the model in characterizing functional group energy interactions in heats of mixing of liquid mixtures, the two parameters, a_{mn}, a_{nm}, are made temperature dependent. The following temperature dependency is investigated in this study:

$$-a_{mn} = A_{mn}T^{n} + B_{mn} \tag{16}$$

and

$$-a_{nm} = A_{nm}T^{n} + B_{nm} \tag{17}$$

where

$$n = -2, -1, \ldots +2$$

Therefore,

$$\psi_{nm} = \mathrm{EXP}(-\frac{a_{nm}}{T}) \tag{18}$$

$$\psi_{nm} = \mathrm{EXP}(A_{nm}T^{n-1} + B_{nm}T^{-1}) \tag{19}$$

$$\psi_{mn} = \mathrm{EXP}(A_{mn}T^{n-1} + B_{mn}T^{-1}) \tag{20}$$

In equations (19) and (20) the two parameters ψ_{mn}, ψ_{nm} have been replaced by the four parameters, namely, A_{mn}, A_{nm}, B_{mn}, B_{nm}.

Therefore it requires two additional equations to make a total of four, in order to solve for the four unknown parameters mentioned above.

The two additional equations are defined by the relationship

$$b_{mn} = \frac{\delta(\psi_{mn})}{\partial T}, \tag{21}$$

$$b_{nm} = \frac{\delta(\psi_{nm})}{\partial T} \tag{22}$$

Differentiating equations (19) and (20) with respect to temperature give

$$b_{mn} = \frac{\partial[\mathrm{EXP}(A_{mn}T^{n-1} + B_{mn}T^{-1})]}{\partial T} \qquad (23)$$

$$b_{mn} = \mathrm{EXP}[A_{mn}T^{n-1} + B_{mn}T^{-1}][(n-1)A_{mn}T^{n-2} - B_{mn}T^{-2}] \qquad (24)$$

$$b_{nm} = \frac{\partial[\mathrm{EXP}(A_{nm}T^{n-1} + B_{nm}T^{-1})]}{\partial T} \qquad (25)$$

$$b_{nm} = \mathrm{EXP}[A_{nm}T^{n-1} + B_{nm}T^{-1}][(n-1)A_{nm}T^{n-2} - B_{nm}T^{-2}] \qquad (26)$$

Where the four parameters, A_{mn}, A_{nm}, B_{mn}, B_{nm} are independent of temperature.

The equation for $T(\frac{\delta \ln \Gamma_k}{\partial T})_{p,x}$ becomes

$$T(\frac{\delta \ln \Gamma_k}{\partial T})_{p,x} = TQ_k \, [\frac{\delta(-\ln(\sum^{m}\theta_m\psi_{mk}))}{\partial T}] - (\frac{\delta(\sum^{n}[\frac{\theta_m\psi_{km}}{\sum^{m}\theta_n\psi_{nm}}])}{\partial T}) \qquad (27)$$

Let

$$C = \frac{\partial(\ln(\sum^{m}\theta_m\psi_{mk}))}{\partial T} \qquad (28)$$

and

$$D = \frac{\partial(\sum^{m}[\frac{\theta_m\psi_{km}}{\sum^{n}\theta_n\psi_{nm}}])}{\partial T} \qquad (29)$$

equation (27) then becomes

$$T(\frac{\partial \ln \Gamma_k}{\partial T})_{p,x} = TQ_k(-C-D) \qquad (30)$$

From equation (28)

$$C = \frac{1}{\sum^{m}\theta_m\psi_{mk}} \sum^{m}\theta_m \frac{\partial\psi_{mk}}{\partial T} \qquad (31)$$

Substitution of equation (21) into (31) gives

$$C = \frac{\sum^{m}\theta_m b_{mk}}{\sum^{m}\theta_m \psi_{mk}} \tag{32}$$

Expanding on equation (29) gives

$$D = \frac{\sum^{m}\theta_m b_{km} \sum^{n}\theta_n \psi_{nm} - \sum^{n}\theta_n b_{nm} \sum^{m}\theta_m \psi_{km}}{(\sum^{n}\theta_n \psi_{nm})^2} \tag{33}$$

Substituting equations (32) and (33) into (30) gives

$$T\left(\frac{\partial \ln \Gamma_k}{\partial T}\right)_{p,x} = TQ_k \sum^{m}\theta_m \left[-\frac{b_{mk}}{\sum^{m}\theta_m \psi_{mk}} - \frac{b_{km}\sum^{n}\theta_n \psi_{nm} - \psi_{km}\sum^{n}\theta_n \psi_{nm}}{(\sum^{n}\theta_n \psi_{nm})^2} \right] \tag{34}$$

