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A STUDY OF THE CLAUSIUS EQUATION OF STATE

by

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ABSTRACT

The purpose of this work is to present an approach and its limitations as applied to the Clausius equation of state to calculate the volume and the heat of mixing.

The investigation was begun to continue the research into volume and heat of mixing, specifically through an evaluation of the latest modification of the Clausius equation of state, simply by considering the three parameters as temperature dependent.

The results of the evaluation indicate that the proposed approach is good for predicting volumes of mixing but not entirely adequate for predicting heats of mixing.

Thus, an alternative approach has been investigated by considering two of the parameters as temperature dependent which appears more adequate and versatile for predicting these thermodynamic properties.

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NOMENCLATURE

A, B, C, a, b, c = parameters of the Clausius equation of state (Equations (3. 1) to (3. 12))

$\Omega_a, \Omega_b, \Omega_c$ = parameters of the Clausius equation of state (Equations (3. 2) to (3. 4))

f = fugacity

h, H = dummy variable of the Clausius equation of state (Equations (3. 6), (3. 7)), or enthalpy

k = interaction constant

n = number of moles

P = pressure

R = gas constant

V = molal volume

ω = acentric factor

x = liquid mole fraction

z = compressibility factor

φ = fugacity coefficient

Δ = difference

SUPERSCRIPTS

E = excess property

$*$ = ideal state

$-$ = partial molal quantity

SUBSCRIPTS

C = critical property

i, j = component identification

L = liquid state

V = vapor state

R = reduced property

CHAPTER 1

INTRODUCTION

The heat of mixing is defined as the change in enthalpy per mole of the mixture when the pure components are mixed at constant temperature and pressure and is given by

$$\Delta H = H - \sum_{i=1} x_i H_i \, . \tag{1}$$

The enthalpy of an ideal solution is given by

$$H^* = \sum x_i H_i^* \tag{2}$$

Combining (1) and (2) gives

$$\Delta H = \sum x_i (H^* - H)_i - (H^* - H)$$

where $(H^* - H)_T$ is the enthalpy departure from ideal behaviour and could be obtained for the pure components and the mixture from the thermodynamic relation$^{(7, 25)}$:

$$(H^* - H)_{T,P} = RT - PV + \int_{\infty}^{V} \left[P - T \left(\frac{\partial P}{\partial T} \right)_V \right] dV \tag{3}$$

Similarily the volume change in mixing pure components at constant temperature and pressure to form one mole of the solution is given by:

$$\Delta V = V - \sum x_i V_i \tag{4}$$

According to Euler's theorem

$$V = \sum x_i \bar{V}_i \qquad (5)$$

Combining (4) and (5) gives

$$\Delta V = \sum x_i (\bar{V}_i - V_i)$$

where $\bar{V}_i$ is the partial molal volume and is given by$^{(8)}$

$$\bar{V}_i = \frac{-\left(\frac{\partial P}{\partial n_i}\right)_{T, V, n_j (i \neq j)}}{\left(\frac{\partial P}{\partial V}\right)_{T, n_j (\text{all } j)}}$$

Both of these quantities, ΔH and ΔV continue to be of primary importance in the design calculations of petroleum and petrochemical industries. The volume of mixing is of economic significance, such as the shrinkage involved in the mixing of hydrocarbon. On the study of distillation efficiency, densities of mixtures along saturation curves are needed.

Also, heat of mixing data are of practical value. Tsao and Smith$^{(55)}$ have pointed out that for solutions which deviate appreciably from ideal behaviour, the heat of mixing may be of considerable importance in comparison with the other heat effects accompanying vaporization and condensation.

Common methods of obtaining these thermodynamic quantities are available in the literature$^{(45)}$. These may involve calculating these values using an adequate equation of state. This approach places the prime focus of attention upon procuring accurate PVT data. Any inadequacies in the functional form of the equation of state are magnified in the resulting expression for the enthalpy departure, $(H^* - H)$, partial molal volume and consequently for heat of mixing and volume of mixing due to the differentiation and integration associated with Equation (8) and Equation (11).

In order to apply an equation of state to vapor-liquid equilibrium for pure component, the equation of state must satisfy the following three conditions

$$V_{V,\,calc} = V_{V,\,exp}$$

$$V_{L,\,calc} = V_{L,\,exp}$$

$$f_{V,\,calc} = f_{L,\,calc}$$

So, the equation must have at least three adjustable parameters to satisfy these conditions at equilibrium. An evaluation of the frequently used equations of state are given elsewhere(10). Mixing rules for combining the pure component parameters are required for extending these equations to mixture.

The aim of this study centers on investigating the applicability of the latest modification(20), considering the parameters of the Clausius equation of state to be temperature dependent, to calculate the heats and the volumes of mixing. The data required to calculate the adjustable parameters Ω_a, Ω_b, and Ω_c are the vapor pressure, the saturated liquid densities and the saturated vapor densities of the pure components.

On the other hand, satisfaction of these three conditions at equilibrium, coupled with the proper mixing rules does not necessitate the suitability of an equation of state, with at least three parameters, to calculate the heat of mixing. Hence, another approach may be endeavoured with the intension of investigating the proper variations of the parameters with temperature so as to modify the Clausius equation of state which can be suitably applied to calculate the heat of mixing.

The different proposed approachs were evaluated and compared with the modified Redlich-Kwong equation of state(8, 30) for the prediction of the compressibility of the pure liquids using oxygen(57) and heptane(18) as examples.

CHAPTER 2

LITERATURE REVIEW

2.1 Equations of State

In view of the large number of equations of state which have been proposed in the literature, it is natural to search for the motivation. There are two rather obvious reasons(34) for the wide-spread activities in this field over an extended period of time. The first is the fact that the problem of developing an equation of state is mathematically fascinating and particularily tantalizing because it seems so simple, at least at the start. The second reason concerns the exceptional power and utility of an equation of state. When combined with appropriate thermodynamic relation, a well behaved equation may predict with high precision isothermal changes in heat capacities, enthalpy departure from ideal gas behaviour, partial molal volume, fugacity, vapor pressure, latent heat of vaporization and vapor liquid equilibria in mixture.

Extensive reviews have been written by many prominent workers, for instance, Shah and Thodes(49), Stewart and Timmerhaus(52), Martin(34), and Tsonopoulos and Prausnitz(56) to compare the relative merits and limitations of the most common equations of state. Despite this prolific outpouring on the subject, some facts are either misunderstood or not fully appreciated and these justify further research in the field.

The degree of complexity of equations of state as indicated by the number of constants, has been deliberately increased to better represent the PVT behaviour of substances over wide ranges of temperature and pressure. In this respect the equation of state proposed by Martin and Hou(31) requires nine constants to predict the PVT behaviour of the substance. Similarily, the Benedict-Webb-Rubin equation requires eight constants(4), while the Beattie-Bridgeman equation(3) uses five constants to predict the PVT behaviour of substances for which the constants are calculated.

These equations have received considerable attention over recommended ranges of temperature and pressure(56). Although these equations are logically developed from the well-known thermodynamic principles, their application is frequently limited by the inaccessibility of the constants for the PVT conditions of interest. Establishing these constants is frequently a lengthy operation, requiring a curve fitting and trial-and-error procedure. What appears to be the limitation is the fact that some PVT data of the substance must be available in order to begin establishing these constants.

Although good accuracy is claimed by these equations, the less complex equations of state, having two or three constants, except the Redlich-Kwong equation of state, which proves to be superior over all the equations examined by Thodes and Shah(49), have been overlooked largely because of their lack of sophistication. This is consistent with the common notion that an equation of state with more constants should produce results that are more consistent with the experimental PVT behaviour of the substance.

2.2 Temperature Dependence of the Parameters of Equations of State

Recently, the literature has indicated a resurgence in the popularity of treating the parameters of equations of state as temperature dependent. However, Benedict and co-workers were primarily interested in applying their equation to hydrocarbon mixture for calculation of K-values and enthalpies; mixing rules for eight constants were proposed(5) in 1942. To obtain eight meaningful constants, extensive experimental data are required and even if such data are at hand, the eight constants obtained from data reduction are probably not unique(56). Several sets of constants are not an important matter as long as the attention is restricted to the properties of pure components but it becomes extremely important when pure component constants are used to predict mixture properties(22, 23). Constants for twelve pure hydrocarbons were given by Benedict, Webb, and Rubin in 1951(6). BWR constants have been obtained for nitrogen(53, 29), hydrogen(29, 37), carbon dioxide(29, 17), hydrogen sulphide(38), argon(62) and carbon monoxide(47).

When fitting liquid saturation pressures, the important constant in the BWR equation is C_o. It was shown in 1951(6) that C_o must be adjusted when the saturation pressure is less than 1 atm, and in 1953(53) Stotler and Benedict showed that for calculations at low temperature, it is necessary to allow C_o to vary with temperature.

This modification has won wide acceptance(29, 38, 61). Barner and Schreiner(2) have pointed out the need for this modification for accurate calculation of enthalpies.

On the other hand, many variations on van der Waals' equation have been proposed but by far the most successful (using only two constants) is that of Redlich and Kwong in 1949(44) which combines simplicity with reasonable accuracy. Since it has only two constants; its primary use is not for representing extensive experimental data but for estimating volumetric and derived properties for non-polar (or slightly polar) fluids and their mixtures from minimum experimental information such as critical temperature and pressure of the pure components. The superiority of the Redlich-Kwong equation over the van der Waals equation and its early variations (Bertheholt, Dietirici), as a limiting case for the two constant equations has been amply demonstrated by Shah and Thodes(49).

To better represent the PVT relation calculated by the Redlich-Kwong equation of state, Wilson(57) proposed that the parameter a be temperature dependent according to the following relation

$$a_{ii}/R\,T_{ci}^{1.5} = 4.934\left[1 + k_i\left(\frac{1}{T_{Ri}} - 1\right)\right] T_{Ri}^{1.5}\, b_i \qquad (2.1)$$

$$a_{ij} = \theta_{ij}\, a_{ii} + (1 - \theta_{ij})\, a_{jj} \qquad (2.2)$$

Where T_{Ri} is the reduced temperature of i, K_i is a constant characteristic of i and θ_{ij} is a binary constant which must be determined from some experimental data for the binary. a_{ij} is a measure of the strength of attraction between a molecule i and a molecule j. If i and j are the same chemical species, the a_{ij} is clearly the Redlich-Kwong a for that substance.

Wilson has also applied his modification of the Redlich-Kwong equation of state to the calculation of enthalpies(59). In this paper he introduced the acentric factor by letting

$$k_i = 1.57 + 1.62\,\omega_i$$

The agreement is good for gaseous mixtures.

In a recent paper(60) Wilson presents a complicated relation which combines equations (2.1), (2.2) and further improves the calculation of mixture properties. A simplified form of this modification has been used by Chang, Chappllear and Kobayashi(12).

As pointed out by the authors, a further modification for the equation of state would be the inclusion of the effect of the inter-molecular forces acting between unlike molecules on the mixing rules which relate the constants of a mixture to these of pure component.

