ABSTRACT

Title of Thesis: Prediction of Heats of Mixing
by Group Contribution Methods

William Rupp, Master of Science, 1982

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

Three group contribution methods used to predict heats of mixing were tested: AGSM, UNIFAC with temperature dependent parameters and the modified UNIFAC of Skjold-Jorgensen et al. The modified UNIFAC provided the best results and was adopted in this study. Primary parameters were obtained for ten groups with alkanes. The simultaneous correlation of cyclic and straight-chain alkanes gave poor results. Attempts to improve the error by changing the group area parameter for cyclic CH_2 failed.

A major problem in correlating the experimental data was the multiplicity of roots. The best set of parameters was obtained by using a grid approach for the initial parameters. The model can be used in the temperature range 0° to $100^\circ C$. 104 systems from the literature were tested of which 78 had a prediction error of less than 20 percent. High errors were observed for some isomers, and long-chain molecules.

PREDICTION OF HEATS OF MIXING BY GROUP CONTRIBUTION METHODS

by

William Walter Rupp

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APPROVAL SHEET

Title of Thesis: Prediction of Heats of Mixing
By Group Contribution Methods

Name of Candidate: William Walter Rupp
Master of Science, 1982

Thesis and Abstract Approved: ______________________

Dr. Dimitrios Tassios
Professor
Department of Chemical
Engineering and Chemistry

____

Dr. John E. McCormick
Professor
Department of Chemical
Engineering and Chemistry

____

Dr. Reginald P.T. Tomkins
Assistant Professor
Department of Chemical
Engineering and Chemistry

Date Approved: 5/6/82

VITA

Name: William Walter Rupp

Permanent address:

Degree and date to be conferred: M.S. Che, 1982

Date of birth:

Place of birth:

Secondary education: Queen of Peace High School, 1974

Collegiate institutions attended	Dates	Degree	Date of Degree
New Jersey Institute of Technology	1974-78	B.S.	May, 1978
New Jersey Institute of Technology	1978-82	M.S.	May, 1982

Major: Chemical Engineering

Publication: Thesis to be published

Positions held:
June 1980 to Present
Vessel Analytical Engineer
M.W. Kellogg, Co.
Hackensack, New Jersey

September 1978 to May 1979
September 1979 to May 1980
Graduate Assistant
New Jersey Institute of Technology
Newark, New Jersey

DEDICATION

To my Father

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To Dr. Tassios, whose "philosophizing" sessions sustained my interest throughout this project;

To Prof. Mal Simon, who although not involved with my thesis became a good friend during my graduate work;

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I. INTRODUCTION

Excess enthalpy (heat of mixing) occurs, as the term suggests, from the mixing of two or more components. Knowledge of heats of mixing is important in several chemical engineering processes, such as fractional, extractive and azeotropic distillation.

A large share of the experimental heats of mixing data are for binary mixtures at 25^oC. However, the more commonly encountered system is a multicomponent mixture at a higher temperature. What is needed is a method that used existing data to calculate the heats of mixing of systems for which there are no data available. One promising method to solve this problem is the group contribution model. Group contribution methods calculate interactions among molecules in terms of the interaction between the functional groups of the molecule. The advantage of this approach is that whereas there are thousands of mixtures in the chemical industry there are only a limited number of functional groups.

The group contribution method assumes that the excess enthalpy is the sum of the contributions of the different groups (i.e. CH_2, OH, ACH) that make up the molecule. This assumption is an approximate representation, of course, in that it implies that a specific group in a molecule is independent of the other groups in that molecule. For example, the OH group in n-propanol is the same as in t-butanol.

According to the group contribution concept, n-butanol would consist of the groups OH, CH_2 and CH_3. Group interaction parameters are used to account for the contribution of each group. For example, in the binary mixture n-butanol + n-heptane the following interaction parameters could be obtained: CH_2/OH and OH/CH_2 (where the interactions for the groups CH_2 and CH_3 are considered the same). The group interaction parameters are found from correlating experimental heats of mixing data. The parameters could then be used to predict other alcohol + alkane mixtures for which no data is available.

Until 1961, when Mrazek and Van Ness (77) published endothermic heats of mixing data for alcohol + aromatic systems, reliable experimental data were scarce. Some other early researchers in this field included Tsao and Smith (42) and Hirobe (13). The main source of error in isothermal calorimetry is due to vaporization-condensation effects. The Van Ness calorimeter contained no vapor space and therefore eliminated this error. Later, Winterhalter and Van Ness (101) modified their calorimeter so that exothermic heats of mixing could also be measured.

In the past 25 years there have been many articles reporting experimental heats of mixing data. There have also been articles which reported a discrepancy between two author's data. For example, Williamson and Scott's (43) data for the system ethanol + benzene at $45^{\circ}C$ differed from those of Brown and Fock (5) by 15 percent. After personal communication between the two groups, Brown and Fock took new measurements which were in close agreement with Williamson's data.

Due to this problem, how does the investigator who is going to use the data know whether it is accurate? There are several things one can look for. In many articles the authors first give data on a test mixture. They then compare their experimental results with other data on the same system, if the comparison is favorable the author assumes his calorimeter and expertise are good. The author then gives new, previously unpublished results on other mixtures. One example of this procedure is an article by Murakami and Fujishiro (78). First, they reported data for benzene + carbon tetrachloride at 25°C which were within a few percent of the generally accepted data. Then they gave new data for n-butanol with other polar liquids. This approach seems reasonable.

According to McGlashan (21), a test mixture should meet the following criteria:

a) a large difference in density between the two components;
b) the liquids should be easily purified;
c) if a vapor space is present the liquids should be chosen (i.e. have very different vapor pressures) so that the errors are at least as large as those which would occur with the mixture to be studied;
d) the heats of mixing should be of the same magnitude as the mixture that will be used; and
e) the test mixture should have been studied by several researchers.

Two popular test mixtures are benzene + carbon tetrachloride and cyclohexane + n-hexane. Some researchers prefer the first pair because of the large difference in density between the two liquids (specific gravity of benzene = 0.879, specific gravity of carbon tetrachloride = 1.595). Due to the significant difference in density it is hard to mix them completely. Therefore, a calorimeter can be used with confidence if accurate results are measured for this system. The maximum experimental heat of mixing for this system at $25^{o}C$ is about 115 J/mole. Despite this argument for the first binary, cyclohexane + n-hexane at $25^{o}C$ is probably the system whose heats of mixing are best known. For example, in the 1969 volume of the _Journal of Chemical Thermodynamics_ there are four articles that report data on this mixture. The maximum experimental heat of mixing for this system is about 220 J/mole.

Some authors do not check their calorimeter with a standard mixture. Instead, they duplicate a system at one temperature already in the literature and then report experimental results on the same mixture at another temperature. For example, Ramalho and Ruel (92) published the heats of mixing of 23 binary alcohol/alkane systems most of which had been previously unreported.

Finally, some researchers develop a reputation for recording good data. A few people in this category include: J.-P.E. Grolier in France, H.C. Van Ness in the United States, R.S. Ramalho and M. Ruel in Canada, and G.C. Benson, also in Canada.

II. PREVIOUS WORK

There have been many papers published on heats of mixing, some have given experimental data and some have presented a new method to correlate and/or predict heats of mixing. This section will discuss some of the methods which have been used to correlate and predict heats of mixing. It will be divided into three parts: Early work, meaning the 1950's and 60's, recent work, and group contribution methods.

A. Early Work

The following equation based on Tsao and Smith (42)

$$G^E = x_1x_2\left[B_0 + B_1(x_1-x_2) + B_2(x_1-x_2)^2 + \ldots\right] \qquad (1)$$

was found to be successful in calculating the excess Gibbs free energy. Therefore, early researchers used a similar expression for the correlation of heats of mixing:

$$\Delta H^M = x_1x_2\left[A_0 + A_1(x_1-x_2) + A_2(x_1-x_2)^2 + \ldots\right] \qquad (2)$$

Tsao and Smith (42) correlated endothermic, exothermic and endoexothermic systems using equation (2). They needed only two constants to correlate the experimental data accurately. Williamson and Scott (43) correlated alcohol + benzene mixtures using the formula

$$\Delta H^M = x_1x_2\left[A_0 + A_1(1-2x_1) + A_2(1-2x_1)^2 + \ldots\right] \qquad (3)$$

However, four constants were needed to adequately represent the data.

Power series equations were also used to predict ternary heats of mixing. For example, equation (4) was developed by Scatchard and co-workers (35) but first proposed by Redlich and Kister (34). For n-constant binary equations the ternary heats of mixing are:

$$\begin{aligned}\Delta H^M = {} & x_1x_2\left[A_{0_{12}} + A_{1_{12}}(x_1-x_2) + \ldots + A_{n_{12}}(x_1-x_2)^n\right] \\ & + x_1x_3\left[A_{0_{13}} + A_{1_{13}}(x_1-x_3) + \ldots + A_{n_{13}}(x_1-x_3)^n\right] \\ & + x_2x_3\left[A_{0_{23}} + A_{1_{23}}(x_2-x_3) + \ldots + A_{n_{23}}(x_2-x_3)^n\right]\end{aligned} \tag{4}$$

This equation successfully predicted the mixture carbon tetrachloride + benzene + cyclohexane but was unsatisfactory when cyclohexane was replaced by methanol. However, if the terms (x_1-x_2) and (x_1-x_3) in equation (4) were arbitrarily replaced by $(2x_1-1)$ then the methanol mixture was accurately predicted. Equation (5) is the result:

$$\begin{aligned}\Delta H^M = {} & x_1x_2\left[A_{0_{12}} + A_{1_{12}}(2x_1-1) + \ldots + A_{n_{12}}(2x_1-1)^n\right] \\ & + x_1x_3\left[A_{0_{13}} + A_{1_{13}}(2x_1-1) + \ldots + A_{n_{13}}(2x_1-1)^n\right] \\ & + x_2x_3\left[A_{0_{23}} + A_{1_{23}}(x_2-x_3) + \ldots + A_{n_{23}}(x_2-x_3)^n\right]\end{aligned} \tag{5}$$

For this specific case component 1 is methanol, in general component 1 is the polar compound. The parameters in equations (1) through (5) are a function of temperature.

Schnaible, Van Ness and Smith (36) presented experimental data for binary and ternary systems and evaluated different methods to predict heats of mixing. They concluded that the prediction of heats of mixing from pure component data only was inadequate. For example, in the regular-solution theory the interaction energy density c_{12} equals

$$c_{12} = (c_{11}c_{22})^n \tag{6}$$

where c_{11} and c_{22} are the cohesive energy densities of the pure components. It was found that just a slight change in the exponent n caused a significant change in the heats of mixing. They also studied equations (4) and (5) for the prediction of heats of mixing and concluded that equation (4) was satisfactory for nonpolar systems while equation (5) was good for polar and nonpolar mixtures.

Goates, Sullivan and Ott (11) studied the effect of mole fraction and temperature on the heats of mixing. They measured the heats of mixing of the binary mixtures that can be developed from benzene, cyclohexane and carbon tetrachloride at several temperatures from 10° to $40^{\circ}C$. All three binaries were successfully correlated and the expression for the cyclohexane + benzene binary was

$$\Delta H^M = x_1x_2\left[3105.0 - 7.98T - (1303.0 - 4.37T)(x_1-x_2) + (1738.0 - 5.486T)(x_1-x_2)^2\right] \tag{7}$$

As can be seen, a lot of the research done in the 1950's and early 60's was for the correlation of experimental data with empirical equations. However, some authors tried other methods, for example, Goates, Snow and James (10) used the quasi-lattice theory to correlate and predict the heats of mixing of alcohol-hydrocarbon systems. They studied three binaries: cyclohexane + ethanol, benzene + methanol and benzene + ethanol. The lattice theory assumes that the liquid has solid-like characteristics, that is, the molecules remain in a regular array in space. For the quasi-lattice theory the number and type of contact points for each molecule and the interaction energies for all combination of contact points are needed. The coefficients needed were obtained from the first two binaries and used to predict the benzene + ethanol mixture. There was a fairly good agreement between the experimental data and the calculated results.

B. Recent Work

The heats of mixing are related to the excess Gibbs free energy by the Gibbs-Helmholtz equation

$$\left[\frac{\partial G^E}{\partial T}\right]_{P,x} = \frac{-\Delta H^M}{T^2} \qquad (8)$$

In the past decade much of the research has been concentrated in the use of this relationship. Investigators have tried to predict VLE data from heats of mixing data, or vice versa. One example of the calculation of binary vapor-liquid equilibrium data from heats of mixing is the paper by Hanks, Gupta and Christensen (12). The authors used two semi-theoretical equations: the Wilson and NRTL equations. The method consisted of evaluating the parameters in the equation from heats of mixing data and then calculating the phase equilibrium data using pure component vapor pressures. The authors studied six mixtures (with their maximum heats of mixing value given in parenthesis): carbon tetrachloride + acetone, 45°C (318 J/mole); benzene + acetone, 45°C (165 J/mole); toluene + acetonitrile, 45°C (500 J/mole); toluene + acetone, 45°C (250 J/mole); toluene + nitroethane, 45°C (350 J/mole); and cyclopentane + tetrachloroethylene, 25°C (230 J/mole). The Wilson equation gave a satisfactory fit of the heats of mixing data for only two systems: carbon tetrachloride + acetone and benzene + acetone. The NRTL equation was used to correlate the other four systems. In general, there was very good agreement between the experimental and predicted VLE data. Even the azeotrope for the toluene + nitroethane system was predicted. (Experimental mole fraction of toluene is 0.71 versus the predicted value of 0.70). Two sets of parameters were found for the toluene + acetonitrile system. The parameters with the lower correlation error for the heats of mixing data also gave a lower prediction error for the VLE data. The authors concluded that their method of obtaining experimental heats of mixing data and then predicting the x-y data is easier then the actual measurement of VLE data. The authors said they chose six "highly nonideal" systems but the maximum heats of mixing was only 500 J/mole.

Nicolaides and Eckert (28) also studied this problem. They wanted to test the ability of several analytical expressions to correlate and predict different types of data (limiting activity coefficients, VLE, heats of mixing and liquid-liquid equilibrium). They also wanted to determine what was the minimum amount of data needed to predict the various types of data. The four expressions studied were the Van Laar, Wilson, UNIQUAC and Zeta equations. The author's results were as follows:

a) The local composition equations gave better VLE correlation than the Van Laar equation. However, the improvement was not as great as might be expected.
b) The two more recent local composition equations, UNIQUAC and Zeta, did not give any significant improvement over the Wilson equation in the correlation of VLE and ΔH^M

data. The Van Laar equation could not be used for heats of mixing prediction because it contains no temperature dependent term.

c) Parameters obtained from VLE data and used to predict ΔH^M data gave poor results, the reverse - the prediction of VLE data from ΔH^M data gave even poorer results. This is the opposite conclusion that was reached by Hanks et al. The systems used were benzene + cyclohexane, acetone + ethanol and acetonitrile + benzene.

d) Parameters obtained from limiting activity coefficients gave very good predictions of VLE data but poor results for heats of mixing.

e) Increasing the number of parameters from two to four by assuming a linear temperature dependence for the parameters was done for the three local composition equations. The prediction of heats of mixing from VLE data improved slightly for most systems. However, the results for VLE prediction from ΔH^M data did not improve.

f) Determining parameters from liquid-liquid equilibria and then predicting x-y data gave fair results. The results for heats of mixing prediction were poor.

The authors concluded that limiting activity coefficients could replace classical VLE measurements. However, heats of mixing data and liquid-liquid equilibria would have to be measured directly. No equation was capable of cross-predicting ΔH^M or LLE data from VLE data. In fact, the choice of equation was not critical, the only improvement of the more recent local composition equations over the Wilson equation was their ability to represent liquid phase separation.

Nagata and Yamada (22) did a study similar to Nicolaides and Eckert (28) and obtained similar results. Their results and conclusions are as follows:

a) For their calculations they used the Wilson, Heil and NRTL equations with parameters that varied linearly with temperature.

b) Heats of mixing were calculated from parameters correlated from VLE data. The authors presented results for two typical systems: methanol + benzene at 35°C and acetone + chloroform at 25°C. The maximum experimental heat of mixing for methanol + benzene is +825 J/mole, for acetone + chloroform the maximum value is -1900 J/mole. The results were fair to poor with no equation predicting the heats of mixing better than the other two. The absolute deviation ranged from 50 J/mole to 825 J/mole.

c) Excess Gibbs free energy was predicted from parameters correlated from heats of mixing data. Poor results were obtained, with typical predictions being less then half the experimental value. The authors stated that the method of Hanks et al (12) should be limited to special cases, i.e. where the heats of mixing are low.

d) The simultaneous correlation of G^E and ΔH^M data was very good for all 3 equations.

e) Ternary heats of mixing were successfully predicted from parameters regressed from binary data. Again the choice of equation did not affect the results.

Liu, Weber and Tao (20) predicted ternary heats of mixing from the simultaneous correlation of binary vapor-liquid equilibrium and heats of mixing data. The authors predicted two ternary systems: acetone + chloroform + methanol at 50°C and chloroform + ethanol + n-heptane at 50°C. In both cases the predicted and experimental values compared favorably.

From these four articles the following conclusions can be reached:

a) The cross-prediction of VLE and ΔH^M data is dubious at best. Only Hanks et al (12) have successfully predicted heats of mixing from vapor-liquid equilibrium data. One article was discussed here but they have presented many more in _Thermochimica Acta_ and _Industrial and Engineering Chemistry_ on the same topic.

b) For the correlation of the data all the local composition equations performed equally well. The advantage of the more recent equations over the Wilson equation is their ability to predict partial miscibility.

c) Although these equations correlated the binary data well and adequately predicted ternary heats of mixing, experimental data were needed for each system to obtain the parameters. This points out the advantage of group contribution methods - only a limited amount of experimental data are needed. Past work on group contribution methods will be discussed in the next section.

C. Group Contribution Methods

Langmuir (16) first proposed the group contribution method in 1925. However, no serious work was done until 1959 when Derr et al (30,33) developed their group contribution model. Some work had been done between 1925 and 1959, see for example Tompa (41), but nothing of significance. Like the models that were developed later, Derr et al assumed that the interaction energy of two molecules could be approximated by the sum of the contributions of the interacting groups. This group contribution was dependent on the group concentrations and two group parameters: interaction coefficient and cross section. The interaction coefficient was due to the interaction between the functional groups in the solution, while the cross section was associated with the size of the groups. Redlich, Derr and Pierotti (33) presented the model. Papadopoulos and Derr (30) predicted the heats of mixing of paraffin and aromatic binaries, and obtained satisfactory results.

Derr's method was extended by Chao et al (6) to include polar substances. They predicted several alcohol + alkane mixtures with best results for high alcohol concentrations for mixtures of higher molecular weight components. Ramalho et al (31) later predicted ketone-ketone systems.

In 1972 Lee, Greenkorn and Chao (17,18,19) developed a group contribution method based on both the cell theory and the quasichemical lattice theory. They have predicted the heats of mixing of alkane/alkane, alcohol/alkane and ketone/alkane systems. Their method can also be used to predict other properties including heat of vaporization and density. However, their model has not gained much use.

UNIFAC (UNIQUAC Functional-group activity coefficients) was developed by Fredenslund et al (9) at Berkeley in 1975. UNIFAC was an extension of UNIQUAC which had also been developed at Berkeley by Abrams and Prausnitz (1). The Fredenslund article presented temperature independent interaction parameters for the prediction of activity coefficients for binary and multicomponent mixtures. Parameters were given for mixtures containing water, hydrocarbons, alcohols, chlorides, nitriles, ketones, amines and other liquids in the temperature range 275° to $400^{\circ}K$. Fredenslund et al (8) later attempted to predict heats of mixing using parameters obtained from VLE data. However, typical results differed from the experimental values by a factor of two.

Nagata and Ohta (23) used the UNIFAC method to predict the heats of mixing of binary systems of alkanes with n-alcohols, ketones, esters and ethers, and ternary n-alcohol + n-alcohol + n-alkane systems. For all cases the prediction error was less than 20 percent, however, only the alcohol data was predicted at more than one temperature. Also, six temperature-independent coefficients were needed to represent the alcohol/alkane interaction:

$$\Psi(CH_2,COH) = 81.35EXP\left[\frac{-2424}{T}\right] + 0.157 \qquad (9)$$

$$\Psi(COH,CH_2) = 330.9EXP\left[\frac{-1682}{T}\right] + 190 \qquad (10)$$

The prediction errors for n-alcohol + branched alkane systems were larger than those for n-alcohol + n-alkane mixtures, also the ethanol systems had larger errors than the other n-alcohols.

Skjold-Jorgensen et al (39) revised and extended the UNIFAC method for the prediction of vapor-liquid equilibria. New and improved parameters were presented based on new data which had become available. The only change of consequence for the prediction of heats of mixing was the new definition of the alcohol group. Previously, the main alcohol group had been defined as CCOH, with different subgroups (CH_2CH_2OH, $CHCH_2OH$, etc). In this work, the alcohol group was redefined as a group containing OH only, but methanol was still kept as a separate group. Unfortunately, the new group cannot distinguish between primary, secondary and tertiary alcohols.

Recently, Skjold-Jorgensen et al (40) modified the UNIFAC and UNIQUAC models by introducing a general temperature dependence for the interaction parameters. The modified model still required two parameters per binary group, the same as the original model. The generalized formula was developed through the simultaneous correlation of vapor liquid equilibrium and heats of mixing data. It was obtained, however, from only a limited number of systems with non-associating components. They obtained very good predictions of x-y data from parameters correlated from heats of mixing data and fair results when they attempted the reverse, prediction of heats of mixing from VLE data. The systems predicted contained the five components: alkanes, alkenes, benzene, toluene and ethers.

The researchers who have dealt with group contribution models the most extensively are Ratcliff and his co-workers at McGill University in Canada. Ratcliff and Chao (32) first presented a Group Solution Model in 1969 for the prediction of vapor-liquid equilibrium, but indicated that the model could be applied to other thermodynamic properties. Like the model of Derr et al, their group model was composed of two independent parts: the skeletal contribution and the energetic interactions between the functional groups in the solution. The skeletal contribution accounts for the differences in size of the molecules but not molecular shape. The Bronsted-Koefoed (4) congruence principle was used to describe this effect.

The group contribution effect is described by the equation

$$\log \gamma_i^G = \sum_k N_{ki} (\log \Gamma_k - \log \Gamma_k^*) \qquad (11)$$

where N_{ki} is the number of groups of type k in component i, Γ_k is the activity coefficient of group k and Γ_k^* is the activity coefficient of group k at standard state. Equation (11) was correlated with experimental data to determine a number for log Γ for each group k.

The model was first checked to see how well it correlated vapor-liquid equilibrium data for 3 systems at 40°C: ethanol + iso-octane, ethanol + n-heptane, and methanol + water; and 3 systems at 90°C: n-propanol + water, n-propanol + n-decane and iso-propanol + n-decane. For all six systems the correlated results compared favorably with the experimental data. The authors then predicted four multicomponent systems at 40°C: methanol + ethanol + water, methanol + ethanol + n-hexane + n-heptane, ethanol + n-hexane + iso-octane and methanol + ethanol + n-hexane + n-heptane + water. The predicted results compared reasonably well with the experimental values.

In 1971 Nguyen and Ratcliff (24) applied this Group Solution Model to heats of mixing. The equation for heats of mixing followed the same format as for activity coefficients

$$\Delta H^M = \Delta H^G + \Delta H^S \tag{12}$$

where ΔH^G represents the heats of mixing due to group interactions and ΔH^S is the skeletal contribution to the heats of mixing. The skeletal contribution was obtained from the heats of mixing of n-alkanes. In most cases this number was negligible, for example, for n-butanol + n-hexane at 25°C the binary n-pentane + n-hexane was used to compute the skeletal contribution, but the heats of mixing were only 1-2 J/mole. ΔH^G was found in the same manner as log γ^G. The authors predicted two alcohol/alkane ternary systems at 25°C: n-octane + n-propanol + n-octanol and n-heptane + n-propanol + n-pentanol. There was good agreement between the calculated and experimental values.

In the same year Nguyen and Ratcliff (25) predicted the heats of mixing of ketone + alkane systems using their Group Solution Model. This time they neglected the skeletal contribution but the prediction error only increased by 1 percent. Ketones were regarded as consisting of carbonyl and methylene groups. The group excess enthalpies were computed from the experimental data for the acetone + n-hexane system at 25°C. They then predicted 10 ketone + n-alkane and ketone + ketone binaries with an average error of 15.7 percent. This error is somewhat high but the heat of mixing for ketone + ketone systems is low (on the order of 100 J/mole).

In 1974 Nguyen and Ratcliff (26) presented the Analytical Group Solution Model (AGSM) for the prediction of heats of mixing. The heat of mixing due to the interactions between the groups was calculated from an analytical expression, namely the Wilson equation. They did not include a skeletal contribution because they felt it was unimportant. In this paper they dealt with alcohol/alkane systems. Five parameters were needed to represent the data adequately:

$$a\ OH/CH_2 = 34.95 EXP \left[\frac{-2908}{T}\right] \tag{13}$$

$$a\ CH_2/OH = 26.69 EXP \left[\frac{-1336}{T}\right] + 7.705 \tag{14}$$

The alcohol/alkane data were predicted in the temperature range 15° to 55°C. Most of the prediction errors were less than 10 percent, except for the ethanol systems where higher errors were found.

In 1975 Nguyen and Ratcliff (27) studied the heats of mixing of alcohols with branched alkanes, the systems studied were pentanol and isopentanol with hexane isomers. For the systems predicted they found no effect on the prediction error due to the branched alkanes.

In 1978 Lai et al (15) extended the model to include liquid mixtures containing alkanes, chloroalkanes and alcohols. They also decided to use a general temperature dependency for the interaction parameters:

$$a_{jk} = EXP\left[A_{jk} + \frac{B_{jk}}{T}\right] \tag{15}$$

Therefore, they had to calculate new parameters for alcohols with alkanes since a (CH_2/OH) from the previous article did not follow this format. They calculated new OH/CH_2 parameters using data from 7 systems including 4 at 15°C, 2 at 30°C and 1 at 45°C. The average Root Mean Square Deviation (RMSD) was 7.4 percent. They also calculated Cl/CH_2 interaction parameters using 7 systems (2 at 15°C, 3 at 25°C, 2 at $35^{o}C$). The average RMSD was 3.2 percent. Using these parameters they were able to calculate Cl/OH parameters. Again they used 7 systems and the average RMSD was 4.8 percent. The temperatures used: 2 at $15^{o}C$, 3 at $25^{o}C$ and 2 at $35^{o}C$. They also predicted two types of ternary systems: with CH_2 and OH groups and CH_2, OH and Cl groups. For these predictions the average RMSD was 8.5 percent.

In a later paper Doan-Nguyen et al (7) evaluated interaction parameters for additional groups presented in Table I.

In 1979 Siman and Vera (38) reevaluated their CH_2/OH interaction parameters. The parameters were obtained by simultaneously fitting G^E and ΔH^M data. Overall, the prediction error for alcohol/alkane systems increased. In the same paper they reported the heats of mixing for alcohol + amine systems, which are exothermic (negative). The AGSM model correlated and predicted these systems well except for those containing methanol.

The work reported here is divided into two phases. The first phase was the evaluation of the AGSM, UNIFAC and modified UNIFAC models on the basis of their ability to correlate and predict the enthalpies of mixing of a selected set of binary systems. The second phase involved the generation of interaction parameters for all the possible combination of groups for which data is available using the best model. These parameters could then be used for the prediction of mixtures for which no experimental data exists.

Most of the work in the first phase was done by Ojini (29), but some contribution was made by the author. This thesis will deal mostly with the modified UNIFAC approach and include the regression for parameters of several active groups with alkanes.

III. GROUP CONTRIBUTION METHODS

The group contribution methods mentioned in the previous sections have used different equations to calculate the heats of mixing but the basic idea for all of them has been the same. Most have assumed that the heats of mixing are due to two contributions: the first part is due to the differences in size and shape of the molecules and the second part accounts for the energetic interactions between the molecules. However, for heats of mixing the second part is more important.

The second contribution, the molecular interactions, is calculated by using group interaction parameters. An example would best illustrate the use of group parameters. The mixture n-pentanol + 1-chlorobutane contains the groups CH_2, OH and Cl (where the interactions for the groups CH_2 and CH_3 are considered the same). In order to predict this mixture the following interactions are considered: CH_2/OH, CH_2/Cl and OH/Cl. As mentioned in the Introduction, OH/CH_2 parameters could be found from the binary n-butanol + n-heptane. The Cl/CH_2 parameters could be correlated from 1-chlorobutane + n-hexane data. Both of these sets of parameters are primary parameters since they are obtained from mixtures containing only two groups. The OH/Cl parameters are secondary parameters. Secondary parameters are parameters obtained from mixtures containing three groups and using the appropriate primary parameters. In this case, Cl/OH parameters could be generated from n-octanol + 1-chlorohexane data. Finally, the system n-pentanol + 1-chlorobutane could be predicted.

A. The Analytical Group Solution Model (AGSM)

The basic equations of the AGSM model as developed by Ratcliff and co-workers (26) are included here. The AGSM method assumes that the contribution of each compound in the mixture is accounted for by summing the contribution of each group that makes up the chemical compound. Therefore, the partial molar excess enthalpy of component i is given by

$$\overline{\Delta H_i} = \sum_k N_{ki}(H_k - H_{ki}^*) \tag{16}$$

where N_{ki} is the number of groups of type k in component i, H_k is the excess enthalpy of group k and H_{ki}^* is the standard state enthalpy of group k in pure component i. It follows that the heat of mixing is

$$\Delta H^M = \sum_i x_i \overline{\Delta H_i} \tag{17}$$

where x_i is the mole fraction of component i. The group excess enthalpy H_k is found from the Wilson equation

$$\frac{H_k}{RT^2} = \frac{\sum_j X_j b_{kj}}{\sum_j X_j a_{kj}} + \sum_j \frac{X_j b_{jk}}{\sum_m X_m a_{jm}} - \sum_j \left[\frac{X_j a_{jk}}{(\sum_m X_m a_{jm})^2} \sum_m X_m b_{jm} \right] \tag{18}$$

where X_k is the group fraction of group k in the mixture and defined as

$$X_k = \frac{\sum_i x_i N_{ki}}{\sum_k \sum_i x_i N_{ki}} \tag{19}$$

H_{ki}^{*} is also calculated from equation (18) using the group fraction of group k in pure component i, instead of the group fraction of group k in the mixture. The temperature dependent group parameters a_{jk} and b_{jk} are related by

$$b_{jk} = \frac{d}{dT}\left[a_{jk}\right] \qquad (20)$$

Ratcliff and co-workers adopted the following expressions for their group parameters

$$a_{jk} = \mathrm{EXP}\left[A_{jk} + \frac{B_{jk}}{T}\right] \qquad (21)$$

$$b_{jk} = \mathrm{EXP}\left[A_{jk} + \frac{B_{jk}}{T}\right]\left[\frac{-B_{jk}}{T}\right] \qquad (22)$$

where A_{jk} and B_{jk} are temperature independent coefficients. Once these coefficients are correlated from experimental data they can be used to predict other mixtures containing the same groups.

