

APPLICATION OF GROUP CONTRIBUTION THEORY  
TO HEATS OF MIXING

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## PREFACE

Chemical engineers and members of other disciplines in science and technology are frequently concerned with the determination of all types of thermodynamic properties. It is generally accepted that these properties must be determined as individual functions of the molecules, or mixtures of molecules, being considered.

This project presents a method by which thermodynamic properties may be evaluated as functions of the groups or radicals composing the molecules. This has the advantage that the group functions, once determined, are valid for all systems containing the same groups. Thus, experimental data for each individual system is no longer necessary.

Details of this theory and results of its application to experimental heat-of-mixing data are presented in this thesis.

I am indebted to Dr. K. C. Chao and Dr. R. L. Robinson, my advisors, for valuable suggestions and guidance in relation to this study. I also wish to express my appreciation to the Air Force Institute of Technology for providing me with the opportunity to pursue graduate studies, and furnishing the financial support for my entire graduate program.

## TABLE OF CONTENTS

Chapter	Page
I. INTRODUCTION . . . . .	1
II. LITERATURE REVIEW . . . . .	3
Surface Area Theory . . . . .	3
Group Contribution Theory . . . . .	4
Local Concentration Effect . . . . .	5
Heat-of-mixing Data . . . . .	5
III. THEORY . . . . .	7
Group Surface-area Model . . . . .	7
Application to Mixtures . . . . .	9
Local Concentration Effect . . . . .	11
Heats of Mixing From Internal Energies of Vaporization . . . . .	13
IV. DATA AND CALCULATIONS . . . . .	15
Alcohol-hydrocarbon Mixtures . . . . .	15
Internal Energy of Vaporization . . . . .	15
Computer Program . . . . .	16
Heats of Mixing . . . . .	18
V. PRESENTATION AND DISCUSSION OF RESULTS . . . . .	22
VI. CONCLUSIONS AND RECOMMENDATIONS . . . . .	37
Conclusions . . . . .	37
Recommendations . . . . .	38
A SELECTED BIBLIOGRAPHY . . . . .	41
APPENDIX A. CALCULATION OF GROUP SURFACE AREAS . . . . .	43
APPENDIX B. COMPUTER PROGRAM . . . . .	49
APPENDIX C. NOMENCLATURE . . . . .	65

## LIST OF TABLES

Table	Page
I. Internal Energies of Vaporization to Ideal Gas for Normal Hydrocarbons . . . . .	17
II. Heats of Mixing of Alcohol-hydrocarbon Mixtures at 30°C . .	19
III. Group Interaction Energies . . . . .	23
IV. Comparison of Hydrocarbon Data with Calculated Values . . .	23
V. Comparison of Heat-of-mixing Results with Data . . . . .	24
VI. Heats of Mixing, Methanol Mixtures . . . . .	34
VII. Exact Model, Butanol-heptane Mixtures . . . . .	34
VIII. Internal Energies of Vaporization of Alcohols . . . . .	35
IX. Hydrocarbon Interaction Energies From Simple Model . . . . .	35
X. Hydrocarbon Internal Energies, Simple Model . . . . .	35
XI. Atomic Radii . . . . .	45
XII. Free Surface Areas of Groups . . . . .	47

## LIST OF ILLUSTRATIONS

Figure	Page
1. Heat of Mixing, Ethanol-hexane, at 30°C . . . . .	26
2. Heat of Mixing, Ethanol-nonane, at 30°C . . . . .	27
3. Heat of Mixing, Propanol-heptane, at 30°C . . . . .	28
4. Heat of Mixing, Butanol-heptane, at 30°C . . . . .	29
5. Heat of Mixing, Pentanol-hexane, at 30°C . . . . .	30
6. Heat of Mixing, Octanol-heptane, at 30°C . . . . .	31
7. Heat of Mixing, Octanol-nonane, at 30°C . . . . .	32
8. Geometry of Bonded Atoms . . . . .	45
9. Differential Element of Surface on a Sphere . . . . .	45
10. Surfaces of Bonded Hydrogen and Carbon . . . . .	47

## CHAPTER I

### INTRODUCTION

Until recently, thermodynamic properties such as heat of vaporization and heat of mixing have been treated as molecular functions. Experiments and theories are normally based on the supposition that the molecule determines the values of thermodynamic functions, and the presentation of data reflects this viewpoint.

Lately, considerable development and refinement have been devoted to the theory that such molecular functions may be reduced to functions of the component groups or radicals comprising the molecule. Once such group functions are evaluated, it follows that it is no longer necessary to experimentally determine values of the thermodynamic functions for all compounds of interest, since the known group functions may be applied to all molecules containing the groups. This has the potential of substantially reducing the experimentation necessary to characterize a given class of compounds.

The following presentation shows the application of a particular type of group contribution theory to heats of mixing. The resultant correlation is shown to give reasonable agreement with experimental data. Thus, one purpose of the development is accomplished by demonstrating that the physical concepts assumed in formulating the correlation are valid. This indicates that the physical model should be applicable not only to heats of mixing, but to other thermodynamic



functions as well.

In fact, the model may prove to have great versatility in liquid theory, just as the lattice theory of solids and the "billiard-ball" theory of gases have demonstrated. The model essentially pictures the liquid molecule and its component groups or radicals as being "bathed" in surrounding liquid, and in constant interaction with these surroundings. It assumes neither the fixed points of a solid lattice nor the necessity for collisions of a gas. It is certainly possible that this might reasonably represent the true physical picture of a liquid system.

There was a second purpose involved in selecting heats of mixing as the thermodynamic function to be tested. The variation of excess free energy with temperature is a simple function of the heat of mixing. Similarly, the variation with temperature of the activity coefficient of a component in solution is a simple function of the partial excess enthalpy of the component. Thus, a correlation for heats of mixing may have great importance in the development of relations for other thermodynamic functions.

## CHAPTER II

### LITERATURE REVIEW

#### Surface Area Theory

Langmuir (13), as early as 1916, proposed that certain characteristics of fluids could be expressed in terms of the chemical groups or radicals comprising the molecules. He suggested that interaction forces among molecules were dependent on the exposed surface areas of these groups in the molecule being considered and in the molecules surrounding it.

He applied this theory primarily to two-phase relations, such as surface tension, film adsorption and vapor pressures. Langmuir recognized that such relations would be strongly influenced by preferential orientation of the molecules at phase interfaces.

Others (2, 5, 6, 7, 9, 10, 11, 26, 27) who have expanded on Langmuir's theory have attempted to account for such orientation effects by applying statistics to a quasi-lattice arrangement of the molecules, in which a molecule is free to rotate about a fixed lattice point, subjecting different groups to contact with surrounding molecules. Guggenheim (9, 10, 11) credits Chang (5, 6) with being the first to propose this theory. The model leads to some fairly tedious, but not necessarily difficult, statistical calculations, even for simple fluids.

Barker (2) attempted to relate excess free energy, enthalpy and

entropy by the quasi-lattice model. He considered solutions of alcohols with non-polar (cyclic) molecules only. After considering both one-dimensional and three-dimensional arrays, he concluded that the three-dimensional array is necessary to represent the data.

Tompa (27) refined Guggenheim's work, and tested his model on the activity coefficients of binary mixtures of linear hydrocarbons. The fit is reasonably good for the three mixtures considered. A similar model was presented by Flory (7) and modified by Tobolsky and Blatz (26), but no tests of the model were presented.

#### Group Contribution Theory

Redlich, et al. (17, 19) used Langmuir's basic idea of separating the molecule into component groups, but their development differed greatly from previous ones. They assumed a characteristic "cross-section" of the groups, a function of the change effected in molar volume by adding the group to a molecule.

Several simplifying assumptions were made in the development. Groups which did not show a positive contribution to molar volume were assumed to be so deeply imbedded within the molecule that they could not interact with other groups. Isomers were all treated as if they were normal, and interactions between paraffinic groups were assumed negligible compared to interactions with other groups. Finally, the interaction energy of a paraffinic  $\text{CH}_3$  group with a group  $u$  was assumed to be the same as for an interaction of a paraffinic  $\text{C}$ ,  $\text{CH}$ , or  $\text{CH}_2$  group with the same group  $u$ . While these assumptions greatly simplified the calculations by reducing the number of different interactions, the effect of introducing them could be determined only by repeating the

calculations without the assumptions. The model also makes no allowance for the possibility that interactions involving higher energies may be mathematically preferred.

The model was tested by calculation of heats of mixing for various binary mixtures. Agreement with data was good. Entropies of mixing were also determined, but results in this case were very poor. This is probably due, at least in part, to the simplifying assumptions.

Other authors (23, 24) have offered basically similar theories. Scheller (24) attempted to determine activity coefficients from partial excess entropies and partial heats of mixing, for alcohol-water and alcohol-hydrocarbon mixtures. Results were good.

#### Local Concentration Effect

Wilson (28) proposed that differences in energy of interaction would cause local concentration effects, with a clustering of the molecules having higher interactions. Others have made similar observations, and it was the application of this principle to group theory which led to modifications of the basic model presented in this paper.

#### Heat-of-mixing Data

A thorough proof of a proposed theory or correlation has in most cases been virtually impossible due to a lack of extensive data on homologous chemical series. Such data has only recently begun to appear in the literature. In the case of heats of mixing, Lundberg (14) has published data on a variety of binary mixtures of hydrocarbons. Van Ness, et al. (16, 21, 22) offer very extensive data on mixtures of

alcohols and hydrocarbons, both aliphatic and cyclic. Van Ness has indicated that he intends to publish data on a wide variety of other mixtures as it becomes available. Rose and Storvick (20) also have data on alcohol-hydrocarbon mixtures.

## CHAPTER III

### THEORY

The following development includes concepts adapted from both the Langmuir and Redlich theories, as well as modifications original to this paper. A model is developed to calculate alcohol-hydrocarbon heats of mixing from group interaction parameters.

#### Group Surface-area Model

We consider a molecule to be composed of individual groups or radicals, linked together. For example, a straight-chain hydrocarbon is made up of  $\text{CH}_3$  groups and  $\text{CH}_2$  groups. Each group,  $i$ , has a certain area of free surface,  $S_i$ , available for contact and interaction with the free surface of other groups. The amount of surface area available is assumed to be dependent not only on the group itself, but on the groups connected to it in the particular molecule. Calculation of the free surface follows closely a method used by Bondi and Simkin (3) involving the van der Waals and covalent radii, and is shown in detail in Appendix A. While this is superficially similar to Redlich's "cross-section", the method used to determine values is entirely different.

It is further assumed that an interaction of any two groups,  $u$  and  $v$ , always produces the same energy contribution,  $\lambda_{uv}$ , per unit area of contacting surfaces. As a first approximation, the probability of an

interaction of a group  $i$  with any group  $j$  is assumed to be dependent on only the fraction of the total free surface area of the molecule which is occupied by group  $j$ . Thus if  $\lambda_{uv}$  is a contribution to the internal energy of vaporization of a pure compound containing  $n_u$  groups of type  $u$  per molecule, each having a surface area  $S_u$ , the total energy of interaction of all  $u$  groups in one molecule with  $v$  groups is

$$\frac{A_u A_v \lambda_{uv}}{A_T} \quad (1)$$

where  $A_u = n_u S_u$

$A_T$  = total surface area of the molecule. Sum of all group areas.

It follows that the total energy contribution of  $u$  groups with all other groups will be

$$A_u \sum_j \left( \frac{A_j}{A_T} \lambda_{uj} \right) \quad (2)$$

and the grand total of all energy contributions for a single molecule is

$$\Delta U_V = \frac{1}{2} \sum_k \left[ A_k \sum_j \left( \frac{A_j}{A_T} \lambda_{jk} \right) \right] \quad (3)$$

Both  $\sum_j$  and  $\sum_k$  represent summation over all types of groups. The necessity for division by two is readily apparent from the fact that each interaction is counted twice in the total summation.

Finally, multiplication by Avogadro's number,  $N$ , gives the molal internal energy of vaporization

$$\Delta U_V = \frac{N}{2} \sum_k \left[ A_k \sum_j \left( \frac{A_j}{A_T} \lambda_{jk} \right) \right]. \quad (4)$$

Note that, from the original assumption,  $\lambda_{jk} = \lambda_{kj}$ .

Using straight-chain hydrocarbons, excluding methane, as a simple example, we have only the  $\text{CH}_2$  and  $\text{CH}_3$  groups to consider. Assigning

the subscripts 2 and 3, respectively, and recognizing that  $n_3$  equals two in all cases, the equations are

$$A_2 = n_2 S_2 \quad (5)$$

$$A_3 = n_3 S_3 = 2S_3 \quad (6)$$

$$A_T = A_2 + A_3 = n_2 S_2 + 2S_3 \quad (7)$$

$$\Delta U_V = \frac{N}{2} \left( \frac{A_2^2}{A_T} \lambda_{22} + 2A_2 \frac{A_3}{A_T} \lambda_{23} + \frac{A_3^2}{A_T} \lambda_{33} \right) \quad (8)$$

While pair interactions are a necessary consequence of this model, this is based on the fact that, from purely physical limitations, a specific area of surface cannot possibly be in contact with more than one other surface at any given time. However, there is nothing in the model to prevent the possibility of different portions of the surface of a given group interacting with other groups of any type. Thus a specific group may be undergoing several different pair interactions at the same time. The only assumption implied is that the interaction energy of a pair of groups is not affected by any other interaction which may be taking place.

#### Application to Mixtures

This concept may be extended to mixtures of any number of different molecules, using a pseudo-molecule concept. The total surface area of a particular group in the pseudo-molecule is simply the area in a particular molecule times the mole fraction of that molecule in the mixture, summed over all types of molecules. For example, in a binary mixture of molecules a and b, the area of group k is

$$A_k = x_a n_{k,a} S_{k,a} + x_b n_{k,b} S_{k,b} \quad (9)$$



where  $x_a$  = mole fraction of molecule a in the mixture.

$n_{k,a}$  = number of k groups in molecule a.

$S_{k,a}$  = surface area of group k in molecule a.

This new definition of area simply replaces the other definition in equation (4). The equation remains exactly the same.

It is apparent, however, as noted in the calculation of surface areas in Appendix A, that  $S_k$  is not necessarily a constant within a given molecule. In an alcohol, for example, all  $\text{CH}_2$  groups except one are linked to two other carbon atoms. The one exception is linked to one carbon and one oxygen atom. Consequently, the free surface area of this group is not the same as the others.

Strictly speaking, the model requires that such a group be treated as a completely different type of group, with an entirely separate set of interactions. However, this approach would appreciably complicate the calculations for all but the simplest molecules. It was decided to simplify the calculations by defining an average group surface area as

$$S_{k,a} = \frac{\sum_i n_{k,a}^i S_{k,a}^i}{\sum_i n_{k,a}^i} \quad (10)$$

where  $S_{k,a}^i$  = a particular area value of group k in molecule a.