Robbinson and Jacoby(45) assumed that both constants a and b are linear functions of temperature. They also found that prediction of properties for multicomponent mixtures was much improved when Equation (2. 2) was used instead of the geometric mean for a_{ij}. Their modification was applied to only restricted ranges of temperature and pressure.

Barner, Pigford and Schreiner used the original Redlich-Kwong mixing rules, but they made the constant a temperature dependent, in order to improve the prediction of the second virial coefficient below the critical temperature. Thus,

$$\frac{a}{T^{\frac{1}{2}}} = \frac{\alpha}{T^{\frac{1}{2}}} + \frac{\gamma}{T^{3/2}} \tag{2. 3}$$

α, γ could be related to critical temperature, critical pressure and acentric factor. This modification provides a considerable improvement in predicting the enthalpies of non-polar condensable vapor(1).

The modification of Barner, Pigford and Schreiner as well as those of Wilson and Robinson and Jacoby, give a critical isotherm which is the same as that of the original Redlich-Kwong equation as they introduced temperature dependence for one or both of the adjustable parameters.

Gray, Rent and Zudkevitch(21) combined Barner's modification with the deviation function approach, in which a function of temperature, pressure and acentric factor is added to the compressibility factor from the original equation to fit the compressibility and enthalpy data for vapor mixture of light hydrocarbons and related non-polar substances. Although the fit near the critical point is improved, the modification has a limited range of applicability.

Chueh and Prausnitz(12) proposed that for gas phase calculation the constant Ω_a, Ω_b be adjusted to the properties of the saturated vapor; for liquid phase properties these constants should be adjusted to liquid density data. In both cases Ω_a, Ω_b are considered to be temperature-independent. The purpose of this adjustment is to facilitate the calculation of fugacity coefficient in saturated vapor mixture, partial molar volumes in liquid mixtures, and critical properties of mixtures. However, this method is restricted to the prediction of partial molal volume at saturation pressure and at a temperature not lower than a reduced pseudocritical temperature of 0.56.

Zudkevitch and Joffe(61) have followed the approach of Wilson(58, 59) and extended it to the quantity Ω_b. They evaluated Ω_a and Ω_b of the Redlich-Kwong equation separately for the saturated vapor phase and the saturated liquid phase. In the establishment of the values of Ω_a and Ω_b the generalized correlation of Lyckman, Eckert and Prausnitz(32) for fugacity coefficient was employed

$$\log \varphi = (\log \varphi)^{(0)} + \omega (\log \varphi)^{(1)}$$

Where $(\log \varphi)^{(0)}$ and $(\log \varphi)^{(1)}$ are functions of the reduced temperature tabulated by Lyckman, Eckert and Prausnitz. The values of Ω_a and Ω_b evaluated from the saturated liquid properties were utilized for both phases due to the fact that for most compounds the values of Ω_a and Ω_b for vapor phase ascend rapidly as T_R decreases. In several cases the vapor values take an erratic course and become negative after passing through a maximum. The parameters of pure component were combined to give that of mixture in the form of the following relation:

$$a_{ij} = (1 - C_{ij})(a_{ii} \cdot a_{jj})^{0.5}$$

Where C_{ij} represents the deviation of a_{ij} from classical geometric mean assumption. The establishment of C_{ij} was found from the experimental data. It should be noted that the temperature-dependent parameters Ω_a and Ω_b obtained with their method would not satisfy the fundamental condition $\varphi_{iV} = \varphi_{iL}$. This drawback is also there in the method of Wilson(58, 59).

Joffe, Schroeder and Zudkevitch recognized the above mentioned pitfalls; subsequently they proposed an alternate procedure for establishing the pure component Ω_a and Ω_b parameters as a temperature function in their very recent publications(26). The procedure is essentially similar to the method proposed by Chang and Lu in the calculation of partial molal volumes(8) and enthalpies of mixing(9) of liquid mixtures. Lyckman's correlated values of φ_L(32) were avoided by facing the equalization of the fugacity coefficient in the saturated vapor and saturated liquid. Therefore the following relation was derived.

$$\Omega_a = \Omega_b \left[\frac{\ln[(V_V - b)/(V_L - b)] - P(V_V - V_L)/RT}{(T_c/T)^{3/2} \ \ln[(V_L + b)/V_L(V_V + b)]} \right] \qquad (2.4)$$

Equation (2. 4) was solved simultaneously with the Redlich-Kwong equation of state at each temperature below the critical point to yield Ω_a and Ω_b. The solution involves a trial-and-error procedure. This Equation (2. 4) becomes indeterminate at the critical point. It is therefore necessary to use the previous method(61) to establish Ω_a and Ω_b at the critical point.

The Redlich-Kwong equation of state has been successfully applied by Chang and Lu to the prediction of partial molar volume$^{(8)}$ and enthalpy of mixing$^{(9)}$ of liquid mixtures by considering both Ω_a and Ω_b temperature-dependent and were obtained through a rigorous thermodynamic approach, therefore, the fundamental condition of equilibrium state $\varphi_{iL} = \varphi_{iV}$ was satisfied. The method has been extended by Hsi and Lu to evaluate Ω_a and Ω_b in the supercritical region$^{(24)}$.

The approach of Zudkevitch and Joffe, Chang and Lu recently extended by Hsi and Lu, relies greatly on the capability of the equation of state to represent the fluid properties for pure components as well as their mixtures. However, in their approach, despite the fact that the fundamental condition at equilibrium $\varphi_{iV} = \varphi_{iL}$ is satisfied, another condition, minimum deviation between experimental and calculated Z_V, is sacrificed. This would not affect the prediction of partial molal volumes and heats of mixing of binary liquid mixtures. This is expected since Redlich-Kwong equation has only two adjustable parameters while we have three conditions to be satisfied at equilibrium. Namely

$$Z_V^{\text{exp}} - Z_V^{\text{calc}} = 0 \qquad \text{(i)}$$

$$Z_L^{\text{exp}} - Z_L^{\text{calc}} = 0 \qquad \text{(ii)}$$

and the fundamental condition $\varphi_{iV} = \varphi_{iL}$ (iii). So, we must have an equation with at least three adjustable parameters to satisfy these conditions at equilibrium.

Thodes and Carlson$^{(7)}$ proposed a simple van der Waals type model based on an analogy between density and enthalpy departure from ideal gas behaviour for pure component, which contains three temperature-independent parameters. Their relation lacks more sophistication and more complex pressure-dependent function of the enthalpy departure would be necessary to describe the behaviour in the liquid state. This was done to by-pass volume, which must be first calculated from equation of state by iteration, altogether by establishing a relationship capable of defining enthalpy departure directly in terms of temperature and pressure and replacing it in an equation of state.

Recently Elshayal and Lu(20) successfully applied a modified Clausius equation of state to calculate the fugacity coefficient, liquid phase activity coefficient and PVT data. In the original equation, Clausius(15, 40) supplemented the van der Waals' equation by the introduction of a third constant. Clausius postulated the existence of clusters of two or more molecules that are temporarily formed by collision at lower temperatures and which break-up very readily at higher temperatures. In such clusters the forces are much greater than if the molecules were separate in the gas and hence the van der Waals term a/V^2 is too small to account for this force at lower temperatures. Further, Clausius considered correction on the cohesive pressure term, i.e., he replaced the term $\frac{a}{V^2}$ by the quantity $\frac{a}{T(V+c)^2}$. This correction is equivalent to treating the parameter a of the van der Waals equation of state as temperature dependent and shifting the calculated critical isotherm.

The technique was not fully appreciated(34) at that time, possibly because Clausius offered a kinetic explanation that was only partially justified rather than a mathematical explanation based on the transformation of the independent variable. In the modification of Elshayal and Lu(20) the parameters Ω_a, Ω_b and Ω_c of the equation were treated as temperature dependent and were obtained through a rigorous thermodynamic approach, therefore, the three conditions for equilibrium state were satisfied. The applicability of treating Ω_a, Ω_b and Ω_c as temperature dependent parameters for representation of vapor-liquid equilibria has been demonstrated$^{(20)}$.

Up to this point, the modified Clausius equation of Elshayal and Lu appears promising to be followed up in calculating heat and volume of mixing because its relative simplicity and wide range of application.

CHAPTER 3

PREDICTION OF THE HEATS AND THE VOLUMES OF MIXING OF BINARY LIQUID MIXTURES WITH THE CLAUSIUS EQUATION OF STATE

A suitable equation of state when combined with appropriate thermodynamic relationships and mixing rules, may be successfully employed for the prediction of the excess thermodynamic properties and vapor-liquid equilibria. In order to satisfy the three conditions at equilibrium, there should be an equation of state which contains three parameters. So, it is desirable to investigate the possibility of utilizing the modified Clausius equation of state as a means of calculating the heat and the volume of mixing of binary liquid mixture.

3.1 Clausius Equation of State

The working equation originally proposed by Clausius$^{(14)}$ is of the following form:

$$P = \frac{RT}{V-b} - \frac{a}{T(V+c)^2} \tag{3.1}$$

Where
$$a = \frac{27}{64}\,\frac{R^2 T_c^3}{P_c} = \Omega_a \frac{R^2 T_c^3}{P_c} \tag{3.2}$$

$$b = \tfrac{1}{4}\, V_c \left(4 - \frac{RT_c}{P_c V_c}\right) = \Omega_b V_c (4-S) \tag{3.3}$$

$$c = \tfrac{1}{8}\, V_c \left(\frac{3RT_c}{P_c V_c} - 8\right) = \Omega_c V_c (3S-8) \tag{3.4}$$

$$S = \frac{1}{Z_c} \tag{3.5}$$

or it could be rearranged as follows

$$Z = \frac{1}{1-h} - \left(\frac{A^2}{C}\right)\left(\frac{H}{(1+H)^2}\right) \tag{3.6}$$

or

$$Z = \frac{1}{1-h} - \left(\frac{A^2}{B}\right)\left(\frac{h}{(1+H)^2}\right) \tag{3.7}$$

Where

$$h = \frac{b}{V} = \frac{BP}{Z} \tag{3.8}$$

$$H = \frac{c}{V} = \frac{CP}{Z} \tag{3.9}$$

$$A^2 = \frac{a}{R^2 T^3} \tag{3.10}$$

$$B = \frac{b}{RT} \tag{3.11}$$

$$C = \frac{c}{RT} \tag{3.12}$$

The values of Ω_a, Ω_b and Ω_c were obtained originally from (3.1) by setting the first and second partial derivatives of pressure with respect to volume equal to zero at the critical point. Namely, $\left(\frac{\partial P}{\partial V}\right)_{T_c} = 0$ and $\left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c} = 0$.