The AGSM model does not include a factor which takes into account the size and shape of the group. Consider for example the case of n-hexane and 2,2 dimethylbutane. The AGSM model does not differentiate between them, since it only considers the total number of groups present. Ratcliff and co-workers have published several articles reporting results which show there is no need to distinguish between specific groups, i.e. CH, CH_2, CH_3 etc. For example, Lai et al (15) predicted chloro/alkane mixtures with good results. Two binaries they predicted were n-hexane with 1- and with 2-chlorobutane at 25°C. The AGSM model predicts the same heats of mixing for both mixtures since it does not distinguish between what carbon atom the Cl group is bonded with. Since the heats of mixing for both systems are similar the prediction error is low. On the other hand, Ratcliff and co-workers have never predicted secondary and tertiary alcohols. However, the difference in heats of mixing of n-heptane with 1- and with 2-propanol is about 20 percent. In this case the AGSM model fails to predict the 2-propanol system accurately.

B. The UNIFAC Method

The prediction of vapor-liquid equilibrium by the UNIFAC method was presented by Fredenslund et al (9) in 1975. The UNIFAC model separates the activity coefficient into two parts: the first part accounts for the difference in size of the molecules while the second part represents energetic interactions. However, when the expression for the heats of mixing is determined using the Gibbs-Helmholtz relationship (equation (8)), the first part does not appear since it is not a function of temperature. Therefore, the UNIFAC model reduces to the same format as the AGSM except that the expression for the group excess enthalpy H_k is different. The equation for H_k is:

$$\frac{H_k}{RT^2} = -Q_k \left[\frac{-\sum_m \Theta_m \Psi'_{mk}}{\sum_m \Theta_m \Psi_{mk}} - \sum_m \left[\frac{\Theta_m \Psi'_{km}}{\sum_n \Theta_n \Psi_{nm}} - \frac{\Theta_m \Psi_{km} (\sum_n \Theta_n \Psi'_{nm})}{(\sum_n \Theta_n \Psi_{nm})^2} \right] \right] \qquad (23)$$

where

Q_k: area parameter for group k

Θ_m: area fraction of group m

$$\Theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \qquad (24)$$

$$\Psi_{mn} = \text{EXP} - \left[\frac{U_{mn} - U_{nn}}{RT} \right] = \text{EXP} - \left[\frac{a_{mn}}{T} \right] \qquad (25)$$

$$\Psi'_{mn} = \frac{d}{dT} \Psi_{mn} \qquad (26)$$

U_{mn}: measure of the energy of interaction between groups m and n

a_{mn}: group-interaction parameter

Once the group interaction parameters are evaluated from experimental data they can be used to predict other mixtures containing the same groups.

Skjold-Jorgensen et al (40) modified the UNIFAC model by introducing a generalized temperature dependency for the interaction parameters. They suggest that the parameter ψ_{mn} can be written as:

$$\psi_{mn} = \text{EXP} - \left[\frac{Za'_{mn}}{2T} \right] \tag{27}$$

where Z is the lattice coordination number which in the original UNIFAC was a constant equal to 10. Therefore, the group-interaction parameter reduced to

$$a_{mn} = \frac{Za'_{mn}}{2} \tag{28}$$

The authors proposed, however, to make Z a function of temperature:

$$Z\ (T) = 35.2 - 0.1272T + 0.00014T^2 \tag{29}$$

The numerical constants were obtained by the simultaneous fit of vapor-liquid equilibrium data for six binaries and heats of mixing data for three binaries. The systems involved were hydrocarbons and ethers, while the temperature range was 25° to 129°C.

One difference in the two expressions for H_k is that the UNIFAC model includes the group area parameter, Q_k, which takes into account the size of the group. The area parameter is obtained from Van der Waals surface areas as given by Bondi (3). As mentioned before, for the AGSM model 2,2 dimethylbutane would consist of 6 CH_2 groups, no distinction would be made between CH_3, CH_2 and C groups. However, for the UNIFAC model 2,2 dimethylbutane would be 1 C, 1 CH_2 and 4 CH_3 groups. The interaction parameters for the three groups would be the same but the area parameter would be different for each group. The group area parameter appears in the equation for H_k not only as Q_k (in front of the bracket in equation (23) but also through Θ_k, which in essence replaces the group fraction of the AGSM model. Table II includes the Q values used in this study.

IV. RESULTS AND DISCUSSION

The Results and Discussion section is divided into four parts: preliminary calculations, evaluation of the models, regression of the data and final parameters. The total work for the heats of mixing project was done by three people: Hetzel (thesis to be completed in October 1982), Ojini (29), and the author. Data or results developed by one person often were necessary to the work of another. While most of the work reported in this thesis was done by the author, some of the preliminary work was shared by all three.

A. Preliminary Calculations

One of the first decisions that had to be made was which group contribution model should be used - AGSM or UNIFAC. Ratcliff and co-workers had published interaction parameters in several papers so it was decided to predict different types of systems using their parameters. Tables III and IV give the results of this analysis. Table III gives predictions for alcohol/alkane systems. The table shows that parameters regressed from heats of mixing data only give better predictions than parameters simultaneously regressed from heats of mixing and vapor-liquid equilibrium data. However, for n-butanol and higher alcohols the results are similar. Table IV presents prediction results for binary systems not containing an alcohol. All the prediction errors are low with only the two benzene + alkane systems at 50°C greater than 15 percent. However, as seen from Table I the benzene/alkane parameters were correlated from 3 systems at 25°C, this would account for the higher prediction errors at 50°C.

For the UNIFAC model no interaction parameters were available which had been obtained from heats of mixing data. Parameters reported in the literature were correlated from vapor-liquid equilibrium data. Ojini (29) had determined that these parameters were inadequate for heats of mixing prediction.

One problem that developed early was the effect of temperature on heats of mixing and the interaction parameters. It was found that the heats of mixing of some systems increased as the temperature increased, for example, alcohols + alkanes and nitroalkanes + alkanes. But for most systems the heats of mixing decreased as the temperature increased. Also, as seen from the AGSM results with benzene + alkanes (Table IV) the experimental data used to correlate the parameters had a significant effect. This can be further seen from Table V which gives the results for the correlation and prediction of n-propanol + n-heptane data using the UNIFAC model. Table V shows that if only n-propanol + n-heptane at 30°C is used to find the parameters the correlation error is 0.9 percent. Using these parameters to predict the same system at 45°C gives a prediction error of 15.6 percent. However, if the data at both temperatures are used to find the parameters the correlation error is 6.7 percent. Therefore, when parameters are obtained it would be best to include data at as many temperatures as possible. The correlation error would be higher but the overall error would be lower.

One advantage of UNIFAC over AGSM is the ability to distinguish between isomers (through the use of the group area parameter Q). Some work was done in this area to see if the UNIFAC was also able to predict heats of mixing for isomers accurately. The alcohols were chosen as the test group and the parameters used were those obtained from n-propanol + n-heptane at 30°C. The groups for n-propanol are 1 CH_2CH_2OH (Q=1.664) and 1 CH_3. Two secondary alcohol + alkane systems were predicted: 2-propanol + n-heptane at 45°C and 2-butanol + n-hexane at 25°C. The groups for 2-propanol are 1 $CHOHCH_3$ (Q=1.660) and 1 CH_3 and for 2-butanol are 1 $CHOHCH_3$, 1 CH_2 and 1 CH_3. The prediction of the heats of mixing of these two systems was poor. The poor results were due to the small difference in Q values between primary and secondary alcohols. Because of the slight difference (Δ = 0.004) in Q, nearly the same heats of mixing was calculated for n-propanol + n-heptane and 2-propanol + n-heptane. However, the heats of mixing of 2-propanol + n-heptane are about 20 percent higher than for n-propanol + n-heptane. A new Q for secondary alcohols was sought using the same parameters. The lowest average error for the two systems was 17.1 percent for Q = 3.5. However, more extensive work would have to be done before changing a Q value. In addition, such a drastic change in Q, from 1.660 to 3.5 cannot be justified. For, once a Q is changed, it would have to be good for all systems, not just alcohol + alkane systems. Though this work was sketchy it did show that predicting isomers later might be difficult.

From the initial calculations the following observations can be made:

a) both the AGSM and UNIFAC models gave low prediction errors ($<$20 percent) for most systems,

b) correlating VLE and ΔH^M data simultaneously gave high errors,

c) both the AGSM and UNIFAC had difficulty predicting isomers, and

d) the temperature dependency of the parameters was an important factor to consider.

In order to choose the appropriate model the three workers on the heats of mixing project developed the Grand Plot.

B. Evaluation of the Models

Since the preliminary calculations were not conclusive enough to choose between the two models, the Grand Plot criteria was developed by the three workers on the heats of mixing project. The Grand Plot was developed to answer two questions:

a) Which model should be used: AGSM or UNIFAC?

b) What form of temperature dependency of the interaction parameters was best?

The Grand Plot relates the temperature exponent β to S_c, the average cumulative prediction error. The Grand Plot included the following:

a) A general temperature dependency expression for the interaction parameters was assumed. For example, for the UNIFAC model the group parameter equals:

$$\psi_{mn} = \text{EXP} - \left[\frac{a_{mn}}{T} \right] \qquad (25)$$

where a_{mn} is the temperature independent parameter. Now a_{mn} would also become a function of temperature by assuming:

$$\psi_{mn} = \text{EXP} - \left[\frac{A_{mn}T^{\beta} + B_{mn}}{T} \right] \qquad (30)$$

A similar expression was used for the AGSM model

$$a_{kj} = \text{EXP} \left[\frac{C_{kj}T^{\beta} + D_{kj}}{T} \right] \qquad (31)$$

Where the coefficients A_{mn}, B_{mn}, C_{kj} and D_{kj} are temperature independent. The value of β, for each model, is determined from the correlation and prediction of heats of mixing data for a selected set of binary systems.

It should be noticed that the temperature dependency of the interaction parameters given by equations (30) and (31) is not the only one possible. For example, Nguyen and Ratcliff (26) used a total of five parameters for the OH/CH_2 interactions with the AGSM model. Later, Lai et al (15) revised these parameters so that only four were necessary. Similarly, Nagata and Ohta (23) used six parameters for the same interactions with the UNIFAC model. Considering the large number of experimental data for n-alcohols/n-alkanes their approach is justified. However, the purpose of the present study is to develop a temperature dependency expression applicable for all group pairs, including several cases where only limited data are available. For this reason a four-parameter expression was sought.

b) The binary systems were classified into two types:

Type I: Heats of mixing increase as temperature increases,

Type II: Heats of mixing decrease as temperature increases.

Preliminary calculations showed that positive exponents

(β) favored Type I systems, while Type II systems did better with negative exponents (β). To obtain an optimum value for β two Type I and two Type II systems were selected as presented in Table VI. Experimental data for the four systems was available at two temperatures.

c) The heats of mixing data were correlated at the lower temperature using values of β from -2 to +2 in intervals of 0.5 excluding $\beta = 0$. For each β, a separate set of interaction parameters was found.

d) The heats of mixing were predicted at the higher temperature using the same value of β and the appropriate set of interaction parameters. In practical applications it is often desirable to extrapolate the heats of mixing data to higher temperatures.

e) The average cumulative prediction error S_c is defined as:

$$S_c = \frac{\sum_i S_j}{L} \qquad (32)$$

where L is the number of systems, and S_j is the average absolute percent error for system j:

$$S_j = \frac{\sum_i \left| \frac{\Delta H^M_{exp} - \Delta H^M_{calc}}{\Delta H^M_{exp}} \right|_i * 100}{V} \qquad (33)$$

where V is the total number of experimental points and the subscripts exp and calc indicate experimental and calculated respectively.

Table VII contains the regression results for UNIFAC and AGSM, while Table VIII gives the prediction results. (Ojini did all the regression and prediction results for UNIFAC, Hetzel did the AGSM regression and prediction for $\beta = +1.0, +0.5, -0.5$ and -1.0). The author did the AGSM regression and prediction for $\beta = +2.0, +1.5, -1.5$ and -2.0.

Three problems arose immediately even before a Grand Plot was made. The three problems were: (1) some prediction errors were very high, (2) for some exponents no parameters were obtained, and (3) for some exponents more than one set of parameters were found. Although three problems are mentioned here they are all due to the problem of multiplicity of roots. This problem will become more apparent when the final parameters are correlated.

For the AGSM predictions there were three systems with a very high error: benzene + n-octane $\beta = +2$, $\beta = -2$ and n-octanol + n-heptane $\beta = +1.5$. A check was made by predicting different systems. For the benzene + alkane systems the prediction error for systems at 25°C was less than 5 percent, but the errors for systems at 50°C were greater than 200 percent. Table IX contains the prediction results for n-octanol + n-heptane at different temperatures. The results seem strange with errors of up to 50,000 percent being indicated. Therefore, it was determined that since similar errors were found for other temperatures the results were correct.

The second problem in the AGSM regression was that the program did not converge and no parameters were found for nitroethane + 2,2-dimethylbutane at 30°C for $\beta = -1.5$. This brings up the question of what parameters should be chosen as initial values. Except for the nitro group Ratcliff and co-workers had reported parameters for the systems studied in the Grand Plot using a linear temperature dependence ($\beta = 1.0$). The initial parameters for the Grand Plot were obtained by prorating Ratcliff's parameters for each temperature dependency. Normally these starting values converged on a new set of parameters. If the program did not converge one of the parameters was changed and the program run again. This approach generally was successful but repeated attempts failed to give a final set of parameters for nitroethane + 2,2-dimethylbutane at 30°C.

Two sets of final parameters for the following systems and temperature dependencies were available: benzene + n-octane, $\beta = -1.5$ and n-octanol + n-heptane, $\beta = 1.5$. Table X presents the results for the two systems. The results for the benzene + alkane systems show that the prediction error at the higher temperature is nearly the same for both sets of parameters. For alcohol + alkane systems the parameters with the higher correlation error gave the lower prediction error. The reason for this is not clear.

Figures 1 and 2 are the Grand Plot for the UNIFAC and AGSM, respectively. From these two graphs and Tables VII and VIII it is noticed that the AGSM gave more erratic results than the UNIFAC. Figure 1, the UNIFAC Grand Plot, shows that β = 0.5 gives the best results with an average absolute error of 7.7 percent. Figure 2, the AGSM Grand Plot, shows the lowest cumulative error was 18 percent for β = -0.5. A closer look at Figure 1 shows that β = 1.0 is not on the smooth curve (11.5 percent) and might be expected to have a lower cumulative error than β = 0.5. Considering the problems with other temperature exponents it was decided to try and improve the error for β = 1.0 (linear temperature dependence) before making the final decision on which model and temperature exponent to use.

Attempts to improve β = 1.0 were unsuccessful. When looking at the percent error for the four systems for β = 1.0 the n-octanol + n-heptane system had the largest error (18.0 percent). Attempts were made to improve the percentage error for this system by using different starting values, but the prediction error did not change.

At this time it looked like β = 0.5 would have to be used with the UNIFAC. However, based on a pre-publication by Skjold-Jorgensen (40) on the Z(T), it was decided to give the modified UNIFAC with the Z(T) the same test as the AGSM and four parameter UNIFAC. Table XI gives the results for the four systems in the Grand Plot. The average cumulative error based on the set of parameters with the lowest correlation error was 5.0 percent. This error is less than that for the UNIFAC with β =0.5. Therefore, since the UNIFAC with Z(T) had the lowest prediction error on the Grand Plot it was decided to use the Z(T) for the future calculations. The Z(T) had the additional advantage in that only two interaction parameters were needed per group pair versus the four parameters that were used before.

A new expression for Z(T) was sought for two reasons: (1) Skjold-Jorgensen's Z(T) was correlated from both vapor liquid equilibrium and heats of mixing data but this study was only interested in the prediction of heats of mixing. It must be remembered, however, that Skjold-Jorgensen et al (40) obtained good predictions for both kinds of data. (2) The data base used to find the Z(T) expression included only alkanes, alkenes, benzene, toluene and ethers. Skjold-Jorgensen et al (40) stated that a special "chemical term" might be needed to predict associating systems. It should be noted that of the four systems predicted in the Grand Plot only the alcohol binary, an associated mixture, had an error greater than 10 percent. An expression for Z(T) was sought that would be applicable for all groups.

In the first attempt to find a new Z(T) only the alcohol binary was used in the data base. Table XII gives the new Z(T) and prediction and correlation results for three systems. The results with Skjold-Jorgensen's Z(T) are also included for comparison and, in most cases, did better. As mentioned before, the lattice coordination number (Z) was a constant set equal to 10 in the original UNIFAC. At 25^{o}C, Skjold-Jorgensen's Z(T) = 9.72 while the Z correlated from n-octanol + n-heptane at 30^{o}C is the unreasonable value of 22.15. Therefore, the first attempt at finding a new expression for Z was unsuccessful.

Finding a general expression for Z is a difficult process. When looking at equation (27) it is noticed that both Z and a'_{mn} are in the numerator, so in effect, the two parameters are estimated from the value of their product. To find a new expression for Z the plan was to include the four systems from the Grand Plot, which would mean regressing for 11 parameters (8 interaction parameters and 3 coefficients for Z). To get good results would be very difficult because of this relation between Z and a'_{mn}. Instead, it was decided to use Skjold-Jorgensens' equation for the final parameters because Skjold-Jorgensen et al (40) had predicted heats of mixing well.

C. Regression of the Data

Appendix I is a print out of a sample regression run and explains how to enter a computer run. Appendix II is the same except that it applies to a prediction run.

Due to the problem of multiplicity of roots, a system of common starting values had to be devised to ensure that the best set of parameters was obtained. A grid of starting values, covering the range +200 to -200 in intervals of 200 as shown in Table XIII was used. This points to a significant advantage of the modified UNIFAC model as compared to the original UNIFAC which needed four interaction parameters. To have the same kind of grid would have involved a very large chart of initial values. The upper value $a'_{mn} = 200$ was chosen because if a'_{mn} becomes too large then $\frac{d\psi}{dT}$ is very small and becomes inconsequential. An example of this will be given later. In the first UNIFAC article by Fredenslund, Jones and Prausnitz (9) they set an upper limit of 3000 for a_{mn} which corresponds to a'_{mn} of 617. For $a'_{mn} = 200$ the corresponding a_{mn} equals 972 and in their article over 80 percent of their reported parameters were less than 972. Therefore, a starting value for a'_{mn} of 200 seems reasonable.

The results for each type of system will be given in three tables:

1) The first table will give the initial and final parameters, FMIN and standard deviation. Also, the correlation

error will be given if the program converged on a set of parameters. The minimization function FMIN was defined as:

$$\mathrm{FMIN} = \frac{1}{V} \sum^{V} \left| \frac{\Delta H^M_{exp} - \Delta H^M_{calc}}{\Delta H^M_{exp}} \right|^2_i \qquad (34)$$

where V is the number of data points used in determining the interaction parameters.

2) The second table will give the correlation errors for each set of parameters. The average and maximum percent error for each binary will be given. The maximum percent error is given in order to see if the parameters correlated the mixture well over the entire range of mole fraction. A column is also included which gives the experimental heat of mixing at its maximum value and the corresponding predicted number. This column was given in order to demonstrate the size of the error. The systems chosen for the regression included data at different temperatures and with various solvents, if possible.

3) The third table is the prediction results for the systems not included in the regression data base. Each system was predicted with each set of parameters. The column marked with an asterisk is the percent error for the set chosen as the final parameters. To demonstrate the size of the error, the maximum error $\Delta H^M_{max} = \left| \Delta H^M_{exp} - \Delta H^M_{calc} \right|$ is also given for each system.

D. Final Parameters

The final part of this thesis was to find interaction parameters for the following groups with CH_2:

1) benzene
2) methanol
3) alcohols
4) primary amines
5) secondary amines
6) tertiary amines
7) CCl, i.e. 1-chlorobutane
8) CCl_2, i.e. dichloromethane
9) CCl_3, i.e. chloroform
10) CCl_4, (carbon tetrachloride as separate group)

Table II contains the Q values for all the groups used in this thesis. All of these parameters are found from binary mixtures where one component is an alkane, for example, n-butanol + n-heptane.

When the final parameters were first correlated cycloalkanes were included in the data base. There were several reasons for including the cycloalkanes:

1) Availability of data. For some systems, such as benzene and alcohols, there is a considerable amount of experimental data in the literature. However, for other systems, for example, dichloromethane and chloroform, there is only a limited amount of data. In these cases including the cycloalkane data would hopefully

give interaction parameters with a wider applicability in terms of temperature range and size of solvent.

2) If cycloalkane data were not included then secondary parameters would be necessary to predict mixtures containing cycloalkanes. The binary system n-butanol + cyclohexane is taken as an example to illustrate the prediction method. If the cyclic CH_2 and the straight chain CH_2 were considered as equal then only the primary parameters a OH/CH_2 and a CH_2/OH would be needed to predict this mixture. However, if cycloalkanes were considered separately and excluded from the data base then secondary parameters would be needed. First, n-butanol + n-hexane would be correlated to find a OH/CH_2 and a CH_2/OH where CH_2 represents straight chain alkanes only. Then cyclohexane + n-hexane data would have to be regressed to find the parameters a $CH_2/\textcircled{CH_2}$ and a $\textcircled{CH_2}/CH_2$ where $\textcircled{CH_2}$ represents cyclic CH_2 as in cyclohexane. Finally, n-propanol + cyclohexane data would be regressed to find the parameters a $OH/\textcircled{CH_2}$ and a $\textcircled{CH_2}/OH$. These interaction parameters would be secondary parameters. After these three sets of parameters were obtained then the binary n-butanol + cyclohexane could be predicted.

3) Principle of group contribution methods. A group contribution method is an approximate method to calculate heats of mixing. It is used when experimental data is

not available. If too many functional groups are defined then the idea behind group contribution methods is defeated.

4) In the first UNIFAC paper by Fredenslund, Jones and Prausnitz (9) they did not include cycloalkanes in their data base when regressing for parameters. They did however predict two cyclohexane systems, cyclohexane + 1,2-dichloroethane and cyclohexane + methyl acetate, and obtained good predictions for both systems. They stated that, "these favorable results suggest that the UNIFAC is applicable to systems containing cyclohexane (6 CH_2 groups) and, perhaps, other cyclic alkanes." Although their paper dealt with VLE predictions it was hoped the same would be true for heats of mixing data.

Table XIV gives experimental data for cyclic alkanes and n-alkanes with a common second component at equal mole fractions. As seen from Table XIV there seems to be no common thread in the data, sometimes there is very little difference in the heats of mixing and, in some cases, the heats of mixing of one system are twice that of the other. Also, for three of the seven cases the heats of mixing of the cyclic system are greater than that of the normal alkane system.

Unfortunately, the simultaneous correlation of straight chain and cyclic alkanes gave poor results. Therefore, it was decided to exclude cyclic alkanes when correlating for the final parameters. A summary of the results follows:

a) methanol. Tables XV to XX give the results for methanol. When the methanol + cyclohexane data at 25°C were correlated the regression results were better than when the 50.5°C binary was used.

b) Secondary amines. Tables XXI to XXV give the results for secondary amines. Ethyleneimine, trimethyleneimine, pyrrolidine, piperidine, hexamethyleneimine and heptamethyleneimine are cyclic amines of the formula $(CH_2)_nNH$ where n is two through seven. When two cyclic amine systems were included in the regression (Table XXI) the prediction results were poor for the other cyclic systems. Including three cyclic amines (Table XXIV) did not improve the results.

c) Tertiary amines. Tables XXVI and XXVII give the results for tertiary amines. The correlation results were poor but this is due more to the low heats of mixing of these systems ($\Delta H^M < 100$ J/mole) than to the two cyclic amine systems included in the regression data base.

d) CCl. Tables XXVIII and XXIX are the results for CCl systems. Two sets of parameters were obtained, however, the value for a CH_2/G was the same for both sets while a G/CH_2 was different (where group G represents a group other than CH_2).

e) CCl_2. Tables XXX and XXXI give the results for CCl_2 systems. Three sets of parameters were obtained but the correlation results were only adequate. Part of the problem may be due to the groups involved in the correlation. Dichloromethane is one group, CH_2Cl_2, while 1,1,2,2-tetrachloroethane is one group twice, $CHCl_2$. By the UNIFAC method the parameters would be the same but the group area parameter would be different. As will be seen later the value of Q can cause unexpected problems.

f) CCl_3. Tables XXXII and XXXIII give the results for CCl_3 systems. Since only two mixtures were included in the data base and their heats of mixing are fairly close (considering the temperature difference) the correlation results were very good.

g) CCl_4. Tables XXXIV and XXXV give the results for CCl_4 systems. Five sets of parameters were obtained where the correlation error was nearly the same - 52 to 53 percent. Closer inspection of the results show that the parameters for sets B and C are reversed, and the same is true for sets E and F. The same problem will appear when the cyclo systems are excluded.

Since the Q value for CH_2 in alkanes and cycloalkanes is the same, and equal to 0.54, it was attempted to improve the correlation results for cycloalkanes by changing the Q value for cyclic CH_2. A similar approach was used by Anderson and Prausnitz (2) to improve the vapor-liquid equilibrium performance of the UNIQUAC model for systems containing water and alcohols. The following procedure was used to find a new Q:

a) Fix a value for Q. Four Q values were used: 0.4, 0.54, 0.65 and 0.75.

b) Regress for CH_2/Group G interaction parameters using the five systems in Table XXXVI. Three Type II systems were used because they make up the majority of binary mixtures.

c) Find the optimum Q from a plot of the overall average absolute error versus Q, as shown in Figure III. It is apparent that no significant improvement was obtained, at least for reasonable values of Q. It was decided, therefore, to treat the cyclic compounds separately.

Although a strong case had been made for considering cyclic and straight chain alkanes the same, there were several reasons for treating them separately:

1) Even if one Q value was more successful than the others and was adopted as the new Q for cyclic CH_2, this Q would also have to work for secondary parameters and beyond. More extensive work would have to be done to see what the effect would be on other systems.

2) As seen from Table XIV sometimes the heats of mixing for cyclic and straight chain alkanes are very close, and this is reflected in the correlation results which are very good. For example, the heats of mixing of chloroform with n-hexane and with cyclohexane were similar. If the Q value were changed it would probably increase the errors for

these systems.

3) Although Fredenslund et al (9) reported good results for two cyclohexane systems, other authors have also had problems with cyclic systems. For example, Kikic et al (14) modified the combinatorial part of UNIFAC to better predict vapor-liquid equilibrium with cycloalkanes. Doan-Nguyen et al (7) reported separate parameters for cyclic CH_2 with benzene and toluene for the AGSM.

Tables XXXVII to LXVI present the correlation and prediction results for the final parameters when cyclic systems are excluded. Table LXVII gives a list of the final parameters for the ten groups along with their correlation error. For six of the ten cases more than one set of parameters gave a correlation error of less than 20 percent. In such cases the set of parameters that were the smallest in absolute value were chosen. The reasoning behind this will be given in more detail when the CCl + alkane systems is discussed. However, a similar conclusion was reached by Silverman and Tassios (37) in the correlation of vapor-liquid equilibrium data with the Wilson equation. Their work involved systems with negative deviations from Raoult's law where up to three sets of parameters are possible. Some specific comments for each type of system follow.

a) CCl. Tables XXXVII to XL give the results for CCl systems. (Please note that not all of the initial parameters in the grid were used. In order to save computer time the final parameters obtained from the cyclic regression were used as starting parameters here). Five sets of parameters were obtained with four sets giving a similar correlation error, especially if the experimental uncertainty of the data is taken into account. It should also be noticed that for sets B, D and E the value for a CH_2/CCl is identical while a CCl/CH_2 varies. In order to determine the final interaction parameters, the four parameters $\psi(1,2)$, $\psi(2,1)$, $d\psi/dT(1,2)$ and $d\psi/dT(2,1)$ that enter into the calculation of heats of mixing were evaluated. The results are given in Table XL and show that only Set A gave reasonable numbers for the four values. Based on these results Set A was chosen as the final parameters. And, for this reason the set of parameters that were the smallest in absolute value were chosen as the final parameters.

Twenty-two systems were predicted as given in Table XXXIX and for thirteen systems the percent error was less than 20 percent. However, when one of the components was either 2-chlorobutane or t-butylchloride the prediction error was high. Figure 4 shows the experimental and predicted heats of mixing for n-hexane with 1-chlorobutane and with 2-chlorobutane at 25°C, the prediction errors were 3.9 percent and 29.4 percent, respectively. As seen from the graph the experimental heats of mixing for both systems are nearly identical. The reason the 2-chlorobutane prediction error is so high is due to the Q values. The groups for 1-chlorobutane are 2 CH_2, 1 CH_3 and 1 CH_2Cl (Q = 1.264), while for 2-chlorobutane are 1 CH_2, 2 CH_3 and 1 CHCl (Q = 0.952). The percentage difference between Q(CH_2Cl) and Q(CHCl) is nearly 25 percent, and this accounts for the difference in the predicted values. Ratcliff and coworkers also predicted these two systems but had much better results. This is due to the fact that the AGSM model does not distinguish between what carbon atom the Cl group is bonded with. The AGSM model predicts the same heats of mixing for the two systems, as a result, since the experimental values are so close the prediction error is very low for both systems.