$n_{k,a}^i$  = number of k groups in molecule a which have area  $S_{k,a}^i$ .

The summation is made to include all k groups in the molecule. Proof of the validity of this assumption would be difficult. However, a check was performed by recalculating values for several data points by the exact method. Results, discussed later, indicate that the assumption is indeed valid.

## Local Concentration Effect

Although there is some possibility that such a simple model as has been proposed will give a reasonable fit to experimental data, the experience of others with somewhat similar models indicates that the likelihood is very small. Results presented later bear this out. Some modification seems necessary to account for the probability that there will be a natural preference for those group interactions having higher interaction energies. The method chosen to reflect these preferential interactions is similar to that used by Wilson (28). However, Wilson applied the concept only to molecules. The present model extends the application to groups.

It is proposed that molecular interactions having higher energies will occur in preference to those with lower energy, rather than being strictly proportional to surface area fractions. Extending this to group interactions, it is logical that those pair interactions exhibiting higher interaction energies will be the more probable.

This influence may be expressed as follows. If the area of contact between the surfaces of groups  $u$  and  $v$  in a single interaction is  $S_{u-v}$ , then the surface interaction energy will be

$$E_S = S_{u-v} \lambda_{uv} \quad (11)$$

The thermal energy of a group is  $kT$ , where  $k$  is the molecular Boltzmann constant and  $T$  is the absolute temperature. Then since  $S_{u-v}/S_u$  is the fraction of the surface area of group  $u$  involved in the interaction, the thermal energy of that portion of the  $u$  group which is involved in the interaction is

$$\frac{S_{u-v}}{S_u} kT \quad (12)$$

Similarly, the thermal energy contribution of the v group is

$$\frac{S_{u-v}}{S_v} kT \quad (13)$$

and the total thermal energy contribution is

$$E_T = \frac{S_{u-v}}{S_u} kT + \frac{S_{u-v}}{S_v} kT \quad (14)$$

The ratio of surface energy to thermal energy is then

$$\frac{E_S}{E_T} = \frac{S_{u-v} \frac{\lambda_{uv}}{S}}{\frac{S_{u-v}}{S_u} kT + \frac{S_{u-v}}{S_v} kT} = \frac{\lambda_{uv}}{\left(\frac{1}{S_u} + \frac{1}{S_v}\right) kT} = \frac{S_u S_v}{S_u + S_v} \frac{\lambda_{uv}}{kT} \quad (15)$$

and the relative contribution of the interaction-energy magnitude to the probability of interaction is assumed to be the exponential function

$$\frac{S_u S_v}{S_u + S_v} \frac{\lambda_{uv}}{kT} \quad (16)$$

e

where e = base of the natural logarithms.

If we define

$$S_{uv} = \frac{S_u S_v}{S_u + S_v} \quad (17)$$

then the term for u-v interactions will be

$$A_u \frac{A_v e^{S_{uv} \lambda_{uv}/kT}}{\sum_i \frac{S_{ui} \lambda_{ui}/kT}{A_i e^{S_{ui} \lambda_{ui}/kT}}} \lambda_{uv} \quad (18)$$

where  $\sum_i$  = summation over all types of groups present. Finally, the molal internal energy of vaporization is

$$\Delta U_V = \frac{N}{2} \sum_k \left[ A_k \sum_j \left( \frac{A_j e^{S_{jk} \lambda_{jk}/kT}}{\sum_i A_i e^{S_{ik} \lambda_{ik}/kT}} \lambda_{jk} \right) \right] \quad (19)$$

This performs a function similar to that of the quasi-lattice theory found in several models cited in Chapter II. Its greatest advantage is that it is free from the assumption of a lattice which actually exists only for crystalline solids.

#### Heats of Mixing From Internal Energies of Vaporization

If the energies mentioned above are internal energies of vaporization to the ideal gas, then heat of mixing may be determined by the following method. Considering a given mixture, if the components are first mixed in the liquid state at a particular temperature, and the mixture is then vaporized to the ideal gas, the total energy change includes both the internal energy of vaporization and the heat of mixing.

If instead, that amount of each pure component equal to its mole fraction in the mixture is vaporized from the same initial temperature to the ideal gas, and the gases are then mixed, the total energy change is the internal energy of vaporization only, since the heat of mixing of ideal gases is zero. Thus the heat of mixing is the difference between the internal energies of vaporization of the pure components and the internal energy of vaporization of the mixture. In equation form,

$$\Delta H_M = \sum_i (x_i \Delta U_{V,i}^*) - \Delta U_{V, \text{Mixture}}^* \quad (20)$$

Then if values of interaction energy,  $\lambda_{jk}$ , can be determined for all

group pairs to fit the internal energies of vaporization to the ideal gas, these same  $\lambda$  values may be used to find the heats of mixing for various mixtures.

This is a much more severe test of the method than a simple fit to internal energy of vaporization data would be, since the heat of mixing is of a much smaller order of magnitude. If, as is common, the energy of vaporization is on the order of 100 times the magnitude of the heat of mixing, then an error of 1% in the energy of vaporization value may result in an error of 100% in the heat of mixing value.

## CHAPTER IV

### DATA AND CALCULATIONS

This section outlines the selection of a set of mixtures on which to test the model, and the development of a computer program to determine the interaction energy values from the data. The exact method of fitting the energy values to the data is explained.

#### Alcohol-hydrocarbon Mixtures

The basic factors considered in selecting a set of mixtures on which to test the model were twofold. First, sufficient data must be available to provide a reasonably thorough test over a variety of mixtures. Second, for the initial test the molecules involved should be simple, involving only a few different groups. Both these criteria are met by mixtures of normal hydrocarbons and normal alcohols. Van Ness, et al., (21) have produced extensive data on these systems, and only three groups ( $\text{CH}_3$ ,  $\text{CH}_2$ ,  $\text{OH}$ ) are involved.

#### Internal Energy of Vaporization

Data on internal energy of vaporization to the ideal gas may be derived from heat of vaporization data by the relation

$$\Delta U_V^* = \Delta H_V + (H^* - H_V) - (1 - z_L) RT \quad (21)$$

where  $(H^* - H_V)$  = enthalpy difference between ideal and actual gases.

$z_L$  = compressibility factor of the liquid.

$R$  = the gas constant, or molal Boltzmann constant.

$T$  = absolute temperature.

The second and third terms may be found from generalized correlations by Lydersen, et al. (15).

The determination of  $\Delta U_V^*$  values for normal hydrocarbons at 25°C is shown in Table I. Values of  $\Delta H_V$  are from API-44 (1).

#### Computer Program

Considering the complexity of attempting to simultaneously optimize several different parameters, and the present state of the art in computer programming, it was inevitable that a computer should be used to optimize the  $\lambda$  values. The basic program selected (4) is a non-linear regression developed at California Research Corporation (now Chevron Research Corporation). It has been adjusted and refined to produce a completely general packaged program for the nonlinear fit of data to any equation, within fairly liberal size limitations. A complete list and explanation of the program are given in Appendix B.

The program was used to find values of the three  $\lambda$  parameters which gave the best fit to  $\Delta U_V^*$  data on hydrocarbons, based on a least-squares criterion. The resultant parameters and the fit they give to the data will be presented later.

TABLE I

INTERNAL ENERGIES OF VAPORIZATION TO IDEAL GAS FOR NORMAL HYDROCARBONS

Hydrocarbon	$\Delta H_V, 25^\circ\text{C}$	$T_r$	$z_L$	$\frac{H^* - H_V}{T_C}$	$H^* - H_V$	$(1 - z_L) RT$	$\Delta U_V^*, 25^\circ\text{C}$
Propane	3605	.806	.029	.77	285	576	3314
n-Butane	5035	.702	.010	.25	106	586	4555
n-Pentane	6316	.635	.005	.09	42	590	5768
n-Hexane	7540	.587	.002	.04	20	591	6969
n-Heptane	8735	.552	.002	.02	11	591	8155
n-Octane	9915				5	592	9328
n-Nonane	11099				2	593	10508
n-Decane	12276				1	593	11684

Units of all the above quantities are cal/g-mole, except for  $T_r$  and  $z_L$ , which are dimensionless, and  $\frac{H^* - H_V}{T_C}$ , which has dimensions of cal/g-mole  $^\circ\text{k}$ .



## Heats of Mixing

The next step would logically seem to be to determine the three parameters involving the hydroxyl group, by fitting internal energies of vaporization of alcohols, considering the three previously determined hydrocarbon parameters to be known constants. However, there are two reasons for not doing this. First, data on heats of vaporization of alcohols at 25°C are not readily available. Second, as mentioned before, parameter values calculated to fit heats of vaporization may give a very poor fit to heats of mixing, since we are obtaining small values by addition and subtraction of large values.

Instead, an alternate method was chosen. It was decided to fit the hydroxyl group parameters directly to the heat-of-mixing data. In this way, closer agreement with the heat-of-mixing values should be possible, and ideally the parameter values this yields should be usable to back-calculate the values of the internal energies of vaporization of the alcohols.

The heat-of-mixing values which were used were extracted from the data of Savini, Winterhalter and Van Ness (21). Since data were not available at 25°C, values for 30°C were used. Although this introduces some bias, the effect should be very nearly equal for all data points, and the error introduced should be quite acceptable.

The original source gives smoothed data for seven different mixtures, covering five different alcohols and three hydrocarbons. The data selected for input to the computer program includes nine equispaced points for each mixture, from ten to ninety mole percent alcohol. These are shown in Table II. For this data, the three hydrocarbon parameters were set at the values previously determined to fit the hydro-

carbon data. Only the three hydroxyl parameters were left free to vary.

TABLE II  
HEATS OF MIXING OF ALCOHOL-HYDROCARBON MIXTURES AT 30°C

Mixture	Mole Fraction Alcohol	$\Delta H_M$ , cal/g-mole (21)
Ethanol- Hexane	0.1	112.3
	0.2	138.0
	0.3	148.5
	0.4	150.3
	0.5	144.0
	0.6	132.5
	0.7	113.9
	0.8	87.9
	0.9	52.3
Ethanol- Nonane	0.1	129.9
	0.2	160.2
	0.3	174.6
	0.4	178.4
	0.5	174.4
	0.6	163.4
	0.7	145.0
	0.8	117.4
	0.9	74.4
Propanol- Heptane	0.1	126.5
	0.2	156.4
	0.3	169.1
	0.4	169.2
	0.5	159.5
	0.6	141.1
	0.7	115.9
	0.8	84.5
	0.9	46.5

TABLE II (Continued)

Mixture	Mole Fraction Alcohol	$\Delta H_M$ , cal/g-mole
Butanol- Heptane	0.1	123.0
	0.2	151.0
	0.3	164.1
	0.4	164.0
	0.5	153.5
	0.6	133.6
	0.7	106.9
	0.8	74.9
	0.9	38.9
Pentanol- Hexane	0.1	109.0
	0.2	131.5
	0.3	141.0
	0.4	139.9
	0.5	129.0
	0.6	109.5
	0.7	85.3
	0.8	58.1
	0.9	29.2
Octanol- Heptane	0.1	105.8
	0.2	122.3
	0.3	128.5
	0.4	126.7
	0.5	118.3
	0.6	103.2
	0.7	81.8
	0.8	56.6
	0.9	28.4
Octanol- Nonane	0.1	120.9
	0.2	141.5
	0.3	149.0
	0.4	148.5
	0.5	140.4
	0.6	122.2
	0.7	98.9
	0.8	69.6
	0.9	35.9

Data on two menthanol-hydrocarbon mixtures were also available from another article (22). These were not included in the computer input since the systems are only partially miscible at 30°C, and the effect of this fact on the model is impossible to predict.

## CHAPTER V

### PRESENTATION AND DISCUSSION OF RESULTS

This section shows and explains the results which were obtained by fitting the interaction energy parameters to experimental data.

The six values of group interaction energy, the first three as determined by hydrocarbon vaporization data, and the three involving the hydroxyl group as fitted to heat-of-mixing data are shown in Table III. Relative values are within expectations, since interactions involving the hydroxyl group may be expected to involve larger energies than those between hydrocarbon groups and the hydroxyl-hydroxyl interaction, in particular, should be quite large.

Table IV is a comparison of the hydrocarbon data from Table I and the values calculated from the three hydrocarbon-hydrocarbon interactions. The fact that the agreement is very good is not particularly significant since the relationships involved are quite simple, and any reasonable three-parameter correlation may be expected to give good results.

A comparison of the heat-of-mixing data with the values calculated from the model is shown in Table V. To better visualize the fit, data for each of the seven mixtures is plotted separately in Figures 1 through 7. The experimental data are indicated by continuous curves, and the computer-calculated points are shown individually.

TABLE III  
GROUP INTERACTION ENERGIES

Interaction	$\lambda \times 10^9, \text{ cal/cm}^2$
CH <sub>2</sub> -CH <sub>2</sub>	861.08
CH <sub>2</sub> -CH <sub>3</sub>	723.71
CH <sub>3</sub> -CH <sub>3</sub>	468.64
OH-OH	3412.50
OH-CH <sub>2</sub>	1533.85
OH-CH <sub>3</sub>	1218.73

TABLE IV  
COMPARISON OF HYDROCARBON DATA WITH CALCULATED VALUES

Hydrocarbon	$\Delta U_V^*$ , cal/g mole		Percent Deviation
	Data	Calculated	
Propane	3,314	3,313	-0.03
n-butane	4,555	4,557	0.04
n-pentane	5,768	5,769	0.02
n-hexane	6,969	6,966	-0.04
n-heptane	8,155	8,152	-0.04
n-octane	9,328	9,332	0.04
n-nonane	10,508	10,509	0.01
n-decane	11,684	11,683	-0.01

TABLE V  
COMPARISON OF HEAT-OF-MIXING RESULTS WITH DATA

Mixture	Mole Fraction Alcohol	$\Delta H_M$ @ 30°C, cal/g mole		Percent Deviation
		Data	Calculated	
Ethanol- Hexane	0.1	112.3	91.9	-18.2
	0.2	138.0	146.9	6.4
	0.3	148.5	172.0	15.8
	0.4	150.3	173.3	15.3
	0.5	144.0	156.8	8.9
	0.6	132.5	127.8	- 3.5
	0.7	113.9	92.0	-19.2
	0.8	87.9	54.7	-37.7
	0.9	52.3	21.9	-58.1
Ethanol- Nonane	0.1	129.9	92.5	-28.8
	0.2	160.2	156.5	- 2.3
	0.3	174.6	193.6	10.9
	0.4	178.4	206.0	15.4
	0.5	174.4	196.3	12.6
	0.6	163.4	168.3	3.0
	0.7	145.0	126.6	-12.7
	0.8	117.4	77.7	-33.9
	0.9	74.4	30.8	-58.6
Propanol- Heptane	0.1	126.5	90.2	-28.7
	0.2	156.4	147.6	- 5.6
	0.3	169.1	177.5	4.9
	0.4	169.2	184.8	9.2
	0.5	159.5	174.1	9.2
	0.6	141.1	149.8	6.2
	0.7	115.9	116.0	0.1
	0.8	84.5	76.9	- 9.0
	0.9	46.5	36.8	-20.9
Butanol- Heptane	0.1	123.0	85.9	-30.2
	0.2	151.0	139.9	- 7.3
	0.3	164.1	168.1	2.4
	0.4	164.0	175.5	7.0
	0.5	153.5	166.6	8.5
	0.6	133.6	145.3	8.7
	0.7	106.9	115.0	7.5
	0.8	74.9	78.8	5.2
	0.9	38.9	39.6	1.7