In the liquid region equation (3.1) failed to predict acceptable values, although good agreement was found to exist in the gaseous region. In many ways, the equation of Clausius embodies a certain definite improvement over the van der Waals equation, which may be attributed(49) to the introduction of temperature and the quantity (V+c). Thus the cohesive pressure term becomes $\frac{a}{T(V+c)^2}$ compared to $\frac{a}{V^2}$ in the van der Waals equation. Hence, a proper adjustment of such cohesive pressure term might produce an equation of state applying better in the liquid and high pressure region.

In this work two different approachs have been investigated. The first approach centers on investigating the applicability of the proposed modification by Elshayal and Lu$^{(20)}$, where Ω_a, Ω_b and Ω_c were treated as temperature dependent, to calculate the heat and the volume of mixing. The parameters were evaluated, for each pure component below its critical temperature, from the saturated liquid density, saturated vapor density and vapor pressure. The method of the evaluation is presented in Section 3. 3.

When the Clausius equation of state is applied to a mixture the following mixing rules are used

$$a = \sum_i \sum_j x_i x_j a_{ij} \tag{3. 13}$$

$$b = \sum_i x_i b_i \tag{3. 14}$$

$$c = \sum x_i c_i \tag{3. 15}$$

Where

$$a_{ij} = \Omega_{a_{ij}} R^2 T_{c_{ij}}{}^3/P_{c_{ij}} \tag{3. 16}$$

$$T_{c_{ij}} = (T_{c_i} T_{c_j})^{0.5} (1 - k_{ij}) \tag{3. 17}$$

$$\Omega_{a_{ij}} = 0.5 (\Omega_{a_{ii}} + \Omega_{a_{jj}}) \tag{3. 18}$$

$$P_{c_{ij}} = Z_{c_{ij}} R T_{c_{ij}} / V_{c_{ij}} \tag{3. 19}$$

$$V_{c_{ij}} = \frac{1}{8} \left(V_{c_i}^{\frac{1}{3}} + V_{c_j}^{\frac{1}{3}}\right)^3 \qquad (3.20)$$

$$Z_{c_{ij}} = 0.291 - 0.08\, \omega_{ij} \qquad (3.21)$$

$$\omega_{ij} = 0.5\, (\omega_i + \omega_j) \qquad (3.22)$$

It should be noted that the quantity k_{ij} in Equation (3.17) is the binary interaction constant, which is a constant characteristic of the interaction of two dissimilar molecules, as a reasonable approximation k_{ij} is assumed to be independent of temperature, density and composition(13). Equation (3.13) to (3.22) are identical to those employed by Elshayal and Lu(20), Chueh and Prausnitz(14).

An extensive comparison was carried out for the results of the proposed approach which indicates that it is more suited for calculating the volume of mixing than the heat of mixing. This appears to stem from the fact that the equations are too sensitive to the temperature derivative of the parameters. Moreover, it appears that c (given by Equation (3.4)) changes rapidly with temperature and does not have a special trend. Hence, it might be thought that an equation of state, even with three parameters to satisfy the three conditions at equilibrium, does not necessitate that it predicts accurately the heat of mixing because the temperature dependence of such an equation is inadequate.

So, another approach has been investigated aiming to simplify the number of primary information needed and to study a proper variation of the parameters with temperature, where Ω_a and Ω_b were treated as temperature dependent while assigning to Ω_c a constant value given by the original equation of Clausius. This minimizes the number of primary information necessary by one, but on the other hand, one of the conditions at equilibrium should be sacrificed. As far as it was of our interest to apply the Clausius equation in the liquid region, the condition of minium deviation between the experimental and calculated Z_V has been sacrificed. The same mixing rules have been used and k_{ij} was assumed independent of temperature, pressure and composition.

3.2.1 Calculation of Heat of Mixing

Heat of mixing is defined by

$$\Delta H = \sum_i x_i (H_i^* - H_i) - (H^* - H) \qquad (3.24)$$

where $(H^* - H)_T$ is the enthalpy departure from ideal gas behaviour and could be obtained from the thermodynamic relation:

$$(H^* - H)_T = RT - PV + \int_\infty^V [P - T(\partial P/\partial T)_V] \, dV \qquad (3.25)$$

Using the Clausius equation of state (3.1), Equations (3.2) to (3.12) and the mixing rules previously mentioned, one can obtain

$$\left(\frac{H_i^* - H_i}{RT}\right) = 1 - Z + \left(\frac{A^2}{B}\right)\left[\left(\frac{2h}{1+H}\right) + \left(\frac{V_c}{RB}\right)\left(\frac{h}{1+H}\right)^2 (3S-8)\right]\frac{d\Omega_c}{dT}$$

$$+ \left(\frac{V_c}{RB}\right)\left(\frac{h}{1-h}\right)(4-S)\frac{d\Omega_b}{dT} - \left(\frac{H}{1+H}\right)\left(\frac{S^2 V_c^2 P_c T_c}{C R^2 T^2}\right)\frac{d\Omega_a}{dT} \qquad (3.26)$$

and

$$\left(\frac{H^{*} - H}{RT}\right) = 1 - Z + \left(\frac{A^{2}}{B}\right)\left[\left(\frac{2h}{1+H}\right) + \left(\frac{1}{RB}\right)\left(\frac{h}{1+H}\right)^{2} \sum x_i \frac{dC_i}{dT}\right]$$

$$+\left(\frac{1}{RB}\right)\left(\frac{h}{1-h}\right)\left(\sum x_i \frac{db_i}{dT}\right) - \left(\frac{H}{1+H}\right)\left(\frac{\sum\sum x_i x_j \frac{da_{ij}}{dT}}{C R^{2} T^{2}}\right) \qquad (3.27)$$

where

$$\frac{da_{ij}}{dT} = a_{ij}\left[\frac{\frac{d(1-k_{ij})}{dT}}{1-k_{ij}} + \frac{\frac{d\Omega_{a}}{dT} + \frac{d\Omega_{aj}}{dT}}{\Omega_{ai} + \Omega_{aj}}\right] \qquad (3.28)$$

$$\frac{db_i}{dT} = V_c\,(4 - S)\,\frac{d\Omega_{bi}}{dT} \qquad (3.29)$$

$$\frac{dc_i}{dT} = V_c\,(3S - 8)\,\frac{d\Omega_{ci}}{dT} \qquad (3.30)$$

In this work, k_{ij} was assumed to be independent of temperature, composition and pressure of the solution so Equation (3.28) reduces to

$$\frac{da_{ij}}{dT} = a_{ij}\left[\frac{\frac{d\Omega_{ai}}{dT} + \frac{d\Omega_{aj}}{dT}}{\Omega_{ai} + \Omega_{aj}}\right] \qquad (3.31)$$

A computer program for performing the calculation is given in Appendix B.

3.2.2 Calculation of Volume of Mixing

The volume of mixing is defined by

$$\Delta V = \sum x_i\,(\overline{V}_i - V_i) \qquad (3.32)$$

Where $\overline{V}_i$ is the partial molal volume at component i in mixture and is defined by

$$\overline{V}_i = \left(\frac{\partial V_T}{\partial n_i}\right)_{P,\,T,\,n_j(i \neq j)} \tag{3.33}$$

Since most equations of state are explicit in pressure, rather than in volume, it is convenient to rewrite Equation (3.25)

$$\overline{V}_i = \frac{-\left(\frac{\partial P}{\partial n_i}\right)_{T,\,V_T,\,n_j(i \neq j)}}{\left(\frac{\partial P}{\partial V_T}\right)_{T,\,n_i\ (\text{all } i)}} \tag{3.34}$$

Combining Equation (3.34) with the Clausius Equation and its mixing rules (Equation (3.1), (3.8), (3.9) and (3.13) to (3.22)) gives

$$\overline{V}_i = \frac{\frac{RT}{V-b}\left(1+\frac{b_i}{V-b}\right) - \frac{2\sum x_j a_{ij} - \frac{2ac_i}{V+c}}{T(V+c)^2}}{\frac{RT}{(V-b)^2} - \frac{2a}{T(V+c)^3}} \tag{3.35}$$

Where V is the liquid molar volume of the mixture. Using V, Equations (3.32) and (3.35), one can readily calculate the volume of mixing of liquid mixtures. A computer program for performing the calculation is given in Appendix B.

3.3 Evaluation of the Adjustable Parameters

The method developed by Elshayal and Lu(20) for the evaluation of the temperature-dependent parameters, Ω_a, Ω_b and Ω_c of the Clausius equation of state was used. The primary information required for the evaluation are the saturated liquid densities, saturated vapor densities and vapor pressure of the pure components.

At equilibrium

$$\varphi_{iV} = \varphi_{iL} \qquad (B.1)$$

The quantity φ_{iV} and φ_{iL} for pure component, i, were obtained from the following equations

$$\ln \varphi_{iL} = \frac{h_L}{1 - h_L} - \ln Z_L - \ln (1 - h_L) - (A^2/B)\, h_L \left[\frac{2 + H_L}{(1 + H_L)^2}\right] \qquad (B.2)$$

$$\ln \varphi_{iV} = \frac{h_V}{1 - h_V} - \ln Z_V - \ln (1 - h_V) - (A^2/B)\, h_V \left[\frac{2 + H_V}{(1 + H_V)^2}\right] \qquad (B.3)$$

Combining Equations (B. 3), (B. 1) and the Clausius equation (Equations (3. 7) and (3. 8) to (3. 11)) one obtains

$$\ln \varphi_{iV} Z_L - \left(\frac{h_L}{1 - h_L}\right) + \ln (1 - h_L) + \left[\frac{1}{(1 - h_L)} - Z_L\right] (2 + H_L) = 0 \quad (B.4)$$

These equations were used to evaluate Ω_a, Ω_b and Ω_c. The calculation procedure contains two iteration loops and is outlined as follows:

1. Assume initial values of Ω_a, Ω_b and Ω_c (e. g., the values at the critical point, 0. 422, 0. 250 and 0. 125, respectively which are given by Equations (3. 2) to (3. 4)).
2. For a given value of Z_L (experimental) and assumed value of φ_{iV}, calculate h_L by means of Equation (B. 4).
3. Calculate A from Equation (3. 8) and B from (3. 7).
4. Substitute the new values of A and B into Equation (3. 7) and (3. 8) and solve simultaneously for another set of roots Z_V and h_V.

5. Calculate φ_{iV} from Equation (B. 3) using the new set of Z_V and h_V.
6. Obtain new value for h_L from Equation (B. 4) and compare it with that of step 2. If they disagree, repeat the calculation starting from step 2. An iteration loop is thus built until the changed h_L value is less than the specified tolerance. The tolerance used in this investigation is 0.0005.
7. The second loop starts by comparing value of Z_V from step 4, with the experimental one. If they disagree, start from the beginning with a new value of Ω_c, i.e., $\Omega_{c,new} = \Omega_{c,old} - \Delta$ and the calculated Ω_a and Ω_b from the last step 6.
8. The second iteration loop is completed when value of Z_V calculated agree with Z_V experimental.

The flow diagram for finding Ω_a, Ω_b and Ω_c is shown in Figure 3.1.1. The computer program is given in Appendix B-1.