Figure 5 shows the experimental and predicted heats of mixing for n-hexane with 1-chlorobutane and with t-butylchloride at 25°C, the prediction errors were 3.9 percent and 55.3 percent, respectively. The Q values again account for the large error for the t-butylchloride system. The groups for t-butylchloride are 3 CH_3 and 1 CCl (Q = 0.724) and the percentage difference between Q(CH_2Cl) and Q(CCl) is nearly 43 percent. This is the main reason for the high prediction error, the 3 CH_3 groups could increase the error slightly but shouldn't be much of a factor. Both of these graphs show that the theoretical advantage of the group area parameter Q is not always adequate in reality.

A test of a group contribution model is the effect of the chain length on the accuracy of the correlation and/or prediction. Figure 6 is for binary mixtures of 1-chlorobutane with an n-alkane at 25°C. No distinct trend is noticed but the error does not increase as the length of the alkane increases. Figure 7 is a graph for molecules containing the group CH_2Cl and n-alkanes. It shows that as the number of carbon atoms in the molecule with the group CH_2Cl increases the prediction error also increases. In general, both of these trends will be followed by other types of systems.

The effect of temperature could not be studied since all but two of the mixtures were at 25°C.

b) CCl_2. Tables XLI and XLII give the results for CCl_2 systems. Only two mixtures were available and both were used for the correlation of the parameters. This is a case where the cycloalkanes would have expanded the data base somewhat. Set A was chosen as the final set of parameters, but this set may be temporary. For sets A and C the value for a CH_2/CCl_2 is very close, while a CCl_2/CH_2 is quite different. However, the difference (0.58) between the two sets for the parameter a CH_2/CCl_2 is somewhat larger than for the other cases (0.15 or less). The true test for these parameters will be when they are used for the evaluation of secondary parameters.

c) CCl_3. Tables XLIII and XLIV give the results for CCl_3 systems. Set B was chosen as the final parameters because it had the lowest correlation error and the parameters had the smallest absolute value. Notice how the value for a CH_2/CCl_3 is identical (11.77) for sets A and E while a CCl_3/CH_2 is different.

An important point should be made here concerning both the CCl_2 and CCl_3 parameters. Only dichloromethane (CH_2Cl_2) was used to find the CCl_2 parameters, and only chloroform ($CHCl_3$) for the CCl_3 parameters. In theory, the CCl_2 parameters can be used to predict mixtures containing the specific groups $-CHCl_2$ and $-CCl_2$, for example, 1,1,2,2-tetrachloroethane (2 $CHCl_2$ groups) + n-hexane. How good the prediction would be is not known, but it would hopefully provide a reasonable approximation. The same reasoning holds for the group $-CCl_3$. This gets back to the cyclo problem mentioned before and the mixture 1,1,2,2-tetrachloroethane + cyclohexane. How much of the difficulty in correlation is due to the cyclos and how much because of the different groups involved is not known. In conclusion, both the CCl_2 and CCl_3 parameters should be used with caution and reevaluated when more data becomes available with different solvents and temperatures.

d) CCl_4 (carbon tetrachloride). Tables XLV to XLVII give the results for CCl_4. Six sets of parameters were obtained, and one is obviously discounted because of its high error. The other five sets have a correlation error in the 7.0 to 7.7 percent range. As mentioned before in the cyclo section, there is a problem with reverse parameters for this system.

The parameters for sets A and B are nearly the reverse, while sets D and E are the reverse also. This situation is unlike the one discussed before with the group CCl where the first parameter a CH_2/CCl was the same (and the FMIN was also the same). Fortunately, set C has a low correlation error and parameters that are small in absolute value. On first inspection, set C would be chosen as the final set of parameters. Sixteen binary mixtures were available for prediction, and as seen from Table XLVII no set of parameters performed significantly better than the others. Therefore, set C was chosen as the final parameters. The problem with reverse parameters was only encountered with this system. Methanol which was considered a separate group and benzene (6 ACH groups) did not have this problem. So carbon tetrachloride being a separate group would not cause this problem.

Since carbon tetrachloride data was relatively plentiful, several topics can be mentioned. Experimental data is available for octane isomers, and as seen from Tables XLVI and XLVII there is only a slight difference in the errors. However, the only two prediction errors greater than 15 percent are for CCl_4 + n-hexadecane, which suggests that the error increases with increasing chain length of alkane. This is the opposite conclusion that was found from the group CCl where no effect was found. Though the errors do increase they are still within reasonable limits.

Figure 8 is a study of the effect of temperature on the correlation and prediction error. In general, there is an increase in error as the temperature increases. However, the temperature range is too small to make a definite conclusion. Also, the CCl_4 + n-hexadecane mixture was not included and the percent error at 40°C was less than that at 20 or 30°C.

The source of experimental data has not been discussed since early in the Introduction, but Figure 8 raises an interesting point. It is noticed for the CCl_4 + n-hexane system that the errors slightly increase with temperature but that the average percent error at 25° is higher than expected. For CCl_4 + n-heptane the average percent error is also higher than anticipated. For CCl_4 + iso-octane the three points fall on a straight line. The reference for the experimental data was the same (69) except for the two systems at 25°C (45). How much of the error is due to the UNIFAC model and how much because of experimental error is not known, but this graph puts into perspective how well the UNIFAC does perform. It should be mentioned that the CCl_2 and CCl_3 parameters were correlated from the same source as the two points at 25°C.

Figure 9 was included to show how the heats of mixing of dichloromethane, chloroform and carbon tetrachloride with a common second component (n-hexane) are related. From the graph it is seen that the heats of mixing increase as the number of chlorine atoms decreases.

e) Primary amines. Tables XLVIII to L give the results for primary amines. Three sets of parameters were obtained, but set A was chosen as the final parameters because it was the only unique set. The other two sets both had a common parameter, the same problem as with the CCl group parameters.

f) Secondary amines. Tables LI to LIII give the results for secondary amines. Set B was clearly the better pair of parameters. The diethylamine mixtures have a relatively high error, 15.5 to 20.9 percent, and are predicted on the low side.

g) Tertiary amines. Tables LIV to LVII give the results for tertiary amines. Of the ten groups that were worked on, the tertiary amine regression was the most difficult one. When the data were first regressed (Table LIV) the two mixtures used were triethylamine + n-heptane at 45°C and tri-n-dodecyclamine ($C_{36}NH_{75}$) + n-octane at 30°C. The first binary was chosen because it had the highest temperature available, the second binary because it had the greatest number of CH_2 groups. It was felt that with these two mixtures the parameters would have a wide range of applicability. However, the computer program could not converge on any parameters. The problem was due to the low heats of mixing of these systems. At equal mole fractions, ΔH^M for the first binary is 95 J/mole, for the second binary it is 62 J/mole. For the UNIFAC model these heats of mixing values are nearly the same, but the number of groups is very different. Therefore, the program could not converge on any set of parameters. When tri-n-dodecyclamine + n-octane was replaced by triethylamine + n-hexane at 30°C (Table LV) a set of parameters was found. But still it was a difficult process, as seen by the many different initial parameters that were used.

The prediction errors are quite high for two of the systems (triethylamine + n-heptane at 25°C and tri-n-dodecyclamine + n-octane at 30°C). For tri-n-dodecyclamine + n-octane at 30°C the UNIFAC predicts a nearly ideal system, while the maximum experimental value is about 80 J/mole. The UNIFAC method tends to overcompensate towards ideality when predicting this system, due to the high number of CH_2 groups.

Figure 10 was included to show how the heats of mixing of n-butylamine, diethylamine and triethylamine with a common second component (n-heptane) are related. Both n-butylamine and diethylamine have three CH_2 or CH_3 groups, so the difference in heats of mixing is due to the amine group. All the experimental data were taken from the same reference (73). This reference also includes experimental data for the same three amines with benzene and chlorobenzene. Looking at this data it is seen how difficult it will be to evaluate secondary parameters. The heats of mixing of diethylamine + benzene and triethylamine + benzene are nearly the same (maximum ΔH^M of about 330 J/mole at 25°C), while their heats of mixing are very different with n-heptane. The secondary parameters will have to account for this difference.

h) Benzene. Tables LVIII to LX give the results for benzene. Benzene was one of the components included in the evaluation of the Z(T) by Skjold-Jorgensen et al (40). And, as a result, the correlation of the benzene systems was easy as shown in Table LVIII. Set A was chosen as the final parameter set, with sets D and E having the same value for a CH_2/ACH and different values for a ACH/CH_2.

Since there are a considerable amount of benzene data several topics can be studied. One of the topics is the prediction of isomeric alkanes. In this case the hexane and iso-octane isomers give very good results. Figure 11 is a graph of average percent error versus the number of carbon atoms in the alkane at two temperatures. It shows that the number of carbon atoms and the temperature have little effect on the prediction and correlation errors.

i) Methanol. Tables LXI to LXIII give the results for methanol. The first question that should be asked is why methanol isn't considered 1 CH_3 and 1 OH group and classified as an alcohol? When Skjold-Jorgensen et al (39) revised and expanded the UNIFAC and defined the alcohol group as OH, they kept methanol as a separate group. They stated that experimental data were readily available and that based on their experience it was "advantageous to treat the first number of a homologous series with special care". This fact is seen from Figure 12, which is a plot for different n-alcohols with n-heptane at 30°C. From the graph it is seen that the heats of mixing decrease with increasing chain length of the alcohol. However, methanol and ethanol do not follow this pattern. In order to ease the situation somewhat methanol is made a separate group.

Parameter set B was chosen as the final parameters with an average regression error of 4.5 percent. The experimental data for methanol + n-propane, + n-butane and + n-pentane at 25°C were recorded by Christensen and co-workers at Brigham Young University (91,76,53). They use a high-pressure flow calorimeter for their experimental data; for example, the methanol + n-propane run was made at 2985 kPa (29.5 atm) and 25°C. In light of this the prediction errors are quite credible.

j) Alcohols. Tables LXIV to LXVI give the results for alcohols. Three sets of parameters were obtained but Set A was chosen as the final parameters. As might be expected the alcohol parameters were similar to the methanol parameters.

One ethanol system was used in the correlation of the parameters and eight more systems were predicted. The average error for the nine ethanol systems was 16.1 percent. Two primary alcohol systems were used in the correlation and twenty were predicted. The average error for the twenty-two primary alcohol systems was 18.1 percent. One secondary alcohol was used in the regression of parameters and four were predicted. The average error for the five secondary alcohcls was 28.6 percent. Two tertiary alcohol systems were included in the correlation and prediction. The average error for the two systems was 28.9 percent.

Figure 13 is a graph that gives the heats of mixing of primary, secondary and tertiary alcohols with a common second component (n-hexane) at 45°C. It shows that the secondary alcohol (2-butanol) have the highest experimental heats of mixing, while the primary alcohol (n-butanol) have the lowest heats of mixing. However, the predicted results are nearly the same for the three mixtures. Since the parameters and the Q value for OH are the same for each type of alcohol, the only difference in the mixtures is the number of C, CH_2 and CH_3 groups. As can be seen from the prediction results these groups make little difference in the final error. It should be noted that the AGSM method would predict the same heats of mixing for the three mixtures. Each alcohol would be considered one OH group and four CH_2 groups.

An effort was made to improve the alcohol results by changing the Q value, the same idea that was done before with the cyclic alkanes. The procedure was as follows:

a) Specify Q(OH). The values ranged from 1.0 to 5.0, the Q value by Bondi (3) is 1.2.

b) Regress for CH_2/OH parameters using the system n-butanol + n-heptane at 30°C.

c) Using these parameters predict 2-propanol + n-heptane at 30°C and 2-methyl-2-propanol + n-hexane at 27°C. However, as seen from Figure 14 no significant improvement was observed for any reasonable value of Q.

V. CONCLUSIONS

1. Group contribution methods are a promising way to predict heats of mixing when experimental data are not available.
2. The three models (AGSM, UNIFAC with temperature dependent parameters and modified UNIFAC) were evaluated on the basis of their ability to correlate and predict the enthalpies of mixing of a selected set of binary systems. The modified UNIFAC model gave the best results and it was adopted in this study.
3. The simultaneous correlation of cyclic and straight chain alkanes gave poor results. Attempts to improve the error by changing the Q value for cyclic CH_2 failed. Therefore, cyclic alkanes will be treated separately.
4. Final interaction parameters were obtained for ten groups with alkanes (primary parameters). Only the correlation error for the alcohols was greater than 10 percent (17.6 percent).
5. A major problem in correlating the data was the multiplicity of roots. The best set of parameters was obtained by using a grid approach for the initial parameters.
6. Most of the experimental data used in the correlation are in the 25°C to 50°C range. Moderate extrapolation to higher temperatures should be satisfactory.

7. A theoretical advantage of UNIFAC over AGSM is the use of the group area parameter Q; however, the prediction of isomers was mixed. When the isomer was the alkane, for example iso-octane, the results were good. But when the isomer was the component containing the group G (where group G is a group other than CH_2) the results were not as good. For example, the high errors for the 2-chlorobutane mixtures were due to the Q value.
8. The results due to the length of the molecule varied. In general, when the chain length of the alkane increased the prediction error did not increase. However, when the length of the component containing the group G increased the prediction error also increased. In this case the calculated heats of mixing were less then the experimental value. UNIFAC tends to overcompensate towards ideality when the number of CH_2 groups is high.
9. The errors for primary alcohols were relatively good (15 - 20 percent), but the prediction errors for secondary and tertiary alcohols were high (25 - 30 percent).
10. 104 systems from the literature were predicted and 78 had a prediction error less than 20 percent.

NOMENCLATURE

a_{jk}, a_{kj} = AGSM temperature dependent parameters, equation (15)

a_{mn}, a_{nm} = UNIFAC parameter, equation (25)

a'_{mn}, a'_{nm} = modified UNIFAC parameter, temperature independent, equation (27)

A_{jk}, B_{jk} = AGSM temperature independent coefficients, equation (15)

A_{mn}, B_{mn} = UNIFAC temperature independent coefficients used in Grand Plot, equation (30)

A_0, A_1, A_2 = temperature dependent parameters, equations (2) and (3)

$A_{n_{12}}$,$A_{n_{13}}$,$A_{n_{23}}$ = temperature dependent parameters, ternary systems, equations (4) and (5)

b_{jk}, b_{kj} = AGSM temperature dependent parameter, equation (20)

B_0, B_1, B_2 = temperature dependent parameters, equation (1)

c_{11}, c_{22} = cohesive energy density of pure component

c_{12} = interaction energy density

C_{kj}, D_{kj} = AGSM temperature independent coefficients used in Grand Plot, equation (31)

FMIN = minimization function, equation (34)

G = group, other than CH_2

G^E = excess Gibbs free energy

H_k = excess enthalpy of group k

H_{ki}^* = standard state enthalpy of group k in pure component i

$\overline{\Delta H_i}$ = partial molar excess enthalpy of component i

ΔH^G = excess enthalpy due to group interactions, equation (12)

ΔH^M = excess enthalpy

ΔH^S = excess enthalpy due to skeletal contribution, equation (12)

$\Delta H^M{}_{max}$ = maximum absolute difference in J/mole between experimental and calculated excess enthalpy

L = number of systems, equation (32)

N_{ki} = number of groups of type k in component i

P = pressure

Q_k = area parameter of group k

R = gas constant, J/K mole

S_c = average cumulative prediction error, equation (32)

S_j = average absolute percent error for system j, equation (33)

t = temperature, ^oC

T = absolute temperature, ^oK

U_{mn} = measure of the energy of interaction between groups m and n

V = number of experimental data points, equations (33) and (34)

x = liquid phase mole fraction

X_k = group fraction of group k in the mixture

Z = lattice coordination number

Greek Symbols

β = temperature exponent, equations (30) and (31)

γ_i^G = activity coefficient due to effect of group contribution, equation (11)

Γ_k = activity coefficient of group k

Γ_k^* = activity coefficient of group k at standard state

Θ_m = area fraction of group m

Ψ_{mn}, Ψ_{nm} = UNIFAC group parameters, equation (25)

Subscripts

calc = calculated

exp = experimental

pre = predicted

i = component i

j, k, m, n = groups j, k, m and n

Superscripts

G = group contribution

S = skeletal

* = reference state

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TABLE I. Data Base for AGSM Group Parameters by Ratcliff and co-workers (7).

Groups	No. of Systems	t, ^{o}C	Avg. RMSD
alkane, ketone	5	$0^{o}(2)$, $20^{o}(1)$, $25^{o}(2)$	6.0
alkane, ester	8	all at 25^{o}	4.5
alkane, ether	1	25^{o}	12.8
alkane, nitrile	1	25^{o}	10.7
alkane, amine	1	25^{o}	3.2
benzene, alkane	3	all at 25^{o}	2.2
toluene, alkane	3	$25^{o}(2)$, $50^{o}(1)$	3.0

TABLE II. Group Area Parameter - Q_k.

Main Group	Subgroup	Q_k	Example
"CH_2"	CH_3	0.848	ethane: 2 CH_3
	CH_2	0.540	butane: 2 CH_3, 2 CH_2
	CH	0.228	2-methylpentane: 3 CH_3, 2 CH_2, 1 CH
	C	0.000	2,2-dimethylbutane: 4 CH_3, 1 CH_2, 1 C
"ACH"	ACH	0.400	benzene: 6 ACH
"OH"	OH	1.200	2-butanol: 2 CH_3, 1 CH_2, 1 CH, 1 CH
"CH_3OH"	CH_3OH	1.432	methanol: 1 CH_3OH
"CNH_2"	CH_3NH_2	1.544	methylamine: 1 CH_3NH_2
	CH_2NH_2	1.236	n-butylamine: 1 CH_3, 2 CH_2, 1 CH_2NH_2
	$CHNH_2$	0.924	isopropylamine: 2 CH_3, 1 $CHNH_2$
"CNH"	CH_3NH	1.244	dimethylamine: 1 CH_3, 1 CH_3NH
	CH_2NH	0.936	diethylamine: 2 CH_3, 1 CH_2, 1 CH_2NH
	CHNH	0.624	diisopropylamine: 4 CH_3, 1 CH, 1 CHNH
"$(C)_3N$"	CH_3N	0.940	trimethylamine: 2 CH_3, 1 CH_3N
	CH_2N	0.632	triethylamine: 3 CH_3, 2 CH_2, 1 CH_2N
"CCL"	CH_2CL	1.264	1-chlorobutane: 1 CH_3, 2 CH_2, 1 CH_2CL
	CHCL	0.952	2-chlorobutane: 2 CH_3, 1 CH_2, 1 CHCL
	CCL	0.724	2-chloro-2-methylpropane: 3 CH_3, 1 CCL
"CCL_2"	CH_2CL_2	1.988	dichloromethane: 1 CH_2CL_2
	$CHCL_2$	1.684	1,1-dichloroethane: 1 CH_3, 1 $CHCL_2$
	CCL_2	1.448	2,2-dichloropropane: 2 CH_3, 1 CCL_2
"CCL_3"	$CHCL_3$	2.410	chloroform: 1 $CHCL_3$
	CCL_3	2.184	1,1,1-trichloroethane: 1 CH_3, 1 CCL_3
"CCL_4"	CCL_4	2.910	carbon tetrachloride: 1 CCL_4
"CCOH"	CH_2CH_2OH	1.664	1-propanol: 1 CH_3, 1 CH_2CH_2CH
	$CHCHCH_3$	1.660	2-butanol: 1 CH_3, 1 CH_2, 1 $CHCHCH_3$
	$CHCHCH_2$	1.352	3-octanol: 2 CH_3, 4 CH_2, 1 $CHCHCH_2$
	CH_3CH_2OH	1.972	ethanol: 1 CH_3CH_2CH
	$CHCH_2CH$	1.352	2-methyl-1-propanol: 2 CH_3, 1 $CHCH_2CH$

TABLE III. Prediction of Alcohol/Alkane Systems Using Ratcliff and co-worker's parameters (7,38) For the AGSM Model.

			Avg. % Error		
System	t, ^{o}C	Data Points	ΔH^M Data	ΔH^M & VLE Data	Ref.
ethanol + n-hexane	30	18	11.1	47.2	93
ethanol + n-hexane	45	18	7.4	52.0	93
ethanol + n-nonane	30	18	19.4	52.4	93
ethanol + n-nonane	45	18	17.1	55.5	93
n-propanol + n-heptane	30	18	2.0	18.7	93
n-propanol + n-heptane	45	18	6.6	17.3	93
n-butanol + n-heptane	30	18	5.7	6.8	93
n-butanol + n-heptane	45	18	9.5	4.8	93
n-pentanol + n-hexane	30	18	7.9	5.6	93
n-pentanol + n-hexane	45	18	10.3	4.6	93
n-octanol + n-heptane	30	18	11.9	9.8	93
n-octanol + n-heptane	45	18	9.2	6.1	93
n-octanol + n-nonane	30	18	10.5	8.9	93
n-octanol + n-nonane	45	18	10.3	6.3	93

TABLE IV. Prediction of Group G/Alkane Systems Using Ratcliff and co-worker's parameters (7) For the AGSM Model.

System	t, °C	Data Points	Avg. % Error	Ref.
2-butanone + n-hexane	25	20	4.6	72
2-pentanone + n-hexane	25	20	5.0	72
3-pentanone + n-hexane	25	20	9.4	72
ethyl acetate + n-hexane	25	17	2.4	63
methyl acetate + n-octane	25	21	2.7	63
methyl acetate + n-hexane	25	16	4.3	63
methyl acetate + n-dodecane	25	21	5.4	63
ethyl acetate + n-octane	25	22	1.9	63
ethyl acetate + n-dodecane	25	20	4.0	63
propyl acetate + n-hexane	25	17	1.8	63
butyl acetate + n-hexane	25	18	4.8	63
n-butylamine + n-heptane	25	6	11.0	73
n-butylamine + n-heptane	45	6	5.3	73
benzene + n-octane	25	21	2.3	54
benzene + n-octane	50	13	17.1	55
benzene + n-dodecane	25	10	3.9	54
benzene + n-dodecane	50	15	18.6	55

TABLE V. Regressing for interaction parameters at one temperature versus regressing at more than one temperature for the UNIFAC model.

System	n-propanol + n-heptane 30°C	
Parameters used	30°	30° + 45°
Avg. % Error	0.9	5.88

System	n-propanol + n-heptane 45°C	
Parameters used	30°	30° + 45°
Avg. % Error	15.6*	7.54

*Prediction Error

TABLE VI. Selected Type I and Type II systems used in evaluating the optimum exponent, β , in equations (30) and (31).

System	Type	t, °C	Data Points	Ref.
nitroethane + 2,2-dimethylbutane	I	30	10	67
nitroethane + 2,2-dimethylbutane	I	40	4	67
n-octanol + n-heptane	I	30	18	93
n-octanol + n-heptane	I	55	10	79
benzene + n-octane	II	25	18	54
benzene + n-octane	II	50	18	55
n-butylamine + n-heptane	II	25	8	73
n-butylamine + n-heptane	II	45	6	73

TABLE VII. Regression Error for AGSM and UNIFAC in the Grand Plot.

System Type I. nitroethane + 2,2-dimethylbutane 30°C

Temperature Exponent	+2.0	+1.5	+1.0	+0.5	-0.5	-1.0	-1.5	-2.0
S_j AGSM	7.1	7.8	8.4	N.C.	7.2	7.5	N.C.	4.9
S_j UNIFAC	1.5	1.4	1.7	0.7	N.A.	5.8	4.7	7.4

n-octanol + n-heptane 30°C

Temperature Exponent	+2.0	+1.5	+1.0	+0.5	-0.5	-1.0	-1.5	-2.0
S_j AGSM	1.7	2.4	1.0	N.C.	1.1	1.5	15.3	15.7
S_j UNIFAC	1.1	1.5	1.1	3.0	1.1	7.7	5.4	3.7

System Type II. benzene + n-octane 25°C

Temperature Exponent	+2.0	+1.5	+1.0	+0.5	-0.5	-1.0	-1.5	-2.0
S_j AGSM	0.3	1.2	0.3	1.5	1.0	0.3	0.3	0.4
S_j UNIFAC	0.3	0.3	0.3	0.7	0.6	0.5	0.5	0.3

n-butylamine + n-heptane 25°C

Temperature Exponent	+2.0	+1.5	+1.0	+0.5	-0.5	-1.0	-1.5	-2.0
S_j AGSM	1.3	1.5	1.8	2.1	1.4	1.4	1.4	1.4
S_j UNIFAC	1.3	1.4	1.4	1.4	1.3	1.5	1.3	1.2

N.C.: No Convergence

N.A.: Not Available

TABLE VIII. Prediction Error for AGSM and UNIFAC in the Grand Plot.

System Type I. nitroethane + 2,2-dimethylbutane 40°C

Temperature Exponent	+2.0	+1.5	+1.0	+0.5	-0.5	-1.0	-1.5	-2.0
S_j AGSM	14.4	10.9	8.1	N.C.	23.9	2.6	N.C.	1.0
S_j UNIFAC	10.6	7.0	12.5	4.0	2.2	3.0	3.0	3.0

n-octanol + n-heptane 55°C

Temperature Exponent	+2.0	+1.5	+1.0	+0.5	-0.5	-1.0	-1.5	-2.0
S_j AGSM	13.9	52597.5	5.5	N.C.	31.9	53.0	30.8	31.7
S_j UNIFAC	1.2	4.5	18.0	12.1	43.0	24.0	22.0	21.1

System Type II. benzene + n-octane 50°C

Temperature Exponent	+2.0	+1.5	+1.0	+0.5	-0.5	-1.0	-1.5	-2.0
S_j AGSM	214.9	78.6	13.5	168.0	14.2	17.5	24.3	278.1
S_j UNIFAC	17.6	13.6	9.3	9.6	7.8	5.9	5.6	7.2

n-butylamine + n-heptane 45°C

Temperature Exponent	+2.0	+1.5	+1.0	+0.5	-0.5	-1.0	-1.5	-2.0
S_j AGSM	59.6	24.8	57.5	107.8	1.8	26.8	5.0	6.3
S_j UNIFAC	10.2	8.1	6.2	5.0	1.7	2.4	5.0	8.6

N.C.: No parameters obtained from data regression.

TABLE IX. Prediction of the system n-octanol + n-heptane by AGSM where $\beta = 1.50$.

t, °C	DATA POINTS	AVG. % ERROR	REF
15	10	54.86	79
30	18	3.71	93
45	18	10737.0	93
55	10	51475.0	79

TABLE X. Examples of Multiplicity of Roots For AGSM in the Grand Plot.

Parameters Correlated from n-octanol + n-heptane at $30^{o}C$ ($\beta = +1.50$).

			S_j		
System	t, °C	Data Points	Correlation Error=3.7%	Correlation Error=14.7%	Ref.
n-octanol + n-heptane	15	10	54.9	16.5	79
n-octanol + n-heptane	30	18	3.7	14.7	93
n-octanol + n-heptane	45	18	10737.0	14.2	93
n-octanol + n-heptane	55	10	51475.0	19.9	79

Parameters Correlated from benzene + n-octane at $25^{o}C$ ($\beta = -1.50$).

			S_j		
System	t, °C	Data Points	Correlation Error=4.7%	Correlation Error=0.4%	Ref.
benzene + n-octane	25	21	4.7	0.4	54
benzene + n-octane	50	13	29.2	28.6	55
benzene + n-dodecane	25	10	5.9	2.1	54
benzene + n-dodecane	50	15	27.7	29.2	55

TABLE XI. Results for the Grand Plot using UNIFAC with the Z(T).

SYSTEM	CORRELATION % ERROR	PREDICTION % ERROR
benzene + n-octane	0.32	1.97
n-butylamine + n-heptane	1.36	2.03
n-butylamine + n-heptane	2.47	4.02
nitroethane + 2,2 dimethylbutane	6.2	3.18
nitroethane + 2,2 dimethylbutane	7.07	2.12
n-octanol + n-heptane	22.93	21.1
n-octanol + n-heptane	41.2	36.79
n-octanol + n-heptane	41.7	34.7
n-octanol + n-heptane	16.2	12.9

TABLE XII. Comparison of Skjold-Jorgensens' Z(T) and Z(T) Correlated from n-octanol + n-heptane Data at 30°C.

	Skjold-Jorgensens' Z(T)	n-octanol + n-heptane 30°C
	$35.2 - 0.1272T + 0.00014T^2$	$39.2 - 0.1105T + 0.000179T^2$
System	Avg. % Error	Avg. % Error
n-octanol + n-heptane 30°C	16.2	11.6
n-octanol + n-heptane 55°C	12.9	35.3
benzene + n-octane 25°C	0.3	0.6
benzene + n-octane 50°C	2.0	3.6
n-butylamine + n-heptane 25°C	1.4	34.9
n-butylamine + n-heptane 45°C	2.0	35.1

TABLE XIII. Grid of Initial Parameters to be Used with the Modified UNIFAC.

$a'_{CH_2/G}$	a'_{G/CH_2}
+200	+200
+200	0.1
+200	-200
0.1	+200
0.1	0.1
0.1	-200
-200	+200
-200	0.1
-200	-200

TABLE XIV. Maximum Experimental ΔH^M Values for Cyclic Alkanes and Normal Alkanes with a Common Second Component at Equal Mole Fractions.

		Normal Alkane			Cyclic Alkane		
Second Component	t, °C	First Component	ΔH^M (J/mole)	Ref.	First Component	ΔH^M (J/mole)	Ref.
n-pentanol	25	n-hexane	495	90	cyclohexane	597	90
benzene	25	n-pentane	850	54	cyclopentane	625	100
carbon tetrachloride	25	n-hexane	315	45	cyclohexane	165	68
dichloromethane	25	n-hexane	1315	45	cyclohexane	1275	59
chloroform	25	n-hexane	750	45	cyclohexane	630	59
n-octene	25	n-hexane	30	71	cyclohexane	250	62
2-nitropropane	25	n-hexane	1470	70	cyclohexane	1500	70

TABLE XV. Correlation of Methanol + Alkane Data including Cyclic Alkanes.

Data used in Correlation:

Methanol + N-hexane 40°C

Methanol + N-hexane 50°C

Methanol + N-heptane 60°C

Methanol + Cyclohexane 50.5°C

Starting Parameters	Final Parameters	Fmin	Standard Deviation	Remarks	Set
+200, +200	326.0, 399.9	5.51	0.43×10^{-5}	Note 1	
+200, 0.1	388.4, 13.71	1.77	0.95×10^{-6}	12.5%	A
+200, -200	388.4, 13.70	1.77	0.95×10^{-6}	12.5%	A
0.1, +200	21.41, 703.1	7.67	0.58×10^{-5}	Note 1	
0.1, 0.1	53.05, -15.53	6.16	0.35×10^{-5}	Note 1	
-200, +200	326.0, 399.8	5.51	0.58×10^{-5}	Note 1	
-200, 0.1	53.08, -15.53	6.16	0.58×10^{-5}	Note 1	
-200, -200	326.0, 399.9	5.51	0.54×10^{-5}	Note 1	

Note:
1. Repeating same Fmin and SD.