TABLE V (Continued)

Mixture	Mole Fraction Alcohol	$\Delta H_M$ @ 30°C, cal/g mole		Percent Deviation
		Data	Calculated	
Pentanol- Hexane	0.1	109.0	78.2	-28.3
	0.2	131.5	123.4	- 6.1
	0.3	141.0	144.6	2.5
	0.4	139.9	148.0	5.8
	0.5	129.0	138.5	7.4
	0.6	109.5	119.8	9.4
	0.7	85.3	94.6	10.9
	0.8	58.1	65.2	12.2
	0.9	29.2	33.2	13.6
Octanol- Heptane	0.1	105.8	65.6	-38.0
	0.2	122.3	103.7	-15.2
	0.3	128.5	122.0	- 5.0
	0.4	126.7	125.9	- 0.6
	0.5	118.3	119.2	0.8
	0.6	103.2	104.6	1.3
	0.7	81.8	84.0	2.7
	0.8	56.6	59.0	4.3
	0.9	28.4	30.7	8.2
Octanol- Nonane	0.1	120.9	69.7	-42.3
	0.2	141.5	114.6	-19.1
	0.3	149.0	139.2	- 6.6
	0.4	148.5	147.7	- 0.5
	0.5	140.4	143.2	2.0
	0.6	122.2	128.2	4.9
	0.7	98.9	104.7	5.9
	0.8	69.6	74.7	7.3
	0.9	35.9	39.3	9.6

Although it is apparent that the overall agreement is not as close as could be desired, the results verify the qualitative validity of the model. A shift of the curve toward the hydrocarbon side is manifest as the length of the alcohol molecule increases. One possible solution to this problem is discussed in Chapter VI.