It should be mentioned that the Newton-Raphson method was used to locate the roots. This method is quadratically convergent, except in the vicinities of the triple point and the critical point. It failed to converge and satisfy the condition of zero deviation between the experimental and calculated Z_V. Thus, the values of the parameters which give a minimum deviation in Z_V were used in this work.

The parameters were determined for most of the substances used in this investigation over the temperature range from the triple point up to the critical point (Table A-1-1). The values of the parameters were correlated as a function of temperature using a polynomial least-square curve fit for the temperature range from the vicinity of the triple point up to the critical point. An improvement

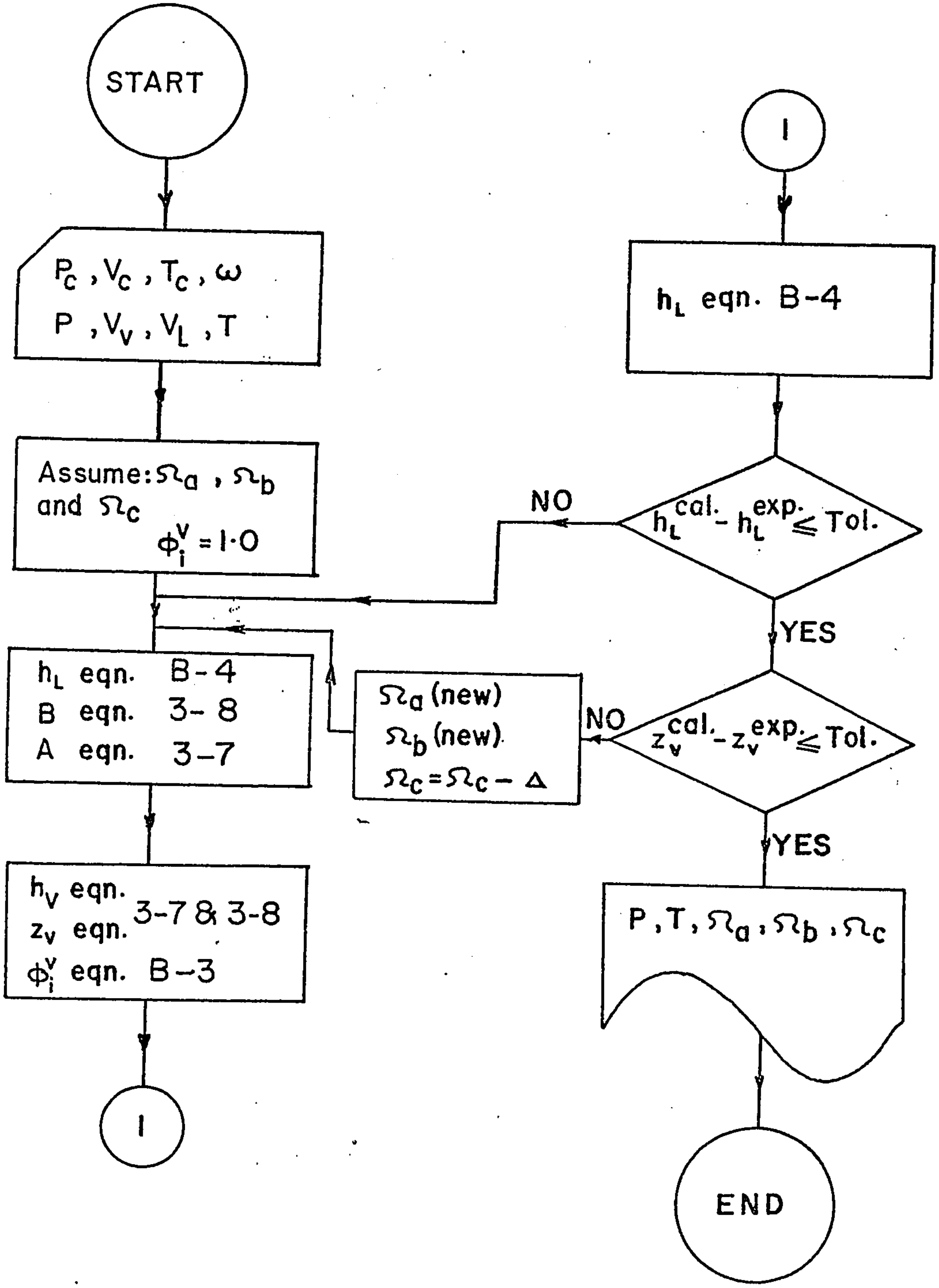

Fig.3. 1. 1 Schematic diagram for calculation of the parameters of the Clausius equation.

has been achieved by correlating the parameters over a limited range of temperature ($0.5 \leq T_R \leq .6$). This range was chosen where the values of the parameters oscillated and did not have the same trend pertinent to the whole range (triple point up to critical point). Unfortunately, most of the data available in the literature for binary liquid mixtures are within that range.

In view of the oscillation of the parameters of the pure component, an alternative procedure for establishing values of Ω_a, Ω_b and Ω_c has been proposed. It involves the utilization of average constant values for the parameters specific for each substance. The values were calculated by averaging the parameters over a limited range for each compound and are given in Table A. 1. 2.

However, the Clausius equation is a three parameter equation with three conditions to satisfy at equilibrium. It should be expected that the parameters obtained by this method were unique whether the iteration loop was started for the parameters A and B or for A and C. Certain difficulties have been encountered in obtaining an initial guess for the value of the parameters when the first iteration loop was designed using A and C. This has not been encountered when the first iteration loop was designed using A and B because a fairly good initial guess for the values of the parameters could be made using the values assigned by Equations (3. 2) to (3. 4).

As far as the critical point is concerned, where $Z_L = Z_V$, the second iteration loop was omitted. This means that only two parameters have been considered as temperature-dependent, i. e., the parameters are not unique, depends whether A and B or A and C were adjusted.

In the second proposed approach where two of the parameters have been considered temperature dependent, the second iteration loop for Z_V was omitted. This approach was used with the expectation that

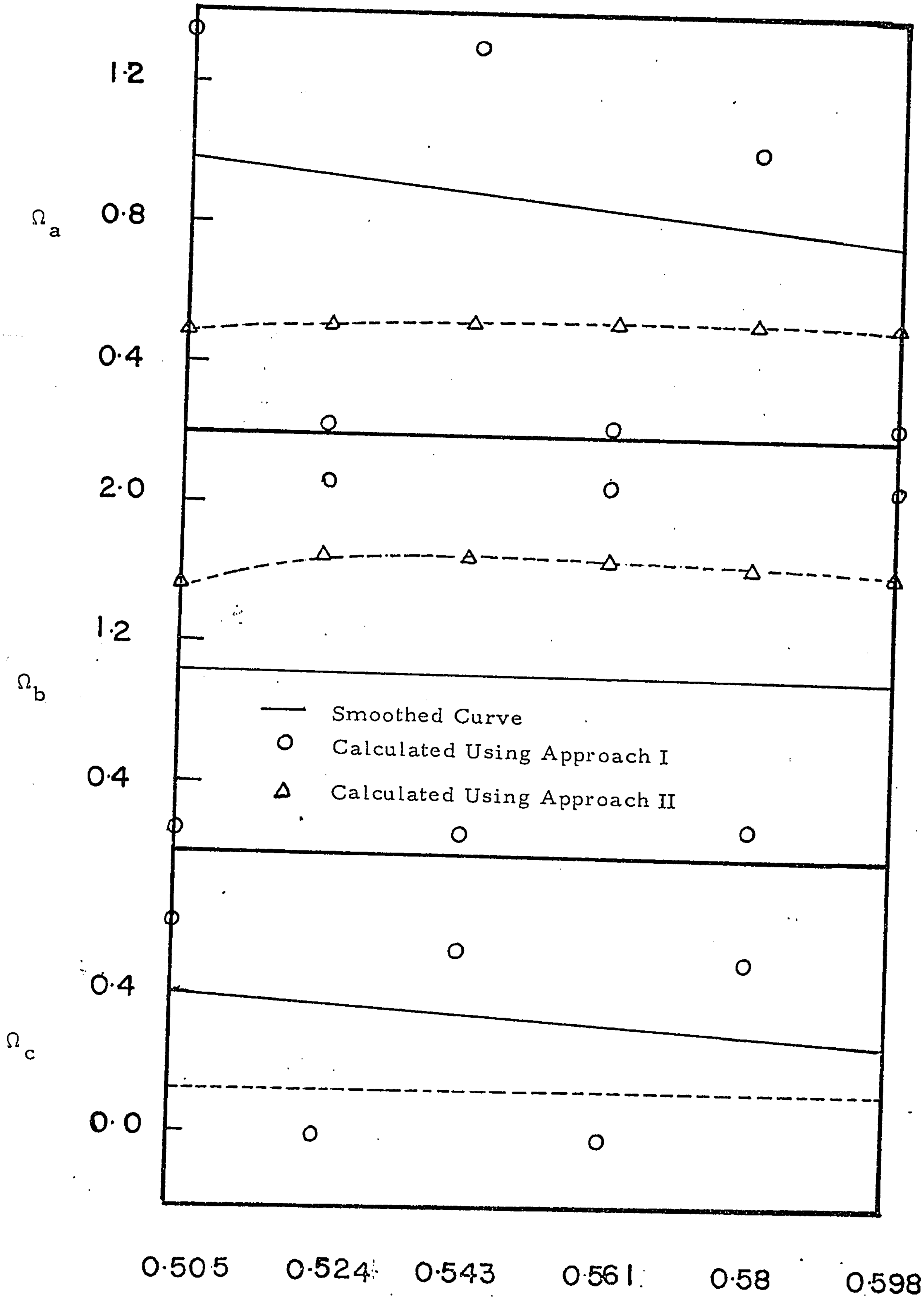

Fig. 3.1.2 Temperature dependent characteristics of Ω_a, Ω_b and Ω_c of heptane.

the parameters would be stable and would not oscillate around a certain value. The variation of Ω_a and Ω_b with temperature would have a specific trend and the derivatives would not change rapidly with temperature and were not difficult to establish. The calculated values of the parameters are given in Table A. 1. 1. The temperature dependent characteristics of heptane are shown in Fig. 3. 1. 2.

3. 4. 1 Comparison of Heats of Mixing Values with Literature Data

The calculated results obtained in this investigation were compared with literature values. Nine systems were arbitrarily chosen in this comparison. A summary of the percentage deviation is listed in Table 3. 1. In this comparison, approach I refers to treating the three parameters of the Clausius equation of state as temperature dependent while approach II refers to treating two of the parameters as temperature dependent.

Oxygen-Nitrogen at 77°K(28): Fairly good agreement between the calculated and the experimental values was observed for approach I while good results were obtained using approach II. The average absolute deviations are 1. 2 and 0. 7 cal/gm mole which are 14. 6 and 8% for approach I and II respectively. The results were adversely affected when a higher than the second order polynomial curve fit was used to represent the variations of the parameters with temperature. The average absolute deviation is 174%. Moreover, the shape of the calculated curve has been changed. The results are given in Table A-3-1 and shown in Figure 3. 2. 1.