TABLE XVI. Correlation Errors for Methanol + Alkane Data Including Cyclic Alkanes.

			Set A		At Max		
System	t, ^{o}C	Data Points	Avg. % Error	Max. % Error	ΔH^{M}_{exp}	ΔH^{M}_{pre}	Ref.
methanol + n-hexane	40	14	8.8	15.3	714.9	777.4	94
methanol + n-hexane	50	13	5.4	17.7	848.7	856.4	94
methanol + n-heptane	60	16	5.0	20.9	1061.0	1074.3	94
methanol + cyclohexane	50.5	11	36.7	43.1	1241.5	794.4	50

TABLE XVII. Prediction Errors for Methanol + Alkane Data Including Cyclic Alkanes.

System	t, °C	Data Points	Avg. % Error Set A	Ref.
methanol + n-hexane	45	17	7.5	94
methanol + n-heptane	30	8	7.6	94

TABLE XVIII. Correlation of Methanol + Alkane Data including Cyclic Alkanes.

Data used in Correlation:

methanol + n-hexane 40°C

methanol + n-hexane 50°C

methanol + n-heptane 60°C

methanol + cyclohexane 25°C

Starting Parameters	Final Parameters	FMIN	Standard Deviation	Remarks	Set
105.98, -38.24	44.65, -12.99	4.48	0.9×10^{-6}	22.9%	A
20, 20	44.64, -12.98	4.48	0.95×10^{-6}	22.9%	A
0.1, +100	44.65, -12.98	4.48	0.67×10^{-6}	22.9%	A
37.37, -11.79	44.66, -12.99	4.48	0.95×10^{-6}	22.9%	A
-100, +100	44.65, -12.99	4.48	0.95×10^{-6}	22.9%	A
+100, -100	44.65, -12.98	4.48	0.0	22.9%	A
+100, +100	398.2, 13.30	0.227	0.22×10^{-6}	5.6%	B
-100, -100	44.66, -12.99	4.48	0.67×10^{-6}	22.9%	A
42,717	20.21, 771.4	5.68	0.95×10^{-6}	24.6%	C

TABLE XIX. Correlation Errors for Methanol + Alkane Data Including Cyclic Alkanes.

System	t, °C	Data Points	Avg. % Error Parameter Set A	 B	 C	Ref.
methanol + n-hexane	40	14	27.0	6.7	28.4	94
methanol + n-hexane	50	13	21.3	3.7	21.4	94
methanol + n-heptane	60	16	20.8	4.3	25.2	94
methanol + cyclohexane	25	6	24.4	10.4	20.9	95

TABLE XX. Prediction Errors for Methanol + Alkane Data Including Cyclic Alkanes.

System	t, °C	Data Points	Avg. % Error Set		Ref.
			A	B	
methanol + n-hexane	45	17	22.0	4.7	94
methanol + n-heptane	30	8	23.3	8.0	94

TABLE XXI. Correlation of Secondary Amines + Alkane Data Including Cyclic Alkanes.

Data Used in Correlation:
diethylamine + n-heptane 45°C
dibutylamine + n-hexane 30°C
ethyleneimine + cyclohexane 25°C
heptamethyleneimine + cyclohexane 25°C

Initial Parameters	Final Parameters	FMIN	Standard Deviation	Remarks	Set
0.1,0.1	50.90,45.29	1.385	0.0	13.2%	A
+100,+100	50.91,45.20	1.385	0.0	13.2%	A
-100,+100	-799.7,38.66	33.595	0.012	note 1	
-100,-100	-857.0,799.5	47.917	0.00938	note 1	
+100,-100	50.89,45.04	1.385	0.44×10^{-5}	note 1	

Note:
1. Repeating same FMIN and Standard Deviation.

TABLE XXII. Correlation Errors for Secondary Amines + Alkane Data Including Cyclic Alkanes.

System	t, °C	Data Points	Avg. % Error	Ref.
diethylamine + n-heptane	45	6	6.1	73
dibutylamine + n-hexane	30	19	10.7	99
ethyleneimine + cyclohexane	25	12	23.0	49
heptamethyleneimine + cyclohexane	25	11	10.7	49

TABLE XXIII. Prediction Errors for Secondary Amines + Alkane Data including Cyclic Alkanes.

System	$t, ^{o}C$	Data Points	Avg. % Error	Ref.
trimethyleneimine + cyclohexane	25	11	32.7	49
pyrrolidine + cyclohexane	25	12	41.1	49
piperidine + cyclohexane	25	14	32.7	49
hexamethyleneimine + cyclohexane	25	11	35.9	49
diethylamine + n-heptane	25	8	11.1	73
diethylamine + n-hexane	30	19	11.8	99

TABLE XXIV. Correlation of Secondary Amines + Alkane Data Including Cyclic Alkanes.

Data used in Correlation:

diethylamine + n-heptane 45°C
dibutylamine + n-hexane 30°C
ethyleneimine + cyclohexane 25°C
pyrrolidine + cyclohexane 25°C
heptamethyleneimine + cyclohexane 25°C

Initial Parameters	Final Parameters	FMIN	Standard Deviation	Remarks	Set
+200,+200	420.8,39.61	27.242	$0.15x10^{-4}$	note 1	
+200,0.1	420.8,39.71	27.242	0.0	62.9%	A
+200,-200	420.8,39.59	27.242	$0.11x10^{-4}$	note 1	
0.1,+200	53.13,42.39	3.474	$0.12x10^{-4}$	note 1	
0.1,0.1	53.07,42.06	3.474	0.0	19.1%	B
0.1,-200	53.09,42.01	3.474	0.0	19.1%	B
-200,+200	-916.8,37.90	43.244	$0.45x10^{-3}$	note 1	
-200,0.1	-4734.2,0.683	59.176	0.1987	note 2	
-200,-200	-902.2,37.76	43.243	$0.18x10^{-2}$	note 1	

Notes:
1. Repeating same FMIN and Standard Deviation.
2. Error Message.

TABLE XXV. Correlation Errors for Secondary Amines + Alkane Data Including Cyclic Alkanes.

No.	System	t, °C	Data Points	At Max ΔH^M_{exp}	Ref.
1	diethylamine + n-heptane	45	6	670.0	73
2	dibutylamine + n-hexane	30	19	280.9	99
3	ethyleneimine + cyclohexane	25	12	1673.6	49
4	pyrrolidine + cyclohexane	25	12	1197.9	49
5	heptamethyleneimine + cyclohexane	25	11	446.9	49

	Set A			Set B		
System No.	Avg. % Error	Max. % Error	At Max ΔH^M_{calc}	Avg. % Error	Max. % Error	At Max ΔH^M_{calc}
1	48.8	55.8	304.2	3.4	6.7	625.3
2	52.0	179.0	153.1	16.9	19.1	326.9
3	73.2	80.5	374.1	21.5	53.6	1271.0
4	75.8	83.7	199.7	39.8	52.0	725.0
5	64.0	76.2	128.5	6.3	10.8	416.7

TABLE XXVI. Correlation of Tertiary Amine + Alkane Data Including Cyclic Alkanes.

Initial Parameters	Final Parameters	FMIN	Standard Deviation	Remarks	Set
+200,+200	2581.6,570.5	56.00	0.0	100.0%	A
+200,0.1	2117.1,-1.02	51.05	0.15×10^{-4}	note 1	
+200,-200	1356.4,-1.02	51.05	0.19×10^{-4}	note 1	
0.1,+200	-1.07,2197.7	51.08	0.15×10^{-4}	note 1	
0.1,0.1	-1.40,0.325	51.08	0.15×10^{-4}	note 1	
0.1,-200	-1.07,6833.5	51.08	0.0	93.1%	B
-200,+200	-346.5,182.7	52.18	0.15×10^{-2}	note 1	
-200,-200	-863.1,539.7	55.26	0.0	99.3%	C

Note:

1. Repeating same FMIN and Standard Deviation.

TABLE XXVII. Correlation Errors for Tertiary Amine + Alkane Data Including Cyclic Alkanes.

No.	System	t, ^{o}C	Data Points	At Max ΔH^{M}_{exp}	Ref.
1	triethylamine + n-heptane	45	5	96.0	73
2	tri-n-dodecylamine + n-octane	30	11	81.2	61
3	tributylamine + n-hexane	25	15	-9.3	48
4	N-methylpyrrolidine + cyclohexane	25	12	244.1	49
5	N-methylpiperidine + cyclohexane	25	13	149.2	49

	Set A			Set B			Set C		
System No.	Avg. % Error	Max. % Error	At Max ΔH^{M}_{calc}	Avg. % Error	Max. % Error	At Max ΔH^{M}_{calc}	Avg. % Error	Max. % Error	At Max ΔH^{M}_{calc}
1	100.0	100.0	0.0	102.4	102.5	-2.2	100.0	100.0	0.0
2	100.0	100.0	0.0	100.3	100.3	-0.2	100.0	100.0	0.0
3	100.0	100.0	0.0	66.7	95.1	-0.7	97.3	100.2	-0.2
4	100.0	100.0	0.0	103.3	105.1	-7.3	100.0	100.0	0.0
5	100.0	100.0	0.0	104.4	106.0	-5.7	100.0	100.0	0.0

TABLE XXVIII. Correlation of CCL + Alkane Data Including Cyclic Alkanes.

Initial Parameters	Final Parameters	FMIN	Standard Deviation	Remarks	Set
+200,+200	406.0,261.5	50.24	0.10×10^{-4}	note 1	
+200,-200	406.0,261.8	50.24	0.18×10^{-4}	note 1	
-200,+200	33.97,1669.7	2.99	0.0	11.7%	A
-200,-200	33.96,1202.2	2.99	0.0	11.7%	B

Note:

1. Repeating same FMIN and Standard Deviation.

TABLE XXIX. Correlation Errors for CCL + Alkane Data Including Cyclic Alkanes.

No.	System	t, ^{o}C	Data Points	At Max ΔH^{M}_{exp}	Ref.
1	1-chlorobutane + n-hexane	35	10	516.4	15
2	2-chlorobutane + n-hexane	35	10	506.1	15
3	1,2 dichloroethane + cyclohexane	25	19	1388.2	75
4	1-chlorohexane + n-octane	25	19	428.1	89
5	1-chloropentane + n-heptane	25	19	486.0	89
6	1-chlorobutane + n-nonane	25	19	603.8	56

		Set A			Set B	
System No.	Avg. % Error	Max. % Error	At Max ΔH^{M}_{calc}	Avg. % Error	Max. % Error	At Max ΔH^{M}_{calc}
1	4.1	8.7	492.9	4.1	8.7	492.8
2	38.9	43.5	304.1	38.9	43.5	304.1
3	22.7	41.9	1722.8	22.7	41.8	1722.6
4	3.8	10.3	414.3	3.8	10.3	414.2
5	4.7	10.1	464.1	4.8	10.1	464.0
6	5.2	9.4	617.0	5.2	9.3	616.9

TABLE XXX. Correlation of CCL_2 + Alkane Data Including Cyclic Alkanes.

Initial Parameters	Final Parameters	FMIN	Standard Deviation	Remarks	Set
+200,+200	302.0,348.3	11.424	0.43×10^{-5}	note 1	
+200,0.1	413.0,17.43	1.891	0.95×10^{-6}	19.0%	A
+200,-200	302.1,348.3	11.424	0.64×10^{-5}	note 1	
0.1,+200	20.76,1335.0	1.140	0.95×10^{-6}	16.4%	B
0.1,0.1	22.18,-1.00	1.135	0.95×10^{-6}	16.2%	C
0.1,-200	22.17,-1.00	1.135	0.95×10^{-6}	16.2%	C
-200,+200	302.1,348.2	11.424	0.63×10^{-5}	note 1	
-200,0.1	22.20,-1.01	1.135	0.95×10^{-6}	16.2%	C
-200,-200	302.1,348.2	11.424	0.35×10^{-5}	note 1	

Note:

1. Repeating same FMIN and Standard Deviation.

TABLE XXXI. Correlation Errors for CCL_2 + Alkane Data Including Cyclic Alkanes.

No.	System	t, °C	Data Points	At Max ΔH^M_{exp}	Ref.
1	dichloromethane + n-heptane	25	11	1403.0	45
2	1,1,2,2-tetrachloroethane + cyclohexane	30	19	1155.9	60
3	dichloromethane + cyclohexane	25	10	1288.0	59

		Set A			Set B			Set C	
System No.	Avg. % Error	Max. % Error	At Max ΔH^M_{calc}	Avg. % Error	Max. % Error	At Max ΔH^M_{calc}	Avg. % Error	Max. % Error	At Max ΔH^M_{calc}
1	21.3	29.4	1038.2	15.5	20.2	1204.8	15.4	18.9	1208.4
2	14.3	48.1	1238.2	14.4	18.8	1341.4	14.1	20.8	1339.3
3	25.3	34.5	935.5	21.3	23.6	1045.9	21.2	23.0	1044.5

TABLE XXXII. Correlation of CCL_3 + Alkane Data Including Cyclic Alkanes.

Initial Parameters	Final Parameters	FMIN	Standard Deviation	Remarks	Set
+200,+200	378.1,324.7	2.605	0.95×10^{-6}	29.1%	A
+200,0.1	486.4,10.20	0.146	0.39×10^{-6}	6.5%	B
+200,-200	378.1,324.7	2.605	0.95×10^{-6}	29.1%	A
0.1,+200	11.34,1438.9	0.043	0.68×10^{-6}	3.3%	C
0.1,0.1	15.49,-3.32	0.022	0.70×10^{-6}	2.9%	D
0.1,-200	11.33,1924.6	0.043	0.60×10^{-6}	3.3%	E
-200,+200	378.0,324.7	2.605	0.95×10^{-6}	29.1%	A
-200,0.1	11.09,0.204	0.045	0.68×10^{-6}	3.4%	F
-200,-200	15.54,-3.35	0.022	0.26×10^{-6}	2.9%	D

TABLE XXXIII. Correlation Errors for CCl_3 + Alkane Data Including Cyclic Alkanes.

No.	System	t, °C	Data Points	At Max ΔH^M_{exp}	Ref.
1	chloroform + n-heptane	25	10	797.0	45
2	chloroform + cyclohexane	40	12	643.9	59

		Set A			Set B			Set C	
System No.	Avg. % Error	Max. % Error	At Max ΔH^M_{calc}	Avg. % Error	Max. % Error	At Max ΔH^M_{calc}	Avg. % Error	Max. % Error	At Max ΔH^M_{calc}
1	36.3	56.0	350.3	7.6	14.8	706.4	3.0	7.7	776.4
2	23.2	61.3	531.2	5.5	14.4	632.6	3.6	8.7	646.3

		Set D			Set E			Set F	
System No.	Avg. % Error	Max. % Error	At Max ΔH^M_{calc}	Avg. % Error	Max. % Error	At Max ΔH^M_{calc}	Avg. % Error	Max. % Error	At Max ΔH^M_{calc}
1	3.1	5.2	780.7	3.0	7.7	776.4	3.2	8.0	776.2
2	2.8	6.3	650.7	3.6	8.7	646.3	3.6	8.9	646.2

TABLE XXXIV. Correlation of CCL_4 + Alkane Data Including Cyclic Alkanes.

Initial Parameters	Final Parameters	FMIN	Standard Deviation	Remarks	Set
+200,+200	569.2,535.6	40.48	0.0	66.9%	A
+200,0.1	721.7,1.72	22.55	0.0	52.1%	B
+200,-200	721.6,1.72	22.55	0.15×10^{-4}	note 1	
0.1,+200	1.74,720.1	22.67	0.0	52.5%	C
0.1,0.1	1.42,0.365	22.77	0.0	52.8%	D
0.1,-200	0.199,1.59	22.77	0.0	52.8%	E
-200,0.1	1.59,0.197	22.77	0.0	52.8%	F

Note:

1. Repeating same FMIN and Standard Deviation.

TABLE XXXV. Correlation Errors for CCL_4 + Alkane Data Including Cyclic Alkanes.

No.	System	t, °C	Data Points	At Max ΔH^M exp	Ref.
1	carbon tetrachloride + iso-octane	30	13	402.7	69
2	carbon tetrachloride + cyclopentane	35	16	73.1	58
3	carbon tetrachloride + cyclohexane	45	13	152.7	58
4	carbon tetrachloride + n-hexadecane	40	12	511.2	69
5	carbon tetrachloride + n-heptane	40	12	327.0	69
6	carbon tetrachloride + n-hexane	20	10	331.1	69

		Set A			Set B			Set C	
System No.	Avg. % Error	Max. % Error	At Max ΔH^M calc	Avg. % Error	Max. % Error	At Max ΔH^M calc	Avg. % Error	Max. % Error	At Max ΔH^M calc
1	82.0	91.6	34.0	62.9	64.0	146.9	62.9	64.8	148.6
2	54.2	178.0	34.4	53.0	81.7	109.9	53.8	61.0	111.1
3	47.6	117.0	66.0	20.1	23.5	118.2	20.6	23.5	119.2
4	65.7	84.8	85.0	63.0	64.6	184.2	64.0	66.2	183.8
5	69.7	82.3	57.9	57.3	61.3	136.2	57.5	58.6	137.6
6	90.7	95.3	15.6	58.7	61.0	135.9	58.3	60.9	137.3

		Set D			Set E			Set F	
System No.	Avg. % Error	Max. % Error	At Max. ΔH^M calc	Avg. % Error	Max. % Error	At Max ΔH^M calc	Avg. % Error	Max. % Error	At Max ΔH^M calc
1	62.5	64.1	151.7	62.6	64.6	151.1	62.5	64.0	151.7
2	54.3	63.7	112.7	54.4	61.2	112.8	54.1	63.9	112.6
3	22.6	23.1	118.8	22.5	24.0	118.8	22.6	23.3	118.7
4	64.2	65.8	185.8	64.4	66.3	184.7	64.3	65.7	185.8
5	57.7	60.9	138.4	57.7	60.3	138.6	57.7	61.0	138.3
6	57.3	60.0	141.0	57.4	59.5	141.1	57.4	60.1	140.8

TABLE XXXVI. Systems Used in Evaluating an Optimum Q for Cyclic CH_2.

System	t, °C	Data Points	Type	Ref.
methanol + cyclohexane	50.5	11	I	50
nitroethane + cyclohexane	25	13	I	70
piperidine + cyclohexane	25	14	II	49
benzene + cyclohexane	50	13	II	57
1,4 dioxane + cyclohexane	60	4	II	44

TABLE XXXVII. Correlation of CCL + Alkane Data.

Initial Parameters	Final Parameters	FMIN	Standard Deviation	Remarks	Set
34.0,1202.2	35.61,1052.8	1.50	$0.44\text{x}10^{-5}$	note 1	
-200,0.1	-5265.9,0.80	74.31	0.746	note 2	
0.1,0.1	47.9,-13.3	1.23	$0.95\text{x}10^{-6}$	7.0%	A
33.9,1314.0	35.6,1313.9	1.50	$0.95\text{x}10^{-6}$	8.7%	B
435.8,27.9	437.7,37.9	18.85	0.0	46.8%	C
41.3,-7.6	47.9,-13.3	1.23	$0.25\text{x}10^{-5}$	note 1	
0.1,-200	35.6,300.3	1.50	$0.95\text{x}10^{-6}$	8.7%	D
34.0,1669.7	35.6,1900.8	1.50	0.0	8.7%	E

Notes:

1. Repeating same FMIN and Standard Deviation.
2. Error Message.

TABLE XXXVIII. Correlation Errors for CCL + Alkane Data.

No.	System	t, ^{o}C	Data Points	At Max ΔH^{M}_{exp}	Ref.
1	1-chlorobutane + n-hexane	35	10	516.4	15
2	2-chlorobutane + n-hexane	35	10	506.1	15
3	1-chlorohexane + n-octane	25	19	428.1	89
4	1-chloropentane + n-heptane	25	19	486.0	89
5	1-chlorobutane + n-nonane	25	19	603.8	56

	Set A			Set B			Set C		
System No.	Avg. % Error	Max. % Error	At Max ΔH^{M}_{calc}	Avg. % Error	Max. % Error	At Max ΔH^{M}_{calc}	Avg. % Error	Max. % Error	At Max ΔH^{M}_{calc}
1	2.8	3.7	497.2	3.6	9.7	518.8	41.6	102.8	292.2
2	33.2	34.8	330.2	35.3	40.0	321.5	56.9	90.0	198.0
3	5.8	7.1	457.0	3.9	7.4	438.6	46.8	84.6	214.9
4	1.9	4.7	490.3	3.2	7.5	486.9	47.5	54.7	229.2
5	4.4	5.8	637.8	7.7	14.5	650.7	43.5	69.3	305.8

	Set D			Set E		
System No.	Avg. % Error	Max. % Error	At Max ΔH^{M}_{calc}	Avg. % Error	Max. % Error	At Max ΔH^{M}_{calc}
1	3.7	9.9	519.6	3.6	9.7	518.9
2	35.3	39.9	321.9	35.3	40.0	321.6
3	3.9	7.5	438.7	3.9	7.4	438.6
4	3.2	7.6	490.3	3.2	7.5	490.1
5	7.7	14.6	651.0	7.7	14.5	650.8

TABLE XXXIX. Prediction Errors for CCL + Alkane Data.

System	t, °C	Data Points	Avg. % Error Parameter Set B^1	C	A^*	ΔH^M max	Ref.
1-chlorohexadecane + n-dodecane	25	15	10.3	35.9	5.2	14.7	96
1-chlorohexadecane + n-hexadecane	25	15	6.3	37.7	22.0	46.3	96
t-butylchloride + n-hexane	25	12	59.4	67.0	55.3	291.7	96
1-chlorobutane + n-octane	25	13	13.1	39.9	11.8	57.2	96
1-chlorobutane + n-dodecane	25	10	6.8	37.4	5.0	59.9	96
1-chlorobutane + n-hexadecane	25	11	5.4	43.4	1.8	20.7	96
1-chlorododecane + n-octane	25	13	9.5	34.9	13.2	21.7	96
1-chlorododecane + n-dodecane	25	13	11.3	36.5	26.9	52.4	96
1-chlorododecane + n-hexadecane	25	11	7.9	37.5	18.8	40.6	96
1-chlorohexadecane + n-octane	25	13	34.7	57.3	23.9	69.8	96
1-chloro-octane + n-octane	25	19	3.2	46.6	6.6	26.5	56
2-chlorobutane + n-hexane	25	19	31.5	60.1	29.4	141.1	56
2-chlorobutane + n-octane	25	19	33.0	59.7	30.5	168.2	56
1-chlorobutane + n-hexane	25	19	6.5	44.7	3.9	25.5	56
1-chloro-octane + n-hexane	25	19	2.6	47.0	4.3	15.6	56
1-chlorohexane + n-hexane	25	14	4.7	48.8	6.9	42.6	87
1-chlorohexane + n-heptane	25	15	4.8	49.7	6.5	35.3	88
t-butylchloride + n-octane	25	12	62.0	63.1	58.1	339.5	96
t-butylchloride + n-dodecane	25	13	63.3	63.0	59.3	442.0	96
t-butylchloride + n-hexadecane	25	14	67.5	68.9	64.0	619.9	96
1-chloropentane + n-hexane	25	14	3.5	51.5	3.6	23.0	85
1-chloropentane + n-octane	25	15	4.6	48.1	4.0	29.2	86

Note:
1. The prediction errors for sets B, D and E are the same.

TABLE XL. Effect of the Parameter Values on ψ_{ij} and $\partial \psi_{ij}/\partial T$.

Set	A(1,2)	A(2,1)	$\psi(1,2)$	$\psi(2,1)$	$\frac{\partial \psi}{\partial T}(1,2)$	$\frac{\partial \psi}{\partial T}(2,1)$
A	47.85	-13.26	0.4585	1.241	0.0028	-.0021
B	35.60	1313.87	0.5597	4.998×10^{-10}	.00255	8.405×10^{-11}
C	437.70	37.87	7.97×10^{-4}	0.5394	4.46×10^{-5}	.0026
D	35.59	300.25	0.5598	7.49×10^{-3}	0.00255	2.878×10^{-4}
E	35.61	1900.76	0.5596	3.50×10^{-14}	0.00255	8.515×10^{-15}

TABLE XLI. Correlation of CCL_2 + Alkane Data.

Initial Parameters	Final Parameters	FMIN	Standard Deviation	Remarks	Set
22.1,-1.00	26.6,-0.389	0.049	0.88×10^{-6}	3.8%	A
413.0,17.4	352.7,20.6	0.165	0.79×10^{-6}	7.5%	B
20.7,1335.0	26.0,1469.4	0.049	0.19×10^{-6}	3.7%	C

TABLE XLII. Correlation Errors for CCL_2 + Alkane Data.

No.	System	t, °C	Data Points	At Max ΔH^M_{exp}	Ref.
1	dichloromethane + n-heptane	25	11	1403.0	45
2	dichloromethane + n-hexane	25	12	1313.0	45

	Set A			Set B			Set C		
System No.	Avg. % Error	Max. % Error	At Max ΔH^M_{calc}	Avg. % Error	Max. % Error	At Max ΔH^M_{calc}	Avg. % Error	Max. % Error	At Max ΔH^M_{calc}
1	2.9	4.5	1456.9	7.5	19.0	1291.7	2.7	4.0	1456.4
2	4.6	12.4	1368.7	7.4	12.6	1215.4	4.6	12.9	1368.4

TABLE XLIII. Correlation of CCL_3 + Alkane Data.

Initial Parameters	Final Parameters	FMIN	Standard Deviation	Remarks	Set
11.30,1924.0	11.77,2172.4	0.021	0.71×10^{-6}	2.9%	A
15.50,-3.3	15.27,-2.78	0.005	0.83×10^{-6}	1.3%	B
378.0,324.0	358.4,304.8	2.404	0.95×10^{-6}	32.2%	C
486.4,10.2	454.1,10.55	0.079	0.36×10^{-6}	5.8%	D
11.09,0.204	15.22,-2.75	0.005	0.24×10^{-6}	1.3%	B
11.34,1438.1	11.77,1554.7	0.021	0.43×10^{-6}	2.9%	E

TABLE XLIV. Correlation Errors for CCL_3 + Alkane Data.

No.	System	t, °C	Data Points	At Max ΔH^M_{exp}	Ref.
1	chloroform + n-heptane	25	10	797.0	45
2	chloroform + n-hexane	25	9	750.0	45

	Set A			Set B			Set C		
System No.	Avg. % Error	Max. % Error	At Max ΔH^M_{calc}	Avg. % Error	Max. % Error	At Max ΔH^M_{calc}	Avg. % Error	Max. % Error	At Max ΔH^M_{calc}
1	2.9	4.2	804.2	0.9	2.0	809.6	29.6	50.7	455.6
2	2.9	6.7	762.7	1.8	3.7	765.0	35.1	58.9	429.1

	Set D			Set E		
System No.	Avg. % Error	Max. % Error	At Max ΔH^M_{calc}	Avg. % Error	Max. % Error	At Max ΔH^M_{calc}
1	5.8	10.3	747.8	2.9	4.2	804.1
2	5.7	10.0	712.5	2.8	6.7	762.6

TABLE XLV. Correlation of Carbon Tetrachloride + Alkane Data.

Initial Parameters	Final Parameters	FMIN	Standard Deviation	Remarks	Set
+200,+200	503.6,447.5	17.843	$0.15\text{x}10^{-4}$	note 1	
+200,0.1	699.5,4.55	0.287	$0.14\text{x}10^{-6}$	7.0%	A
+200,-200	486.7,1464.4	29.633	$0.11\text{x}10^{-4}$	note 1	
0.1,+200	4.53,677.3	0.301	$0.60\text{x}10^{-6}$	7.2%	B
0.1,0.1	2.75,1.79	0.315	$0.26\text{x}10^{-6}$	7.4%	C
0.1,-200	0.20,4.44	0.334	$0.60\text{x}10^{-6}$	7.7%	D
-200,+200	4.53,682.7	0.301	$0.17\text{x}10^{-3}$	note 2	
-200,0.1	4.39,0.20	0.322	$0.84\text{x}10^{-6}$	7.4%	E
-200,-200	503.5,447.4	17.843	0.0	57.2%	F

Notes:

1. Repeating same FMIN and Standard Deviation.
2. Ran Out of Time.

TABLE XLVI. Correlation Errors for Carbon Tetrachloride + Alkane Data.

No.	System	t, ^oC	Data Points	At Max ΔH^M_{exp}	Ref.
1	carbon tetrachloride + iso-octane	30	13	402.7	69
2	carbon tetrachloride + n-hexadecane	40	12	511.2	69
3	carbon tetrachloride + n-heptane	40	12	327.0	69
4	carbon tetrachloride + n-hexane	20	10	331.1	69

		Set A			Set B			Set C	
System No.	Avg. % Error	Max. % Error	At Max ΔH^M_{calc}	Avg. % Error	Max. % Error	At Max ΔH^M_{calc}	Avg. % Error	Max. % Error	At Max ΔH^M_{calc}
1	6.2	10.6	374.8	5.6	8.8	379.4	5.4	9.5	382.3
2	8.2	13.1	463.6	8.8	12.6	469.7	9.8	13.7	468.5
3	7.7	18.8	348.2	7.4	12.4	348.1	7.0	11.6	349.2
4	5.8	8.9	349.7	7.0	13.4	348.2	7.5	13.1	355.0

		Set D			Set E			Set F	
System No.	Avg. % Error	Max. % Error	At Max ΔH^M_{calc}	Avg. % Error	Max. % Error	At Max ΔH^M_{calc}	Avg. % Error	Max. % Error	At Max ΔH^M_{calc}
1	6.1	12.1	380.4	5.3	7.9	383.0	60.8	75.7	98.0
2	10.0	16.0	464.4	9.6	12.2	471.3	55.2	128.9	218.7
3	7.1	10.3	351.4	7.2	13.0	347.9	44.5	80.4	157.6
4	7.5	9.7	356.7	7.8	14.8	352.8	70.0	84.7	52.1

TABLE XLVII. Prediction Errors for Carbon Tetrachloride + Alkane Data.