Substituting equations (20) and (24) into (34) gives

$$T\left(\frac{\partial \ln \Gamma_k}{\partial T}\right)_{p,x} = TQ_k \sum^{m}\theta_m \{ - \frac{EXP(A_{mk}T^{n-1} + B_{mk}T^{-1})[(n-1)A_{mk}T^{n-2} - B_{mk}T^{-2}]}{\sum^{m}\theta_m EXP[A_{mk}T^{n-1} + B_{mk}T^{-1}]}$$

$$- \frac{(EXP(A_{mk}T^{n-1} + B_{mk}T^{-1})((n-1)A_{mk}T^{n-2} - B_{mk}T^{-2}) - \sum^{n}\theta_n EXP(A_{mk}T^{n-1} + B_{mk}T^{-1}))}{[\sum^{n}\theta_n EXP(A_{mk}T^{n-1} + B_{mk}T^{-1})]^2}$$

$$- \frac{(EXP(A_{km}T^{n-1} + B_{km}T^{-1}) \cdot \sum^{n}\theta_n \cdot EXP(A_{nm}T^{n-1} + B_{nm}T^{-1}))}{[\sum^{n}\theta_n \cdot EXP(A_{mk}T^{n-1} + B_{mk}T^{-1})]^2} \} \tag{35}$$

Similarly, following equation (34)

$$\left(\frac{\partial \ln \Gamma_k^{(i)}}{\partial T}\right)_{p,x} = TQ_k \sum^{m}\theta_m^{(i)} \; \frac{b_{mk}}{\sum^{m}\theta_m^{(i)} \psi_{mk}} - \frac{(b_{km}\sum^{n}\theta_n^{(i)} \psi_{nm} - \psi_{km}\sum^{n}\theta_n^{(i)} b_{nm})}{(\sum^{n}\theta_n^{(i)} \psi_{nm})^2} \; . \tag{36}$$

where b_{jk}, b_{kj} retain their definitions in equations (21), (22) and $\theta_m^{(i)}$ = the group surface area fraction of group m in pure component i.

Substitutions of equations (19), (20), (24) and (26) into (36) gives the complete expression for that equation. Substituting equations (35) and (36) into (5), gives the heat-of-mixing expression for group k.

Check: the correctness of the heat-of-mixing expressions (equation 5) can be verified by substituting $A_{mn} = 0$, $B_{mn} = a_{mn}$, into the four-parameter version; this substitution should revert the four-parameter version to the two-parameter version.

APPENDIX 2

COMPUTER PROGRAMS

The Fortran programs for heat-of-mixing calculations are presented in this section. Also included is the nomenclature for the actual use of the programs. There are three main programs and one subroutine for obtaining parameters for the various correlations.

Main Program Titles

HM1X2	UNIFAC two-parameter program, calculates heats of mixing
HM1X4	UNIFAC four-parameter program, calculates heats of mixing
AGSM	AGSM Program calculates heats of mixing
REG	Non-linear Regression Subroutine used with each of the above main programs to calculate the group interaction parameters

Nomenclature for Main Programs & Variables in Common

A(J,K),B(J,K)	Group temperature independent coefficients for groups j and k interactions
ERROR	Percentage difference between calculated and experimental heats of mixing
HEMIX(I)	Calculated heats of mixing of component i in solution
HK(K)	Heats of mixing of group k in the solution
HKS(K,I)	Standard heats of mixing of group k in component i

HMIXE	Experimental heats of mixing
HMIX	Calculated heats of mixing
HSUM(I)	Partial molar heats of mixing of component i in solution
I	Molecular components
J,K	Groups
NDATA	Number of data points
N(K,I)	Number of groups of type K in component i
Q(J)	Group J group area parameter
R	Universal gas constant
T	Absolute temperature in degrees Kelvin
TH(J)	Group J surface area fraction
THS(J,I)	Group surface area fraction of group J in pure component i
U(J,K)	UNIFAC binary temperature dependent parameters
W_{SUM}	Sum of group surface areas for all groups in solution
X(J)	Group fraction of group J
XM(I)	Mole fraction of component i
XT	Group interaction parameter determined by data reduction