Argon-Nitrogen at 84°K(41): When the unsmoothed values of the parameters were used, no minimum of the sum of the absolute differences between the experimental and the calculated values of heats of mixing, or even a reasonable and acceptable value, have been obtained even at higher values of k_{ij} using approach I. An improvement has been achieved by using the smoothed values of the parameters. The average absolute deviation is 1.8 which is 21.3%. When the calculated values of the parameters, using approach I, were used and the values of the derivatives were computed from the smoothed relations of the parameter with temperature, the average absolute deviation is 3 cal/gm mole which is 31.4%. For approach II, the average absolute deviation is 1.2 cal/gm mole and the percentage deviation is 9.9%. The calculated results are less scattered. The comparison is made in Figure 3.2.2 and Table A.3.2.

<u>Oxygen-Argon at 84°K</u>$^{(41)}$: An improvement has been achieved by using the smoothed values of the parameters. The results are very sensitive to the calculated values of the derivatives of Ω_a, Ω_b and Ω_c with temperature, based on different polynomial curve fit. The average absolute deviation is 1.8 cal/gm mole which is 15.8%, for a smoothed linear relation of the parameters with temperature. Very good results have been obtained for the two parameter temperature dependent approach. The average absolute deviation is 0.5 cal/gm mole which is 3.9%. The comparison is made in Figure 3.2.3 and Table A.3.3.

<u>Oxygen-Argon at 86°K</u>$^{(28)}$: The average absolute deviations are 1.9 and 5.7 cal/gm mole depending on whether nothing but a linear or a linear and second order fit were used to represent the variations of Ω_a, Ω_b and Ω_c with temperature. Thus, the percentage deviations are 19.7 and 60.2 respectively. The results are given in Table A.3.4 and are shown in Figure 3.3.4.

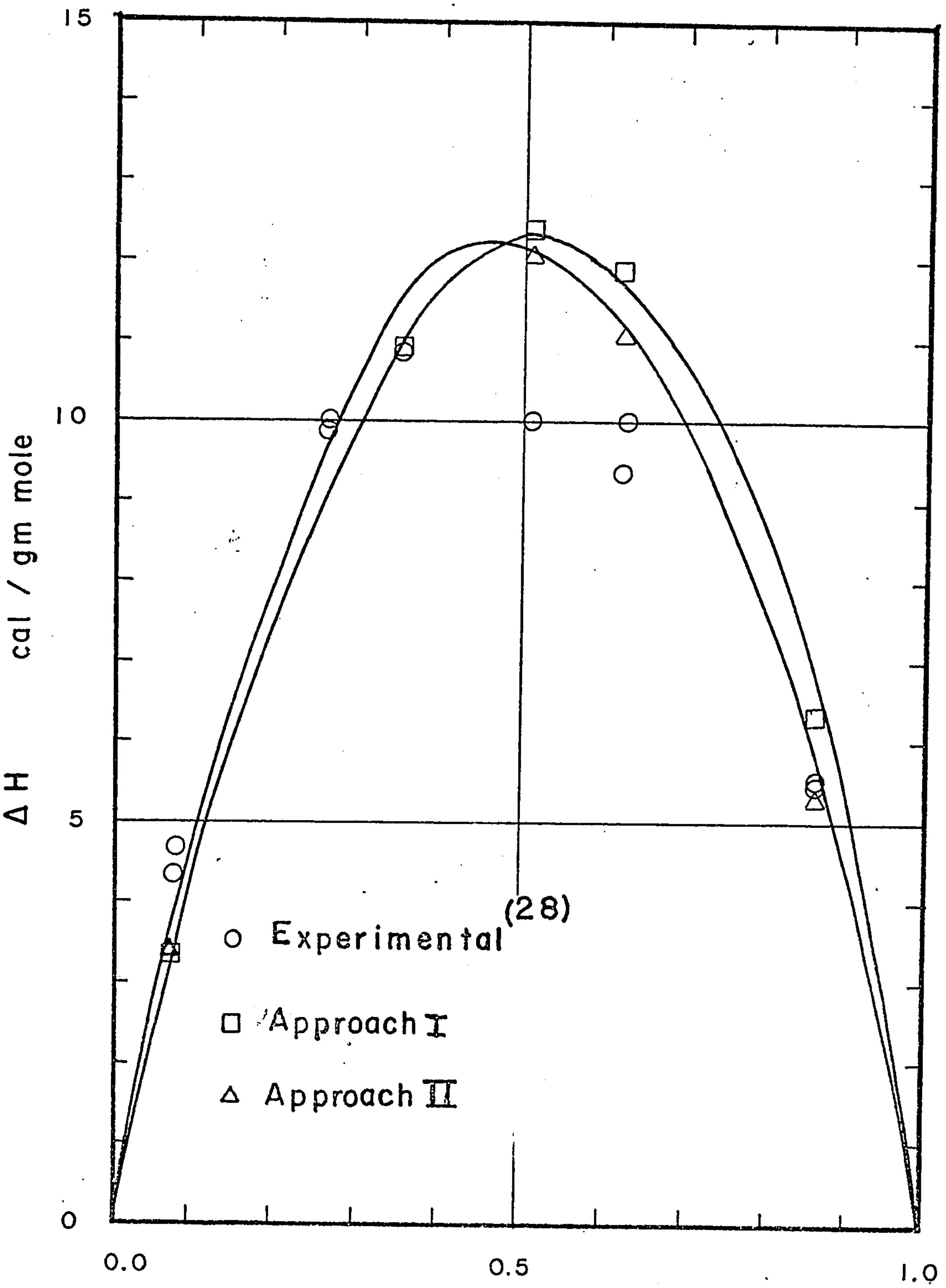

Fig. 3. 2. 1 Comparison of calculated and literature values of heat of mixing for oxygen-nitrogen at 77°K.