			Avg. % Error Parameter Set							
Second Component	t, ^{o}C	Data Points	A	B	D	E	F	C*	ΔH^{M} max	Ref.
n-hexadecane	20	8	21.2	20.1	19.7	19.1	84.0	19.3	129.9	69
n-hexadecane	30	8	16.2	16.2	15.6	15.8	59.4	15.8	91.3	69
iso-octane	20	9	4.7	4.2	3.5	3.0	83.3	2.8	17.1	69
iso-octane	40	14	7.0	7.2	7.8	7.7	46.5	7.9	36.9	69
n-decane	25	21	2.4	2.6	1.4	1.9	75.9	1.6	11.4	65
n-octane	30	8	3.4	4.4	4.3	5.7	83.8	4.9	22.4	69
n-octane	40	13	8.6	8.3	7.8	8.0	40.7	7.6	30.1	69
n-octane	20	11	3.4	5.6	5.3	6.3	79.7	5.7	25.8	69
n-nonane	25	21	2.4	2.6	1.8	2.2	75.9	1.8	13.5	64
n-hexane	30	10	9.1	8.6	10.5	9.0	52.8	9.5	33.1	69
n-hexane	25	10	8.7	9.2	10.1	10.2	64.8	10.2	37.5	45
n-heptane	25	10	6.2	7.2	7.8	8.2	69.4	7.9	37.9	45
n-dodecane	25	21	4.7	4.9	3.5	3.9	76.6	3.6	43.3	66
n-heptane	30	8	4.7	5.8	5.6	6.6	57.8	6.0	22.6	69
n-heptane	20	6	3.8	5.2	5.8	6.3	76.5	5.8	26.2	69
n-hexane	40	12	10.5	10.3	9.5	9.8	42.1	9.5	32.2	69

TABLE XLVIII. Correlation of Primary Amines + Alkane Data.

Initial Parameters	Final Parameters	FMIN	Standard Deviation	Remarks	Set
+200,+200	305.3,39.54	8.524	0.12×10^{-4}	note 1	
+200,0.1	305.3,39.59	8.524	0.11×10^{-4}	note 1	
+200,-200	305.3,39.54	8.524	0.96×10^{-5}	note 1	
0.1,+200	81.36,-5.94	0.361	0.77×10^{-6}	8.8%	A
0.1,0.1	81.31,-5.88	0.361	0.67×10^{-6}	8.8%	A
0.1,-200	81.36,-5.95	0.361	0.42×10^{-6}	8.8%	A
-200,+200	-1701.5,38.95	25.805	0.15×10^{-4}	note 1	
-200,0.1	-5265.9,0.804	34.475	0.14652	note 2	
-200,-200	-1002.9,38.38	25.811	0.22×10^{-3}	note 1	
86.0,-6.8	81.55,-5.85	0.390	0.38×10^{-5}	note 1	
77.8,491.7	76.21,199.4	0.378	0.50×10^{-5}	note 1	
25,200	81.28,-5.86	0.361	0.31×10^{-5}	note 1	
77.8,+500	76.56,220.2	0.379	0.64×10^{-6}	9.2%	B
77.8,+790	76.71,926.4	0.381	0.56×10^{-6}	9.3%	C
77.8,0.1	81.31,-5.88	0.361	0.97×10^{-6}	8.8%	A

Notes:

1. Repeating same FMIN and Standard Deviation.
2. Error Message.

TABLE XLIX. Correlation Errors for Primary Amines + Alkane Data.

No.	System	t, ^{o}C	Data Points	At Max ΔH^{M}_{exp}	Ref.
1	n-butylamine + n-heptane	45	6	1281.0	73
2	n-hexylamine + n-hexane	30	19	973.1	99
3	n-butylamine + n-hexane	25	10	994.1	78

	Set A			Set B			Set C		
System No.	Avg. % Error	Max. % Error	At Max ΔH^{M}_{calc}	Avg. % Error	Max. % Error	At Max ΔH^{M}_{calc}	Avg. % Error	Max. % Error	At Max ΔH^{M}_{calc}
1	6.3	8.5	1189.0	4.7	8.4	1203.2	5.3	8.9	1195.3
2	7.0	13.5	919.7	7.3	11.1	912.1	7.4	11.3	911.3
3	13.5	20.7	1175.2	15.3	22.1	1190.3	15.1	21.8	1188.7

TABLE L. Prediction Errors for Primary Amines + Alkane Data.

			Avg. % Error Parameter Set				
System	t, °C	Data Points	B	C	A^*	ΔH^M_{max}	Ref.
n-propylamine + n-hexane	30	19	3.2	3.2	5.4	82.1	99
n-butylamine + n-heptane	25	6	7.3	7.4	3.5	96.6	73

TABLE LI. Correlation of Secondary Amines + Alkane Data.

Initial Parameters	Final Parameters	FMIN	Standard Deviation	Remarks	Set
420.8,39.71	486.3,38.28	16.738	0.0	62.7%	A
53.07,42.06	50.02,8.16	0.598	0.98×10^{-6}	8.4%	B
50.9,45.3	49.99,8.15	0.598	0.14×10^{-5}	note 1	

Note:

1. Repeating same FMIN and Standard Deviation.

TABLE LII. Correlation Errors for Secondary Amines + Alkane Data.

No.	System	t, ^oC	Data Points	Ref.
1	diethylamine + n-heptane	45	19	73
2	dibutylamine + n-hexane	30	19	99

	Set A				Set B			
			At Max				At Max	
System No.	avg. % error	max. % error	ΔH^M_{exp}	ΔH^M_{calc}	avg. % error	max. % error	ΔH^M_{exp}	ΔH^M_{calc}
1	62.5	159.8	671.0	213.1	15.5	35.9	671.0	530.8
2	62.9	73.4	280.9	88.7	1.4	3.5	280.9	283.7

TABLE LIII. Prediction Errors for Secondary Amines + Alkane Data.

System	t, ^{o}C	Data Points	Avg. % Error Parameter Set A	Avg. % Error Parameter Set B*	ΔH^{M}_{max}	Ref.
diethylamine + n-heptane	25	8	77.1	14.7	142.8	73
diethylamine + n-hexane	30	19	73.9	20.9	139.3	99

TABLE LIV. Correlation of Tertiary Amines + Alkane Data.

Data used in Correlation:

Triethylamine + N-heptane 45°C

Tri-n-dodecylamine + N-octane 30°C

Starting Parameters	Final Parameters	Fmin	Standard Deviation	Remarks	Set
+200, +200	32.18, 470.7	8.538	0.25×10^{-4}	Note 1	
+200, 0.1	32.15, 0.120	8.540	0.35×10^{-5}	Note 1	
+200, -200	89.0, -47.56	7.174	0.12×10^{-5}	Note 1	
0.1, +200	88.56, -47.38	7.174	0.32×10^{-3}	Note 1	
0.1, 0.1	88.28, -47.22	7.174	0.79×10^{-4}	Note 1	
0.1, -200	32.19, 575.6	8.538	0.15×10^{-4}	Note 1	
-200, +200	-1045.4, 38.63	18.554	0.20×10^{-2}	Note 1	
-200, 0.1	-862.2, 0.148	29.864	0.693	Note 2	
-200, -200	-1069.8, 39.48	18.561	0.25×10^{-2}	Note 1	

Notes:
1. Repeating same Fmin and Standard Deviation.
2. Error Message.

TABLE LV. Correlation of Tertiary Amines + Alkane Data.

Data used in Correlation:
triethylamine + n-heptane 45°C
triethylamine + n-hexane 30°C

Initial Parameters	Final Parameters	FMIN	Standard Deviation	Remarks	Set
+200,+200	22.62,66.51	0.160	$0.19\mathrm{x}10^{-4}$	note 1	
+200,0.1	22.86,0.118	0.282	$0.13\mathrm{x}10^{-5}$	note 1	
+200,-200	20.72,40.14	0.179	$0.43\mathrm{x}10^{-3}$	note 2	
0.1,+200	22.54,65.84	0.160	$0.18\mathrm{x}10^{-4}$	note 1	
0.1,0.1	22.63,66.66	0.160	$0.22\mathrm{x}10^{-4}$	note 2	
0.1,-200	22.59,66.21	0.160	$0.35\mathrm{x}10^{-4}$	note 2	
-200,+200	-950.2,35.63	16.532	$0.13\mathrm{x}10^{-2}$	note 1	
-200,0.1	-4734.2,0.68	36.765	0.3178	note 3	
-200,-200	-1083.9,35.43	16.537	$0.87\mathrm{x}10^{-3}$	note 1	
22.7,67.90	22.70,67.32	0.160	$0.23\mathrm{x}10^{-4}$	note 1	
32.2,100.0	22.56,65.95	0.160	$0.34\mathrm{x}10^{-5}$	note 1	
32.2,575.6	28.94,576.0	0.283	$0.10\mathrm{x}10^{-5}$	note 1	
88.5,-47.5	22.74,67.89	0.160	$0.10\mathrm{x}10^{-4}$	note 2	
89.0,-47.56	21.50,54.99	0.163	$0.28\mathrm{x}10^{-2}$	note 2	
32.2,0.12	22.71,67.60	0.160	$0.15\mathrm{x}10^{-4}$	note 2	
22.7,67.60	22.60,66.35	0.160	$0.20\mathrm{x}10^{-5}$	note 1	
21.5,55.00	22.58,66.19	0.160	$0.19\mathrm{x}10^{-5}$	note 1	
22.7,200.0	22.65,66.91	0.160	$0.86\mathrm{x}10^{-6}$	5.2%	A
+200,67.0	22.76,68.23	0.160	$0.68\mathrm{x}10^{-6}$	5.2%	A
0.1,67.0	22.63,66.77	0.160	$0.30\mathrm{x}10^{-5}$	note 1	
-200,67.0	-963.6,35.82	16.526	$0.35\mathrm{x}10^{-2}$	note 1	
22.7,-200	22.62,66.43	0.160	$0.86\mathrm{x}10^{-5}$	note 1	
22.7,0.1	28.87,0.114	0.282	$0.25\mathrm{x}10^{-5}$	note 1	

Notes:
1.Repeating same FMIN and Standard Deviation.
2.Ran out of time.
3.Error Message.

TABLE LVI. Correlation Errors for Tertiary Amines + Alkane Data.

					SET A	
System	t, °C	Data Points	Avg. % Error	Max. % Error	At Max. $\Delta H^M_{exp} - \Delta H^M_{calc}$	Ref.
triethylamine + n-heptane	45	19	7.5	16.7	94.8 - 84.4	73
triethylamine + n-hexane	30	19	3.0	5.0	78.2 - 80.7	99

TABLE LVII. Prediction Errors for Tertiary Amines + Alkane Data.

			Avg. % Error		
System	t, ^{o}C	Data Points	Set A	ΔH^{M}_{max}	Ref.
triethylamine + n-heptane	25	7	40.5	23.4	73
triethylamine + n-hexane	25	19	2.2	2.3	48
tributylamine + n-octane	25	18	15.5	6.7	48
tri-n-dodecylamine + n-octane	30	11	90.0	73.7	61
triethylamine + n-octane	25	19	13.1	14.8	48

TABLE LVIII. Correlation of Benzene + Alkane Data.

Initial Parameters	Final Parameters	FMIN	Standard Deviation	Remarks	Set
10.8,2.6	12.07,1.90	0.135	0.60×10^{-6}	3.2%	A
+200,+200	516.8,312.2	23.688	0.0	50.9%	B
+200,0.1	665.6,14.50	0.522	0.48×10^{-6}	6.9%	C
+200,-200	516.6,312.3	23.688	0.0	50.9%	B
0.1,+200	14.24,1624.1	0.152	0.16×10^{-6}	3.2%	D
0.1,0.1	12.09,1.89	0.135	0.81×10^{-6}	3.2%	A
0.1,-200	12.08,1.89	0.135	0.73×10^{-6}	3.2%	A
-200,+200	14.23,1452.5	0.152	0.75×10^{-6}	3.1%	E
-200,0.1	12.08,1.89	0.135	0.45×10^{-6}	3.2%	A
-200,-200	12.09,1.89	0.135	0.63×10^{-6}	3.2%	A

TABLE LIX. Correlation Errors for Benzene + Alkane Data.

No.	System	t, °C	Data Points	At Max ΔH^M_{exp}	Ref.
1	benzene + iso-octane	25	8	1003.0	74
2	benzene + n-decane	50	14	1009.0	55
3	benzene + n-hexadecane	25	11	1345.0	54
4	benzene + n-docosane	50	10	1295.0	55
5	benzene + n-pentane	25	11	867.0	54
6	benzene + n-tetradecane	50	13	1128.0	55

	Set A			Set B			Set C		
System No.	Avg. % Error	Max. % Error	At Max ΔH^M_{calc}	Avg. % Error	Max. % Error	At Max ΔH^M_{calc}	Avg. % Error	Max. % Error	At Max ΔH^M_{calc}
1	2.1	3.2	1026.7	62.0	77.8	279.0	7.9	15.9	995.4
2	0.7	2.0	1013.2	42.8	198.1	643.4	5.7	17.7	989.5
3	3.8	8.3	1306.9	71.1	78.7	309.9	12.2	21.3	1215.9
4	3.6	11.1	1323.3	32.7	82.4	813.1	7.3	24.0	1277.6
5	7.3	13.3	852.4	62.5	76.2	246.6	2.6	3.9	839.2
6	2.0	4.3	1142.6	39.8	105.7	710.9	6.7	14.7	1108.5

	Set D			Set E		
System No.	Avg. % Error	Max. % Error	At Max ΔH^M_{calc}	Avg. % Error	Max. % Error	At Max ΔH^M_{calc}
1	1.3	1.7	1019.6	1.2	1.6	1019.2
2	1.4	3.2	1014.9	1.3	3.1	1014.4
3	3.7	6.5	1307.6	3.8	6.5	1307.0
4	2.9	8.7	1328.9	2.8	8.6	1328.2
5	8.8	16.5	844.2	8.8	16.6	843.9
6	1.3	2.2	1146.2	1.3	2.3	1145.7

TABLE LX. Prediction Errors for Benzene + Alkane Data.

Second Component	t, °C	Data Points	Avg. % Error Parameter Set B	C	D	E	A*	ΔH^M max	Ref.
n-heptane	50	4	32.7	2.3	2.7	2.6	2.5	22.1	74
n-hexane	25	10	64.1	6.7	1.5	1.5	2.3	21.0	80
n-heptane	25	8	61.7	6.6	2.3	2.2	2.6	32.0	74
2-methylpentane	25	15	67.6	5.8	1.0	1.0	0.9	23.0	81
3-methylpentane	25	11	63.6	7.6	1.4	1.4	1.8	30.8	82
2,3-dimethylbutane	25	10	65.4	10.0	1.8	1.8	2.5	40.7	84
2,2-dimethylbutane	25	10	68.6	8.7	1.2	1.2	2.4	28.2	83
n-octane	25	21	64.5	6.4	2.3	2.3	3.2	38.2	54
n-undecane	25	11	67.4	8.3	3.5	3.4	4.3	48.5	54
n-dodecane	25	10	73.1	8.9	2.4	2.4	3.2	35.0	54
n-tetradecane	25	10	64.9	7.9	1.6	1.7	0.6	14.8	54
n-pentadecane	25	10	67.3	10.3	0.8	0.9	1.4	15.4	54
n-heptadecane	25	11	67.7	11.8	3.7	3.8	3.6	60.9	54
n-hexane	50	13	55.3	5.9	2.9	2.9	2.8	25.0	55
n-octane	50	13	61.9	7.7	2.0	2.0	2.3	26.7	55
n-dodecane	50	15	74.0	6.8	1.6	1.6	0.7	11.1	55
n-hexadecane	50	16	31.3	6.0	1.7	1.6	2.3	49.6	55
n-octadecane	50	11	37.1	6.6	2.4	2.4	2.8	55.9	55
eicosane	50	13	42.4	6.7	2.2	2.2	2.3	45.7	55
iso-octane	50	4	34.8	3.8	0.6	0.6	1.1	17.5	74

TABLE LXI. Correlation of Methanol + Alkane Data.

Initial Parameters	Final Parameters	FMIN	Standard Deviation	Remarks	Set
44.6,-13.0	52.39,-16.19	3.838	0.95×10^{-6}	22.9%	A
398.2,13.3	394.4,12.90	0.145	0.16×10^{-6}	4.5%	B
53.1,-15.5	52.41,-16.19	3.838	0.95×10^{-6}	22.9%	A
326.0,400.0	322.5,406.2	3.637	0.67×10^{-6}	25.5%	C
21.4,703.1	20.06,748.1	5.221	0.67×10^{-6}	25.0%	D

TABLE LXII. Correlation Errors for Methanol + Alkane Data.

No.	System	t, ^{o}C	Data Points	At Max ΔH^{M}_{exp}	Ref.
1	methanol + n-hexane	40	14	714.9	94
2	methanol + n-hexane	50	13	848.7	94
3	methanol + n-heptane	60	16	1061.0	94

	Set A			Set B			Set C		
System No.	Avg. % Error	Max. % Error	At Max ΔH^{M}_{calc}	Avg. % Error	Max. % Error	At Max ΔH^{M}_{calc}	Avg. % Error	Max. % Error	At Max ΔH^{M}_{calc}
1	26.3	69.7	976.5	5.3	8.8	733.6	33.3	45.3	548.7
2	21.8	73.4	930.2	3.5	13.1	808.4	24.8	45.1	818.0
3	20.7	73.7	900.2	4.8	16.6	1016.8	19.2	47.1	1224.2

	Set D		
System No.	Avg. % Error	Max. % Error	At Max ΔH^{M}_{calc}
1	28.0	80.7	828.0
2	21.3	83.2	710.4
3	25.5	83.5	640.5

TABLE LXIII. Prediction Errors for Methanol + Alkane Data.

			Avg. % Error Parameter Set					
System	t, ^oC	Data Points	A	C	D	B*	ΔH^M_{max}	Ref.
methanol + n-hexane	45	17	24.9	28.9	32.0	4.4	52.5	94
methanol + n-pentane	25	23	33.9	38.4	42.5	17.0	111.9	53
methanol + n-butane	25	23	33.9	49.0	46.0	16.1	112.6	76
methanol + n-propane	25	25	74.3	48.5	73.0	40.3	164.3	91

TABLE LXIV. Correlation of Alcohol + Alkane Data.

Initial Parameters	Final Parameters	FMIN	Standard Deviation	Remarks	Set
398.2,13.3	323.4,49.20	2.623	$0.17x10^{-5}$	note 1	
+200,+200	323.4,49.15	2.623	$0.95x10^{-6}$	17.6%	A
+200,0.1	323.4,49.05	2.623	$0.42x10^{-5}$	note 1	
+200,-200	323.4,49.13	2.623	$0.95x10^{-6}$	17.6%	A
0.1,+200	50.51,131.3	12.448	$0.43x10^{-4}$	note 1	
0.1,0.1	138.1,-35.87	6.971	$0.58x10^{-5}$	note 1	
0.1,-200	50.42,131.0	12.448	$0.81x10^{-5}$	note 1	
-200,+200	-1231.8,43.47	35.717	0.0	80.5%	B
-200,0.1	-4734.2,0.684	53.157	0.21688	note 2	
-200,-200	-1306.0,44.02	35.718	0.0	80.5%	C

Notes:

1. Repeating same FMIN and Standard Deviation.
2. Error Message.

TABLE LXV. Correlation Errors for Alcohol + Alkane Data.

No.	System	t, °C	Data Points	At Max ΔH^M_{exp}	Ref.
1	ethanol + n-hexane	45	14	837.5	93
2	n-butanol + n-nonane	55	10	1255.4	79
3	n-pentanol + 2,2-dimethylbutane	25	10	506.6	27
4	2-propanol + n-heptane	60	14	1490.8	98
5	2-methyl-2-propanol + n-hexane	45	6	1046.0	47

	Set A			Set B			Set C		
System No.	Avg. % Error	Max. % Error	At Max ΔH^M_{calc}	Avg. % Error	Max. % Error	At Max ΔH^M_{calc}	Avg. % Error	Max. % Error	At Max ΔH^M_{calc}
1	13.4	41.4	919.5	69.7	92.0	216.5	69.9	92.0	216.5
2	15.6	29.5	1346.8	86.0	96.3	143.5	86.0	96.3	143.5
3	12.3	45.4	469.2	76.1	93.9	93.5	76.1	93.9	93.3
4	24.9	40.2	1219.1	86.0	95.9	190.8	86.0	95.9	190.8
5	22.7	52.5	837.7	90.8	96.4	114.3	90.8	96.4	114.2

TABLE LXVI. Prediction Errors for Alcohol + Alkane Data.

			Avg. % Error Parameter Set			
System	t, ^{o}C	Data Points	B^{1}	A*	ΔH^{M}_{max}	Ref.
n-propanol + n-hexane	45	8	80.4	12.3	159.0	46
n-butanol + n-hexane	45	7	83.3	10.4	129.9	46
n-pentanol + n-hexane	45	18	89.5	20.5	189.7	93
n-hexanol + n-hexane	45	7	88.6	15.7	199.4	46
n-octanol + n-hexane	45	7	91.6	18.2	204.7	46
ethanol + n-heptane	10	14	57.1	17.6	87.3	97
ethanol + n-heptane	20	12	59.4	19.0	140.8	92
ethanol + n-heptane	25	12	61.4	16.2	162.0	92
ethanol + n-heptane	30	16	64.4	18.5	189.2	92
ethanol + n-heptane	45	13	71.9	16.6	258.2	97
ethanol + n-heptane	60	15	79.3	15.1	287.9	97
ethanol + n-heptane	75	14	82.4	11.4	248.3	97
ethanol + n-decane	25	19	61.7	17.0	284.3	51
n-propanol + n-decane	25	18	73.1	16.7	200.4	51
n-butanol + n-decane	25	18	79.2	20.1	183.2	51
n-pentanol + n-decane	25	17	81.9	21.9	184.6	51
n-hexanol + n-decane	25	19	85.5	20.3	207.7	51
n-heptanol + n-decane	25	19	86.2	18.6	196.9	51
n-octanol + n-decane	25	19	87.6	19.9	207.3	51
n-pentanol + n-hexane	25	10	77.7	15.4	128.3	27
n-pentanol + n-heptane	25	12	79.9	20.5	146.9	92
n-pentanol + n-octane	25	13	82.0	24.6	165.6	92
n-pentanol + n-nonane	25	18	81.9	19.5	184.5	52
n-pentanol + n-tetradecane	25	13	83.0	33.3	273.4	92
n-pentanol + n-pentane	25	16	74.7	11.9	89.7	53
n-pentanol + n-butane	25	17	74.0	11.0	81.4	76
2-methyl-1-propanol + n-hexane	25	10	85.1	22.0	221.9	47
2-methyl-1-propanol + n-hexane	45	10	89.0	17.5	271.9	47
2-butanol + n-hexane	25	6	88.9	33.3	440.7	47
2-butanol + n-hexane	45	6	90.8	25.2	499.3	47
2-methyl-2-propanol + n-hexane	27	8	87.9	35.1	463.1	47
2-propanol + n-heptane	30	20	78.8	31.7	313.6	98
2-propanol + n-heptane	45	21	82.6	28.1	349.5	98

Note:

1. The prediction errors for sets B and C are the same.

TABLE LXVII. Group Interaction Parameters, $-CH_2$ with Group G.

Group G	CH_2 / G	G / CH_2	Avg. % Error
CCL	47.85	-13.26	7.0
CCL_2	26.60	-0.389	3.8
CCL_3	15.22	-2.75	1.3
CCL_4	2.75	1.79	7.4
CNH_2	81.36	-5.95	8.8
CNH	50.02	8.16	8.4
$(C)_3N$	22.65	66.91	5.2
ACH	12.09	1.89	3.2
CH_3OH	394.4	12.90	4.5
OH	323.4	49.15	17.6

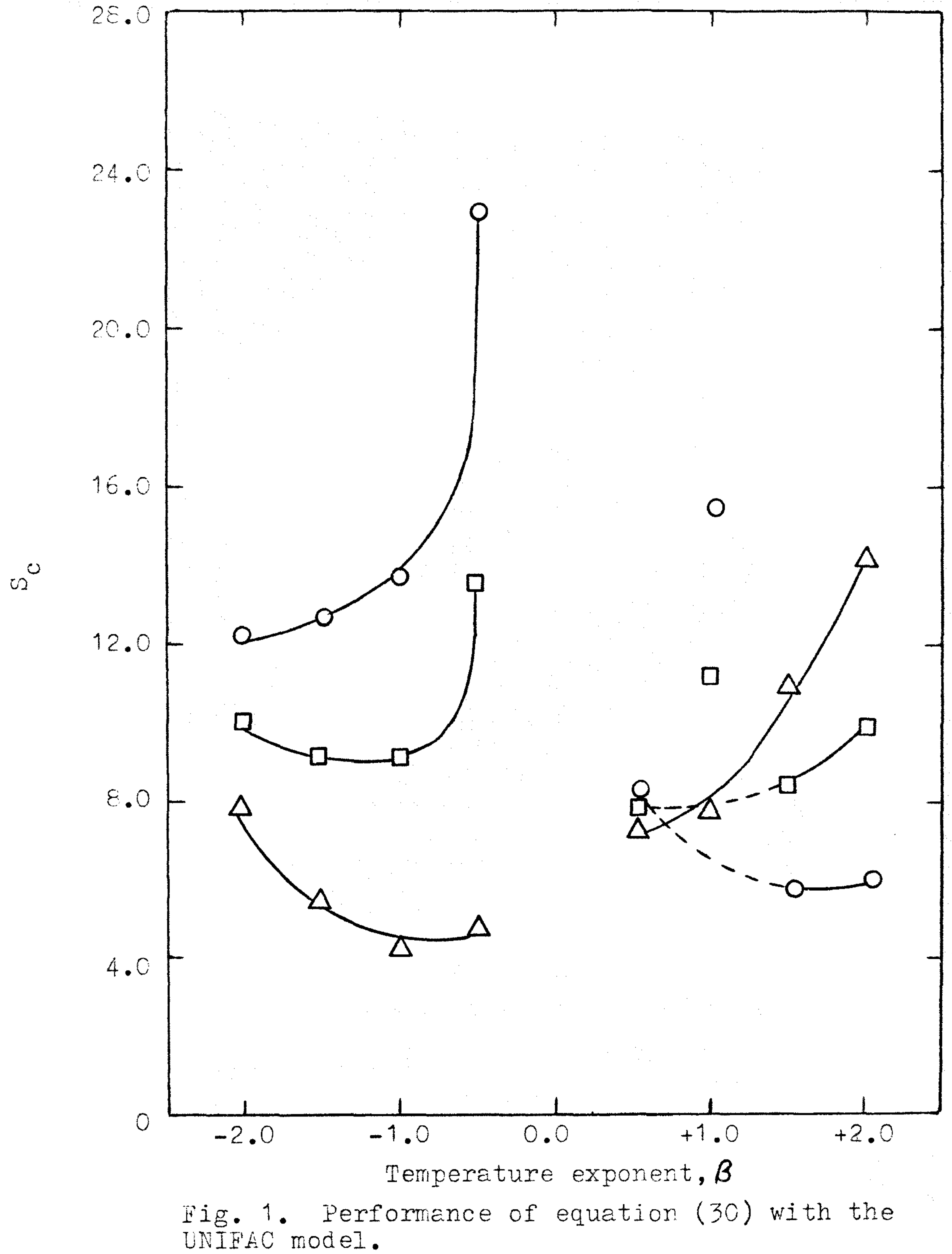

Fig. 1. Performance of equation (30) with the UNIFAC model.

○ Type I systems
△ Type II systems
□ Overall error

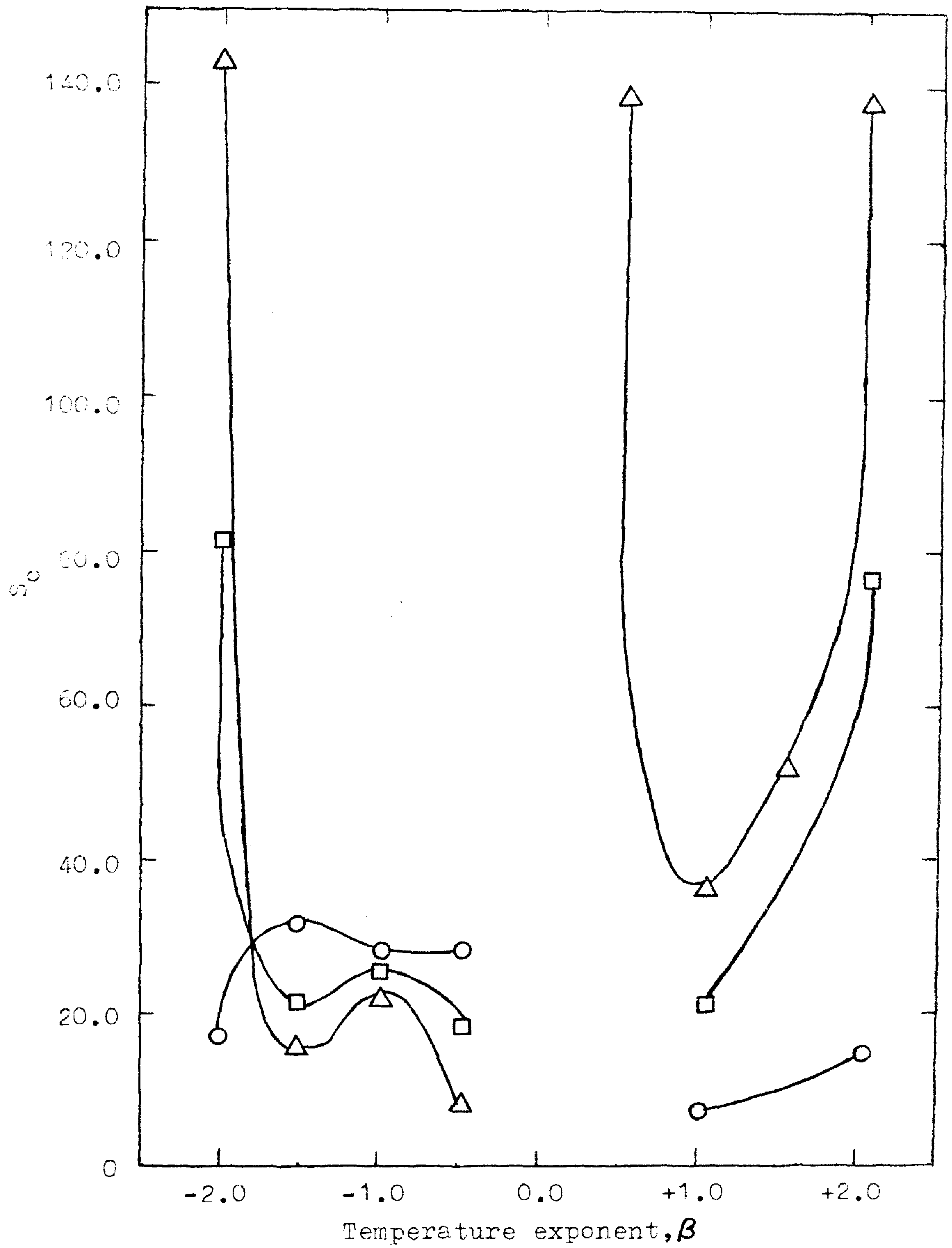

Fig. 2. Performance of equation (31) with the AGSM model.