HMIX2

```
C        PROGRAM USING UNIFAC REGRESSION SUBRUOTINE
C        MAIN PROGRAM
C        BUTANOL/HEPTANE SYSTEM
         COMMON XM1(40),HMIXE(40),HMIX(40),ERROR(40),NDATA,T
         DIMENSION XT(15,15)
         REAL*8 NAME1,NAME2,NAME3
         INTEGER F,H
         READ 12,NAME1,NAME2,NAME3
   12    FORMAT (3A8)
         PRINT 12,NAME1,NAME2,NAME3
         READ 1, NDATA
    1    FORMAT (I10)
         READ 11, T
   11    FORMAT (F10.5)
         READ 2,(XM1(I),HMIXE(I),I=1,NDATA)
 2       FORMAT(F5.3,F10.4)
         READ 1 ,NPAR
         NN=NPAR+1
         N=NPAR
         READ 702,(XT(1,I),I=1,NPAR)
 702     FORMAT (F15.7)
         SA=1.E-6
         DO 20 J=2,NN
         DO 20 I=1,N
         IF(J-I-1)2002,2003,2002
 2003    XT(J,I)=1.1*XT(1,I)
         GO TO 20
 2002    XT(J,I)=XT(1,I)
 20      CONTINUE
         PRINT 4
 4       FORMAT ('-',10X,'INITIAL PARAMETERS')
         PRINT 301, (XT(1,I),I=1,N)
 301     FORMAT('-',10X,F10.6)
         ALFA=1.
         BETA=0.5
         GAMMA=2.
         CALL REG(NPAR,XT,ALFA,BETA,GAMMA,SA,NN,N)
         PRINT 9,(XM1(J),HMIXE(J),HMIX(J),ERROR(J),J=1,NDATA)
 9       FORMAT (4F15.5)
         STOP
         END
```

```
      SUBROUTINE FMIN(XT,FF)
      COMMON XM1(40),HMIXE(40),HMIX(40),ERROR(40),NDATA,T
      DIMENSION BS(10,10),HEAT(10,10),HEMIX(20)
      DIMENSION U(10,10),AX(10),HK(10),HKS(10,10),DN(10,10),BSUM
      DIMENSION DS(10,10),CS(10,10),ES(10),FS(10),GS(10)
      DIMENSION C(10,10),D(10,10),E(10),F(10),G(10)
      DIMENSION BX(10), M(10),N(10,10),X(10)
      DIMENSION CSUM(10),P(10,10),YSUM(10),CSSUM(10),BSSUM(10)
      DIMENSION HSUM(10),WSUM(10),VSUM(10),PPSSUM(10),PPSUM(10)
      DIMENSIONTH(20),THS(20,20),PP(10,10),PPS(10,10),Q(10)
      DIMENSION XT(10)
      YS=0.
      Q(2)=0.540
      Q(3)=0.848
      Q(4)=1.664
      N(2,2)=1
      N(2,3)=5
      N(3,2)=1
      N(3,3)=2
      N(4,2)=1
      N(4,3)=0
      U(3,2)=1.
      U(2,3)=1.
      U(2,2)=1.
      U(3,3)=1.
      U(4,4)=1.
      KA=4
      IS=3
      IA=3
      MA=4
      JA=4
      IB=3
      JB=4
      MB=4
      JS=4
      KS=4
      MS=4
      IH=3
      KH=4
      JC=4
      MC=4
      ID=3
      JD=4
      MD=4
      R=8.314
      U(2,4)=XT(1)
      U(4,2)=XT(2)
      U(2,4)=ABS(U(2,4))
      U(4,2)=ABS(U(4,2))
      U(3,4)=U(2,4)
```

```
      U(4,3)=U(4,2)
      DO 777 KPN=1,NDATA
      XM(2)=XM1(KPN)
      XM(3)=1.-XM(2)
      BX(1)=0.
      AX(1)=0.
      AXSUM=0.
      DO 30 M=2,MA
      DO 40 I=2,IA
      DO 50 K=2,KA
      AX(K)=AX(K-1)+XM(I)*N(K,I)
   50 CONTINUE
      BX(I)=BX(I-1)+XM(I)*N(M,I)
      AXSUM=AXSUM+AX(KA)
   40 CONTINUE
      X(M)=BX(IA)/AXSUM
      AXSUM=0.
   30 CONTINUE
      WSUM(1)=0.
      DO 99 J=2,JC
      DO 88 M=2,MC
      WSUM(M)=WSUM(M-1)+Q(M)*X(M)
   88 CONTINUE
      TH(J)=Q(J)*X(J)/WSUM(MC)
   99 CONTINUE
      D(1,1)=0.
      C(1,1)=0.
      F(1)=0.
      E(1)=0.
      G(1)=0.
      CSUM(1)=0.
      BSUM(1)=0.
      P(1,1)=0.
      PPSUM(1)=0.
      PP(1,1)=0.
      DO 3 K=2,KA
      DO 1 J=2,JA
      DO 2 M=2,MA
      C(J,M)=TH(M)*U(M,J)*ALOG(U(K,J)/U(M,J))
      P(J,M)=TH(M)*U(M,J)
      PP(M,K)=TH(M)*U(M,K)
      CSUM(M)=CSUM(M-1)+C(J,M)
      BSUM(M)=BSUM(M-1)+P(J,M)
      PPSUM(M)=PPSUM(M-1)+PP(M,K)
      D(J,M)=BSUM(M)**2.
    2 CONTINUE
      E(J)=E(J-1)+U(K,J)*CSUM(MA)/D(J,MA)
      F(J)=F(J-1)+U(J,K)*ALOG(U(J,K))/PPSUM(MA)
      G(J)=G(J-1)+TH(J)*(F(J)+E(J))
    1 CONTINUE
```

```
        HK(K)=Q(K)*G(JA)
  3     CONTINUE
        YSUM(1)=0.
        DO 5 I=2,IB
        DO 10 J=2,JB
        DO 20 M=2,MB
        YSUM(M)=YSUM(M-1)+N(M,I)
  20    CONTINUE
        DN(J,I)=FLOAT(N(J,I))/YSUM(MB)
  10    CONTINUE
  5     CONTINUE
        VSUM(1)=0.
        DO 77 I=2,ID
        DO 66 J=2,JD
        DO 55 M=2,MD
        VSUM(M)=VSUM(M-1)+Q(M)*DN(M,I)
  55    CONTINUE
        THS(J,I)=Q(J)*DN(J,I)/VSUM(MD)
  66    CONTINUE
  77    CONTINUE
        DS(1,1)=0.
        CS(1,1)=0.
        ES(1)=0.
        FS(1)=0.
        GS(1)=0.
        BS(1,1)=0.
        CSSUM(1)=0.
        BSSUM(1)=0.
        PPS(1,1)=0.
        PPSSUM(1)=0.
        DO 44 I=2,IS
        DO 33 K=2,KS
        DO 11 J=2,JS
        DO 22 M=2,MS
        CS(J,M)=THS(M,I)*U(M,J)*ALOG(U(K,J)/U(M,J))
        BS(J,M)=THS(M,I)*U(M,J)
        PPS(M,K)=THS(M,I)*U(M,K)
        CSSUM(M)=CSSUM(M-1)+CS(J,M)
        BSSUM(M)=BSSUM(M-1)+BS(J,M)
        PPSSUM(M)=PPSSUM(M-1)+PPS(M,K)
        DS(J,M)=BSSUM(M)**2.
  22    CONTINUE
        ES(J)=ES(J-1)+U(K,J)*CSSUM(MS)/DS(J,MS)
        FS(J)=FS(J-1)+U(J,K)*ALOG(U(J,K))/PPSSUM(MS)
        GS(J)=GS(J-1)+THS(J,I)*(FS(J)+ES(J))
  11    CONTINUE
        HKS(K,I)=Q(K)*GS(JS)
  33    CONTINUE
  44    CONTINUE
        HEMIX(1)=0.
```

```
      HSUM(1)=0.
      HEAT(1,1)=0.
      DO 60 I=2,IH
      DO 70 K=2,KH
      HEAT(K,I)=N(K,I)*(HK(K)-HKS(K,I))
      HSUM(K)=HSUM(K-1)+HEAT(K,I)
   70 CONTINUE
      HEMIX(I)=HEMIX(I-1)+XM(I)*HSUM(KH)
   60 CONTINUE
      HEMIX(3)=-R*T*HEMIX(IH)
      HMIX(KPN)=HEMIX(3)
      ERROR(KPN)=100.*(HMIXE(KPN)-HMIX(KPN))/HMIXE(KPN)
      DIFF=ABS(HMIXE(KPN)-HMIX(KPN))
      Y=(DIFF/HMIXE(KPN))**2.
      YS=YS+Y
  777 CONTINUE
      FF=YS
      RETURN
      END
```