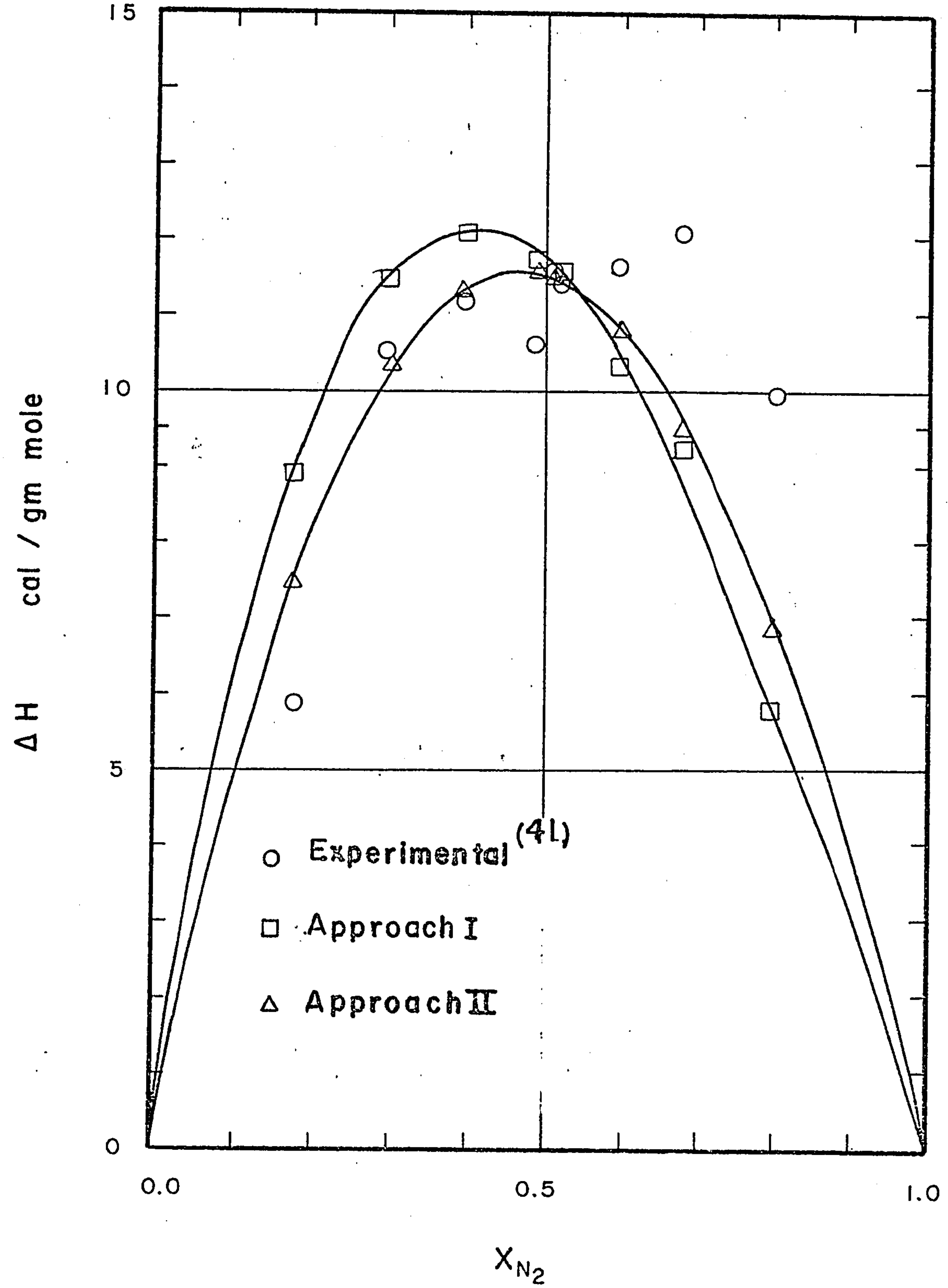

Fig. 3.2.2 Comparison of calculated and literature values of

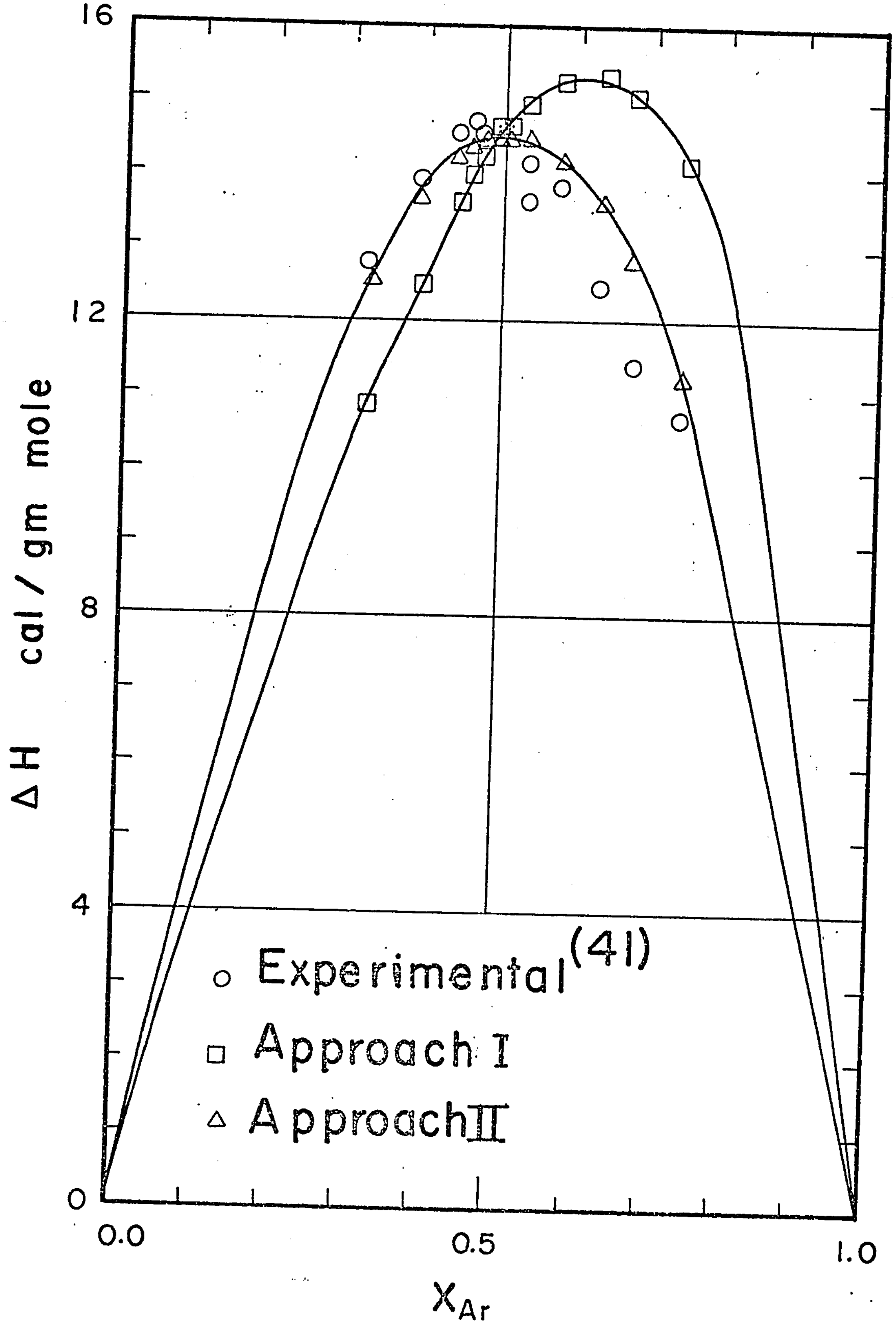

Fig. 3.2.3 Comparison of calculated and literature values of heat of mixing for oxygen-argon at 84°K.

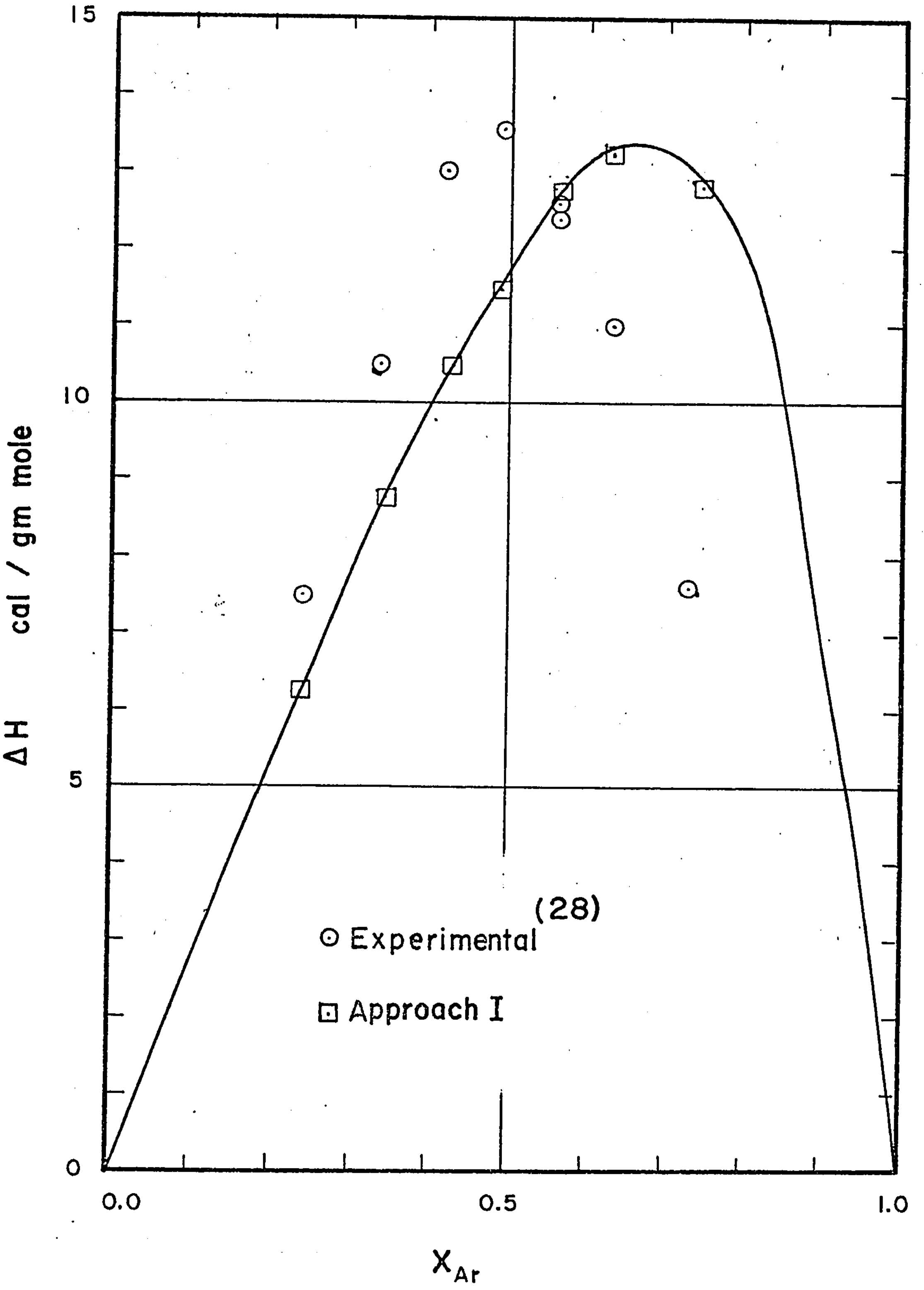

Fig. 3.2.4 Comparison of calculated and literature values of heat of mixing for oxygen-argon at 86°K.

Benzene-Hexane at 25°C(27): Excellent results have been obtained by both approaches as seen from Figure 3. 2. 5 and Table A. 3. 5. The average absolute deviation is 2 cal/gm mole which is less than 2%.

Benzene-Hexane at 20°C(35): As shown in Figure 3. 2.6 and Table A. 3. 6, approach II proved to be better than approach I. The average absolute deviation is 43 J/gm mole which is 6. 7%, for approach I, while it is 10 J/gm mole which is 1. 6% for approach II. When the average constant values of the parameters for both hexane and benzene were used the percentage deviation is 1..9%. The unmodified original equation of Clausius gives a deviation of 1. 8%.

Benzene-Heptane at 50°C(31): For approach II, the average absolute deviation is 6. 1 J/gm mole which is less than 1%. Approach I gives very poor results when the unsmoothed values of the parameters were used. Better results have been obtained by smoothing the values of the parameters up to the critical point or over a limited range of temperature ($0.5 \leq T_R \leq 0.6$). The average absolute deviations are 13. 2 and 12. 5 J/gm mole which are 1. 73 and 1. 74% respectively. When the average values of the parameters were used, the average absolute deviation is 24. 7 J/gm mole which is 4%. It is interesting to report that the percentage deviation is 1. 1% when the modified Clausius equation of state was used. The results are shown in Figure 3. 2. 7 and Table A. 3. 7.

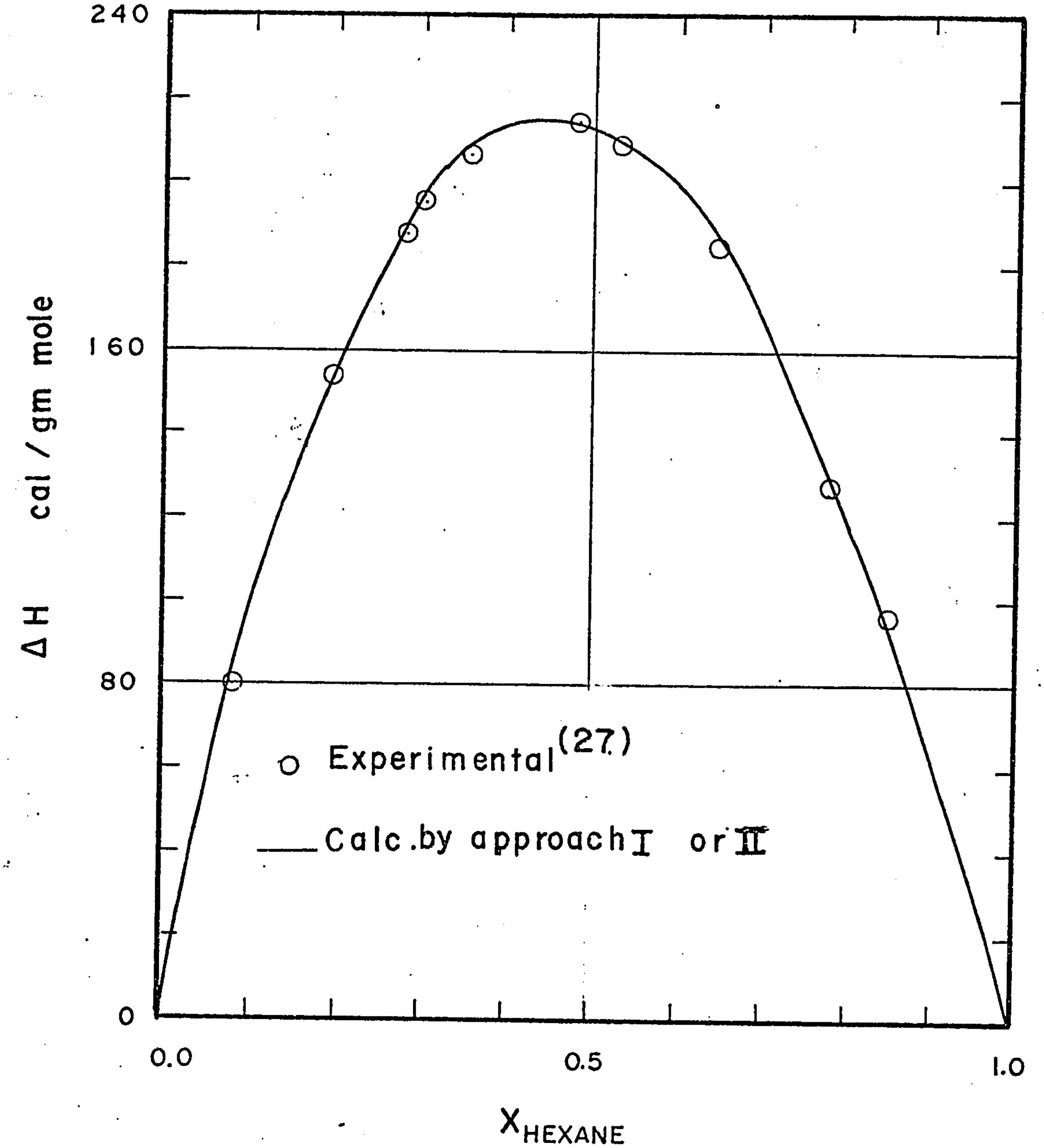

Fig. 3.2.5 Comparison of calculated and literature values of heat of mixing for benzene-hexane at 25°C.