- ○ Type I systems
- △ Type II systems
- □ Overall error

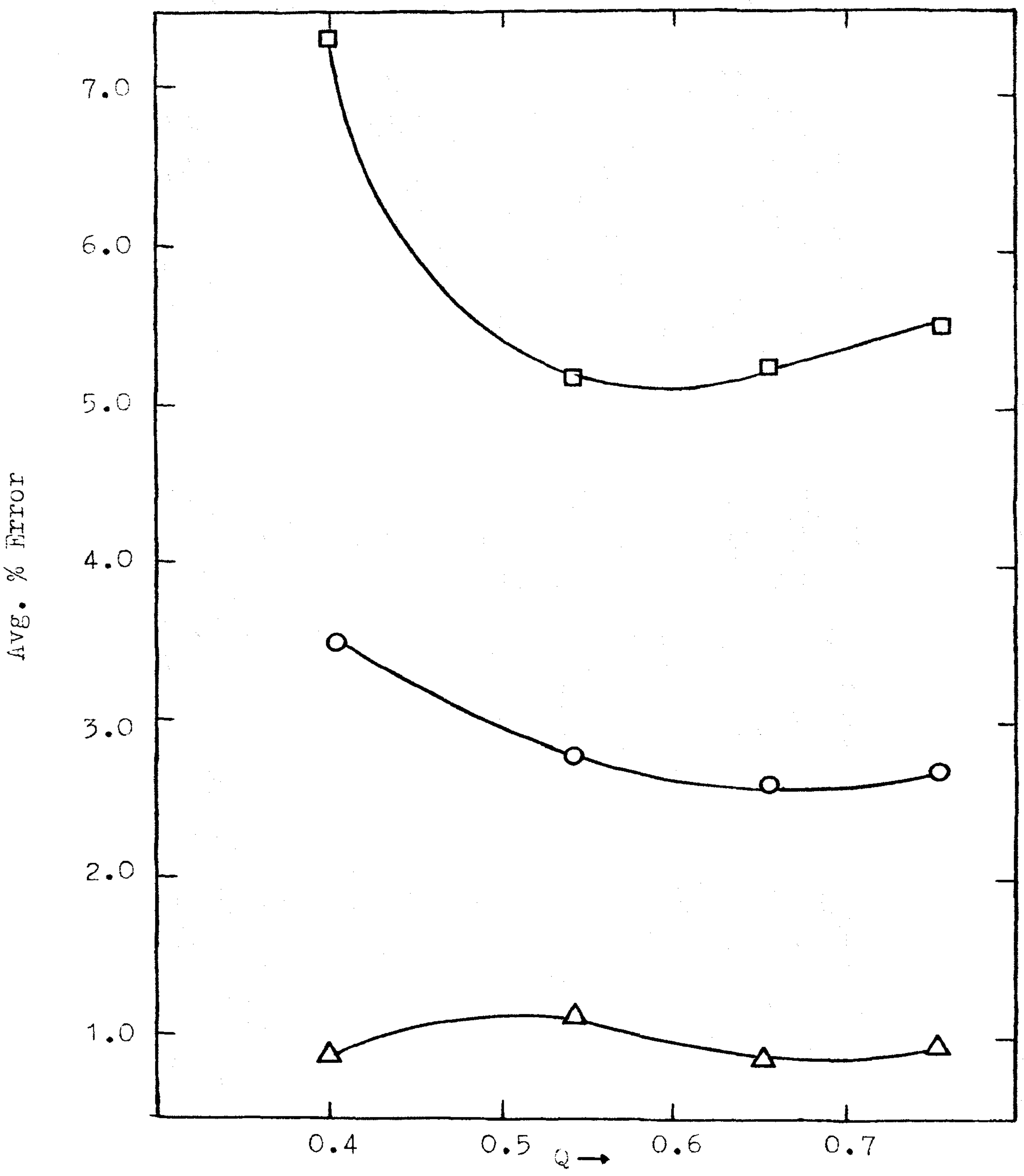

Fig. 3. Effect of the Value of Q on the accuracy of correlation for systems containing cycloalkanes.

- ○ Overall error
- □ Two Type I systems
- △ Three Type II systems

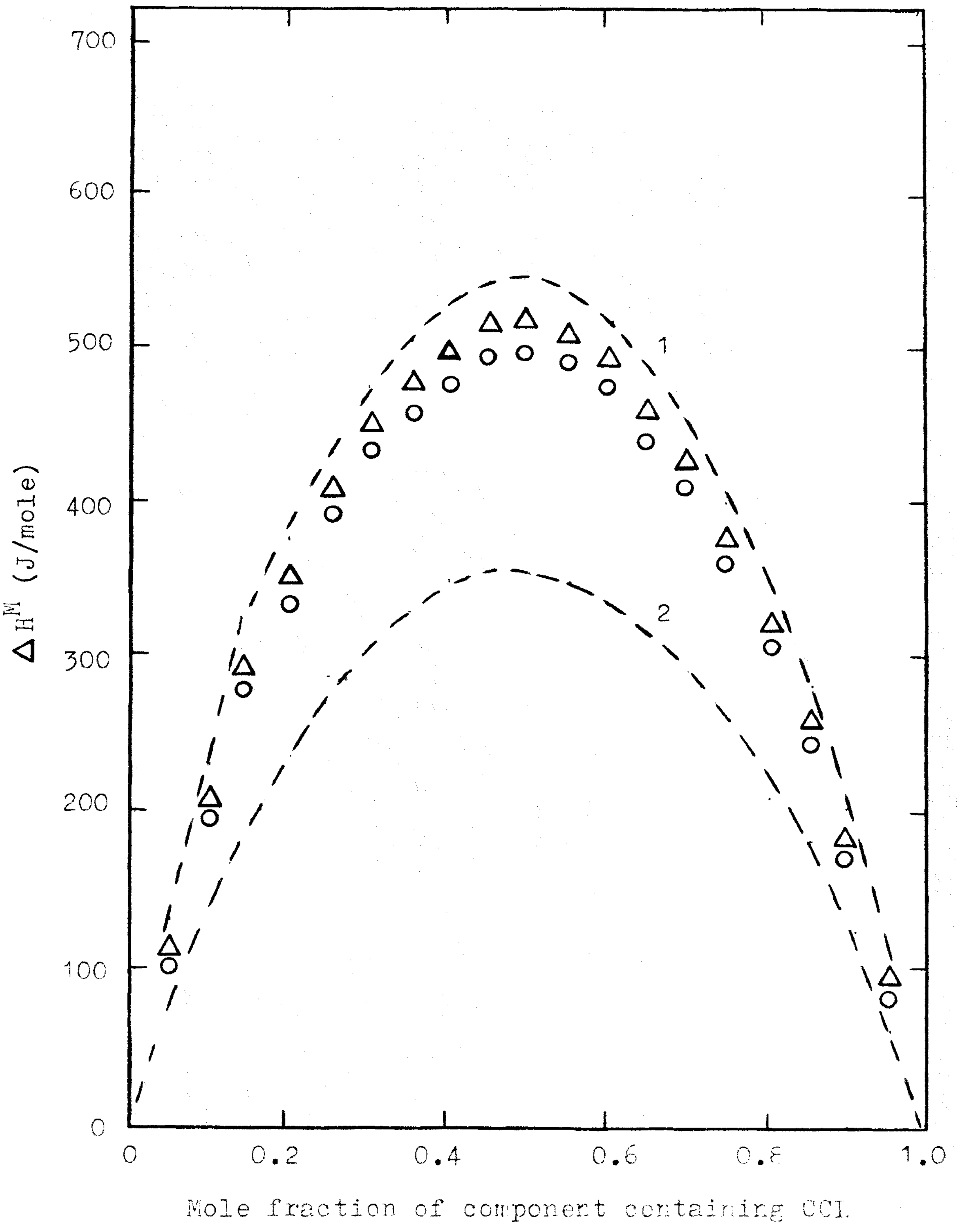

Fig. 4. Comparison of experimental and predicted heats of mixing for n-hexane with 1-chlorobutane and with 2-chlorobutane at 25°C.
Experimental data: 56.

△ experimental, and - - 1pre:1-chlorobutane
○ experimental, and - - 2pre:2-chlorobutane

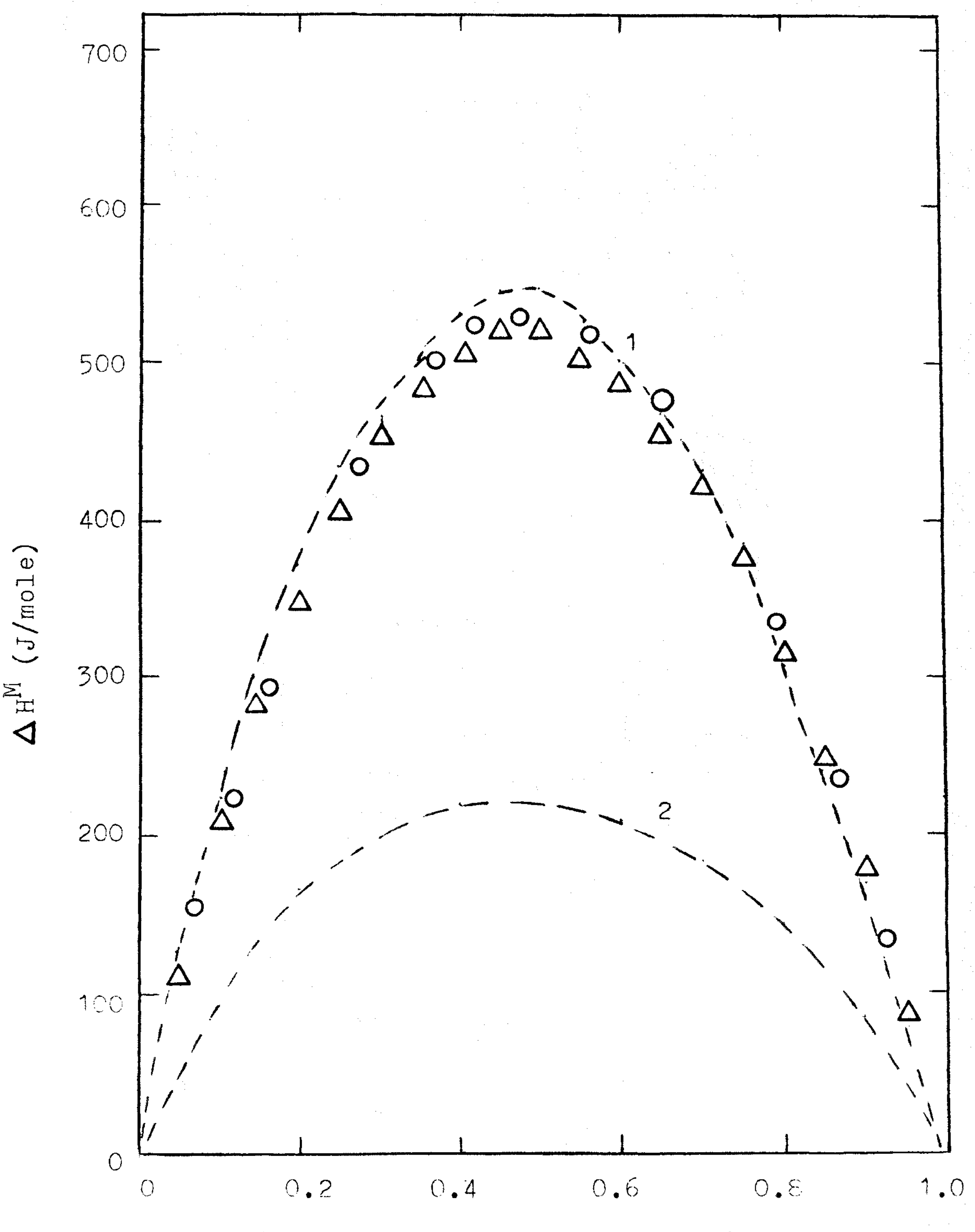

Fig. 5. Comparison of experimental and predicted heats of mixing for n-hexane with 1-chlorobutane and with t-butylchloride at 25°C. (Experimental data: 56,96).

△ experimental, and - - 1 (pre.): 1-chlorobutane
○ experimental, and - - 2 (pre.): t-butylchloride

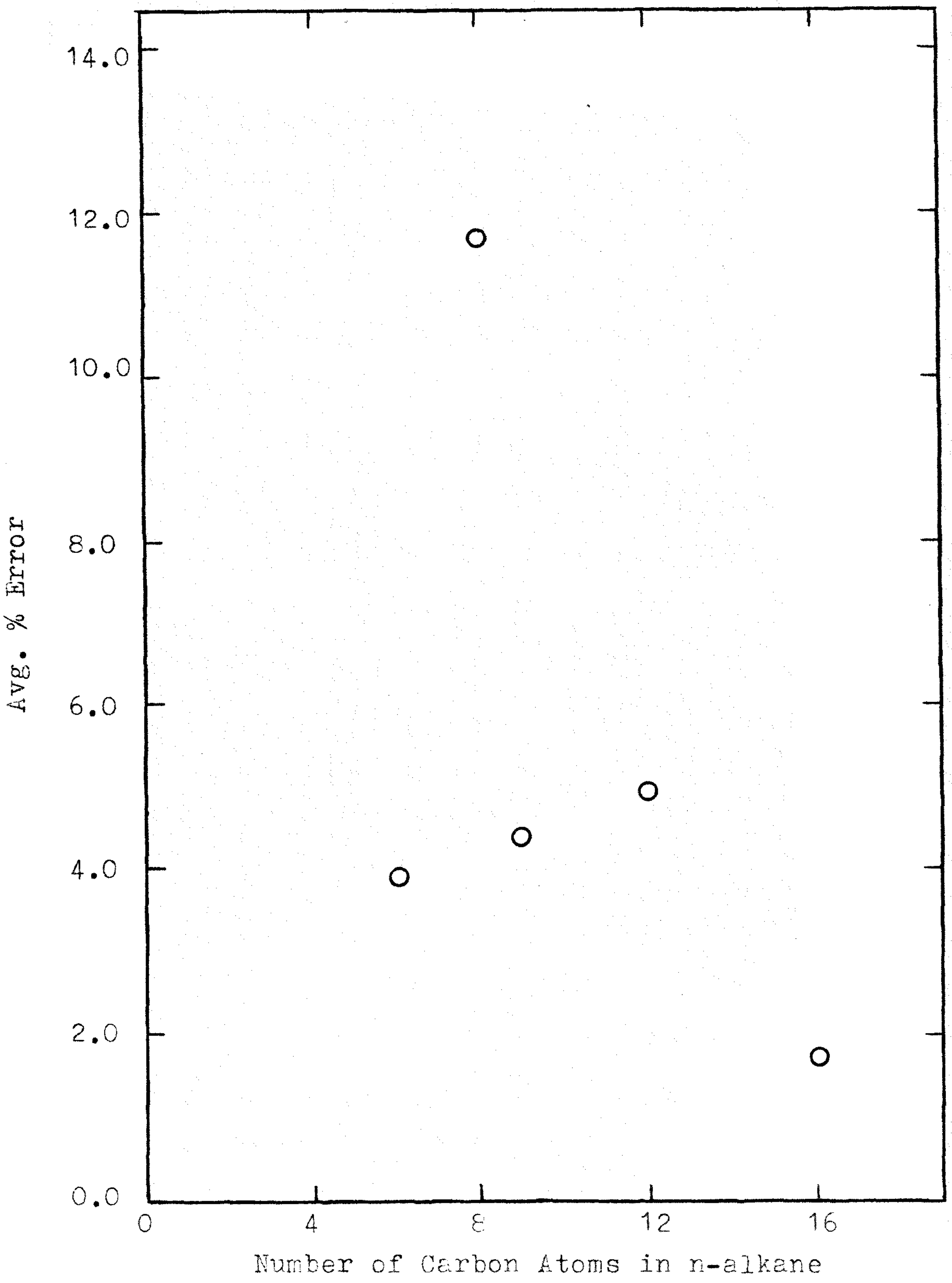

Fig. 6. Effect of alkane chain length on prediction error for 1-chlorobutane + n-alkane data at 25°C. (Experimental data: 56, 96).

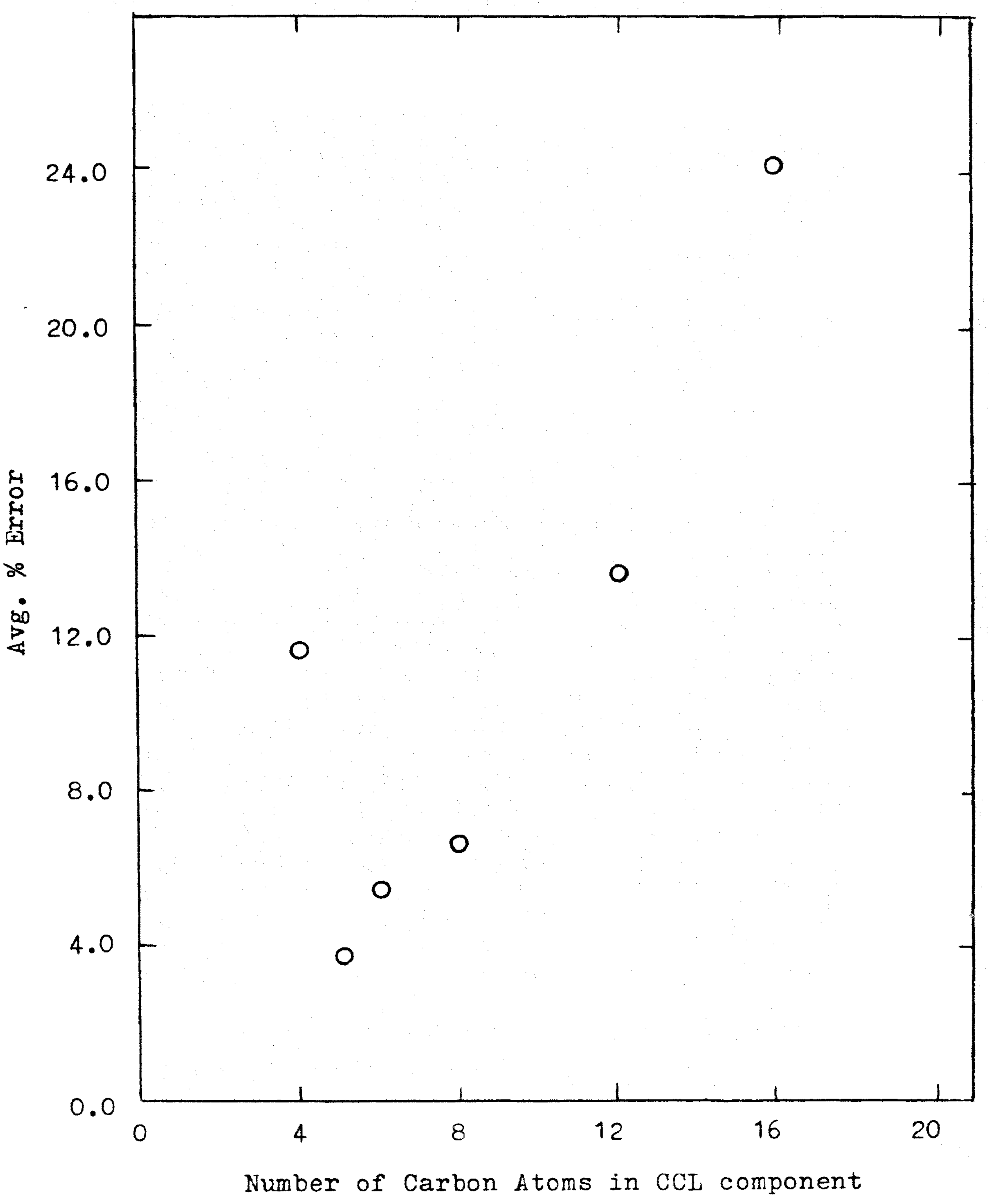

Fig. 7. Effect of length of component containing group CCL on prediction error for n-octane data at 25°C. (Experimental data: 56,86,89,96).

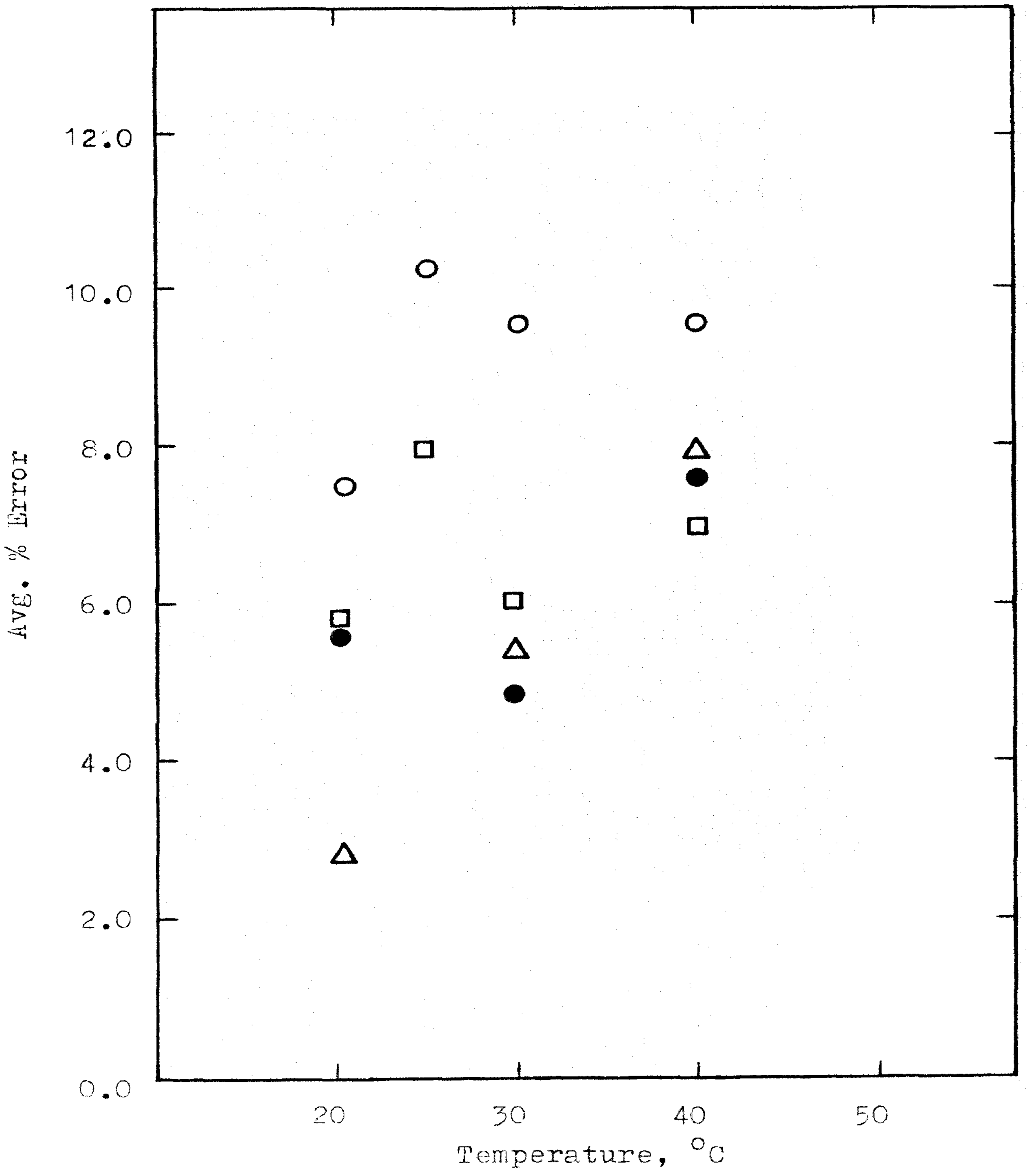

Fig. 8. Prediction errors for carbon tetrachloride mixtures at several temperatures. (Experimental data: 45,69).

○ CCl_4 + n-hexane

☐ CCl_4 + n-heptane

● CCl_4 + n-octane

△ CCl_4 + iso-octane

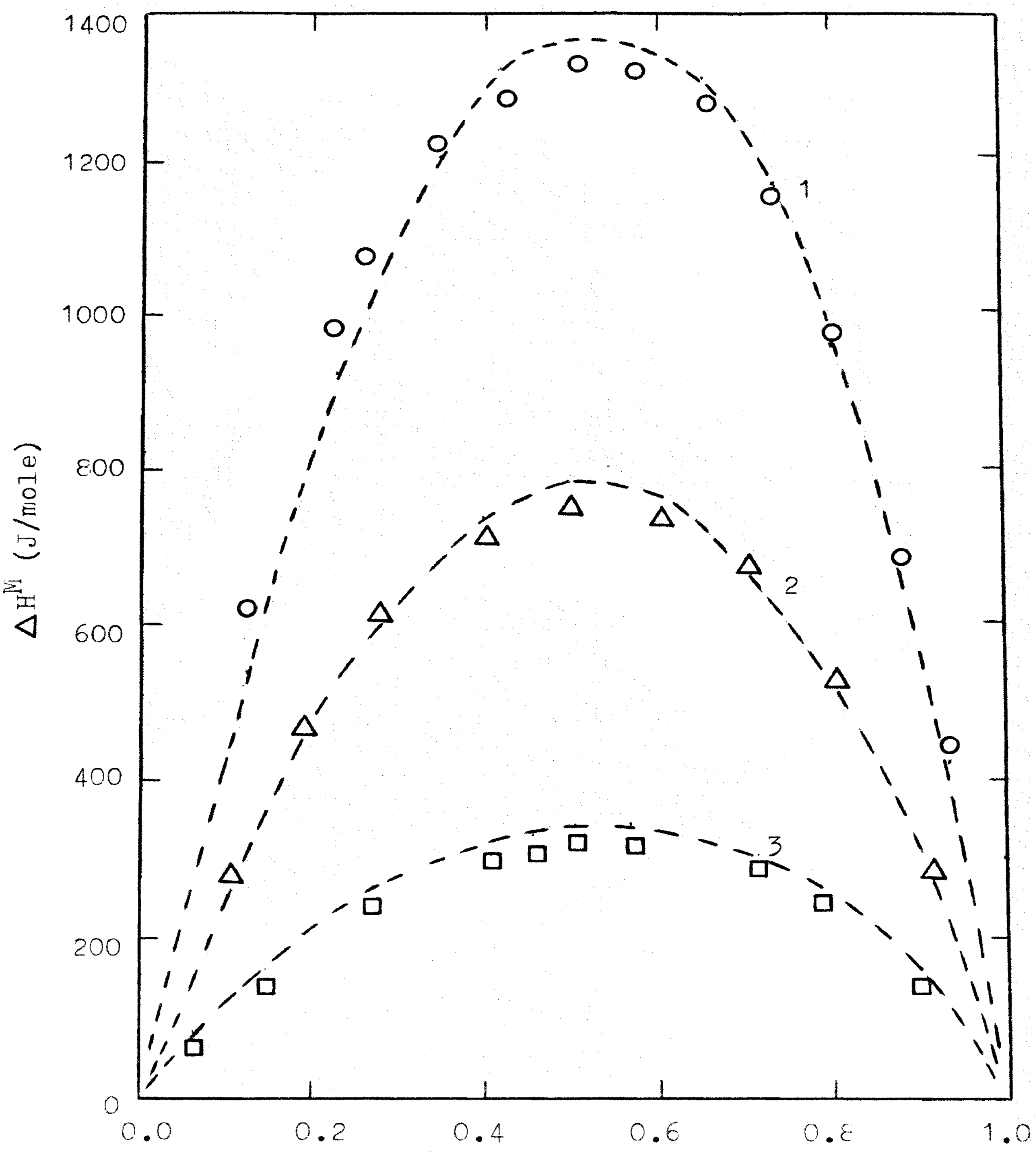

Fig. 9. Comparison of experimental and predicted heats of mixing for n-hexane with dichloromethane, chloroform and carbon tetrachloride at 25°C. (Experimental data: 45).