Several points for the methanol mixtures were also calculated from



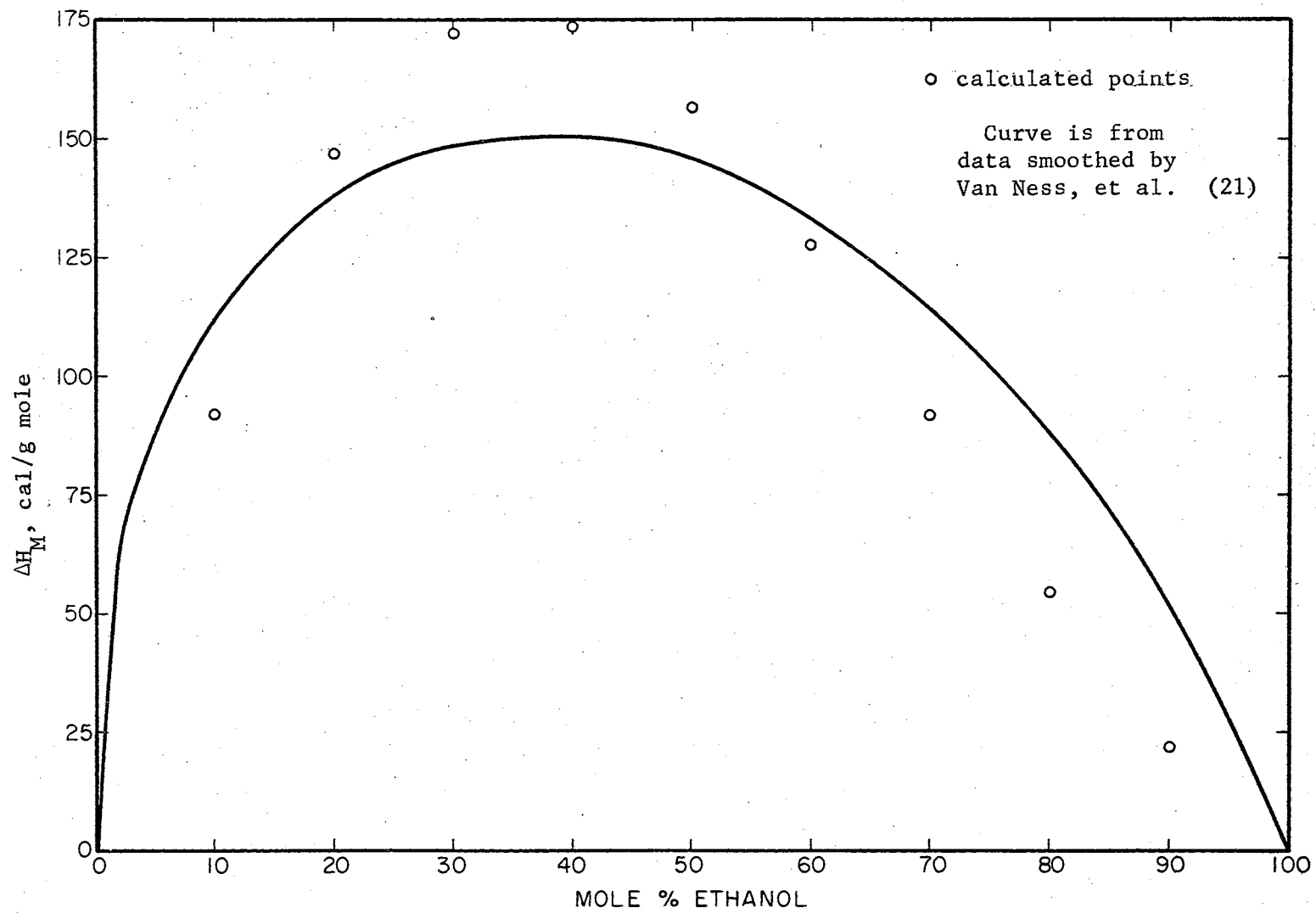


Figure 1. Heat of Mixing, Ethanol-hexane, at 30°C

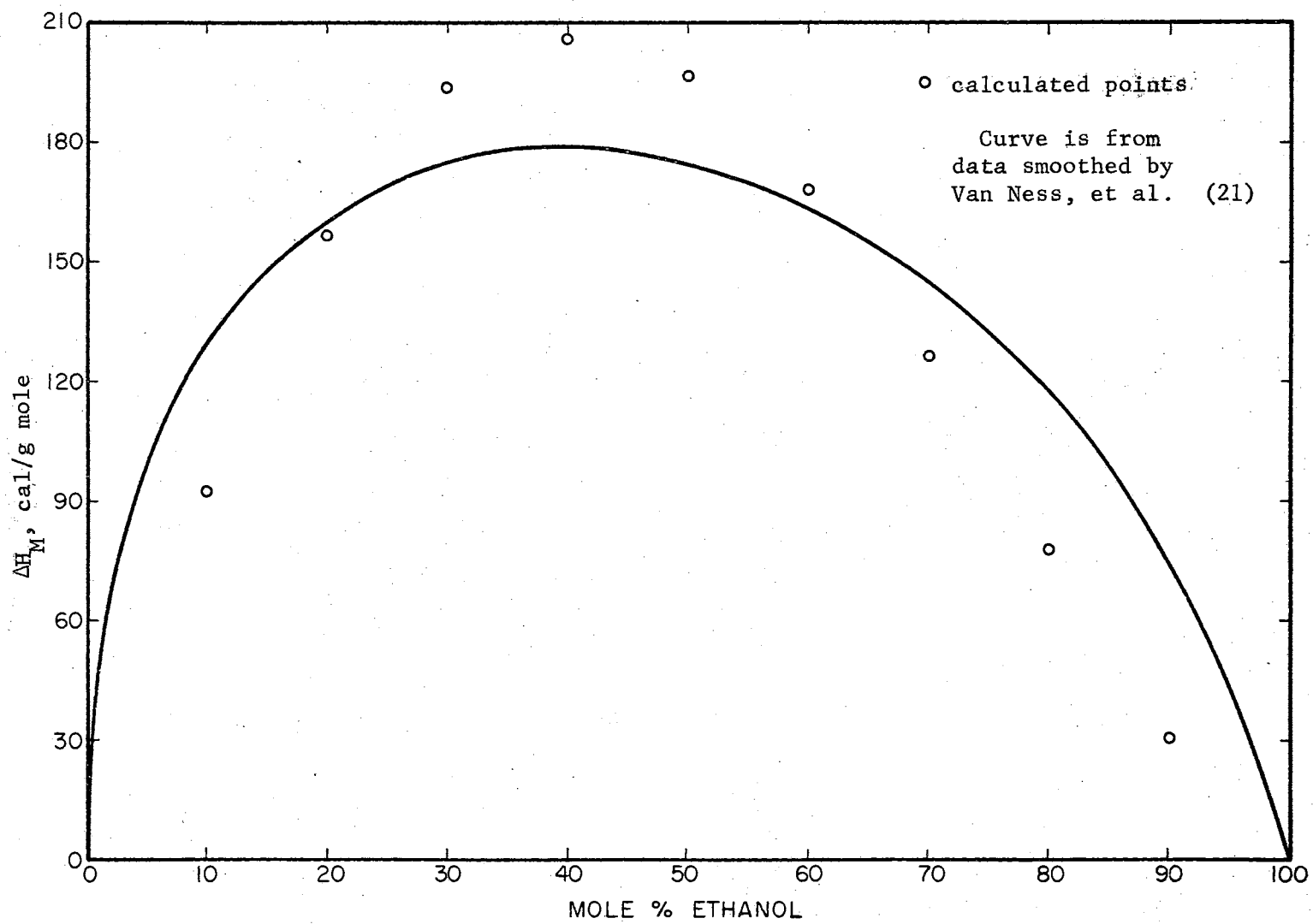


Figure 2. Heat of Mixing, Ethanol-nonane, at 30°C

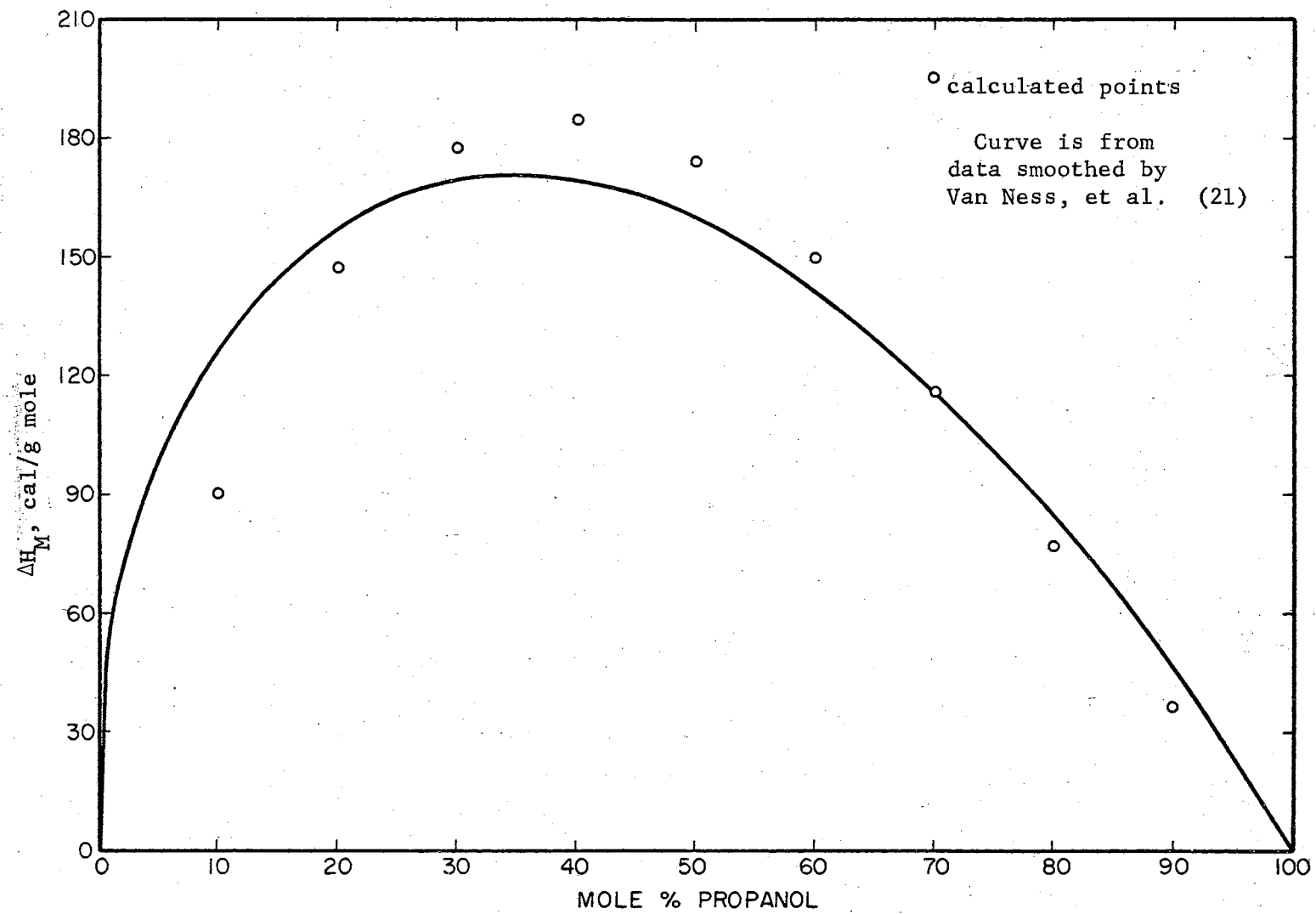


Figure 3. Heat of Mixing, Propanol-heptane, at 30°C

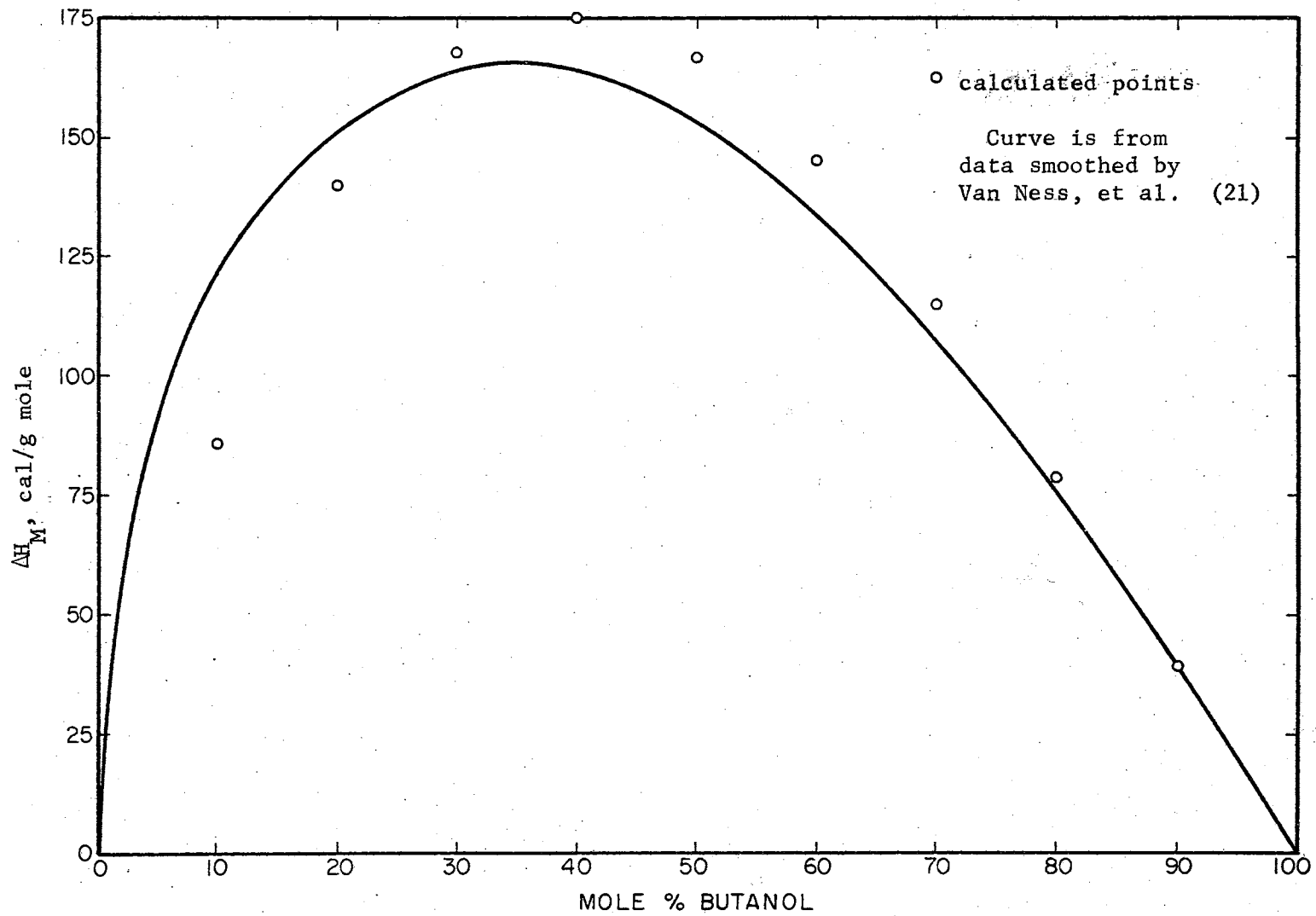


Figure 4. Heat of Mixing, Butanol-heptane, at 30°C

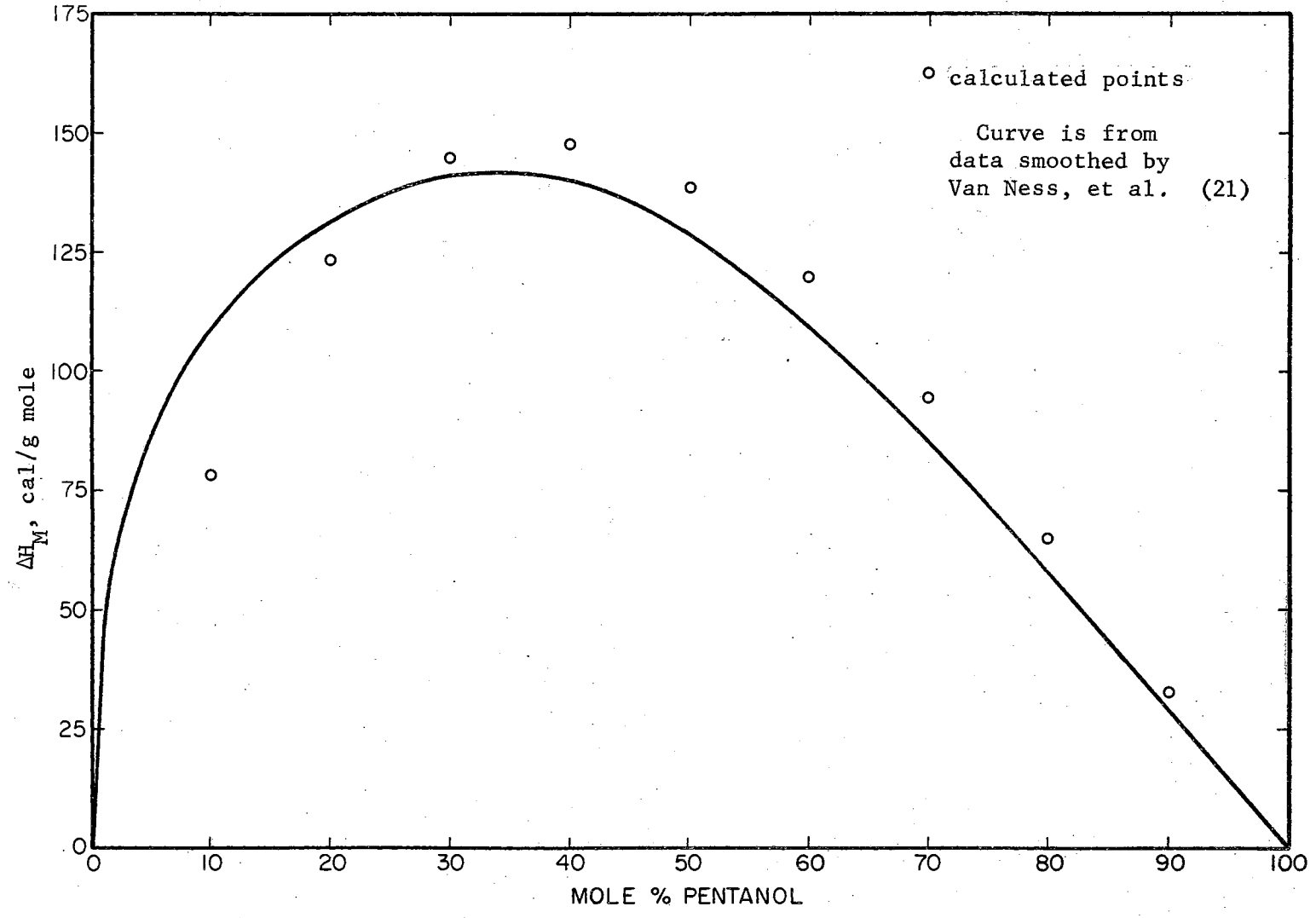


Figure 5. Heat of Mixing, Pentanol-hexane, at 30°C

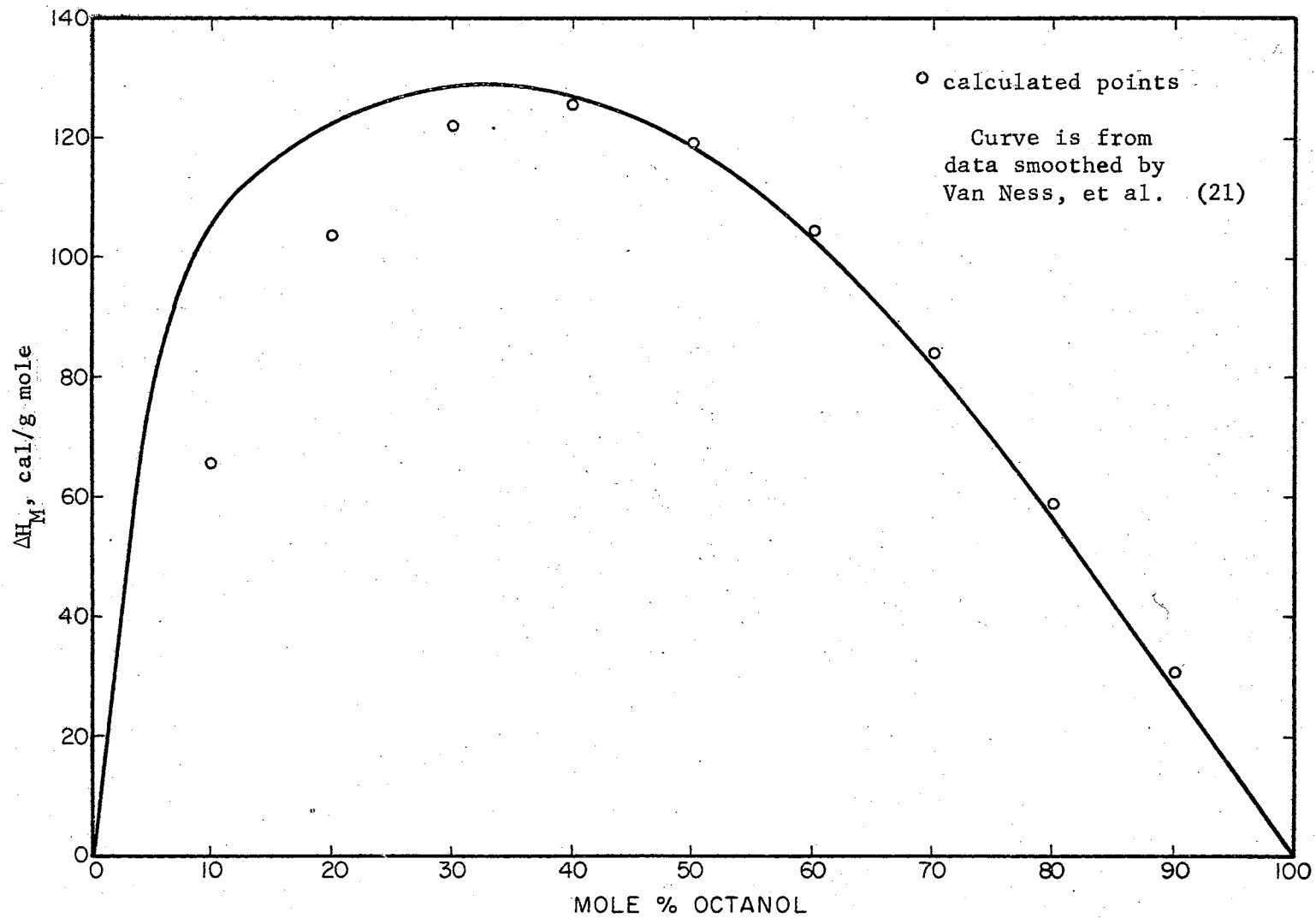


Figure 6. Heat of Mixing, Octanol-heptane, at 30°C

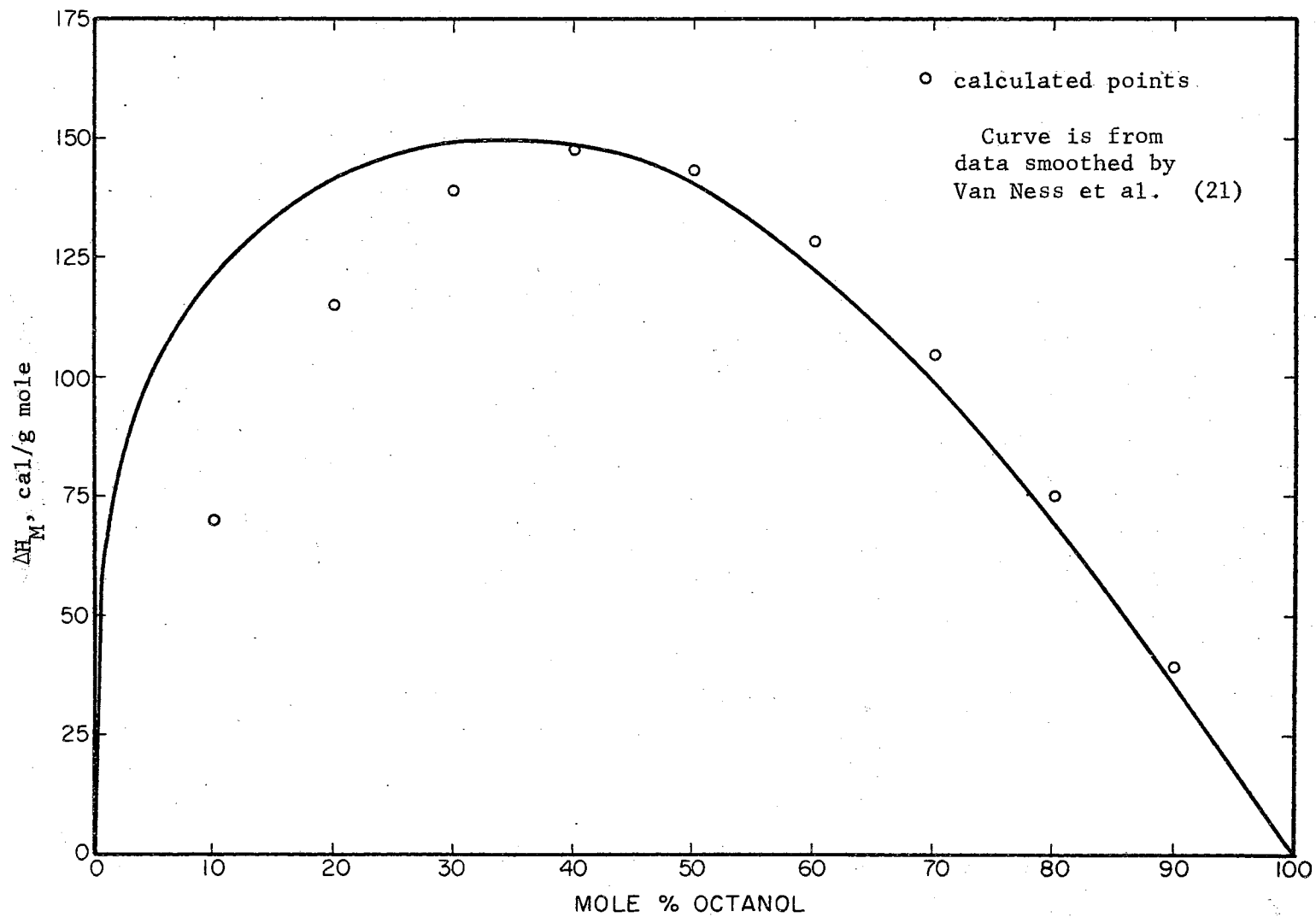


Figure 7. Heat of Mixing, Octanol-nonane, at 30°C

the same  $\lambda$  values. These are shown in Table VI. As expected, the agreement is poor, indicating that application of the model to partially miscible systems is doubtful. However, further refinement of the model might possibly give a much better fit to this data.