Hmix4

```
      PROGRAM USING UNIFAC REGRESSION SUBROUTINE
C     MAIN PROGRAM
        COMMON XM1(40),HMIXE(40),HMIX(40),ERROR(40),NDATA,T
        DIMENSION XT(17,20)
         READ(5,1) NDATA
  1      FORMAT(I4)
```

```
 1    FORMAT(F10.5)
      READ(5,2)(XM1(I),HMIXE(I),I=1,NDATA)
 2    FORMAT(F6.4,F8.1)
      READ(5,1)NPAR
     NN=NPAR+1
     N=NPAR
     SA=1.E-6
      READ(5,702)(XT(1,I),I=1,NPAR)
 702  FORMAT(F15.7)
     DO 20 J=2,NN
     DO 20 I=1,N
     IF(J-I-1)2002,2003,2002
2003 XT(J,I)=1.1*XT(1,I)
     GO TO 20
2002 XT(J,I)=XT(1,I)
20   CONTINUE
     WRITE(6,4)
4    FORMAT ('-',10X,'NITIAL PARAMETERS')
     WRITE(6,301) (XT(1,I),I=1,N)
301  FORMAT (///,10X,F15.7)
     ALFA=1.
     BETA=0.5
     GAMMA=2.
     CALL REG(NPAR,XT,ALFA,BETA,GAMMA,SA,NN,N)
     WRITE(6,9)(XM1(J),HMIXE(J),HMIX(J),ERROR(J),J=1,NDATA)
9    FORMAT (4F15.5)
     STOP
     END
     SUBROUTINE FMIN(XT,FF)
     COMMON XM1(40),HMIXE(40),HMIX(40),ERROR(40),NDATA,T
C   UNIFAC---TEMPERATURE-INDEPENDENT PARAMETERS
     DIMENSIONHS(10),BS(10,10),HEAT(10,10),HEMIX(50)
     DIMENSION A(10,10),AX(10),HK(10),HKS(10,10),DN(10,10),BSUM(10)
     DIMENSION DS(10,10),CS(10,10),ES(10), FS(10),GS(10)
     DIMENSION C(10,10),D(10,10),E(10),F(10),G(10),H(10),B(10,10)
     DIMENSION BX(10), XM(10),N(10,10),X(10), H1(10),H1S(10)
     DIMENSION CSUM(10),P(10,10),YSUM(10),CSSUM(10),BSSUM(10)
     DIMENSION HSUM(10)
     DIMENSION WSUM(10),TH(10),THS(10,10),Q(10)
     DIMENSION VSUM(10)
     DIMENSION XT(10)
     YS=0.
     KA=4
     IS=3
     IA=3
     MA=4
     JA=4
     IB=3
     JB=4
     MB=4
     JS=4
     KS=4
     MS=4
     IH=[illegible]
     KH=4
     JC=4
     MC=4
     ID=3
     JD=4
     MD=4
     Q(2)=0.540
     Q(3)=0.848
      Q(4)=1.664
      N(2,2)=5
      N(3,2)=1
```

```
       N(2,3)=5
       N(3,3)=2
      N(4,3)=0
      R=8.314
      A(2,2)=0.
      A(3,3)=0.
      B(2,2)=0.
      B(3,3)=0.
      A(4,4)=0.
      A(2,3)=0.
      A(3,2)=0.
      B(2,3)=0.
      B(3,2)=0.
      B(4,4)=0.
      A(2,4)=XT(1)
      A(4,2)=XT(2)
      B(2,4)=XT(3)
      B(4,2)=XT(4)
      A(3,4)=A(2,4)
      A(4,3)=A(4,2)
      B(3,4)=B(2,4)
      B(4,3)=B(4,2)
      DO 777 KPN=1,NDATA
      XM(2)=XM1(KPN)
      XM(3)=1.-XM(2)
      BX(1)=0.
      AX(1)=0.
      AXSUM=0.
      DO  30 M=2,MA
      DO  40 I=2,IA
      DO  50 K=2,KA
      AX(K)=AX(K-1)+XM(I)*N(K,I)
  50  CONTINUE
      BX(I)=BX(I-1)+XM(I)*N(M,I)
      AXSUM=AXSUM+AX(KA)
   40 CONTINUE
      X(M)=BX(IA)/AXSUM
      AXSUM=0.
   30 CONTINUE
      WSUM(1)=0.
      DO 99 J=2,JC
      DO 88 M=2,MC
      WSUM(M)=WSUM(M-1)+Q(M)*X(M)
88    CONTINUE
      TH(J)=Q(J)*X(J)/WSUM(MC)
99    CONTINUE
      D(1,1)=0.
      C(1,1)=0.
      F(1)=0.
      E(1)=0.
      G(1)=0.
      H(1)=0.
      B(1,1)=0.
      CSUM(1)=0.
      BSUM(1)=0.