○ exp., and - - 1 pre.: dichloromethane
△ exp., and - - 2 pre.: chloroform
□ exp., and - - 3 pre.: carbon tetrachloride

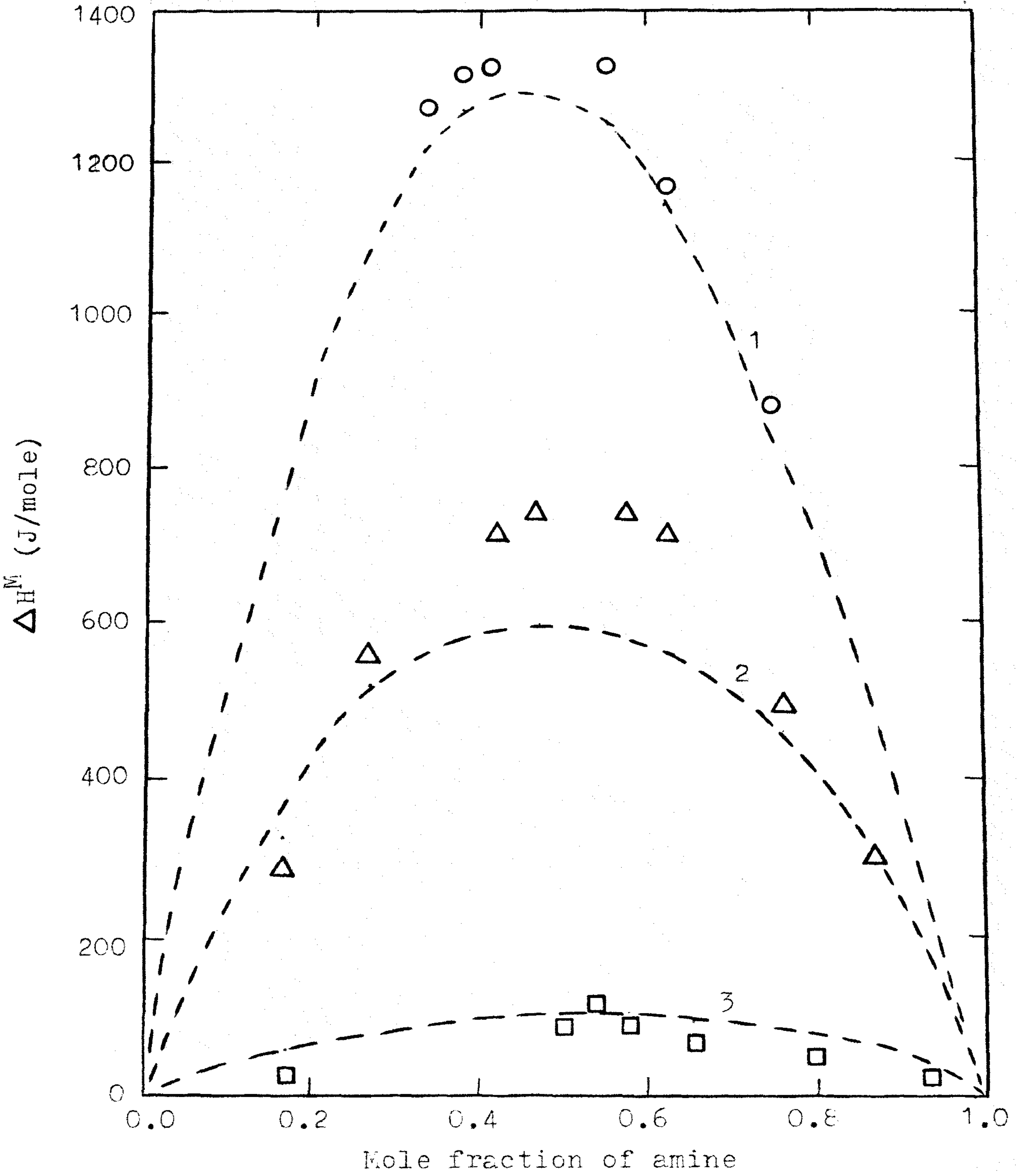

Fig. 10. Comparison of experimental and predicted heats of mixing for n-heptane with n-butylamine, diethylamine and triethylamine at 25°C. (Experimental data: 73).

○ exp., and - - 1 pre.: n-butylamine
△ exp., and - - 2 pre.: diethylamine
□ exp., and - - 3 pre.: triethylamine

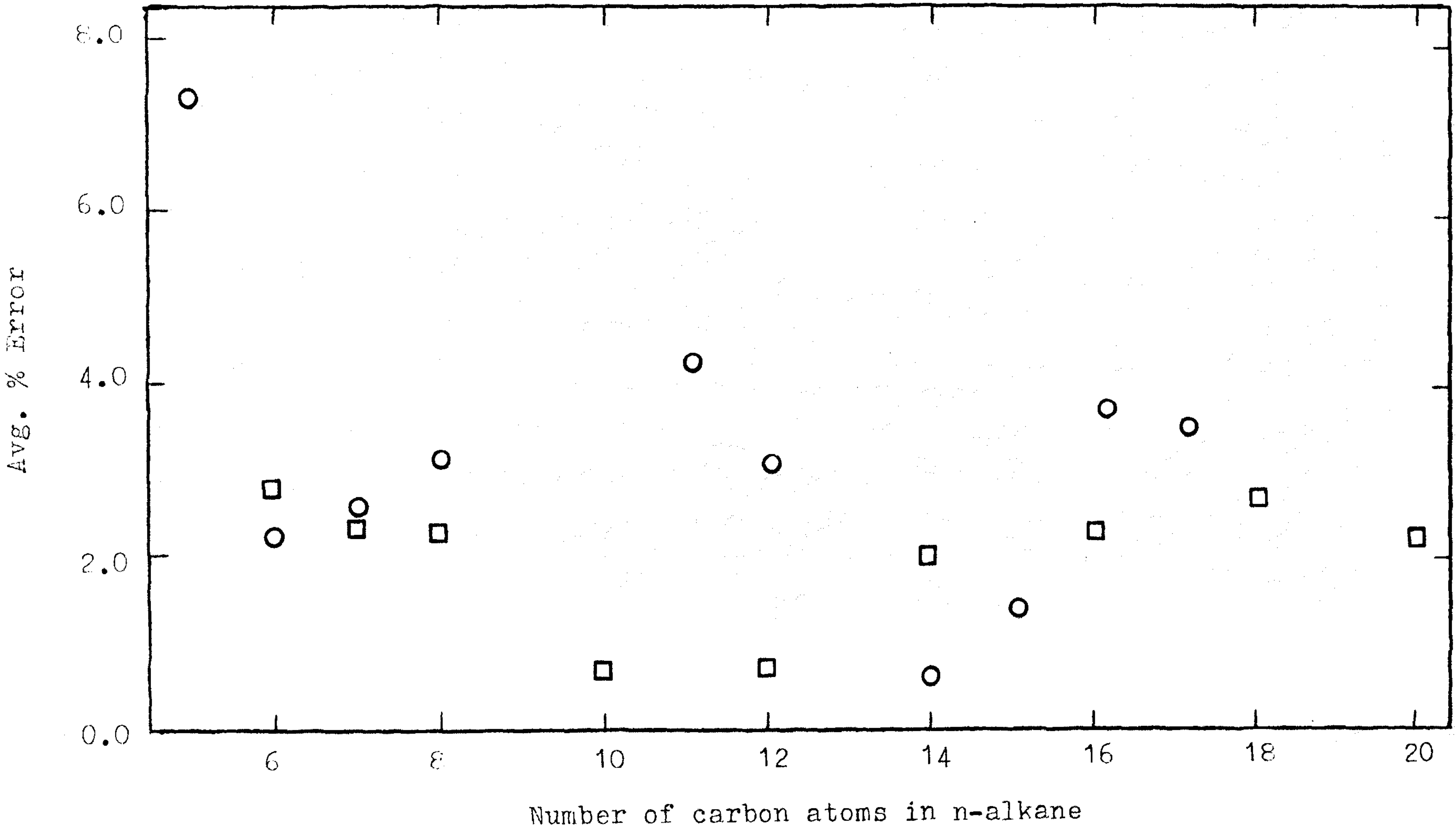

Fig. 11. Effect of alkane chain length on correlation and prediction error for benzene + n-alkane data at 25°C and 50°C. (Experimental data: 54,55,74,80).

○ benzene + n-alkane 25°C

□ benzene + n-alkane 50°C

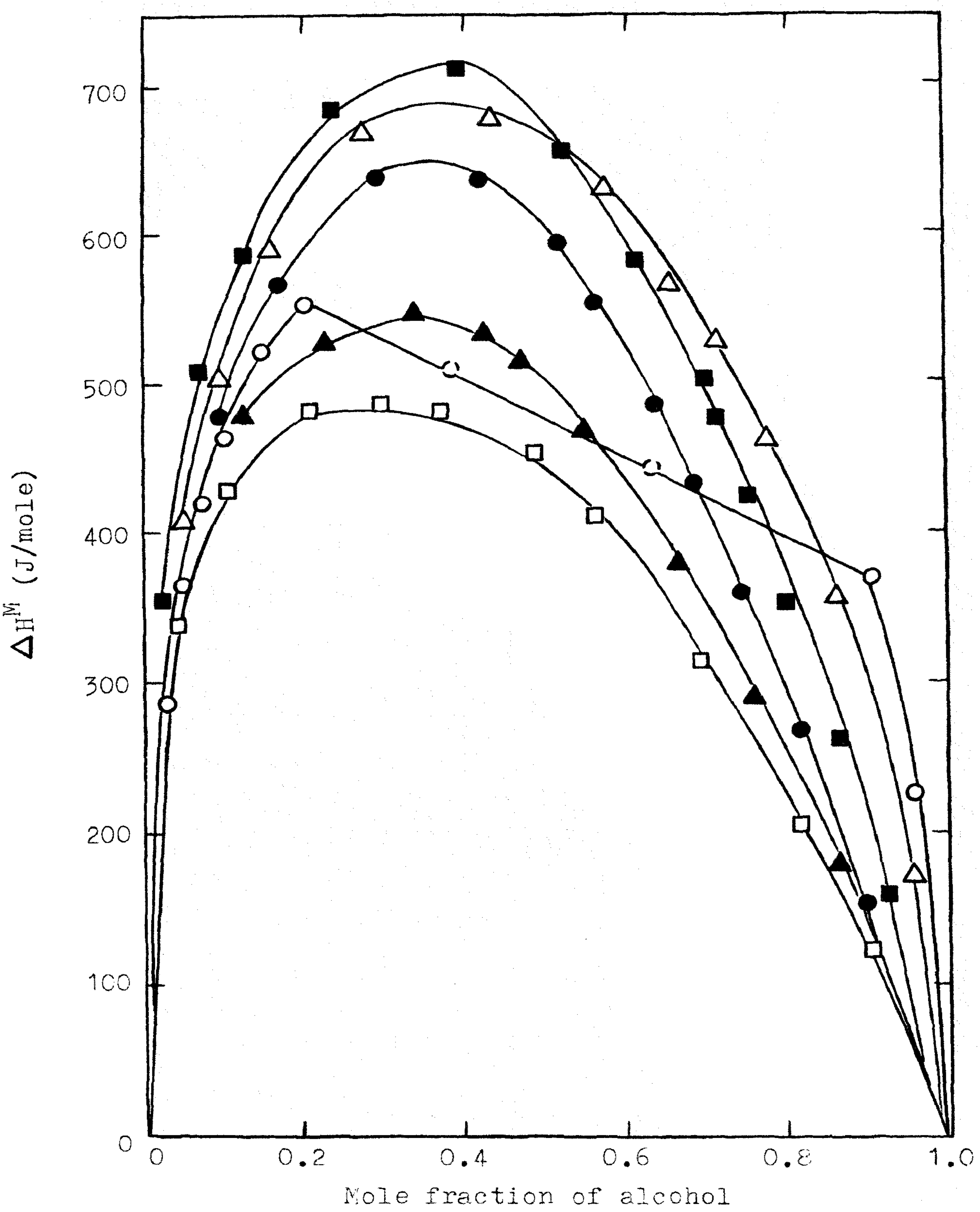

Fig. 12. Comparison of experimental data of n-heptane with several n-alcohols at 30°C. (Experimental data: 92,93,94).

○	methanol	●	n-pentanol
△	ethanol	▲	n-octanol
■	n-propanol	□	n-decanol

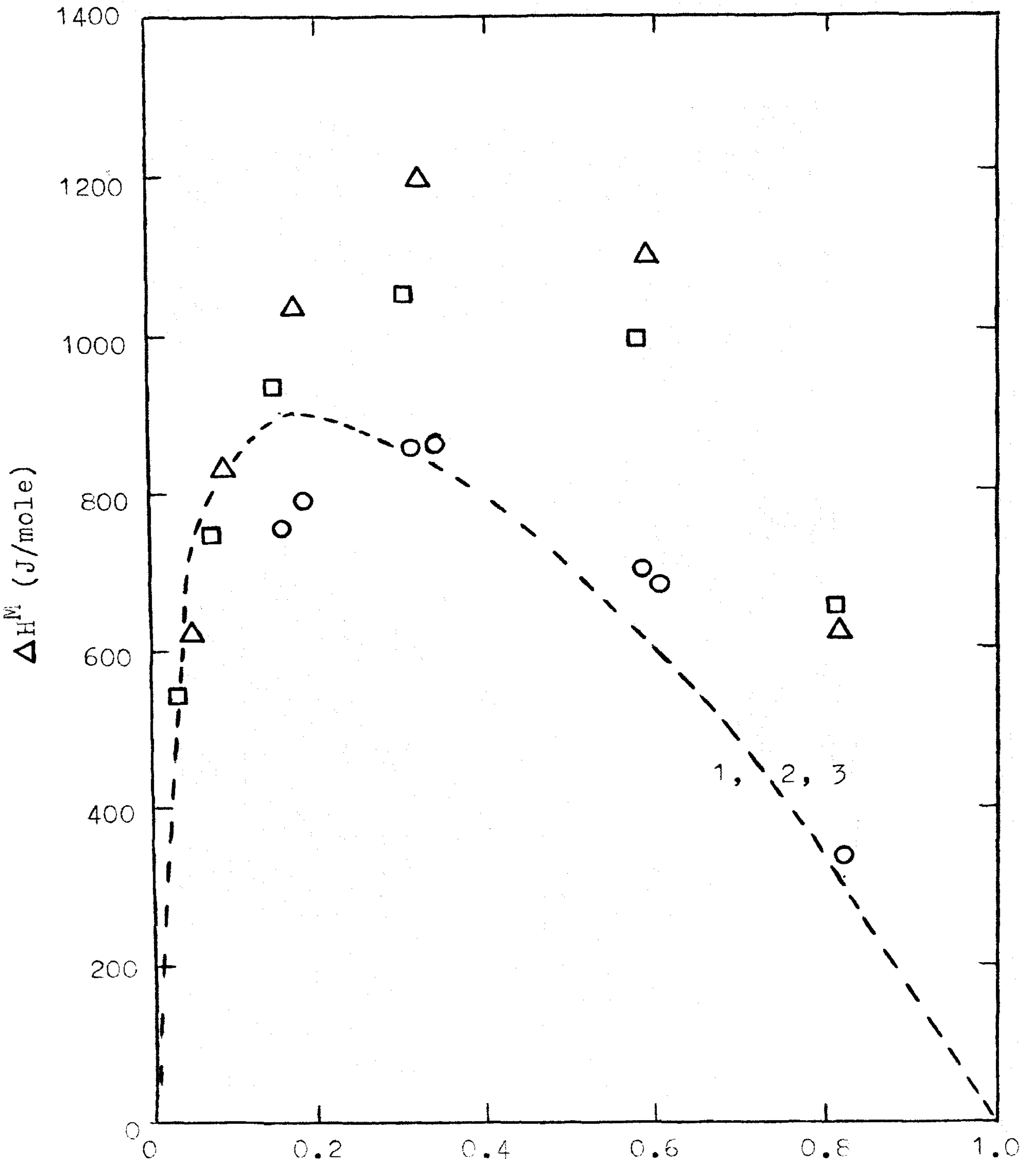

Fig. 13. Comparison of experimental and predicted heats of mixing of n-hexane with n-butanol, 2-butanol and 2-methyl-2-propanol at 45°C. (Experimental data: 47).

○ exp., and - - 1 (pre): n-butanol
△ exp., and - - 2 (pre): 2-butanol
□ exp., and - - 3 (pre): 2-methyl-2-propanol

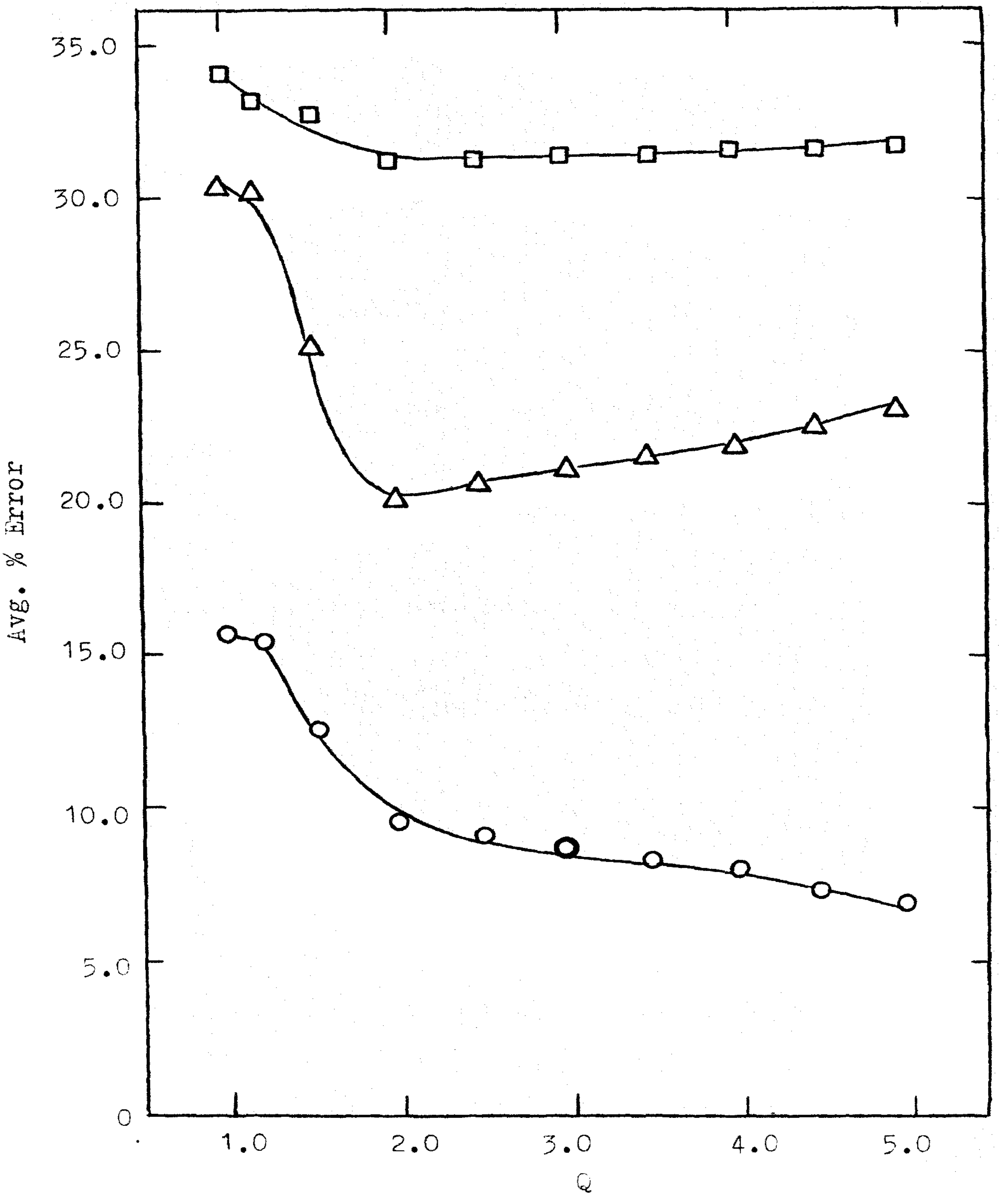

Fig. 14. Effect of the value of Q on the accuracy of correlation and prediction for alcohol systems. (Experimental data: 47,93,98).

○ n-butanol + n-heptane 30°C

△ 2-propanol + n-heptane 30°C

□ 2-methyl-2-propanol + n-hexane 27°C

Appendix I

Regression Computer Program

This appendix presents the regression computer program using the modified UNIFAC (with the Z(T)). Before explaining how to enter the program in the computer it might be good at this time to explain what is involved in the regression of interaction parameters. The regression computer program has three parts: main program, subroutine REG and subroutine FMIN. The main program has two parts, in the first part the information is read in by the computer. The data needed by the program is the number of experimental data points, the experimental data given as mole fraction and heats of mixing in J/mole, the number of parameters, and the starting values for the interaction parameters. The second part prints out the results when the program has converged on a good set of parameters.

The regression of the experimental data was accomplished using the subroutine REG which was identified in the book by Fredenslund et al (8). There were three subroutines available to us and REG was chosen because it took the least amount of computer time. The subroutine FMIN is where the prediction of heats of mixing by the UNIFAC method takes place.

The regression computer program does the following:

1) read in data,

2) call subroutine REG which in turn calls subroutine FMIN,

3) the heats of mixing is calculated for each data point in this subroutine,

4) the minimization function (FMIN) is defined by equation (34) (on page 47)

5) the program returns to REG where the parameters are changed in order to reduce FMIN and then returns to the other subroutine with this new set of parameters,

6) the computer program repeats this procedure until one of the following occurs:

   a) the program converges when the standard deviation is less than 1 x 10^{-5}, and the final results are printed out,

   b) the program reaches 200 iterations and stops calculating. This limit is needed because sometimes the program goes in the wrong direction and the FMIN gets large. Also, sometimes the program gets stuck on a set of parameters and repeats the same FMIN and standard deviation over and over.

   c) The program uses all the computer time it was allotted. In order to run the program on the school computer a time limit had to be given when the program was entered. The amount of time depended on the number of data points and the type of system. Some systems converged on a set of parameters more easily than others, for example, the alcohol regression took longer than the benzene regression.

An example of a computer run will be given for the benzene/alkane regression. Below is a listing of the input data (program name = BENZENE-ALKANE-REG-DATA):

line 1 = number of experimental data points

lines 2-68 = experimental data for all the systems used, given as mole fraction of benzene and heats of mixing in J/mole

line 69 = number of interaction parameters

lines 70-71 = initial values of parameters

```
 1    67              31  0.7088  1319.0  61  0.4760   1047.0
 2  0.2651   698.0    32  0.7642  1252.0  62  0.5463   1108.0
 3  0.4200   931.0    33  0.8436  1016.0  63  0.6131   1128.0
 4  0.5207  1000.0    34  0.9193   645.0  64  0.6859   1111.0
 5  0.5909  1003.0    35  0.1873   524.0  65  0.7553   1035.0
 6  0.6868   939.0    36  0.3089   827.0  66  0.8283    887.0
 7  0.7449   862.0    37  0.4077  1034.0  67  0.8855    694.0
 8  0.8145   716.0    38  0.5053  1184.0  68  0.9410    417.0
 9  0.8975   467.0    39  0.5809  1263.0  69    2
10  0.0794   216.0    40  0.6893  1295.0  70         0.1
11  0.1503   394.0    41  0.7572  1249.0  71         0.1
12  0.2111   534.0    42  0.8177  1129.0
13  0.2655   650.0    43  0.8949   829.0
14  0.3118   739.0    44  0.9482   485.0
15  0.3910   867.0    45  0.1006   256.0
16  0.4535   940.0    46  0.2104   492.0
17  0.5046   980.0    47  0.2851   629.0
18  0.5665  1009.0    48  0.3461   721.0
19  0.6294  1002.0    49  0.4465   828.0
20  0.7059   943.0    50  0.5289   867.0
21  0.7944   817.0    51  0.5938   866.0
22  0.8799   575.0    52  0.6655   831.0
23  0.9496   277.0    53  0.7576   714.0
24  0.1454   476.0    54  0.8346   562.0
25  0.2689   816.0    55  0.9188   314.0
26  0.3499  1013.0    56  0.0609   178.0
27  0.4289  1145.0    57  0.1306   370.0
28  0.5062  1263.0    58  0.2292   618.0
29  0.5675  1321.0    59  0.3126   797.0
30  0.6262  1345.0    60  0.3985   946.0
```

The nomenclature for the main computer program is given below:

ERROR	Percentage difference between calculated and experimental heats of mixing
HEMIX(I)	Calculated heats of mixing of component i in the mixture
HK(K)	Heats of mixing of group k
HKS(K,I)	Standard state heats of mixing of group k in pure component i
HMIXE	Experimental heats of mixing
HMIX	Calculated heats of mixing
HSUM(I)	Partial molar heats of mixing of component i in the mixture
I	component i
J,K	groups j, k
NDATA	number of experimental data points
N(K,I)	Number of groups of type k in component i
Q(J)	Area parameter of group j
R	Gas constant, J/K mole
T	Absolute temperature, ^{o}K
TH(J)	Area fraction of group j
THS(J,I)	Area fraction of group j in pure component i
X(J)	Group fraction of group j
XM(I)	Mole fraction of component i
XT	Group interaction parameter determined by data reduction