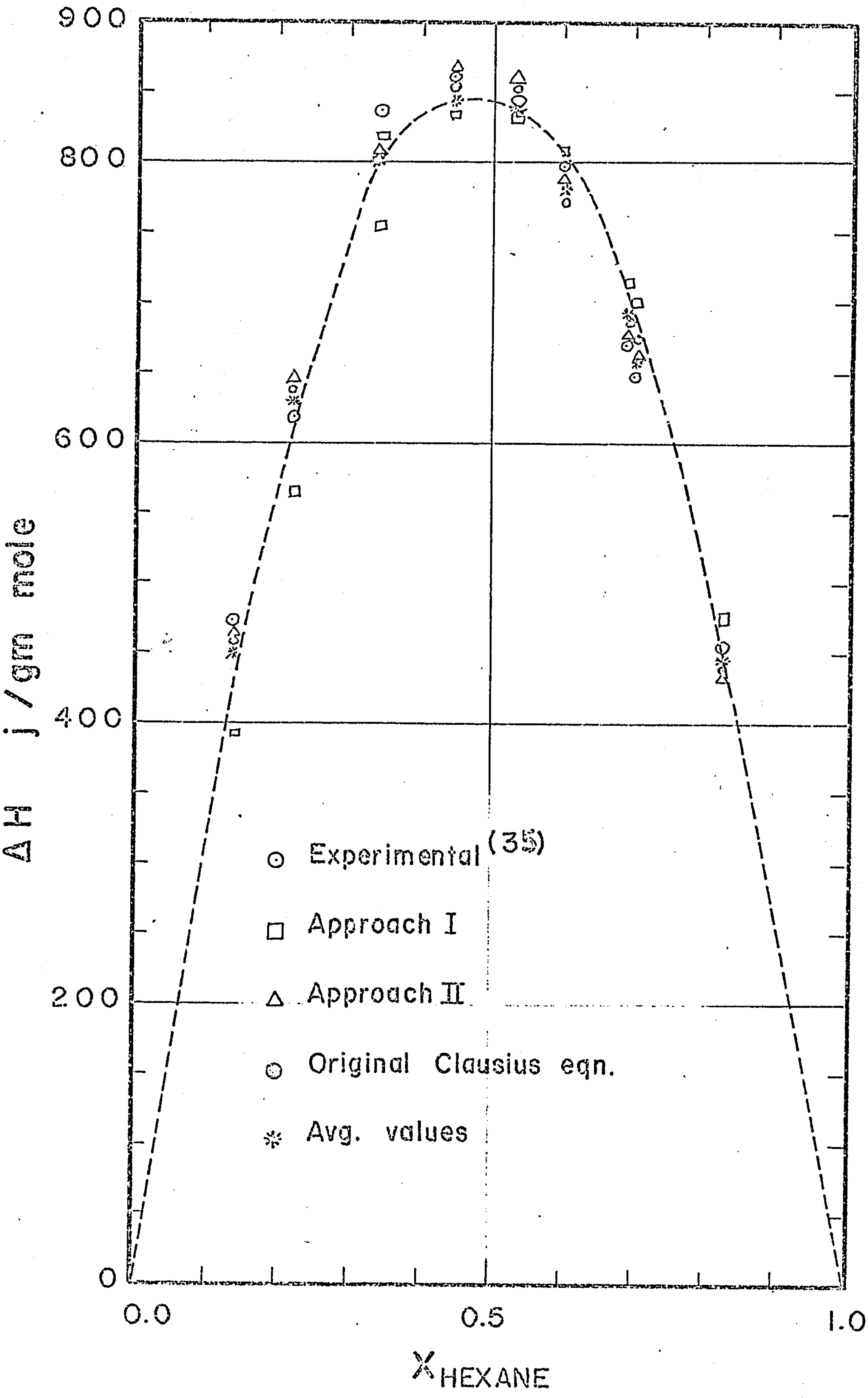

Fig. 3.2.6 Comparison of calculated and literature values of heat of mixing for benzene-hexane at 20°C.

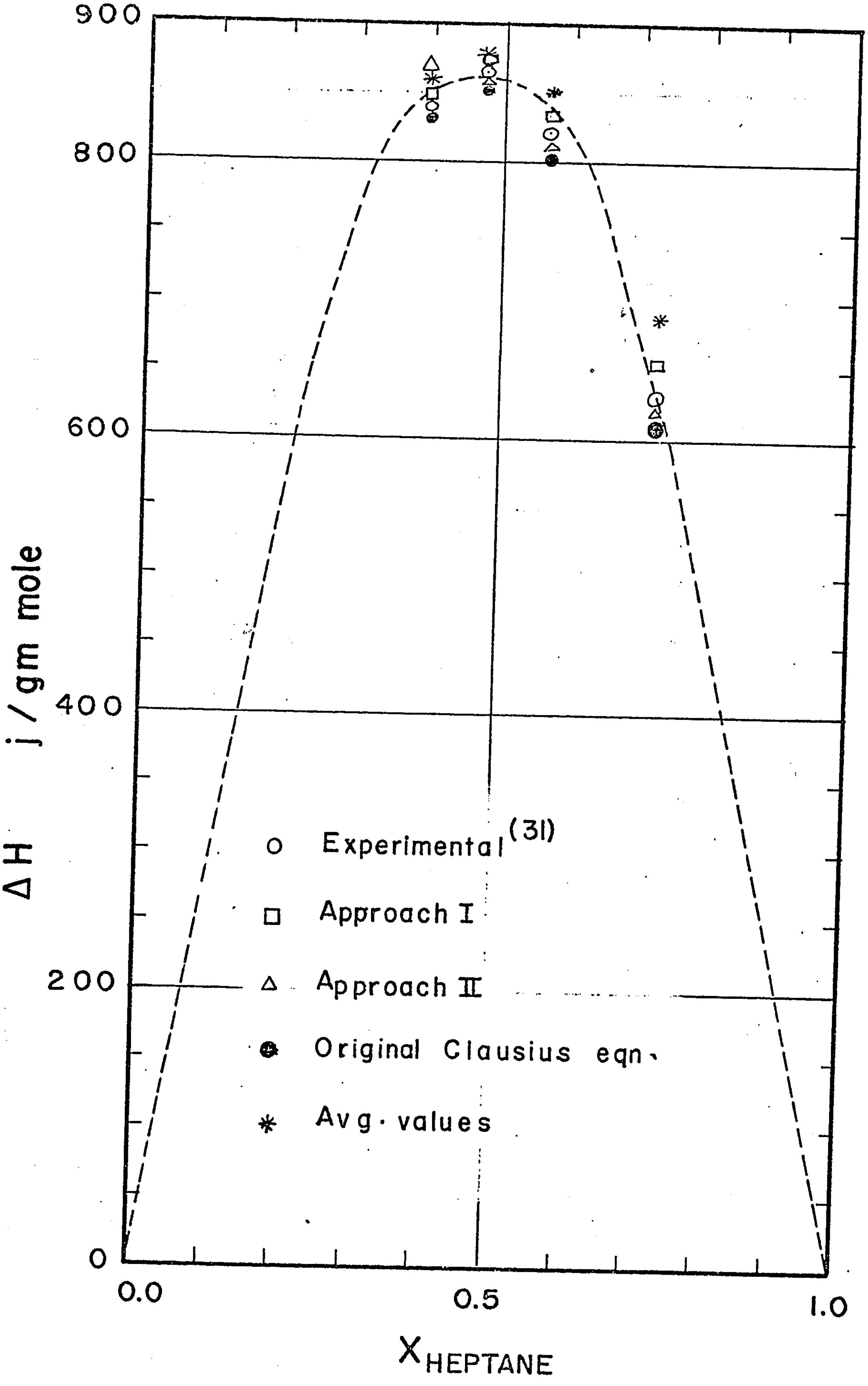

Fig. 3. 2. 7 Comparison of calculated and literature values of heat of mixing for benzene-heptane at 50°C.

TABLE 3.1

Comparison of the Calculated and Literature Values of Heat of Mixing

% Average Absolute Deviation

System	Three Parameter Approach	Two Parameter Approach	Constant Values of the Parameters	Original Equation
Oxygen-Nitrogen at 77°K(28)	14.6 *174	8.	-	-
Argon-Nitrogen at 84°K(41)	21.3 Δ31.4	9.9	-	-
Oxygen-Argon at 84°K(41)	15.8	3.9	-	-
Oxygen-Argon at 86°K(28)	19.7 * 60.2	-		
Benzene-Hexane at 25°C(27)	1.7	1.8		
Benzene-Hexane at 20°C(35)	6.7	1.6	1.9	1.8
Benzene-Heptane at 50°C(31)	1.73 ○ 1.74	0.85	4	1.1
Benzene-Heptane at 25°C(48)	○ 17.8 21.5	27.3	17.0	27.1
Heptane-Hexane at 20°(35)	13.4 ○ 45.6	21.5	57.3	35.6

(TABLE 3. 1)... continued...

* Higher order of the polynomial curve fit was used.

Δ Unsmoothed values of the parameters with the values of the derivatives computed from a first order relation of the parameters with temperature.

o Limited range curve fit for heptane.