      DO  3 K=2,KA
      DO 1 J=2,JA
      DO  2 M=2,MA
      C(J,M)=TH(M)*EXP(A(M,J)+B(M,J)/T)*(-B(M,J)/(T*T))
      P(J,M)=TH(M)*EXP(A(M,J)+B(M,J)/T)
      CSUM(M)=CSUM(M-1)+C(J,M)
      BSUM(M)=BSUM(M-1)+P(J,M)
      D(J,M)=(ABS(BSUM(M)))**2.
      CONTINUE
      E(J)=E(J-1)+TH(J)*EXP(A(K,J)+B(K,J)/T)*CSUM(MA)/D(J-
```

```
     GMA)
      F(J)=F(J-1)+TH(J)*EXP(A(K,J)+B(K,J)/T)*(-B(K,J)/(T*
     GT))/BSUM(MA)
      G(J)=G(J-1)+TH(J)*EXP(A(J,K)+B(J,K)/T)*(-B(J,K)/(T*
     GT))
      H(J)=H(J-1)+TH(J)*EXP(A(J,K)+B(J,K)/T)
    1 CONTINUE
      H1(JA)=G(JA)/H(JA)
      HK(K)=Q(K)*(H1(JA)+F(JA)-E(JA))*R*T*T
    3 CONTINUE
      YSUM(1)=0.
      DO 5 I=2,IB
      DO 10 J=2,JB
      DO 20 M=2,MB
      YSUM(M)=N(M,I)+YSUM(M-1)
20    CONTINUE
      DN(J,I)=FLOAT(N(J,I))/YSUM(MB)
10    CONTINUE
5     CONTINUE
      VSUM(1)=0.
      DO 77 I=2,ID
      DO 66 J=2,JD
      DO 55 M=2,MD
      VSUM(M)=VSUM(M-1)+Q(M)*DN(M,I)
55    CONTINUE
      THS(J,I)=Q(J)*DN(J,I)/VSUM(MD)
66    CONTINUE
77    CONTINUE
      DS(1,1)=0.
      CS(1,1)=0.
      ES(1)=0.
      FS(1)=0.
      GS(1)=0.
      HS(1)=0.
      BS(1,1)=0.
      CSSUM(1)=0.
      BSSUM(1)=0.
      DO 44 I=2,IS
      DO 33 K=2,KS
      DO 11 J=2,JS
      DO 22 M=2,MS
      CS(J,M)=THS(M,I)*EXP(A(M,J)+B(M,J)/T)*(-B(M,J)/(T*T
     G))
      BS(J,M)=THS(M,I)*EXP(A(M,J)+B(M,J)/T)
      CSSUM(M)=CSSUM(M-1)+CS(J,M)
      BSSUM(M)=BSSUM(M-1)+BS(J,M)
      DS(J,M)=(ABS(BSSUM(M)))**2.
   22 CONTINUE
      ES(J)=ES(J-1)+THS(J,I)*EXP(A(K,J)+B(K,J)/T)*CSSUM(M
     GS)/DS(J,MS)
      FS(J)=FS(J-1)+THS(J,I)*EXP(A(K,J)+B(K,J)/T)*(-B(K,J)
     G/(T*T))/BSSUM(MS)
      GS(J)=GS(J-1)+THS(J,I)*EXP(A(J,K)+B(J,K)/T)*(-B(J,K)
     G/(T*T))
      HS(J)=HS(J-1)+THS(J,I)*EXP(A(J,K)+B(J,K)/T)
   11 CONTINUE
      H1S(JS)=GS(JS)/HS(JS)
      HKS(K,I)=Q(K)*(H1S(JS)+FS(JS)-ES(JS))*R*T*T
   33 CONTINUE
   44 CONTINUE
      HEMIX(1)=0.
      HSUM(1)=0.
      HEAT(1,1)=0.
      DO 60 I=2,IH
      DO 70 K=2,KH
```

```
      HSUM(K)=HSUM(K-1)+HEAT(K,I)
   70 CONTINUE
      HEMIX(I)=XM(I)*HSUM(KH)+ HEMIX(I-1)
   60 CONTINUE
      HEMIX(3)=HEMIX(IH)
      HMIX(KPN)=HEMIX(3)
      ERROR(KPN)=100.*(HMIXE(KPN)-HMIX(KPN))/HMIXE(KPN)
      DIFF=ABS(HMIXE(KPN)-HMIX(KPN))
      Y=(DIFF/HMIXE(KPN))**2
      YS=YS+Y
  777 CONTINUE
      FF=YS
      RETURN
      END
```

```
C     AGSM
      DIMENSIONHS(10),BS(10,10),HEAT(10,10),HEMIX(50)
      DIMENSION A(10,10),AX(10),HK(10),HKS(10,10),DN(10,10),BSUM(10)
      DIMENSION DS(10,10),CS(10,10),ES(10), FS(10),GS(10)
      DIMENSION C(10,10),D(10,10),E(10),F(10),G(10),H(10),B(10,10)
      DIMENSION BX(10), XM(10),N(10,10),X(10), H1(10),H1S(10)
      DIMENSION CSUM(10),P(10,10),YSUM(10),CSSUM(10),BSSUM(10)
      DIMENSION HSUM(10)
      XM(2)=0.
100   XM(2)=XM(2)+0.1