The computer program that follows is the main regression program adapted for the benzene/alkane correlation (lines 20 - 94 in subroutine FMIN). This program is called ZT-BENZENE-REG.

```
C   PROGRAM USING UNIFAC REGRESSION SUBROUTINE
C   REGRESSION FOR Z(T)
C   MAIN PROGRAM
        COMMON XM1(100),HMIXE(100),HMIX(100),ERROR(100),NDATA,T
        COMMON Q(100),N(100,100),AERROR
        DIMENSION XT(50,50)
        READ1,NDATA
  1     FORMAT(I4)
  11    FORMAT(F10.5)
        READ2, (XM1(I),HMIXE(I),I=1,NDATA)
  2     FORMAT(F6.4,F8.1)
        READ1, NPAR
        NN=NPAR+1
        SA=1.E-6
        READ702,(XT(1,I),I=1,NPAR)
  702   FORMAT(F15.7)
        DO 20 J=2,NN
        DO 20 I=1,NPAR
        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
        PRINT4
  4     FORMAT('-',10X,'INITIAL PARAMETERS')
        PRINT301, (XT(1,I),I=1,NPAR)
   301  FORMAT(///,10X,F15.7)
        ALFA=1.
        BETA=0.5
        GAMMA=2.0
        CALL REG(NPAR,XT,ALFA,BETA,GAMMA,SA,NN)
        AEROR=AERROR/FLOAT(NDATA)
        PRINT7
  7     FORMAT(1H0,4X,'MOLE FRACTION',3X,'EXP. HMIX',5X,
       %'CALC. HMIX',8X,'% ERROR')
        PRINT9,(XM1(J),HMIXE(J),HMIX(J),ERROR(J),J=1,NDATA)
  9     FORMAT(4F15.5)
        PRINT10, AEROR
  10    FORMAT(1H0,'AVERAGE % ERROR =',2X,F12.6)
        STOP
        END
```

```
          SUBROUTINE FMIN(XT,FF)
          COMMON XM1(100),HMIXE(100),HMIX(100),ERROR(100),NDATA,T
          COMMON G(100),N(100,100),AERROR
   C   UNIFAC---TEMPERATURE-  INDEPENDENT PARAMETERS
          DIMENSION HS(100),BS(100,100),HEAT(100,100),HEMIX(100)
          DIMENSION A(100,100),AX(100),HK(100),HKS(100,100)
          DIMENSION DN(100,100),BSUM(100),DS(100,100)
          DIMENSION ES(100),FS(100),GS(100),CS(100,100)
          DIMENSION C(100,100),D(100,100),E(100),F(100),G(100)
          DIMENSION H(100),B(100,100),BX(100),XM(100),X(100)
          DIMENSION H1(100),H1S(100),CSUM(100),P(100,100)
          DIMENSION YSUM(100)
          DIMENSION CSSUM(100),BSSUM(100),HSUM(100),WSUM(100)
          DIMENSION TH(100),THS(100,100),VSUM(100),XT(100)
          YS=0.
          AERROR=0.
          R=8.314
           DO 777 KPN=1,NDATA
           IS=3
           IF(KPN.LE.8)GO TO 725
           IF(KPN.LE.22)GO TO 735
           IF(KPN.LE.33)GO TO 745
           IF(KPN.LE.43)GO TO 755
           IF(KPN.LE.54)GO TO 765
           GO TO 775
   C  BENZENE + 2,2,4 TRIMETHYLPENTANE(ISO-OCTANE)  25 C
     725   T=298.15
           N(2,2)=0
           N(3,2)=0
           N(4,2)=0
           N(5,2)=0
           N(6,2)=6
           N(2,3)=1
           N(3,3)=1
           N(4,3)=1
           N(5,3)=5
           N(6,3)=0
           KA=6
           Q(2)=0.0
           Q(3)=.228
           Q(4)=.54
           Q(5)=.848
           Q(6)=.4
           DO 730 KK20=2,KA
           DO 730 KK21=2,KA
              A(KK20,KK21)=0.
     730   CONTINUE
           A(2,6)=XT(1)
           A(6,2)=XT(2)
           A(3,6)=A(2,6)
           A(4,6)=A(2,6)
           A(5,6)=A(2,6)
```

```
      A(6,3)=A(6,2)
      A(6,4)=A(6,2)
      A(6,5)=A(6,2)
      GO TO 780
C  BENZENE + N-DECANE  50 C
  735 T=323.15
      N(2,3)=8
  740 N(2,2)=0
      N(3,2)=0
      N(4,2)=6
      N(3,3)=2
      N(4,3)=0
      KA=4
      Q(2)=.54
      Q(3)=.848
      Q(4)=0.4
      A(2,2)=0.
      A(3,3)=0.
      A(4,4)=0.
      A(2,3)=0.
      A(3,2)=0.
      A(2,4)=XT(1)
      A(4,2)=XT(2)
      A(3,4)=A(2,4)
      A(4,3)=A(4,2)
      GO TO 780
C  BENZENE + N-C16  25 C
  745 T=298.15
      N(2,3)=14
      GO TO 740
C  BENZENE + N-C22  50 C
  755 T=323.15
      N(2,3)=20
      GO TO 740
C  BENZENE + N-PENTANE  25 C
  765 T=298.15
      N(2,3)=3
      GO TO 740
C  BENZENE + N-C14  50 C
  775 T=323.15
      N(2,3)=12
      GO TO 740
  780 XM(2)=XM1(KPN)
      XM(3)=1.0-XM(2)
      BX(1)=0.
      AX(1)=0.
      AXSUM=0.0
      DO 30 M=2,KA
      DO 40 I=2,IS
      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(IS)/AXSUM
      AXSUM=0.0
 30   CONTINUE
      WSUM(1)=0.0
      DO 99 J=2,KA
      DO 88 M=2,KA
      WSUM(M)=WSUM(M-1)+Q(M)*X(M)
 88   CONTINUE
      TH(J)=Q(J)*X(J)/WSUM(KA)
 99   CONTINUE
      D(1,1)=0.0
      C(1,1)=0.0
      F(1)=0.0
      E(1)=0.0
      G(1)=0.0
      H(1)=0.0
      B(1,1)=0.0
      CSUM(1)=0.0
      BSUM(1)=0.0
      DO 3 K=2,KA
      DO 1 J=2,KA
      DO 2 M=2,KA
      C(J,M)=TH(M)*EXP(-((35.2-0.1272*T+0.00014*T*T)*A(M,J)
     %)/(2*T))*(((35.2-0.1272*T+0.00014*T*T)*A(M,J))/(2*T*T
     %)-(A(M,J)*(0.00028*T-0.1272))/(2*T))
      P(J,M)=TH(M)*EXP(-((35.2-0.1272*T+0.00014*T*T)*A(M,J)
     %)/(2*T))
      CSUM(M)=CSUM(M-1)+C(J,M)
      BSUM(M)=BSUM(M-1)+P(J,M)
      D(J,M)=(ABS(BSUM(M)))**2.0
 2    CONTINUE
      E(J)=E(J-1)+TH(J)*EXP(-((35.2-0.1272*T+0.00014*T*T)
     %*A(K,J))/(2*T))*CSUM(KA)/D(J,KA)
      F(J)=F(J-1)+TH(J)*EXP(-((35.2-0.1272*T+0.00014*T*T)
     %*A(K,J))/(2*T))*(((35.2-0.1272*T+0.00014*T*T)*A(K,J)
     %)/(2*T*T)-(A(K,J)*(0.00028*T-0.1272))/(2*T))/BSUM(KA)
      G(J)=G(J-1)+TH(J)*EXP(-((35.2-0.1272*T+0.00014*T*T)
     %*A(J,K))/(2*T))*(((35.2-0.1272*T+0.00014*T*T)*A(J,K)
     %)/(2*T*T)-(A(J,K)*(0.00028*T-0.1272))/(2*T))
      H(J)=H(J-1)+TH(J)*EXP(-((35.2-0.1272*T+0.00014*T*T)
     %*A(J,K))/(2*T))
 1    CONTINUE
      H1(KA)=G(KA)/H(KA)
      HK(K)=Q(K)*(H1(KA)+F(KA)-E(KA))*R*T*T
 3    CONTINUE
      YSUM(1)=0.0
      DO 5 I=2,IS
      DO 10 J=2,KA
      DO 20 M=2,KA
```

```
      YSUM(M)=N(M,I)+YSUM(M-1)
 20   CONTINUE
      DN(J,I)=FLOAT(N(J,I))/YSUM(KA)
 10   CONTINUE
 5    CONTINUE
      VSUM(1)=0.0
      DO 77 I=2,IS
      DO 66 J=2,KA
      DO 55 M=2,KA
      VSUM(M)=VSUM(M-1)+Q(M)*DN(M,I)
 55   CONTINUE
      THS(J,I)=Q(J)*DN(J,I)/VSUM(KA)
 66   CONTINUE
 77   CONTINUE
      DS(1,1)=0.0
      CS(1,1)=0.0
      ES(1)=0.0
      FS(1)=0.0
      GS(1)=0.0
      HS(1)=0.0
      BS(1,1)=0.0
      CSSUM(1)=0.0
      BSSUM(1)=0.0
      DO 44 I=2,IS
      DO 33 K=2,KA
      DO 11 J=2,KA
      DO 22 M=2,KA
      CS(J,M)=THS(M,I)*EXP(-((35.2-0.1272*T+0.00014*T*T)
     %*A(M,J))/(2*T))*(((35.2-0.1272*T+0.00014*T*T)*A(M,J)
     %)/(2*T*T)-(A(M,J)*(0.00028*T-0.1272))/(2*T))
      BS(J,M)=THS(M,I)*EXP(-((35.2-0.1272*T+0.00014*T*T)
     %*A(M,J))/(2*T))
      CSSUM(M)=CSSUM(M-1)+CS(J,M)
      BSSUM(M)=BSSUM(M-1)+BS(J,M)
      DS(J,M)=(ABS(BSSUM(M)))**2.0
 22   CONTINUE
      ES(J)=ES(J-1)+THS(J,I)*EXP(-((35.2-0.1272*T+0.00014*T
     %*T)*A(K,J))/(2*T))*CSSUM(KA)/DS(J,KA)
      FS(J)=FS(J-1)+THS(J,I)*EXP(-((35.2-0.1272*T+0.00014*T
     %*T)*A(K,J))/(2*T))*(((35.2-0.1272*T+0.00014*T*T)*A(K,J)
     %)/(2*T*T)-(A(K,J)*(0.00028*T-0.1272))/(2*T))/BSSUM(KA)
      GS(J)=GS(J-1)+THS(J,I)*EXP(-((35.2-0.1272*T+0.00014*T
     %*T)*A(J,K))/(2*T))*(((35.2-0.1272*T+0.00014*T*T)*A(J,K)
     %)/(2*T*T)-(A(J,K)*(0.00028*T-0.1272))/(2*T))
      HS(J)=HS(J-1)+THS(J,I)*EXP(-((35.2-0.1272*T+0.00014*T
     %*T)*A(J,K))/(2*T))
 11   CONTINUE
      H1S(KA)=GS(KA)/HS(KA)
      HKS(K,I)=Q(K)*(H1S(KA)+FS(KA)-ES(KA))*R*T*T
 33   CONTINUE
 44   CONTINUE
      HEMIX(1)=0.0
```

```
         HSUM(1)=0.0
         HEAT(1,1)=0.0
         DO 60 I=2,IS
         DO 70 K=2,KA
         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(KA)+HEMIX(I-1)
   60    CONTINUE
         HEMIX(3)=HEMIX(IS)
         HMIX(KPN)=HEMIX(3)
         ERROR(KPN)=100.0*(HMIXE(KPN)-HMIX(KPN))/HMIXE(KPN)
         AERROR=AERROR+ABS(ERROR(KPN))
         DIFF=ABS(HMIXE(KPN)-HMIX(KPN))
         Y=(DIFF/HMIXE(KPN))**2.0
         YS=YS+Y
   777   CONTINUE
         FF=YS
         RETURN
         END
```

```
      SUBROUTINE REG(NPAR,X,ALFA,BETA,GAMMA,SA,NN)
      DIMENSION X(50,50),F(100),XS(100),XM(100),XE(100)
      DIMENSION XX(100),XR(100),XK(100),XB(100)
      N=NPAR
      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=1.0
      BETA=0.5
      GAMMA=2.0
      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
      DO 131 I=1,N
  131 XR(I)=XM(I)+ALFA*(XM(I)-XS(I))
      CALL FMIN(XR,FR)
      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=0.0
      DO 20 J=1,NN
   20 FM=FM+F(J)
      FM=FM/FLOAT(NN)
      FRMS=0.0
      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-200)500,500,23
  500 CONTINUE
      IF(JPR-1)902,902,903
  903 CONTINUE
      IF(JPR-6)901,904,904
  904 JPR=1
  902 CONTINUE
      PRINT107,ITER,NF
  107 FORMAT(1H0,´    ITERATION ´,I4,´   NUMBER OF
     %CALLS FOR THE SUBROUTINE´,I5)
      PRINT109
  109 FORMAT(´-´,´  PARAMETERS´)
      PRINT400,(X(JS,I),I=1,N)
      PRINT106,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
```

```
FORTRAN IV (VER 5  ) SOURCE LISTING: REG     SUBROUTINE  09/16/80  20:12:19
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))16,18,30
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)=XH(I)+BETA*(XS(I)-XH(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))/2.0
38      CONTINUE
        GO TO 27
23      PRINT905
905     FORMAT(1H0,'        FINAL PARAMETERS')
        PRINT906
906     FORMAT(1H0,5X,'A(3,4)',10X,'A(4,3)')
        PRINT400,(X(JS,I),I=1,N)
        PRINT106,F(JS),RMS
635     CONTINUE
        RETURN
        END
```

The procedure to run the program follows:

1) Write a mini-program

```
/LOGON JR301923,JCHE701,c'43conove'
/PARAM LIST=YES,DEBUG=YES,MAP=NO,WRLST=YES
/SYSFILE SYSDTA=(main program name)
/EXEC $BGFOR
/SYSFILE SYSDTA=(data program name)
/EXEC *
/LOGOFF
```

where JR301923 is the student I.D. number. For this case the main program is ZT-BENZENE-REG, and the data program is BENZENE-ALKANE-REG-DATA. Call this mini-program BENZ-ALKANE-ONE.

2) Return to the system (@SY), the computer will give a /.

3) Then type

```
/ENTER BENZ-ALKANE-ONE,TIME=XXX
```

then hit control C, the computer will give a / and give the job number for this run. The amount of time you enter depends on the particular system and the number of data points, the range is 200-800 seconds but could be higher. The same amount of time should not be entered for each type of system. Sometimes the parameters get stuck on the same value, and repeat the same predictions over and over. If an excessive amount of time is given then the computer will continue calculating until the limit is reached, as a result, a lot of computer time is wasted.

4) The output is obtained from the computer room. A typical printout is given on the following pages.

```
              INITIAL PARAMETERS


                      0.1000000

                      0.1000000

       ITERATION     1    NUMBER OF                                 CALLS FOR THE SUBROUTINE     5

    PARAMETERS
       0.1150000          0.1150000
      FMIN=    0.64652E 02      SD=    0.11542E 00

       ITERATION     6    NUMBER OF                                 CALLS FOR THE SUBROUTINE    13

    PARAMETERS
       0.2124999          0.1774999
      FMIN=    0.63095E 02      SD=    0.60484E 00

       ITERATION    11    NUMBER OF                                 CALLS FOR THE SUBROUTINE    23

    PARAMETERS
       1.0631976          1.2505436
      FMIN=    0.40838E 02      SD=    0.74672E 01

       ITERATION    16    NUMBER OF                                 CALLS FOR THE SUBROUTINE    32

    PARAMETERS
       6.4906321          4.6460209
      FMIN=    0.24686E 01      SD=    0.10138E 01

       ITERATION    21    NUMBER OF                                 CALLS FOR THE SUBROUTINE    40

    PARAMETERS
       7.9325562          5.6652679
      FMIN=    0.20225E 00      SD=    0.70724E-01

       ITERATION    26    NUMBER OF                                 CALLS FOR THE SUBROUTINE    49

    PARAMETERS
       8.1061287          5.7309484
      FMIN=    0.19049E 00      SD=    0.27951E-03
```

```
     ITERATION   31   NUMBER OF                                 CALLS FOR THE SUBROUTINE   58

   PARAMETERS
      8.2580070        5.5741062
    FMIN=   0.16026E 00     SD=   0.14792E-02

     ITERATION   36   NUMBER OF                                 CALLS FOR THE SUBROUTINE   67

   PARAMETERS
      9.6239319        3.9830103
    FMIN=   0.16717E 00     SD=   0.74403E-02

     ITERATION   41   NUMBER OF                                 CALLS FOR THE SUBROUTINE   77

   PARAMETERS
     11.9496760        1.9615959
    FMIN=   0.13626E 00     SD=   0.62943E-03

     ITERATION   46   NUMBER OF                                 CALLS FOR THE SUBROUTINE   86

   PARAMETERS
     12.1233080        1.8621721
    FMIN=   0.13543E 00     SD=   0.30410E-04

     ITERATION   51   NUMBER OF                                 CALLS FOR THE SUBROUTINE   96

   PARAMETERS
     12.0808630        1.8896055
    FMIN=   0.13540E 00     SD=   0.34944E-05

       FINAL PARAMETERS

        A(2,4)            A(4,2)
     12.0871460        1.8873072
    FMIN=   0.13540E 00     SD=   0.60632E-06

   MOLE FRACTION    EXP. HMIX      CALC. HMIX        % ERROR
        0.24510     492.00000      495.26342         0.39236
        0.42000     931.00000      940.69042        -1.04086
        0.52070    1000.00000     1018.18460        -1.81848
        0.59090    1003.00000     1026.71430        -2.36434
        0.66630     939.00000      967.99475        -3.08837
        0.74490     862.00000      887.19750        -2.92314
        0.81450     716.00000      738.67236        -3.16653
        0.89750     467.00000      476.62817        -2.06171
```

0.07940	216.00000	218.40753	-1.11460
0.15030	394.00000	397.53466	-0.89712
0.21110	534.00000	537.66064	-0.68551
0.26550	650.00000	651.24564	-0.19167
0.31140	739.00000	739.22631	0.10469
0.39100	867.00000	863.80322	0.36872
0.45350	940.00000	939.43603	0.06000
0.50460	980.00000	983.68652	-0.37618
0.56650	1009.00000	1013.19330	-0.41560
0.62940	1002.00000	1012.22530	-1.02049
0.70590	943.00000	961.56445	-1.96866
0.79440	817.00000	820.46484	-0.42409
0.87990	575.00000	578.16992	-0.55129
0.94960	277.00000	282.41088	-1.95339
0.14540	476.00000	436.57324	8.28293
0.26890	816.00000	763.35791	6.45123
0.34990	1013.00000	948.71240	6.34626
0.42890	1145.00000	1101.21430	3.82407
0.50620	1263.00000	1216.57710	3.67560
0.56750	1321.00000	1278.34270	3.22916
0.62620	1345.00000	1306.90110	2.83263
0.70880	1319.00000	1282.42110	2.77323
0.76420	1252.00000	1211.34690	3.24705
0.84360	1016.00000	1005.10810	1.07203
0.91930	645.00000	647.58618	-0.40096
0.18730	524.00000	509.65380	2.73782
0.30890	827.00000	803.96069	2.76589
0.40770	1034.00000	1012.02220	2.12551
0.50530	1184.00000	1179.05390	0.41774
0.58090	1263.00000	1271.95890	-0.70934
0.68930	1295.00000	1323.29390	-2.18486
0.75720	1249.00000	1282.78580	-2.70503
0.81770	1129.00000	1175.54050	-4.12228
0.89490	829.00000	889.66064	-7.31732
0.94870	485.00000	538.91235	-11.11595
0.10060	256.00000	290.03222	-13.29384
0.21040	492.00000	541.18237	-9.99641
0.28510	629.00000	671.40771	-6.74208
0.34610	721.00000	752.44946	-4.36192
0.44650	828.00000	834.52758	-0.73836
0.51890	867.00000	852.33452	1.63575
0.59380	866.00000	833.78808	3.71962
0.66550	831.00000	773.56398	6.30758
0.75760	714.00000	652.23779	8.65017
0.83460	562.00000	496.76611	11.60745
0.91830	314.00000	272.45556	13.23070
0.96090	178.00000	170.41716	4.26002
0.13060	370.00000	355.43554	3.93634
0.22920	616.00000	595.63065	3.61960
0.31260	797.00000	774.96264	2.76504

```
            0.39850        946.00000        931.33544         1.55016
            0.47600       1047.00000       1041.86030         0.49089
            0.54630       1108.00000       1110.96690        -0.26796
            0.61310       1128.00000       1142.61100        -1.29531
            0.66590       1111.00000       1129.71060        -1.68413
            0.75530       1035.00000       1058.62470        -2.28258
            0.82830        887.00000        902.30273        -1.72522
            0.88550        694.00000        702.59472        -1.23843
            0.94100        417.00000        422.59790        -1.34242

    AVERAGE % ERROR =        3.166955
```

Appendix II

Prediction Computer Program

This appendix will give a listing of the prediction computer program and explain how to use it. The prediction program is the subroutine FMIN in the regression program with some minor changes in format statements and input data. The binary benzene + n-octane at 50°C will be predicted using the parameters from Appendix I. The input data needed to predict this mixture follows:

```
 1  13                      13  0.8984   418.0
 2  0.0600   160.0          14  0.9636   168.0
 3  0.1607   413.0          15  0.54
 4  0.2456   591.0          16  0.848
 5  0.3172   718.0          17  0.40
 6  0.3765   800.0          18   0
 7  0.4484   872.0          19   0
 8  0.5182   910.0          20   6
 9  0.5818   917.0          21   6
10  0.6622   883.0          22   2
11  0.7598   760.0          23   0
12  0.8318   609.0          24  323.15
```

where

line 1 = number of experimental data points

lines 2 -14 = experimental data, given as mole fraction of benzene and heats of mixing in J/mole

lines 15 - 17 = group area parameters for groups CH_2, CH_3 and ACH, respectively

lines 18 - 23 = number of groups of type k in component i

line 24 = temperature, ^oK

Call this program BENZ-NC8-323-PRE. The following pages give a listing of the prediction program.

```
253.      @P

C PROGRAM TO CALCULATE HEATS OF MIXING USING UNIFAC
C MAIN PROGRAM
C XM1=MOLE FRACTION READ IN, HMIXE=EXPERIMENTAL HEATS OF
C MIXING, HMIX=PREDICTED EXCESS ENTHALPY, XT=INTERACTION
C PARAMETERS(TEMPERATURE-INDEPENDENT)
      DIMENSION XM1(40), HMIXE(40),HMIX(40),ERROR(40)
      DIMENSION XT(10)
      SUMER=0.
C NDATA=NUMBER OF DATA POINTS
      READ 1,NDATA
    1 FORMAT(I2)
      DO 3 I=1,NDATA
      READ 2,XM1(I),HMIXE(I)
    3 CONTINUE
    2 FORMAT(F6.4,F8.1)
C NPAR=NUMBER OF PARAMETERS
      NPAR=2
C ORDER OF PARAMETERS = A(CH2,G), A(G,CH2)
      XT(1)=53.07
      XT(2)=42.06
      CALL FMIN(XM1,HMIXE,HMIX,ERROR,NDATA,XT,NPAR,SUMER)
      PRINT 6
    6 FORMAT('OMOLE FRACTION OF',5X,'EXPERIMENTAL',8X,
     G'PREDICTED',12X,'%')
      PRINT 7
    7 FORMAT('    COMPONENT 2',5X,'HEATS OF MIXING',4X,
     G'HEATS OF MIXING',7X,'ERROR')
      DO 10 J=1,NDATA
      PRINT 9,XM1(J),HMIXE(J),HMIX(J),ERROR(J)
   10 CONTINUE
    9 FORMAT(F12.4,F19.3,F20.4,F15.4)
C ASUMER=AVERAGE ERROR
      ASUMER=SUMER/(FLOAT(NDATA))
      PRINT 14,ASUMER
   14 FORMAT('0 THE AVERAGE ERROR =',F7.4)
      STOP
      END
      SUBROUTINE FMIN(XM1,HMIXE,HMIX,ERROR,NDATA,XT,NPAR,SUME
R)
C UNIFAC - TEMPERATURE-INDEPENDENT PARAMETERS
      DIMENSION XM1(40),HMIXE(40),HMIX(40),ERROR(40)
      DIMENSION HS(10),BS(10,10),HEAT(10,10),HEMIX(50)
      DIMENSION A(10,10),AX(10),HK(10),HKS(10,10),DN(10,10)
      DIMENSION BSUM(10),DS(10,10),CS(10,10),ES(10),FS(10)
      DIMENSION GS(10),C(10,10),D(10,10),E(10),F(10),G(10)
      DIMENSION H(10),B(10,10),BX(10),XM(10),N(10,10)
      DIMENSION X(10),H1(10),H1S(10),CSUM(10),P(10,10)
      DIMENSION YSUM(10),CSSUM(10),BSSUM(10),HSUM(10)
      DIMENSION WSUM(10),TH(10),THS(10,10),Q(10),VSUM(10)
      DIMENSION XT(10)
C I=NUMBER OF COMPONENTS
```

```
       READ 100,I
100    FORMAT(I2)
       IC=I+1
C K=NUMBER OF GROUPS
       READ 100,K
       KG=K+1
C Q=AREA BY BONDI
C Q(CH3)=0.848, Q(CH2)=0.540, Q(CH)=0.228, Q(C)=0.0
C Q(ACH)=0.4,Q(OH)=1.20,Q(CH2CH2OH)=1.664,Q(CHOHCH3)=1.660
       DO 120 K3=2,KG
          READ 110,Q(K3)
120    CONTINUE
110    FORMAT(F6.4)
C N(K,I)=NUMBER OF GROUP K IN COMPONENT I
C READ IN ORDER N(2,2),N(3,2),N(4,2)...N(2,3),N(3,3),ETC.
       DO 150 I4=2,IC
          DO 140 K5=2,KG
             READ 100, N(K5,I4)
140       CONTINUE
150    CONTINUE
C R=GAS CONSTANT, UNITS ARE (JOULE)/(G MOLE)(K)
       R=8.314
C T=TEMPERATURE IN DEG. K
       READ 170,T
170    FORMAT(F7.3)
       PRINT 190
190    FORMAT('0 PREDICTION OF HEATS OF MIXING')
       PRINT 195
195    FORMAT('  USING THE UNIFAC METHOD')
       PRINT 200,I
200    FORMAT('0NUMBER OF COMPONENTS=',I3)
       PRINT 210,K
210    FORMAT(' NUMBER OF GROUPS=',I3)
       PRINT 500
       DO 230 J12=2,KG
          PRINT 220,J12,Q(J12)
220       FORMAT(' Q(',I2,')=',F6.4)
230    CONTINUE
       PRINT 500
       DO 260 J14=2,IC
          DO 250 J15=2,KG
             PRINT 240,J15,J14,N(J15,J14)
240          FORMAT(' N(',I2,',',I2,')=',I2)
250       CONTINUE
260    CONTINUE
500    FORMAT('0')
       PRINT 280,T
280    FORMAT('0 THE TEMPERATURE=',F10.3,' DEG. K')
C A(K,M)=TEMPERATURE-INDEPENDENT PARAMETERS
       DO 330 K20=2,KG
```

```
       DO 330 K21=2,KG
          A(K20,K21)=0.
 330   CONTINUE
C LAST GROUP = GROUP G, IT IS NOT AN ALKANE GROUP
       DO 340 J33=2,KG
          IF(J33.EQ.KG)GO TO 340
          A(J33,KG)=XT(1)
          A(KG,J33)=XT(2)
 340   CONTINUE
       PRINT 350
 350   FORMAT('0 THE TEMPERATURE-INDEPENDENT PARAMETERS=')
       PRINT 360, XT(1)
 360   FORMAT('  A(CH2/G)=',F15.5)
       PRINT 370, XT(2)
 370   FORMAT('  A(G/CH2)=',F15.5)
      ALPHA=35.2
       BETA=-.1272
       GAMMA=.00014
       PRINT 372,ALPHA,BETA,GAMMA
 372   FORMAT('0 Z(T) =',F6.2,' ',F10.7,'*T  +',F10.7,
     G'*T*T')
       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,KG
       DO 40 I=2,IC
       DO 50 K=2,KG
       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(KG)
  40   CONTINUE
       X(M)=BX(IC)/AXSUM
       AXSUM=0
  30   CONTINUE
       WSUM(1)=0
       DO 99 J=2,KG
       DO 88 M=2,KG
       WSUM(M)=WSUM(M-1)+Q(M)*X(M)
  88   CONTINUE
       TH(J)=Q(J)*X(J)/WSUM(KG)
  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,KG
      DO 1 J=2,KG
      DO 2 M=2,KG
      C(J,M)=TH(M)*EXP(-((ALPHA+BETA*T+GAMMA*T*T)*A(M,J)
     G)/(2*T))*(((ALPHA+BETA*T+GAMMA*T*T)*A(M,J))/(2*T*T
     G)-(A(M,J)*(2*GAMMA*T+BETA))/(2*T))
      P(J,M)=TH(M)*EXP(-((ALPHA+BETA*T+GAMMA*T*T)*A(M,J)
     G)/(2*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)+TH(J)*EXP(-((ALPHA+BETA*T+GAMMA*T*T)
     G*A(K,J))/(2*T))*CSUM(KG)/D(J,KG)
      F(J)=F(J-1)+TH(J)*EXP(-((ALPHA+BETA*T+GAMMA*T*T)
     G*A(K,J))/(2*T))*(((ALPHA+BETA*T+GAMMA*T*T)*A(K,J)
     G)/(2*T*T)-(A(K,J)*(2*GAMMA*T+BETA))/(2*T))/BSUM(KG)
      G(J)=G(J-1)+TH(J)*EXP(-((ALPHA+BETA*T+GAMMA*T*T)
     G*A(J,K))/(2*T))*(((ALPHA+BETA*T+GAMMA*T*T)*A(J,K)
     G)/(2*T*T)-(A(J,K)*(2*GAMMA*T+BETA))/(2*T))
      H(J)=H(J-1)+TH(J)*EXP(-((ALPHA+BETA*T+GAMMA*T*T)
     G*A(J,K))/(2*T))
1     CONTINUE
      H1(KG)=G(KG)/H(KG)
      HK(K)=Q(K)*(H1(KG)+F(KG)-E(KG))*R*T*T
3     CONTINUE
      YSUM(1)=0.
      DO 5 I=2,IC
      DO 10 J=2,KG
      DO 20 M=2,KG
      YSUM(M)=N(M,I)+YSUM(M-1)
20    CONTINUE
      DN(J,I)=FLOAT(N(J,I))/YSUM(KG)
10    CONTINUE
5     CONTINUE
      VSUM(1)=0.
      DO 77 I=2,IC
      DO 66 J=2,KG
      DO 55 M=2,KG
      VSUM(M)=VSUM(M-1)+Q(M)*DN(M,I)
55    CONTINUE
      THS(J,I)=Q(J)*DN(J,I)/VSUM(KG)
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,IC
      DO 33 K=2,KG
      DO 11 J=2,KG
      DO 22 M=2,KG
      CS(J,M)=THS(M,I)*EXP(-((ALPHA+BETA*T+GAMMA*T*T)
     G*A(M,J))/(2*T))*(((ALPHA+BETA*T+GAMMA*T*T)*A(M,J)
     G)/(2*T*T)-(A(M,J)*(2*GAMMA*T+BETA))/(2*T))
      BS(J,M)=THS(M,I)*EXP(-((ALPHA+BETA*T+GAMMA*T*T)
     G*A(M,J))/(2*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(-((ALPHA+BETA*T+GAMMA*T
     G*T)*A(K,J))/(2*T))*CSSUM(KG)/DS(J,KG)
      FS(J)=FS(J-1)+THS(J,I)*EXP(-((ALPHA+BETA*T+GAMMA*T
     G*T)*A(K,J))/(2*T))*(((ALPHA+BETA*T+GAMMA*T*T)*A(K,J)
     G)/(2*T*T)-(A(K,J)*(2*GAMMA*T+BETA))/(2*T))/BSSUM(KG)
      GS(J)=GS(J-1)+THS(J,I)*EXP(-((ALPHA+BETA*T+GAMMA*T
     G*T)*A(J,K))/(2*T))*(((ALPHA+BETA*T+GAMMA*T*T)*A(J,K)
     G)/(2*T*T)-(A(J,K)*(2*GAMMA*T+BETA))/(2*T))
      HS(J)=HS(J-1) +THS(J,I)*EXP(-((ALPHA+BETA*T+GAMMA*T
     G*T)*A(J,K))/(2*T))
   11 CONTINUE
      H1S(KG)=GS(KG)/HS(KG)
      HKS(K,I)=Q(K)*(H1S(KG)+FS(KG)-ES(KG))*R*T*T
   33 CONTINUE
   44 CONTINUE
      HEMIX(1)=0.
      HSUM(1)=0.
      HEAT(1,1)=0.
      DO 60 I=2,IC
      DO 70 K=2,KG
      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(KG)+HEMIX(I-1)
   60 CONTINUE
      HEMIX(3)=HEMIX(IC)
      HMIX(KPN)=HEMIX(3)
      ERROR(KPN)=100.*(HMIXE(KPN)-HMIX(KPN))/HMIXE(KPN)
      SUMER=SUMER+ABS(ERROR(KPN))
  777 CONTINUE
      RETURN
      END
```

```
 253.      @SY
%BKPT PCOUNT 3691F2
/LOGOFF
%  E420 LOGOFF AT 14:13 ON 10/11/80, FOR TSN 0464.
%  E421 CPU TIME USED : 8.38 SECONDS.
```

To run the program use the following procedure:

1) read the prediction program (@REA 'program name')
2) type @RUN
3) the computer will print the following:

```
**FASTFOR (CONVERSATIONAL.VER 9)**
```

4) just as the computer finishes printing hit the break key
5) the computer will give a slash(/)
6) type

```
/SYSFILE SYSDTA=BENZ-NC8-323-PRE
/R
```

then hit control C and the computer will print out the calculations. A listing for this system is given on the next page.

7) This program could also be run the same way the regression program was done. In that case the amount of time needed is only a few seconds. The procedure outlined above prints the output at the computer terminal.

```
PREDICTION OF HEATS OF MIXING USING
THE MODIFIED UNIFAC METHOD

  BENZENE(1) + N-OCTANE(2)   323.15 K

REF:  DIAZ PENA, M. AND C. MENDUINA,
      J.CHEM.THERMO.,6,1097(1974).

  GROUP 1 = CH2         Q(1) = 0.54
  GROUP 2 = CH3         Q(2) = 0.848
  GROUP 3 = ACH         Q(3) = 0.4

N(K,I) = NUMBER OF GROUPS OF TYPE K IN COMPONENT I
 N(1,1) = 0
 N(2,1) = 0
 N(3,1) = 6
 N(1,2) = 6
 N(2,2) = 2
 N(3,2) = 0

 THE TEMPERATURE = 323.15 DEG. K

THE TEMPERATURE-INDEPENDENT PARAMETERS ARE
  A(CH2,ACH) = 12.09
  A(ACH,CH2) =  1.90

Z(T) = 35.20 - 0.1272*T + 0.00014*T*T

MOLE FRACTION OF  EXPERIMENTAL HEATS  PREDICTED HEATS      %

 COMPONENT 1      OF MIXING (J/MOLE) OF MIXING (J/MOLE) ERROR
    0.0600             160.0               165.8          -3.6
    0.1607             413.0               415.5          -0.6
    0.2456             591.0               594.8          -0.6
    0.3172             718.0               720.9          -0.4
    0.3765             800.0               805.9          -0.7
    0.4484             872.0               882.8          -1.2
    0.5182             910.0               926.8          -1.8
    0.5818             917.0               937.4          -2.2
    0.6622             883.0               905.2          -2.5
    0.7598             760.0               786.7          -3.5
    0.8318             609.0               633.7          -4.1
    0.8984             418.0               433.8          -3.8
    0.9636             168.0               175.2          -4.3

     THE AVERAGE ERROR = 2.3 %
```