It was necessary to check the validity of the previously outlined assumption of an average area value, where groups of the same type have different areas within one molecule. This was done by recalculating the heats of mixing for the butanol-heptane system, using an exact model, in which those groups with different cross-sections were treated as having separate interactions, but the same interaction energy. Results are compared with those of the "average area" model in Table VII. The discrepancies are fully explained by the fact that the averaged areas used were rounded to the third decimal place. Thus, the value  $1.41 \times 10^9 \text{ cm}^2$  was used for the  $\text{CH}_2$  groups in butanol, while the value should actually be 1.41333.... This indicates that the averaging method is valid.

As a final check, values of internal energy of vaporization were calculated for three alcohols from the previously determined  $\lambda$  values. The actual values are determined from heats of vaporization given in the International Critical Tables (12). These are compared in Table VIII. Agreement is not very good. A discussion of possible reasons and remedies is included in Chapter VI.

In order to determine the effect of the local concentration concept (exponential function) on the model, calculation of the six interaction coefficients was repeated, substituting the simple linear model, equation (4), for the more refined model, equation (19). Determination of the hydrocarbon parameters gave good results. The parameter values



are shown in Table IX. The fit to hydrocarbon internal energies of vaporization is shown in Table X.

TABLE VI  
HEATS OF MIXING, METHANOL MIXTURES

Mixture	Mole Fraction Methanol	$\Delta H_M$ @ 30°C, cal/g mole		Percent Deviation
		Data (22)	Calculated	
Methanol-Hexane	0.1	102.7	94.6	- 7.9
	0.2	126.9	150.7	18.8
	0.3	139.6	174.1	24.4
	0.8	117.3	22.0	-81.2
	0.9	80.3	- 4.2	-105.2
Methanol-Heptane	0.1	108.2	94.4	- 12.8
	0.2	130.5	153.8	17.9
	0.9	87.9	-4.0	-104.6

TABLE VII  
EXACT MODEL, BUTANOL-HEPTANE MIXTURES

Mole Fraction Butanol	$\Delta H_M$ , cal/g mole		Percent Deviation
	Exact Areas	Averaged Areas	
0.1	85.6	85.9	0.3
0.2	139.3	139.9	0.4
0.3	167.3	168.1	0.5
0.4	174.5	175.5	0.6
0.5	165.6	166.6	0.6
0.6	144.3	145.3	0.7
0.7	114.2	115.0	0.7
0.8	78.2	78.8	0.8
0.9	39.3	39.6	0.8

TABLE VIII  
INTERNAL ENERGIES OF VAPORIZATION OF ALCOHOLS

Alcohol	$\Delta U_V^*$ @ 25°C, cal/g mole		Percent Deviation
	Data	Calculated	
Methanol	8,420	5,946	-29.4
Ethanol	9,500	7,216	-24.0
Propanol	10,540	8,367	-20.6

TABLE IX  
HYDROCARBON INTERACTION ENERGIES FROM SIMPLE MODEL

Interaction	$\lambda \times 10^9$ , cal/cm <sup>2</sup>
CH <sub>2</sub> - CH <sub>2</sub>	856.32
CH <sub>2</sub> - CH <sub>3</sub>	732.87
CH <sub>3</sub> - CH <sub>3</sub>	474.04

TABLE X  
HYDROCARBON INTERNAL ENERGIES, SIMPLE MODEL

Hydrocarbon	$\Delta U_V^*$ @ 25°C, cal/g mole		Percent Deviation
	Data	Calculated	
Propane	3,314	3,314	0.01
n-Butane	4,555	4,555	0.00
n-Pentane	5,768	5,769	0.01
n-Hexane	6,969	6,966	-0.04
n-Heptane	8,155	8,153	-0.02
n-Octane	9,328	9,334	0.06
n-Nonane	10,508	10,509	0.01
n-Decane	11,684	11,681	-0.02

However, in attempting to find values of the three hydroxyl group interaction energies to fit heat-of-mixing data, the simplified model failed entirely. The computer made sixty iterations in an attempt to find a convergence. Results indicated that dependence of the calculated heats of mixing on the parameter values is so small for this model that the computer could not find "best" values. The average deviation changed only slightly over wide ranges of parameter values, from very large positive to very large negative values. The smallest root mean square deviation for any iteration was 44.2, compared with a value of 18.8 for the refined model. This indicates that the local concentration concept is not only a valid modification of the simple model, but in fact a practical necessity for all but the simplest calculations.

## CHAPTER VI

### CONCLUSIONS AND RECOMMENDATIONS

#### Conclusions

The results presented in this work are in semi-quantitative agreement with data, for mixtures which are highly non-ideal. This substantiates the validity of the proposed group-interaction model. Thus, the primary purpose of this work has been achieved.

Further refinements to the model, based on sound theory and properly applied, should yield improved results. The more refined model may then be thoroughly evaluated and extended to other thermodynamic functions, including excess free energies and activity coefficients.

One of the primary advantages of this model is that, once a value of  $\lambda$  for any pair interaction has been determined, it is applicable to the same type of interaction in any other system. Thus, by judicious selection of successive systems, values may be determined for a wide range of interactions in a "building-block" fashion, using those values which have been previously determined as known constants.

Also, the model is as valid for multi-component mixtures as it is for binary mixtures. Obviously, a mixture of more than two components will increase the complexity of the calculations and make the work more tedious, but there is nothing at all in the theory to prevent such an application. It is entirely possible to determine values of pair interaction energies from very simple systems, and to then apply these

known values to multi-component systems which, from a molecular viewpoint, are much more complex.

### Recommendations

One concept which, at least in theory, might well provide the modification to the present model necessary to bring it into closer agreement with experimental data is that of degrees of freedom of thermal motion. This has not yet been explored, due solely to time limitations. However, since the present model includes thermal energy as a factor, the modification is relatively simple.

From Prigogine (18), the degrees of thermal freedom of a molecule may be expressed as

$$F = 2r + 1 \quad (22)$$

where  $r$  may be considered to be the number of groups in the molecule. Then, assuming each individual group has the same degrees of freedom, the value per group is

$$f = \frac{F}{r} = \frac{2r + 1}{r} \quad (23)$$

From the principle of equipartition of energy, each degree of freedom has associated with it an average thermal energy of motion of  $kT/2$ .

Then the average energy of each group is

$$E_{rT} = \frac{kT}{2} \frac{2r + 1}{r} \quad (24)$$

If we define

$$\alpha = \frac{2r}{2r + 1} \quad (25)$$

then

$$E_{rT} = kT/\alpha \quad (26)$$

The value of  $\alpha$  for any molecule can be simply calculated.

Inclusion of this factor in the model gives a new expression for the ratio of surface energy to thermal energy,

$$\frac{E_S}{E_T} = \frac{\lambda_{uv}}{\frac{kT}{S_u \alpha_u} + \frac{kT}{S_v \alpha_v}} \quad (27)$$

and a modified expression for the interaction probability

$$\frac{\lambda_{uv}}{kT} e^{\left( \frac{1}{S_u \alpha_u} + \frac{1}{S_v \alpha_v} \right)} \quad (28)$$

This may be substituted directly for the exponential expression in equation (19). Note, however, that since  $\alpha$  is a function of the molecule containing the group, a group in one molecule must now be treated as having separate interactions from the same type of group in another molecule, except in the special case where the value of  $\alpha$  is the same for both molecules. The primary assumption, that the interaction energy  $\lambda$ , is always a constant for a given pair interaction, still holds true. Thus, this concept increases the number of possible interactions for a particular case, but does not otherwise complicate the model.

It is recommended that the effect of this concept be thoroughly evaluated.

It is further recommended that, if sufficient data can be obtained on heats of vaporization of alcohols, the hydroxyl interaction parameters should be evaluated by direct fit to internal energies of vaporization of the alcohols. All six parameters could then be refined by using the predetermined values as initial estimates and allowing all six parameters to be refit to the heats of mixing. In this way it should be possible to find values which will best fit both the energy

of vaporization data and the heat of mixing data.

Finally, and again presuming the availability of data, the model should be applied to multi-component mixtures. This is an area in which very little theoretical work has been possible to date.

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## APPENDIX A

### CALCULATION OF GROUP SURFACE AREAS

The following is based on a method outlined by Bondi and Simkin (3). The surface of each atom in a molecule is considered to be a spherical segment whose radius is the van der Waals radius of the atom. The point of intersection of two atoms bonded to each other is a function of the covalent radii. The free surface of an atom is then that portion outside any points of intersection with other surfaces. The free surface of a group is simply the sum of the free surfaces of the component atoms.

A two-dimensional representation of this model is shown in Figure 8. Since there is symmetry about the common centerline, the figure represents any plane surface through the centerline.  $R_1$  and  $R_2$  are the van der Waals radii, and  $L$  is the sum of the covalent radii. Note that  $L_1$  and  $L_2$  are not necessarily the individual covalent radii, but may easily be determined by geometry as explained below.

The values of both the van der Waals and covalent radii are known to two or three places for the more common atoms. Values for the atoms of present interest are given in Table XI.

#### Determination of $L_1$ and $L_2$

From Figure 8,

$$L_1 + L_2 = L \quad (29)$$

$$R_1^2 - L_1^2 = R_2^2 - L_2^2 \quad (30)$$

Combining (29) and (30),

$$R_1^2 - L_1^2 = R_2^2 - (L - L_1)^2 = R_2^2 - L^2 + 2LL_1 - L_1^2 \quad (31)$$

$$L_1 = \frac{R_1^2 - R_2^2 + L^2}{2L} \quad (32)$$

and

$$L_2 = L - L_1 \quad (33)$$

### Surface Area of a Spherical Segment

As indicated in Figure 9, the area of an elemental ring of width  $d\theta$  on a spherical surface is

$$dS = R \sin\theta (Rd\theta) 2\pi = 2\pi R^2 \sin\theta d\theta \quad (34)$$

Then the surface area of a spherical segment subtended by an angle  $\theta$  is

$$S = 2\pi R^2 \int_0^\theta \sin\theta d\theta = -2\pi R^2 \cos\theta \Big|_0^\theta = 2\pi R^2 (1 - \cos\theta) \quad (35)$$

### Free Surface Area of Hydrogen Bonded to Carbon

From equation (32), using the subscripts H for hydrogen and C for carbon,

$$L_H = \frac{R_H^2 - R_C^2 + L^2}{2L} = \frac{(1.20)^2 - (1.70)^2 + (0.77+0.28)^2}{2(0.77+0.28)} = -0.165 \text{ \AA} \quad (36)$$

The negative value may be surprising at first glance, but it simply indicates a physical structure such that the center of the hydrogen atom

TABLE XI  
ATOMIC RADII

Atom	van der Waal's Radius, $\text{\AA}$	Covalent Radius, $\text{\AA}$ (8)
C	1.70 (3)	0.77
H	1.20 (3)	0.28
O	1.40 (8)	0.74

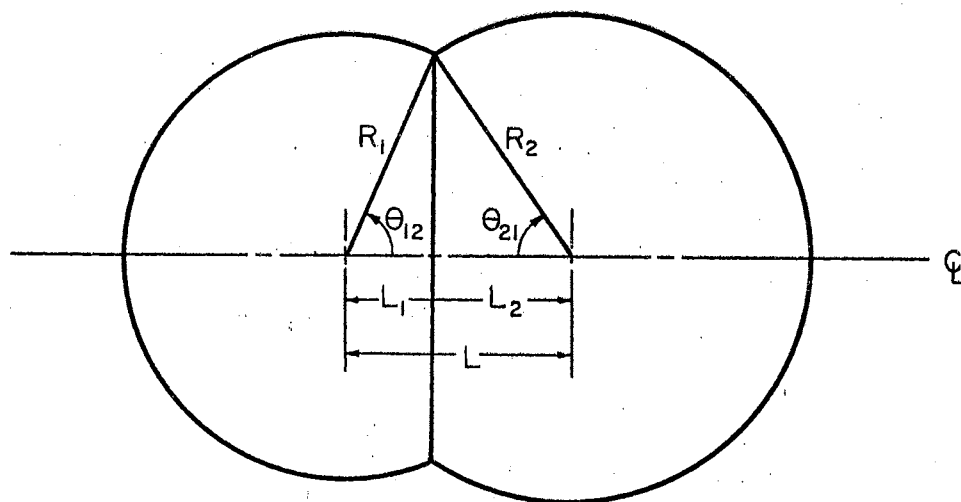


Figure 8. Geometry of Bonded Atoms

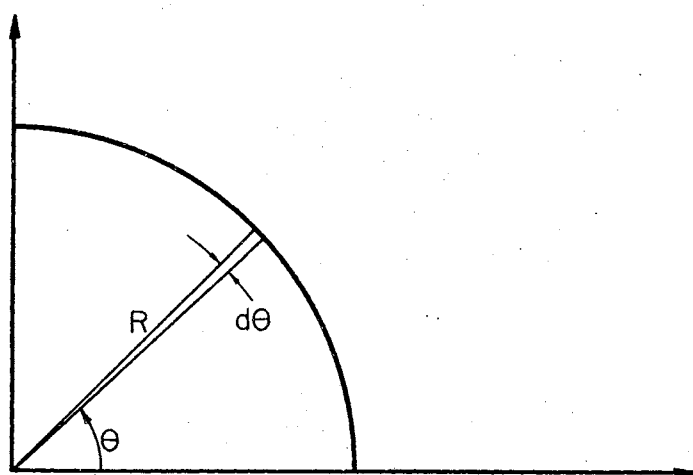


Figure 9. Differential Element of Surface on a Sphere

lies to the carbon side of the plane of intersection of the two atoms, rather than to the hydrogen side. This is entirely possible and poses no problem. The geometry is shown in Figure 10, which is drawn to scale.