      IF(XM(2)-1.) 300,200,200
300   XM(3)=1.-XM(2)
      KA=3
      IS=3
      IA=3
      MA=3
      JA=3
      IB=3
      JB=3
      MB=3
      JS=3
      KS=3
      MS=3
      IH=3
      KH=3
      N(2,3)=7
      N(3,2)=1
      N(2,2)=3
      N(3,3)=0
      R=8.314
      T=303.15
      A(2,2)=0.
      A(3,3)=0.
      B(2,2)=0.
      B(3,3)=0.
```

```
      B(3,2)=-3316.1
      BX(1)=0.
      AX(1)=0.
      AXSUM=0.
      DO  30 M=2,MA
      DO  40 I=2,IA
      DO  50 K=2,KA
      AX(K)=AX(K-1)+XM(I)*N(K,I)
 50   CONTINUE
      BX(I)=BX(I-1)+XM(I)*N(M,I)
      AXSUM=AXSUM+AX(KA)
 40   CONTINUE
      X(M)=BX(IA)/AXSUM
      AXSUM=0.
 30   CONTINUE
      D(1,1)=0.
      C(1,1)=0.
      F(1)=0.
      E(1)=0.
      G(1)=0.
      H(1)=0.
      B(1,1)=0.
      CSUM(1)=0.
      BSUM(1)=0.
      DO  3 K=2,KA
      DO 1 J=2,JA
      DO  2 M=2,MA
      C(J,M)=X(M)*EXP(A(J,M)+B(J,M)/T)*(-B(J,M)/(T*T))
      P(J,M)=X(M)*EXP(A(J,M)+B(J,M)/T)
      CSUM(M)=CSUM(M-1)+C(J,M)
      BSUM(M)=BSUM(M-1)+P(J,M)
      D(J,M)=(ABS(BSUM(M)))**2.
  2   CONTINUE
      E(J)=E(J-1)+X(J)*EXP(A(J,K)+B(J,K)/T)*CSUM(MA)/D(J,M
     1A)
      F(J)=F(J-1)+X(J)*EXP(A(J,K)+B(J,K)/T)*(-B(J,K)/(T*T)
     1)/BSUM(MA)
      G(J)=G(J-1)+X(J)*EXP(A(K,J)+B(K,J)/T)*(-B(K,J)/(T*T)
     1)
      H(J)=H(J-1)+X(J)*EXP(A(K,J)+B(K,J)/T)
      H1(J)=G(J)/H(J)
   1  CONTINUE
      HK(K)=(H1(JA)+F(JA)-E(JA))*R*T*T
   3  CONTINUE
      YSUM(1)=0.
      DO 5 I=2,IB
      DO 10 J=2,JB
      DO 20 M=2,MB
      YSUM(M)=N(M,I)+YSUM(M-1)
0     CONTINUE
      DN(J,I)=FLOAT(N(J,I))/YSUM(MB)
 10   CONTINUE
 5    CONTINUE
      DS(1,1)=0.
      CS(1,1)=0.
      ES(1)=0.
      FS(1)=0.
      GS(1)=0.
      HS(1)=0.
      BS(1,1)=0.
      CSSUM(1)=0.
      BSSUM(1)=0.
      DO 44 I=2,IS
```

```
      DO 33 K=2,KS
      DO 11 J=2,JS
      DO 22 M=2,MS
      CS(J,M)=DN(M,I)*EXP(A(J,M)+B(J,M)/T)*(-B(J,M)/(T*T))
      BS(J,M)=DN(M,I)*EXP(A(J,M)+B(J,M)/T)
      CSSUM(M)=CSSUM(M-1)+CS(J,M)
      BSSUM(M)=BSSUM(M-1)+BS(J,M)
      DS(J,M)=(ABS(BSSUM(M)))**2.
   22 CONTINUE
      ES(J)=ES(J-1)+DN(J,I)*EXP(A(J,K)+B(J,K)/T)*CSSUM(MS)
     1/DS(J,MS)
      FS(J)=FS(J-1)+DN(J,I)*EXP(A(J,K)+B(J,K)/T)*(-B(J,K)/
     1(T*T))/BSSUM(MS)
      GS(J)=GS(J-1)+DN(J,I)*EXP(A(K,J)+B(K,J)/T)*(-B(K,J)/
     1(T*T))
      HS(J)=HS(J-1)+DN(J,I)*EXP(A(K,J)+B(K,J)/T)
      H1S(J)=GS(J)/HS(J)
   11 CONTINUE
      HKS(K,I)=(H1S(JS)+FS(JS)-ES(JS))*R*T*T
   33 CONTINUE
   44 CONTINUE
      HEMIX(1)=0.
      HSUM(1)=0.
      HEAT(1,1)=0.
      DO 60 I=2,IH
      DO 70 K=2,KH
      HEAT(K,I)=N(K,I)*(HK(K)-HKS(K,I))
      HSUM(K)=HSUM(K-1)+HEAT(K,I)
   70 CONTINUE
      HEMIX(I)=XM(I)*HSUM(KH)+ HEMIX(I-1)
   60 CONTINUE
      HEMIX(3)=HEMIX(IH)
      WRITE(2,400) XM(2),HEMIX(3)
  400 FORMAT (F5.3,F15.5)
      GO TO 100
  200 STOP
      END
```