For the carbon, from equation (33),

$$L_C = (0.77 + 0.28) - (-0.165) = 1.215 \text{ \AA} \quad (37)$$

The angle of the plane of intersection in the carbon is

$$\cos\theta_{CH} = \frac{L_C}{R_C} = \frac{1.215}{1.70} = 0.715 \quad (38)$$

The angle in the hydrogen is

$$\cos\theta_{HC} = \frac{L_H}{R_H} = \frac{-0.165}{1.20} = -0.1375 \quad (39)$$

Then the free surface of the hydrogen is

$$S_H = 4\pi R_H^2 - 2\pi R_H^2 (1 - \cos\theta_{HC}) = 2\pi R_H^2 (1 + \cos\theta_{HC}) \quad (40)$$

Substituting the known values,

$$S_H = 2\pi (1.20)^2 (1 - 0.1375) = 7.80 \text{ \AA}^2 \quad (41)$$

#### Methylene Group Attached to Two Other Carbons

Considering the carbon-carbon bond, since we have two spheres of equal size, the values of  $L_1$  and  $L_2$  are the same and are equal to the covalent radius. Then the angle in the carbon is

$$\cos\theta_{CC} = \frac{0.77}{1.70} = 0.453 \quad (42)$$

and

$$\begin{aligned} S_C &= 4\pi R_C^2 - 2 \left[ 2\pi R_C^2 (1 - \cos\theta_{CC}) \right] - 2 \left[ 2\pi R_C^2 (1 - \cos\theta_{CH}) \right] \\ &= 4\pi R_C^2 (\cos\theta_{CC} + \cos\theta_{CH} - 1) \\ &= 4\pi (1.70)^2 (0.453 + 0.715 - 1) = 6.09 \text{ \AA}^2 \quad (43) \end{aligned}$$

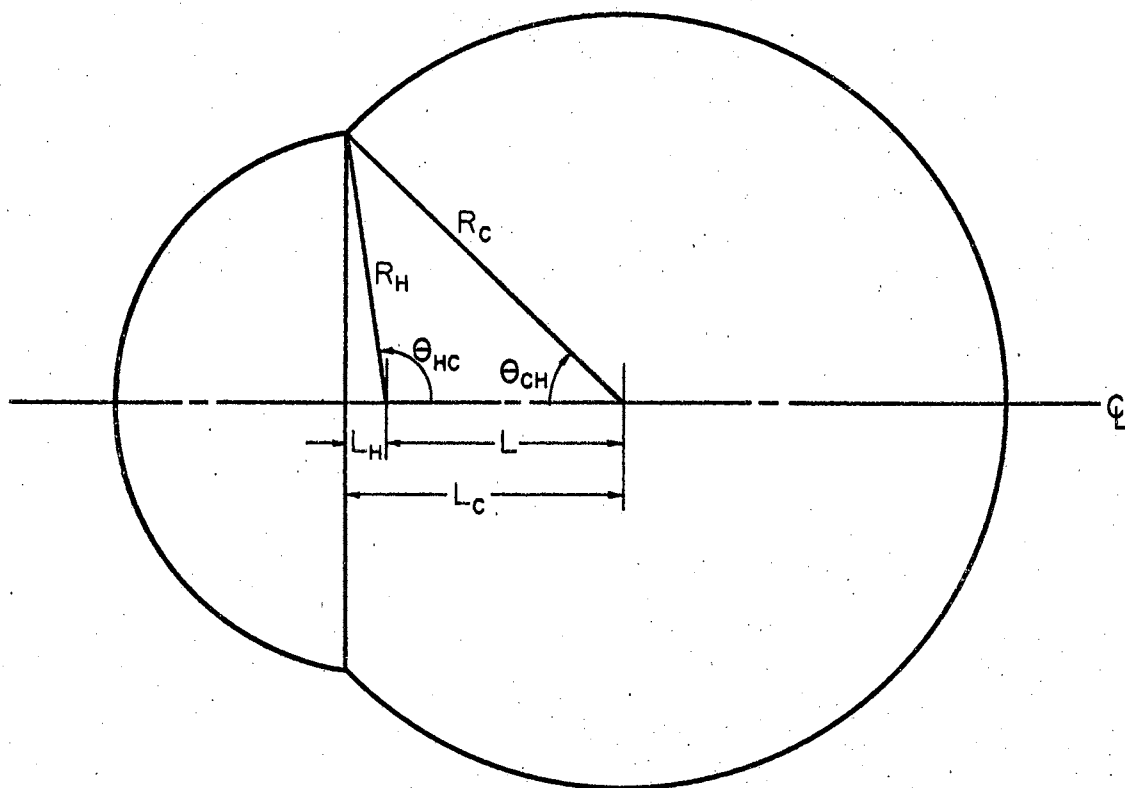


Figure 10. Surfaces of Bonded Hydrogen and Carbon

TABLE XII

FREE SURFACE AREAS OF GROUPS

Group	Bonded to	$S \times 10^{-9}$ , $\text{cm}^2/\text{mole}/\text{group}$
$\text{CH}_2$	two carbons	1.35
$\text{CH}_2$	one carbon, one oxygen	1.54
$\text{CH}_3$	carbon	2.13
$\text{CH}_3$	oxygen	2.32
OH	carbon	1.30

Then the total free surface area of the methylene group linked to two other carbons is

$$S_{\text{CH}_2} = S_{\text{C}} + 2S_{\text{H}} = 6.09 + 2(7.80) = 21.70 \text{ \AA}^2/\text{group} \quad (44)$$

In molal terms,

$$S_{\text{CH}_2} = 21.70 \times 6.02 \times 10^{23} / 10^{16} = 1.35 \times 10^9 \text{ cm}^2/\text{mole/group} \quad (45)$$

Similarly, for a methyl group attached to a carbon,

$$\begin{aligned} S_{\text{C}} &= 4\pi R_{\text{C}}^2 - 2\pi R_{\text{C}}^2 (1 - \cos\theta_{\text{CC}}) - 3 \left[ 2\pi R_{\text{C}}^2 (1 - \cos\theta_{\text{CH}}) \right] \\ &= 2\pi R_{\text{C}}^2 (\cos\theta_{\text{CC}} + 3 \cos\theta_{\text{CH}} - 2) \\ &= 2\pi (1.70)^2 (0.453 + 2.145 - 2) = 10.86 \text{ \AA}^2 \end{aligned} \quad (46)$$

The total area of the methyl is

$$S_{\text{CH}_3} = S_{\text{C}} + 3S_{\text{H}} = 10.86 + 3(7.80) = 34.26 \text{ \AA}^2 \quad (47)$$

In molal terms,

$$S_{\text{CH}_3} = 34.26 \times 6.02 \times 10^{23} / 10^{16} = 2.13 \times 10^9 \text{ cm}^2/\text{mole/group} \quad (48)$$

Calculations for the other groups are exactly analogous. Results are summarized in Table XII.

It is apparent from the above examples that the assumption is made throughout that there is no intersection or overlapping of areas except between groups which are bonded together. For instance, the hydrogens on a carbon are assumed to be so situated that they intersect only with that particular carbon.

## APPENDIX B

### COMPUTER PROGRAM

The basic program, written at Chevron Research Corporation (4), accepts as input the data values to be fitted and initial estimates of the parameter values. Using subroutines outlined below, the parameter estimates are improved until successive estimates give changes in all parameter values which are no greater than a percentage specified by the programmer. The set giving the least-sum-of-squares fit is then taken as a convergence. Printout includes the specified and calculated values of the dependent variable, and the percent deviation, for each data point, as well as the parameter values. Average and maximum deviations are also printed out.

The program is written in FORTRAN IV language, and has been run on both IBM 7040 and 7090 computers. It is fully standardized so that the only additions needed for a particular problem are as follows:

- 1) Data, including initial estimates of parameter values and specifications such as number of data points, number of parameters, etc.
- 2) The particular equation to be fitted.

Limitations of the program are a maximum of three hundred data points, twelve variables, and twenty parameters.



## Subroutine YCOMP

This routine accepts the equation to which the data are to be fitted, and calculates the value of the dependent variable for each data point using successive estimates of the parameters as determined in the main routine.

## Subroutine DERIV

In this section, the values of partial derivatives of the correlating equation are estimated by a differencing method. Thus, we avoid the problem of determining and programming partial derivatives which may be very complex. Comparisons of the results obtained by this method with those obtained by use of actual partial derivatives show no appreciable advantage in convergence from mathematically accurate derivatives.

This routine obtains the current parameter values from the main program, and changes each parameter successively by a small percentage, both plus and minus. Subroutine YCOMP is then used to find the dependent variable values for these slightly differing parameter values. The result gives estimates of the partial derivatives, which are used to establish the parameter values for the succeeding iteration.

## Subroutine SOLV

The values obtained from the YCOMP and DERIV subroutines are used by the main program to formulate a matrix which is fed to the SOLV subroutine for solution. The results are returned to the main program, which uses them to determine the parameter values for the next iteration.

This routine uses the largest available element of each row as a pivotal element, rather than solving on the diagonal. The major advantage of this is that it eliminates the possibility of using a zero element as a pivot unless there is an entire zero row or column in the matrix. This eventuality is also provided for. If it occurs, the program terminates with a printout informing the programmer of the reason.

#### Parabolic Fit

After each third iteration, the next estimate is made by applying a parabolic fit to the three previous sum-of-squares values. In general, this will materially increase the convergence rate.

#### Programming of Correlating Equation

The program statement of the equation must have the digit 1 (one) in column 5. This controls a DO loop which cycles through the data points. The dependent variable must be specified as CY(N), where the subscript, N, is the index for the DO loop.

The independent variables are designated as Z (i, N), where the i identifies the particular variable. The parameters are identified as B, subscripted.

For example, the equation

$$W = (A+BX^2) e^{(CX-DY)}$$

where the parameter values to be optimized are A, B, C, and D, and the independent variables are X and Y, can be programmed as

```
1 CY(N) = (B(1)+B(2)*Z(1,N)**2)* EXP(B(3)* Z(1,N)-B(4)* Z(2,N))
```

This is inserted in subroutine YCOMP after the statement

DO 1 N = 1,NUMBER

### Programming of Data

The first data card contains specifications in 12I6 format which are listed in the program as subscripted MM. They represent the following:

- MM(1) = number of data points
- MM(2) = index of dependent variable, or one digit higher than the highest indexed independent variable
- MM(3) = number of parameters
- MM(4) = limit on number of iterations. A value of 30 to 60 is usually sufficient for convergence.
- MM(5), if negative, skips reading of Z(i, N) values from input.
- MM(6) = -1 gives results of calculations for each iteration.
- MM(6) = 0 gives final results only.
- MM(6) = 1 gives results for only the first and last iterations.
- MM(7) = 1 gives straight fit.
- MM(7) = 0 gives parabolic fit. Recommended.
- MM(8) = 1 for input. This value is changed internally during the program run.
- MM(9) = 1 prints input data as part of output.
- MM(9) = 0 bypasses this recording.
- MM(10) = -1 records each matrix.
- MM(10) = 0 bypasses these.
- MM(10) = 1 records first matrix only.
- MM(11) = number of problems in the run. Allows multiple problems on one computer run.
- MM(12) = if negative, nullifies printing of all output except final solution.

The second through fifth data cards are the initial estimates of parameter values in 6F12.12 format. The maximum number of parameters is twenty. The twenty-first through twenty-fourth fields are used as follows:

B(21) = tolerance on convergence. Recommend 0.0001.

B(22) is used internally in DERIV routine. Leave this field blank.

B(23) = limit on magnitude of iteration changes. Recommend 1.0.

B(24) is not normally used. May be used to control entry point in YCOMP for multiple program runs or for other purposes.

The program reads 24 values regardless of the number of parameters actually used. Therefore, there must be four data cards in this section, even though one or more may be blank.

The remaining cards contain the  $Z(i, N)$  in 6F12.12 format. All variable values for the first data point are listed first, followed by those of the second data point, etc. The dependent variable is the last value listed for each point. There are no unused fields. The first value of one data point must be in the first field following that of the last value of the previous data point.

#### Program Lists

The following program lists are shown on succeeding pages:

List I: The general program excluding YCOMP subroutine.

List II: YCOMP subroutine and data for hydrocarbon parameters.

List III: YCOMP subroutine and data for heats of mixing, used to determine parameters involving the hydroxyl group.

## LIST I

```

$IBFTC DKNAME NODECK
C   EMBEDDING PROGRAM FOR GAUSS
    DIMENSION B(24), Z(12,300), MM(12)
    COMMON NUMBER,B,Z
    COMMON /COMA/ MM
    COMMON /COMB/ JJ
    1 READ (5,2) (MM(J),J=1,12)
    2 FORMAT (12I6)
    NUMBER=MM(1)
    NSET=MM(2)
    JJ=MM(3)
    IF (NUMBER) 4,4,10
    4 WRITE (6,5)
    CALL EXIT
    5 FORMAT (40H0 GAUSS INPUT ZERO, PROGRAM STOP /1H1)
    10 READ(5,11) (B(J),J=1,24)
    11 FORMAT (6F12.12)
    IF (MM(5)) 15,14,14
    14 READ (5,11) ((Z(J,N),J=1,NSET),N=1,NUMBER)
    15 CALL GAUSS
    IF (MM(8)-2) 30,20,30
    20 WRITE (6,21)
    21 FORMAT (40H0 GAUSS CONVERGENCE //)
    MM(8)=1
    30 MM(11)=MM(11)-1
    IF (MM(11)) 1,1,14
    END
$IBFTC GAUSS NODECK
SUBROUTINE GAUSS
DIMENSION A(20,21),B(24),BMIN(20),BSTART(20),C(20,1),X(20,1),
X Z(12,300),DEL(20),E(20),MM(12),RECORD(100),CY(300),FP(20,300)
COMMON NUMBER,B,Z
COMMON /COMA/ MM
COMMON /COMB/ JJ
COMMON /COMC/ CY
COMMON /COMD/ FP
COMMON /COME/ A,C,M
EQUIVALENCE (A,X)
NUMBER = MM(1)
NSET = MM(2)
JJ = MM(3)
LIMIT = MM(4)
NULL = MM(12)
MM(12) = MM(12) + 1
IDNTFC = MM(12)
TZERO = 1.0
SCALE 1 = 0.2
SCALE 2 = 1.5
SCALE 3 = 1.0
TOL1 = B(21)
X NORM = 0.0
MARK P = 0
KKPATH = -1
NDOWN = 0
NN = 0
NNPARA = 0
NPATH = 1
NTZERO = -1
SUMSQ = 0.0
T = 0.0
X3 = 3.0
X2 = 2.0

```

```

DECK0010
DECK0020
DECK0030
DECK0040
DECK0050
DECK0060
DECK0070
DECK0080
DECK0090
DECK0100
DECK0110
DECK0120
DECK0130
DECK0140
DECK0150
DECK0160
DECK0170
DECK0180
DECK0190
DECK0200
DECK0201
DECK0210
DECK0220
DECK0230
DECK0240
DECK0250
GAUS0030
GAUS0040
GAUS0050
GAUS0060
GAUS0061
GAUS0062
GAUS0063
GAUS0064
GAUS0065
GAUS0070
GAUS0490
GAUS0500
GAUS0510
GAUS0520
GAUS0530
GAUS0540
GAUS0550
GAUS0570
GAUS0580
GAUS0590
GAUS0600
GAUS0610
GAUS0620
GAUS0640
GAUS0650
GAUS0660
GAUS0670
GAUS0680
GAUS0690
GAUS0700
GAUS0710
GAUS0720
GAUS0730
GAUS0740

```

## LIST I (Continued)

```

Y2 = 2.0
Y3 = 3.0
IF (LIMIT - 100) 2,47,47
2 IF (TOL1) 420,420,1
1 DO 4 J=1,JJ
  BMIN(J) = B(J)
  BSTART(J) = B(J)
  X NORM = X NORM + B(J)**2
  DEL(J) = 0.05*ABS (B(J))
  IF (DEL(J)) 4,3,4
3 DEL(J) = 0.05
4 CONTINUE
  WRITE (6,5)
5 FORMAT (51H1      GAUSSIAN PARAMETER SUBROUTINE      Z(12,300) )
  WRITE (6,412)      (MM(L), L=1,12)
  WRITE (6,108)      (B(J), J = 1,24)
  IF (MM(9)) 400,6,400
6 IF (MM(8) - 1) 7,80,7
7 IF (B(23)) 8,8,430
8 JPARA = -1
  MPATH = -1
  T = 0.0
  MM(8) = 2
  WRITE(6,59)
  DO 9 J=1,JJ
9 BSTART(J) = B(J)
10 SQLAST = SUMSQ
  SUMSQ = 0.0
  NTZERO = NTZERO + 1
  NN = NN+1
  IF (NN - LIMIT) 12,12,11
11 MM(8) = -2
  GO TO 80
12 CALL YCOMP
  DO 17 N= 1,NUMBER
  YC = CY(N)
  DELY = YC - Z(NSET,N)
  SUMSQ = SUMSQ + DELY**2
  IF (NULL) 17,13,13
13 IF (MM(6)) 14,17,14
14 IF (N-1) 16,15,16
15 WRITE (6,410)
16 WRITE (6,18)      N,YC,Z(NSET,N),DELY
  MARK P = 1
17 CONTINUE
  RECORD(NN) = SUMSQ
18 FORMAT (16,4E18,7)
  GO TO 440
19 IF (NN - 1) 20,22,30
20 IF (SUMSQ-SQMIN) 21,21,27
21 NDOWN = 1
22 SQMIN = SUMSQ
  DO 24 J=1,JJ
24 BMIN(J) = B(J)
25 IF (MPATH) 301,200,38
27 IF (NDOWN) 28,28,29
28 NDOWN = -1
29 IF (MPATH) 301,200,36
30 IF (MM(6)) 32,32,31
31 MM(6) = 0
32 IF (MM(10)) 20,20,33
33 NNZERO = 01
38 DO 39 J=1,JJ
  B(J) = BMIN(J)

```

```

GAUS0750
GAUS0760
GAUS0780
GAUS0790
GAUS0810
GAUS0820
GAUS0830
GAUS0840
GAUS0850
GAUS0860
GAUS0870
GAUS0880
GAUS0900
GAUS0910
GAUS0930
GAUS0940
GAUS0960
GAUS0980
GAUS1000
GAUS1010
GAUS1020
GAUS1030
GAUS1040
GAUS1050
GAUS1060
GAUS1070
GAUS1090
GAUS1100
GAUS1110
GAUS1120
GAUS1130
GAUS1150
GAUS1160
GAUS1180
GAUS1181
GAUS1190
GAUS1200
GAUS1210
GAUS1220
GAUS1230
GAUS1240
GAUS1250
GAUS1260
GAUS1270
GAUS1280
GAUS1290
GAUS1300
GAUS1310
GAUS1330
GAUS1360
GAUS1370
GAUS1380
GAUS1390
GAUS1400
GAUS1410
GAUS1430
GAUS1440
GAUS1450
GAUS1470
GAUS1480
GAUS1490
GAUS1500
GAUS1560
GAUS1570

```

## LIST I (Continued)

```

39  BSTART(J) = BMIN(J)
    Y1 = SQMIN
    X1 = 0.0
    JPARA = -1
    MPATH = -1
    GO TO 301
40  SUM2 = SUM1
    SUM1 = SUMSQ
    NNPARA = 0
    IF (SUM1 - SUM2) 19,45,19
45  TZERO = SCALE1*TZERO
    NDOWN = 0
    T = 0.0
    GO TO 8
47  LIMIT = 99
    GO TO 2
49  T = -0.5*((X1*X1-X2*X2)*(Y1-Y3)-(X1*X1-X3*X3)*(Y1-Y2))/
    X ((X1-X3)*(Y1-Y2)-(X1-X2)*(Y1-Y3))
    MPATH = 1
    JPARA = -1
    NNPARA = 1
    NDOWN = 0
    GO TO 366
53  WRITE (6,54)
54  FORMAT (24H0 OVER-UNDERFLOW          //)
    MM(8) = -1
    MM(10) = -1
    GO TO 301
56  WRITE (6,57)
57  FORMAT (24H0 MATRIX IS SINGULAR      //)
    MM(8) = -1
    MM(10) = -1
    GO TO 301
59  FORMAT (114H0CYCLE   SUM OF SQUARES *****GAUS2020
X***** PARAMETERS *****//) GAUS2030
58  FORMAT (I6, F18.5, 5E18.6/(E42.6,4E18.6)) GAUS2040
60  DO 66 J=1,JJ
    BTEST = B(J)-BSTART(J)-DEL(J)
    IF (BTEST) 63,63,62
62  B(J) = BSTART(J) + DEL(J)
63  CONTINUE
    BTEST = B(J) - BSTART(J) + DEL(J)
    IF (BTEST) 65,65,66
65  B(J) = BSTART(J)-DEL(J)
66  CONTINUE
    MPATH = -1
67  DO 69 J=1,JJ
69  BSTART(J) = B(J)
    GO TO 10
80  IF (NULL) 1000,82,82
82  AV = 0.0
    AV1 = 0.0
    AV2 = 0.0
    YMAX = 0.0
    ZMAX = 0.0
    ZZMAX = 0.0
    DO 81 J=1,JJ
81  B(J) = BMIN(J)
    N = 1
    DO 90 J=1,JJ
90  WRITE (6,91) J,B(J)
91  FORMAT (4H B I2, E14.5)
    WRITE (6,100)
92  WRITE (6,93)

```

## LIST I (Continued)

```

93  FORMAT (82HONUMBER          Y OBSERVED      Y CALCULATED          GAUS2420
X   DELTA Y          PCT DEVIATION ///)          GAUS2430
94  CALL YCOMP          GAUS2450
98  YC = CY(N)          GAUS2451
    DELY = YC - Z(NSET,N)          GAUS2460
    RATIO = 100.0 * (DELY / Z(NSET,N))          GAUS2470
    ABSRAT = ABS (RATIO)          GAUS2480
    AV = AV + DELY          GAUS2490
    AV1 = AV1 + RATIO          GAUS2500
    AV2 = AV2 + ABSRAT          GAUS2510
    WRITE (6,95)          N,Z(NSET,N),YC,DELY,RATIO          GAUS2520
95  FORMAT (15,E23.5,E17.5,2E19.5)          GAUS2530
    ABSVAL = ABS (DELY)          GAUS2540
    IF (YMAX - ABSVAL) 96,96,97          GAUS2550
96  YMAX = ABSVAL          GAUS2560
    YYMAX = DELY          GAUS2570
    MARK = N          GAUS2580
97  IF (ZMAX-ABSRAT) 971,971,972          GAUS2590
971 ZMAX = ABSRAT          GAUS2600
    ZZMAX = RATIO          GAUS2610
    MARK1 = N          GAUS2620
972 N = N+1          GAUS2630
    IF (N - NUMBER) 98,98,99          GAUS2640
99  D = NUMBER          GAUS2660
    AV = AV/D          GAUS2670
    AV1 = AV1/D          GAUS2680
    AV2 = AV2/D          GAUS2690
    RTMNSQ = SQRT (SUMSQ/D)          GAUS2700
    WRITE (6,100)          GAUS2710
100 FORMAT(118H0*****GAUS2720
X*****//GAUS2730
X/)          GAUS2740
    WRITE (6,101)          AV,AV1,AV2          GAUS2750
101 FORMAT (30H0  AVERAGE DEVIATION          E14.5,          GAUS2760
X           20H    AVERAGE PCT DEV          E14.5,          GAUS2770
X           20H    AVE ABS PCT DEV          E14.5)          GAUS2780
    WRITE (6,103)          YYMAX,MARK          GAUS2790
103 FORMAT (30H0  MAXIMUM DEVIATION          E14.5,I6)          GAUS2800
    WRITE (6,104)          ZMAX,MARK1          GAUS2810
104 FORMAT (30H0  MAXIMUM PCT DEV          E14.5,I6)          GAUS2820
    WRITE (6,105)          RTMNSQ          GAUS2830
105 FORMAT (30H0  ROOT MEAN SQUARE DEVIATION E14.5)          GAUS2840
107 FORMAT ( 21H0          AT ITERATION I3, 24H, THE SUM OF SQUARES IS GAUS2860
X           E16.7/ 22H0 FOR PARAMETER VALUES /1H0//(6E20.7))          GAUS2870
108 FORMAT (5F20.5)          GAUS2880
109 FORMAT (//)          GAUS2890
110 FORMAT (I20, F20.8)          GAUS2900
    WRITE (6,5)          GAUS2910
    IF (MM(8) + 2) 114,111,114          GAUS2920
111 WRITE (6,112)          GAUS2930
112 FORMAT (30H0 EXCEEDED ITERATION LIMIT          //)          GAUS2940
    GO TO 999          GAUS2950
114 IF (MM(8) - 1) 999,8,999          GAUS2970
200 IF (NDOWN) 201,201,202          GAUS2990
201 T = T*SCALE1          GAUS3000
    GO TO 203          GAUS3010
202 T = T*SCALE2          GAUS3020
203 MPATH = 0          GAUS3030
    JPARA = JPARA + 1          GAUS3040
    GO TO 366          GAUS3050
301 MPATH = 0          GAUS3070
302 NDOWN5=N01,JJ          GAUS3080
305 A(M,N) = 0.0          GAUS3120
    CALL DERIV          GAUS3170

```



## LIST I (Continued)

```

CALL YCOMP
DO 313 N = 1,NUMBER
DO 313 K = 1,JJ
C(K,1) = C(K,1) + FP(K,N) * (Z(INSET,N) - CY(N))
DO 313 J = K,JJ
313 A(K,J) = A(K,J) + FP(K,N) * FP(J,N)
IF (NTZERO) 318,318,317
317 TZERO = 1.0
318 T = TZERO
DO 316 I=2,JJ
II=I-1
DO 316 J=1,II
316 A(I,J) = A(J,I)
IF (MM(10)) 319,331,319
319 WRITE (6,320) NN
320 FORMAT (19H0 MATRIX, ITERATION I3)
MMPATH = 0
322 DO 323 I=1,JJ
323 WRITE (6,324) (A(I,J), J=1,JJ)
324 FORMAT (9E13.5)
DO 328 I=1,JJ
328 WRITE (6,324) C(I,1)
IF (MMPATH) 350,331,350
331 DO 340 I=1,JJ
DENOM = ABS (A(I,1))
DO 336 J=2,JJ
IF (DENOM-ABS (A(I,J))) 335,336,336
335 DENOM = ABS (A(I,J))
336 CONTINUE
DO 338 K=1,JJ
338 A(I,K) = A(I,K)/DENOM*SCALE3
340 C(I,1) = C(I,1)/DENOM*SCALE3
MMPATH = 1
IF (MM(10)) 322,350,322
350 DD = 1.0
IF (MM(8)) 999,354,354
354 CALL SOLV
GO TO (351,53,56), M
351 IF (MM(6)) 352,363,352
352 WRITE (6,353) (X(J,1), J=1,JJ)
353 FORMAT (13H0 DELTA B(J) / (9E13.5))
363 Y NORM = 0.0
DO 364 J=1,JJ
364 Y NORM = Y NORM + X(J,1)**2
IF (Y NORM - X NORM) 366,366,365
365 T = 0.5*SQRT (X NORM)/SQRT (Y NORM)
X1 = T
366 DO 367 J=1,JJ
367 B(J) = BSTART(J) + T*X(J,1)
371 DO 376 J=1,JJ
IF (B(J)) 372,374,372
372 XX = ABS ((B(J) - BSTART(J))/B(J))
GO TO 375
374 XX = ABS (B(J) - BSTART(J))
375 IF (XX-TOL1) 376,376,378
376 CONTINUE
MM(8) = 2
GO TO 80
378 IF (MM(7)) 60,379,60
379 IF (NDOWN) 10,10,380
380 IF (JPARA) 10,10,49
400 IF (NULL) 6,401,401
401 WRITE (6,100)
IF (MM(5)) 406,403,403

```

```

GAUS3160
GAUS3210
GAUS3220
GAUS3230
GAUS3240
GAUS3250
GAUS3300
GAUS3310
GAUS3320
GAUS3330
GAUS3340
GAUS3350
GAUS3360
GAUS3370
GAUS3390
GAUS3410
GAUS3420
GAUS3430
GAUS3440
GAUS3450
GAUS3460
GAUS3480
GAUS3490
GAUS3500
GAUS3520
GAUS3530
GAUS3540
GAUS3550
GAUS3560
GAUS3570
GAUS3580
GAUS3590
GAUS3600
GAUS3620
GAUS3630
GAUS3650
GAUS3660
GAUS3670
GAUS3680
GAUS3690
GAUS3700
GAUS3710
GAUS3730
GAUS3740
GAUS3750
GAUS3770
GAUS3780
GAUS3790
GAUS3800
GAUS3810
GAUS3820
GAUS3830
GAUS3840
GAUS3850
GAUS3860
GAUS3870
GAUS3880
GAUS3890
GAUS3900
GAUS3920
GAUS3940
GAUS3960
GAUS3980
GAUS3990
GAUS3991

```

## LIST I (Continued)

```

403 WRITE (6,402)
402 FORMAT (15H OBSERVATIONS//)
DO 404 N=1,NUMBER
404 WRITE (6,405) N, (Z(J,N), J=1,12)
405 FORMAT (14,8E14.5/(E18.5,7E14.5))
406 WRITE (6,5) IDNTFC
GO TO 6
410 FORMAT ( 60H0 DATA Y COMP Y OBS
XRENCE )
411 FORMAT (16,F20.7)
412 FORMAT (12I6)
420 TOL1 = 0.0001
GO TO 1
430 IF (B(23) - 1.0) 431,8,8
431 T ZERO = B(23)
WRITE (6,433) TZERO
433 FORMAT ( 30H0 VECTOR SCALE FACTOR = B(23), E12.4//)
GO TO 8
440 IF (NULL) 446,441,441
441 N SPIN = N SPIN + 1
442 IF(MARK P) 444,443,444
443 IF (N SPIN - 15) 445,444,444
444 N SPIN = 0
WRITE (6,59)
445 WRITE (6,58) NN, SUMSQ, (B(J), J=1,JJ)
446 X3 = X2
X2 = X1
X1 = T
Y3 = Y2
Y2 = Y1
Y1 = SUMSQ
IF (NNPARA) 40,19,40
999 WRITE (6,991)
DO 990 J=1,NN
990 WRITE (6,405) J, RECORD(J)
991 FORMAT ( 28H0 RECORD OF SUM OF SQUARES // )
993 FORMAT (24H0 MINIMIZING PARAMETERS //)
WRITE (6,993)
WRITE (6,108) (BMIN(J), J=1,JJ)
1000 RETURN
END
$IBFTC SOLV NODECK
SUBROUTINE SOLV
DIMENSION A(20,21), C(20,1), LOC(20), CK(20)
COMMON /COMB/ JJ
COMMON /COME/ A,C,M
M = 1
NP = JJ+ 1
DO 11 I = 1,JJ
CK(I) = 0.
11 A(I,NP) = C(I,1)
DO 50 I = 1,JJ
IP = I + 1
C*****FIND MAX ELEMENT IN I' TH COLUMN.
AMAX = 0.
DO 2 K = 1,JJ
IF (AMAX - ABS(A(K,I))) 3,2,2
C*****IS NEW MAX IN ROW PREVIOUSLY USED AS PIVOT
3 IF (CK(K)) 4,4,2
4 LOC(I) = K
AMAX = ABS(A(K,I))
2 CONTINUE
CK(L) = 1.
C*****PERFORM ELIMINATION. L IS PIVOT ROW, A(L,I) IS PIVOT ELEMENT.