REG

```
      SUBROUTINE REG(NPAR,X,ALFA,BETA,GAMMA,SA,NN,N)
      DIMENSION X(17,20),F(10),XS(10),XM(10),XE(10),XX(10)
       DIMENSION XR(10),XK(10),XB(10)
      NP=6
      DO 1 J=1,NN
      DO 21 I=1,N
21    XX(I)=X(J,I)
      CALL FMIN(XX,FF)
1     F(J)=FF
      NF=NN
C     NF IS THE NUMBER OF CALCULATIONS OF F
      ALFA=1.
      BETA=0.5
      GAMMA=2.
      ITER=0
      JPR=0
 400   FORMAT(8F16.7)
C     ESTIMATION OF THE LOWEST VALUE OF F=FB
25    FB=F(1)
      DO 98 I=1,N
98    XB(I)=X(1,I)
      JB=1
      DO 31 J=2,NN
      IF(FB-F(J))31,31,108
108   FB=F(J)
      JB=J
      DO 41 I=1,N
41    XB(I)=X(J,I)
31    CONTINUE
C     ESTIMATION OF THE HIGHEST VALUE OF F=FS
      FS=F(1)
      DO 51 I=1,N
51    XS(I)=X(1,I)
      JS=1
      DO 61 J=2,NN
      IF(FS-F(J))111,61,61
111   FS=F(J)
      JS=J
      DO 71 I=1,N
71    XS(I)=X(J,I)
61    CONTINUE
C     CALCULATION OF THE CENTROID XM(I) OF POINTS
C     EXCLUDING XS(I)
      DO 81 I=1,N
81    XM(I)=-XS(I)
      DO 9 J=1,NN
      DO 122 I=1,N
122   XM(I)=XM(I)+X(J,I)
9     CONTINUE
      DO 121 I=1,N
121   XM(I)=XM(I)/FLOAT(N)
C      REFLECTION
```

```
      NF=NF+1
C     EXPANSION
      IF(FR-FB)141,151,151
141   DO 161 I=1,N
161   XE(I)=XM(I)+GAMMA*(XR(I)-XM(I))
      CALL FMIN(XE,FE)
      NF=NF+1
      IF(FE-FB)17,18,18
17    DO 19 I=1,N
      X(JS,I)=XE(I)
19    XS(I)=XE(I)
      F(JS)=FE
C     CALCULATION OF THE HALTING CRITERION
27    FM=0.
      DO 20 J=1,NN
20    FM=FM+F(J)
      FM=FM/FLOAT(NN)
      FRMS=0.
      DO 22 J=1,NN
22    FRMS=(F(J)-FM)**2+FRMS
      RMS=SQRT(FRMS/FLOAT(N))
      ITER=ITER+1
      JPR=JPR+1
       IF(ITER.EQ.101)GO TO 23
500   CONTINUE
      IF(JPR-1)902,902,903
903   CONTINUE
      IF(JPR-6)901,904,904
904   JPR=1
902   CONTINUE
      WRITE(NF,107)ITER,NF
107   FORMAT(1H0,'    ITERATION ',I4,'   NUMBER OF CALLS FOR THE SUBRO
     GUTINE',I5)
      WRITE(NF,109)
109   FORMAT('       PARAMETERS')
      WRITE(NP,400)(X(JS,I),I=1,N)
      WRITE(NP,106)F(JS),RMS
106   FORMAT(1H ,'    FMIN=',E14.5,'    SD=',E14.5)
901   CONTINUE
      IF(RMS-SA)23,23,25
C     NEW SIMPLEX
C     FE GREATER THAN FB
18    DO 26 I=1,N
      X(JS,I)=XR(I)
26    XS(I)=XR(I)
      F(JS)=FR
      FS=FR
      GO TO 27
C     NEW SIMPLEX
C     FR GREATER THAN FB
151   DO 30 J=1,NN
      IF(J-JS)28,30,28
28    IF(FR-F(J))18,18,30
30    CONTINUE
      IF(FR-FS)91,91,32
91    DO 33 I=1,N
      X(JS,I)=XR(I)
33    XS(I)=XR(I)
      F(JS)=FR
      FS=FR
32    DO 34 I=1,N
34    XK(I)=XM(I)+BETA*(XS(I)-XM(I))
      CALL FMIN(XK,FK)
```

```
      NF=NF+1
C     NEW SIMPLEX
C     AFTER CONTRACTION
      IF(FK-FS)35,35,36
35    DO 37 I=1,N
      X(JS,I)=XK(I)
37    XS(I)=XK(I)
      F(JS)=FK
      FS=FK
      GO TO 27
36    DO 38 J=1,NN
      DO 39 I=1,N
39    X(J,I)=(X(J,I)+XB(I))/2.
38    CONTINUE
      GO TO 27
23    WRITE(NP,905)
905   FORMAT(1H0,'        FINAL PARAMETERS')
      WRITE(NP,400)(X(JS,I),I=1,N)
      WRITE(NP,106)F(JS),RMS
833   CONTINUE
      RETURN
      END
```