```

## LIST I (Continued)

DO 50 J = 1,JJ	SOLV0260
IF (L-J) 6,50,6	SOLV0261
6 F = -A(J,I) / A(L,I)	SOLV0262
DO 40 K = IP,NP	SOLV0270
40 A(J,K) = A(J,K) + F * A(L,K)	SOLV0280
50 CONTINUE	SOLV0290
DO 200 I = 1,JJ	SOLV0300
L = LOC(I)	SOLV0310
200 A(I,1) = A(L,NP) / A(L,I)	SOLV0320
RETURN	SOLV0330
99 M = 3	SOLV0340
RETURN	SOLV0350
END	SOLV0360
\$IBFTC DERIV NODECK	DERIV010
SUBROUTINE DERIV	DERIV020
DIMENSION B(24),Z(12,300),CY(300),FP(20,300),H(20),Y(300)	DERIV030
COMMON NUMBER,B,Z	DERIV040
COMMON /COMB/ JJ	DERIV050
COMMON /COMC/ CY	DERIV060
COMMON /COMD/ FP	DERIV070
IF (B(22)) 20,1,20	DERIV080
1 B(22) = 1.	DERIV090
DO 7 J = 1,JJ	DERIV100
TEST = ABS(B(J))	DERIV110
IF (TEST - 0.001) 5,6,6	DERIV120
5 H(J) = 0.001	DERIV130
GO TO 7	DERIV140
6 H(J) = 0.0001 * TEST	DERIV150
7 CONTINUE	DERIV160
20 DO 22 J = 1,JJ	DERIV170
TEMP = B(J)	DERIV180
B(J) = TEMP + H(J)	DERIV190
CALL YCOMP	DERIV200
DO 21 N = 1,NUMBER	DERIV210
21 Y(N) = CY(N)	DERIV220
B(J) = TEMP - H(J)	DERIV230
CALL YCOMP	DERIV240
B(J) = TEMP	DERIV250
DO 22 N = 1,NUMBER	DERIV260
22 FP(J,N) = (Y(N) - CY(N)) / (2. * H(J))	DERIV270
RETURN	DERIV280
END	

## LIST II

```

$IBFTC YCOMP NODECK
SUBROUTINE YCOMP
DIMENSION B(24),Z(12,300),CY(300)
COMMON NUMBER,B,Z
COMMON /COMC/ CY
E1 = EXP(0.675 * B(1) / 592.52)
E2 = EXP(0.826 * B(2) / 592.52)
E3 = EXP(1.065 * B(3) / 592.52)
DO 1 N = 1,NUMBER
F1 = 1.35 * Z(1,N) * E1
F2 = 1.35 * Z(1,N) * E2
F3 = 4.26 * E2
F4 = 4.26 * E3
D1 = F1 + F3
D2 = F2 + F4
1 CY(N)=1.35*Z(1,N)*F1/D1*B(1)+1.35*Z(1,N)*F3/D1*B(2)+4.26*F2/D2*
X B(2)+4.26*F4/D2*B(3)
RETURN
END

```

YCOMP010  
YCOMP020  
YCOMP030  
YCOMP040  
  
YCOMP100  
  
YCOMP200  
YCOMP210

```

$ENTRY
8 3 3 60 -1 1 1 -1 1 1
861.08 723.71 468.64

```

		.0001		1.	
1.	3314.	2.	4555.	3.	5768.
4.	6969.	5.	8155.	6.	9328.
7.	10508.	8.	11684.		

\$IBSYS

## LIST III

```

$IBFTC YCOMP NODECK
SUBROUTINE YCOMP
DIMENSION B(24),Z(12,300),CY(300)
COMMON NUMBER,B,Z
COMMON /COMC/ CY
E1 = EXP (0.675 * 861.08 / 592.52)
E2 = EXP ( 0.826 * 723.71 / 592.52)
E3 = EXP ( 1.065 * 468.64 / 592.52)
F3 = 4.26 * E2
F4 = 4.26 * E3
E4 = EXP(0.65 * B(1) / 592.52)
F5 = 1.3 * E4
DO 1 N = 1,NUMBER
F1 = 1.35 * Z(2,N) * E1
F2 = 1.35 * Z(2,N) * E2
D1 = F1 + F3
D2 = F2 + F4
U1=1.35*Z(2,N)*F1/D1*861.08+1.35*Z(2,N)*F3/D1*723.71+4.26*F2/
X D2*723.71+4.26*F4/D2*468.64
S02 = 1.3 * Z(4,N) / (1.3 + Z(4,N))
S22 = Z(4,N) ** 2 / (2. * Z(4,N))
S23 = Z(4,N) * Z(5,N) / (Z(4,N) + Z(5,N))
E6 = EXP (0.807* B(3) / 592.52)
E9 = E3
2 E5 = EXP( S02 * B(2) / 592.52)
E7 = EXP ( S22 * 861.08 / 592.52)
E8 = EXP ( S23 * 723.71 / 592.52)
F6 = 1.3 * E5
F7 = 1.3 * E6
F8 = Z(4,N) * Z(1,N) * E5
F9 = Z(4,N) * Z(1,N) * E7
F10 = Z(4,N) * Z(1,N) * E8
F11 = Z(5,N) * E6
F12 = Z(5,N) * E8
F13 = Z(5,N) * E9
D3 = F5 + F8 + F11
D4 = F6 + F9 + F12
D5 = F7 + F10 + F13
U2=1.3*F5/D3*B(1)+Z(1,N)*Z(4,N)*F6/D4*B(2)+Z(5,N)*F7/D5*B(3)+
X 1.3*F8/D3*B(2)+Z(1,N)*Z(4,N)*F9/D4*861.08+Z(5,N)*F10/D5*723.71
X +1.3*F11/D3*B(3)+Z(1,N)*Z(4,N)*F12/D4*723.71+Z(5,N)*F13/D5*468.64
S2=(Z(3,N)*Z(4,N)*Z(1,N)+(1.-Z(3,N))*Z(2,N)*1.35)/(Z(3,N)*Z(1,N)
X +(1.-Z(3,N))*Z(2,N))
S3 = 2.13
3 S02 = 1.3 * S2 / (1.3 + S2)
S03 = 1.3 * S3 / (1.3 + S3)
S22 = S2 ** 2 / (2. * S2)
S23 = S2 * S3 / (S2 + S3)
S33 = S3 ** 2 / (2. * S3)
E10 = EXP( S02 * B(2) / 592.52)
E11 = EXP ( S03 * B(3) / 592.52)
E12 = EXP ( S22 * 861.08 / 592.52)
E13 = EXP ( S23 * 723.71 / 592.52)
E14 = EXP ( S33 * 468.64 / 592.52)
F14 = 1.3 * Z(3,N)
F15 = S2 * (Z(3,N) * Z(1,N) + (1. - Z(3,N)) * Z(2,N))
F16 = S3 * (2. - Z(3,N))
D6 = F14 * E4 + F15 * E10 + F16 * E11
D7 = F14 * E10 + F15 * E12 + F16 * E13
D8 = F14 * E11 + F15 * E13 + F16 * E14
U3=F14**2*E4/D6*B(1)+F14*F15*B(2)*E10*(1./D6+1./D7)+F14*F16*
X B(3)*E11*(1./D6+1./D8)+F15**2*E12/D7*861.08+F15*F16*723.71*E13
YCOMP010
YCOMP020
YCOMP030
YCOMP040
YCOMP050
YCOMP060
YCOMP070
YCOMP080
YCOMP090
YCOMP100
YCOMP110
YCOMP100
YCOMP130
YCOMP140
YCOMP150
YCOMP160
YCOMP170
YCOMP171
YCOMP180
YCOMP190
YCOMP200
YCOMP210
YCOMP220
YCOMP260
YCOMP270
YCOMP280
YCOMP290
YCOMP300
YCOMP310
YCOMP320
YCOMP330
YCOMP340
YCOMP350
YCOMP360
YCOMP370
YCOMP380
YCOMP390
YCOMP400
YCOMP401
YCOMP402
YCOMP410
YCOMP411
YCOMP420
YCOMP460
YCOMP470
YCOMP480
YCOMP490
YCOMP500
YCOMP510
YCOMP520
YCOMP530
YCOMP540
YCOMP550
YCOMP560
YCOMP570
YCOMP580
YCOMP590
YCOMP600
YCOMP610
YCOMP620
YCOMP621

```

## LIST III (Continued)

$X * (1./D7 + 1./D8) + F16 ** 2 * E14 / D8 * 468.64$   
 $1 \text{ CY}(N) = (1. - Z(3,N)) * U1 + Z(3,N) * U2 - U3$   
 SENTRY  
 63      6      3      60      -1      1      1      -1      1      1  
 3209.      1490.      1142.

YCOMP622  
YCOMP630

		.0001		1.	
1.	4.	.1	1.54	2.13	112.3
1.	4.	.2	1.54	2.13	138.
1.	4.	.3	1.54	2.13	148.5
1.	4.	.4	1.54	2.13	150.3
1.	4.	.5	1.54	2.13	144.
1.	4.	.6	1.54	2.13	132.5
1.	4.	.7	1.54	2.13	113.9
1.	4.	.8	1.54	2.13	87.9
1.	4.	.9	1.54	2.13	52.3
1.	7.	.1	1.54	2.13	129.9
1.	7.	.2	1.54	2.13	160.2
1.	7.	.3	1.54	2.13	174.6
1.	7.	.4	1.54	2.13	178.4
1.	7.	.5	1.54	2.13	174.4
1.	7.	.6	1.54	2.13	163.4
1.	7.	.7	1.54	2.13	145.
1.	7.	.8	1.54	2.13	117.4
1.	7.	.9	1.54	2.13	74.4
2.	5.	.1	1.44	2.13	126.5
2.	5.	.2	1.44	2.13	156.4
2.	5.	.3	1.44	2.13	169.1
2.	5.	.4	1.44	2.13	169.2
2.	5.	.5	1.44	2.13	159.5
2.	5.	.6	1.44	2.13	141.1
2.	5.	.7	1.44	2.13	115.9
2.	5.	.8	1.44	2.13	84.5
2.	5.	.9	1.44	2.13	46.5
3.	5.	.1	1.41	2.13	123.
3.	5.	.2	1.41	2.13	151.
3.	5.	.3	1.41	2.13	164.1
3.	5.	.4	1.41	2.13	164.
3.	5.	.5	1.41	2.13	153.5
3.	5.	.6	1.41	2.13	133.6
3.	5.	.7	1.41	2.13	106.9
3.	5.	.8	1.41	2.13	74.9
3.	5.	.9	1.41	2.13	38.9
4.	4.	.1	1.40	2.13	109.
4.	4.	.2	1.40	2.13	131.5
4.	4.	.3	1.40	2.13	141.
4.	4.	.4	1.40	2.13	139.9
4.	4.	.5	1.40	2.13	129.
4.	4.	.6	1.40	2.13	109.5
4.	4.	.7	1.40	2.13	85.3
4.	4.	.8	1.40	2.13	58.1
4.	4.	.9	1.40	2.13	29.2
7.	5.	.1	1.38	2.13	105.8
7.	5.	.2	1.38	2.13	122.3
7.	5.	.3	1.38	2.13	128.5
7.	5.	.4	1.38	2.13	126.7
7.	5.	.5	1.38	2.13	118.3
7.	5.	.6	1.38	2.13	103.2
7.	5.	.7	1.38	2.13	81.8
7.	5.	.8	1.38	2.13	56.6
7.	5.	.9	1.38	2.13	28.4

## LIST III (Continued)

7.	7.	.1	1.38	2.13	120.9
7.	7.	.2	1.38	2.13	141.5
7.	7.	.3	1.38	2.13	149.
7.	7.	.4	1.38	2.13	148.5
7.	7.	.5	1.38	2.13	140.4
7.	7.	.6	1.38	2.13	122.2
7.	7.	.7	1.38	2.13	98.9
7.	7.	.8	1.38	2.13	69.6
7.	7.	.9	1.38	2.13	35.9

\$IBSYS

## APPENDIX C

### NOMENCLATURE

- $A_i$  - total free surface area of  $i$  groups in one molecule.
- $\overset{\circ}{A}$  - Angstrom unit,  $10^{-8}$  cm.
- B - Parameter in computer program.
- CY - Dependent variable in computer program.
- $E_S$  - group surface energy.
- $E_T$  - group thermal energy.
- F - degrees of freedom of a molecule.
- f - degrees of freedom of a group.
- $\Delta H_M$  - heat of mixing.
- $H_V$  - enthalpy of a real gas.
- $H_V^*$  - enthalpy of an ideal gas.
- $\Delta H_V$  - heat of vaporization.
- k - molecular Boltzmann constant.
- L - sum of covalent radii of bonded atoms.
- $L_1$  - distance from center of atom 1 to plane of intersection of bond.
- MM - specification in computer program.
- N - Avogadro's number.
- $n_i$  - number of  $i$  groups in a molecule.
- R - universal gas constant, or molal Boltzmann constant.
- $R_1$  - van der Waals radius of atom 1.
- r - total number of groups in a molecule.



- $S_i$  - free surface area of group  $i$ .  
 $S_{ij}$  - defined by equation (17).  
 $T$  - absolute temperature.  
 $T_c$  - critical temperature.  
 $T_r$  - reduced temperature,  $T/T_c$ .  
 $\Delta U_V^*$  - internal energy of vaporization to the ideal gas.  
 $x_A$  - mole fraction of molecule A in a mixture.  
 $Z$  - independent variable in computer program.  
 $z_L$  - liquid compressibility factor.

#### Greek Letters

- $\alpha$  - thermal freedom factor, defined by equation 25.  
 $\lambda_{uv}$  - energy of interaction between  $u$  and  $v$  groups.  
 $\theta_{12}$  - angle subtended in atom 1 bonded to atom 2.  
 $\pi$  - 3.14159....  
 $\sum_i$  - summation over all types of groups.

#### Subscripts

- $2$  -  $\text{CH}_2$  group.  
 $3$  -  $\text{CH}_3$  group.  
 $C$  - carbon atom.  
 $H$  - hydrogen atom.

VITA

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