NOMENCLATURE

Arabic Numerals

ΔH_{EXP} = Experimental heats of mixing per mole of mixture

ΔH_{CAL} = Calculated heats of mixing per mole of mixture

ΔH = Heats of mixing per mole of mixture

$\Delta \overline{H}_i$ = Partial molar heats of mixing of component i

$V_k^{(i)}$ = Number of groups of type k in component i

X_i = Mole fraction of component i

H_k = Group heats of mixing of group k

$H_k^{(i)}$ = Standard state heats of mixing of group k in component i

X_m = Group fraction of group m

P = Pressure

T = Temperature

a_{jk}, b_{jk} = UNIFAC group parameters (temperature dependent)

A_{jk}, B_{jk} = Group parameters (temperature independent)

Q_k = Group k surface area parameter

R = Universal gas constant

U_{kj}, U_{jk} = UNIFAC binary interaction parameters

G^E = Excess Gibbs Energy

F_{MIN} = Function minimized by data reduction

Greek Letters

γ_i^R = Residual activity coefficient of component i in mixture

γ_i = Activity Coefficient of component i

Γ_k = Activity coefficient of group k

$\Gamma_k^{(i)}$ = Activity coefficient of group k in pure component i

θ_m = Area fraction of group m

$\theta_m^{(i)}$ = Group surface area fraction of group m in pure component i

γ_i^C = the combinatorial activity coefficient which is independent of temperature

τ_{ij}, τ_{ji} = the two adjustable parameters obtained by data reduction. No ternary or higher parameters are needed for multicomponent systems.

Φ_i = molecular volume fraction

θ_i = molecular surface area fraction

x_i = component i mole fraction

z = lattice combination number (here equal to 10)

q_i = van der Waals surface area for component i

r_i = van der Waals volume for component i

l_i = pure component (i) constant

$k = 1, 2 \ldots . N$

N = number of groups in molecule i

$j = 1, 2 \ldots . M$

M = number of components in mixture

where

M^E = excess property (extensive)

$\bar{m}_i^E$ = partial excess property

n_i = number of moles of i

$i = 1, 2 \ldots . M$

M = number of components in the mixture

G^E = Gibbs free energy

N = number of different groups in the mixture

T = temperature in degrees Kelvin

$X_m^{(i)}$ = group fraction of group m in pure component i

γ_i = component i activity coefficient in mixture

j,k,m = groups in the mixture

$x_j^{(i)}$ = group fraction of group j in pure component i

$N_k^{(i)}$ = number of the group type k in component i

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INDEX