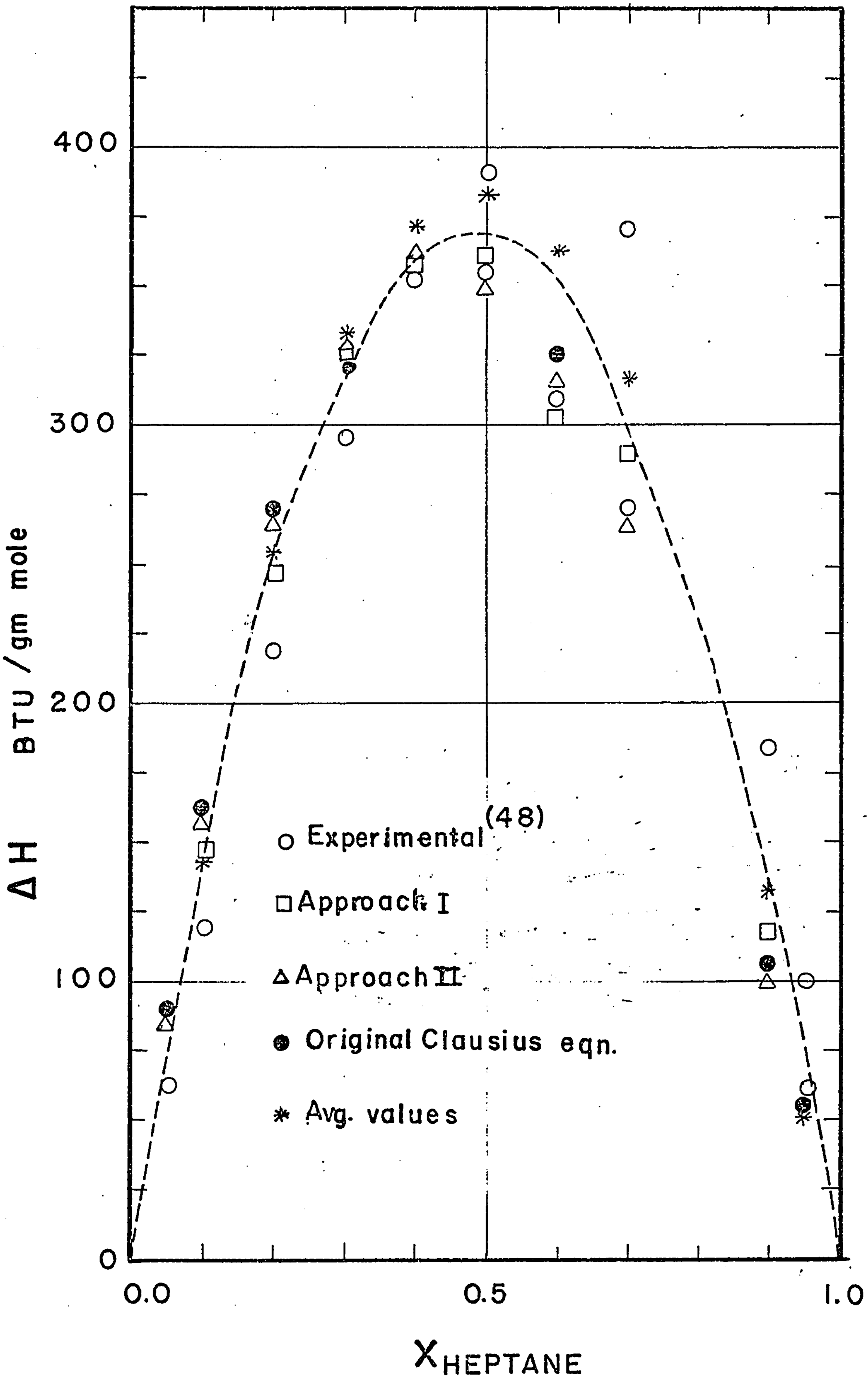

Fig. 3. 2. 8 Comparison of calculated and literature values of heat of mixing for benzene-heptane at 25°C.

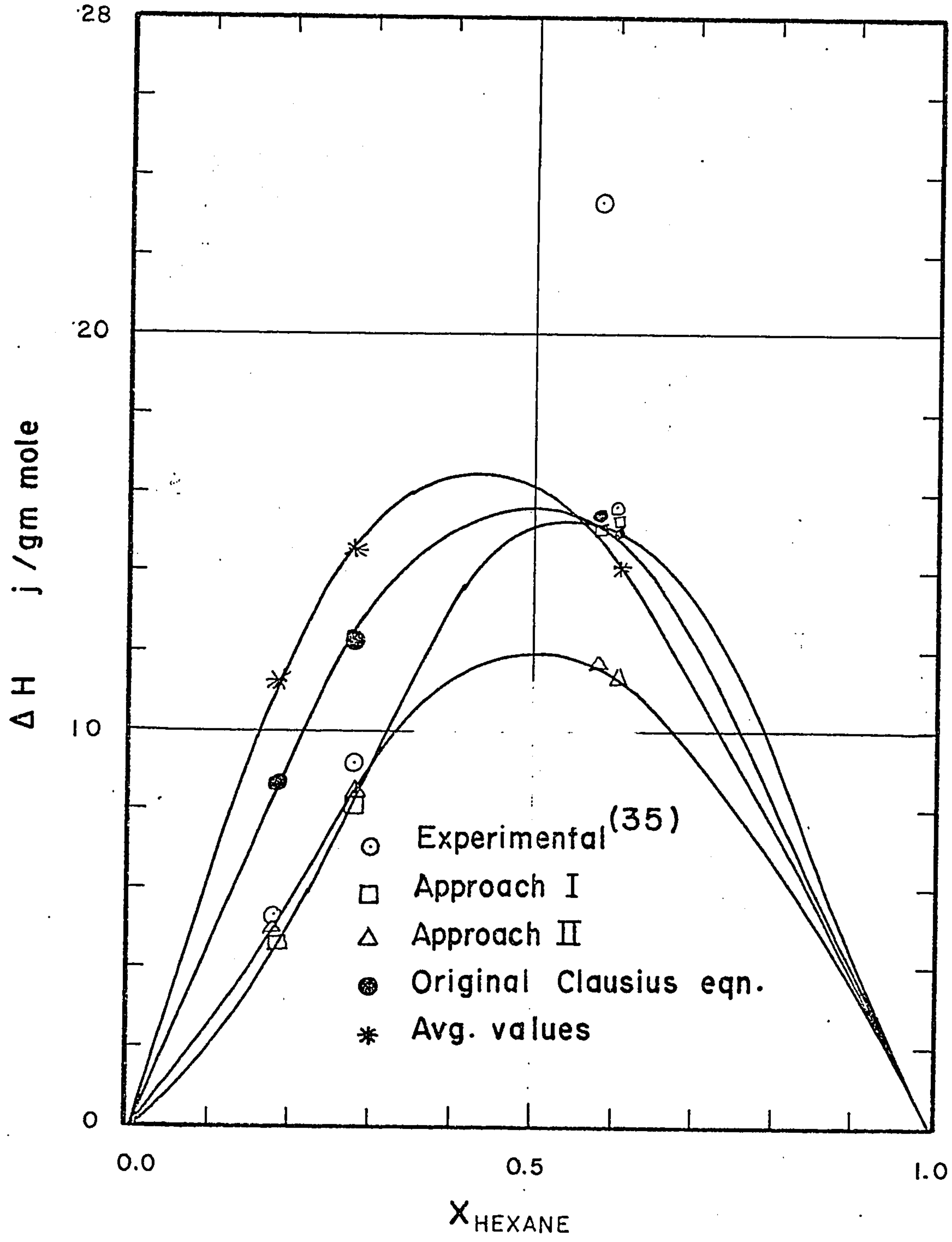

Fig. 3.2.9 Comparison of calculated and literature values of heat of mixing for hexane-heptane at 20°C.

Benzene-Heptane at 25°C(48): Very poor results were obtained for approach I. An improvement was achieved by using smoothed values of the parameters. The average absolute deviations are 37.6 and 40.6 Btu/gm mole depending on whether the parameters are smoothed over a limited range, as mentioned before, or over the whole range up to the critical point. The percentage deviations are 17.8 and 21.5 respectively. When the original unmodified equation of Clausius was used the average absolute deviation was 50.2 Btu/gm mole which is comparable to 51.6 Btu/gm mole for approach II. The percentage deviations are 27.1 and 27.3 respectively. However, when an average constant value for the parameters was used, the average absolute deviation was 30.4 Btu/gm mole which is 17%. The comparison is made in Figure 3.2.8 and Table A.3.8.

Heptane-Hexane at 20°C(35): The average absolute deviation when the unmodified equation of Clausius, the average constant values of the parameters and approach II are 3.8, 5.5 and 4.2 J/gm mole respectively, the percentage deviations are 35.6, 57.3 and 21.5 respectively. The average absolute deviation for approach I depends upon the range over which the parameters were fitted. For the whole range, from near the triple point up to the critical point, and over a limited temperature range ($0.5 \leq T_R \leq 0.6$). The average absolute deviations were 2.5 and 4.5 J/gm mole. The percentage deviations are 13.4 and 45.6% respectively. The comparison is shown in Figure 3.2.9 and Table A.3.9.

3.4.2 Discussion

The binary interaction constant has been assumed to be independent of temperature, pressure and composition. It was determined in a manner such as that the sum of the absolute differences between the experimental and calculated values is minimum.

Different values for the parameters of the Clausius equation of state have been used (as shown in Tables A. 1. 1 and A. 1. 2). As has been shown in the present work, the approach of treating two of the parameters as temperature dependent yields better results than that of treating the three parameters as temperature dependent. The reported k_{ij}'s values differ from the values reported in literature$^{(8, 62)}$ and varies with temperature. It is difficult, at this stage, to draw a conclusion with certainty because the change with temperature in the value of k_{ij} may be due to the unreliability of data of systems studied.

The derivatives, $\frac{d\Omega_{ai}}{dt}$, $\frac{d\Omega_{bi}}{dt}$ and $\frac{d\Omega_{ci}}{dt}$ are obtained by numerical$^{(36)}$ or graphical differentiation of the Ω_{ai}, Ω_{bi} and Ω_{ci} with temperature for each pure component. The two temperature dependent parameters approach gives better results than the three parameters approach. This can be explained by the fact that Ω_c does change rapidly with temperature compared to Ω_a and Ω_b. Hence, when the value of Ω_c was fixed, the sensitivity of the equations (3. 26 and 3. 27) to calculate the heat of mixing is decreased and it was possible to establish both the variations of Ω_a and Ω_b with temperature. The necessity for a smoothed value of the parameters has been demonstrated by the improvement which has been obtained by using smoothed values of the parameters. The equations do not seem sensitive to the values of the parameters used. It is rather more sensitive to the derivatives of the parameters with temperature. A linear variation of the parameters with temperature appears to be adequate over the whole range up to the critical point for nitrogen, argon and oxygen or over a limited range for heptane ($0.5 \leq T_R \leq 0.6$). It might be advantageous to use smoothed PVT data rather than smoothed values of the parameters. A comparison of the calculated PVT using the smoothed values of the parameters with the experimental one is given in Tables A. 5. 1 and A. 5. 2.

The suitability of the two parameter temperature dependent approach and its superiority over the three parameter temperature dependent may suggest that an equation of state could be used satisfactorily to predict heat of mixing of binary liquid mixtures even without satisfying the condition of minimum deviation between the calculated and the experimental value of the vapor compressibility factor of the pure component at equilibrium. It may be feasible to satisfy the condition of $(H^* - H)_L - (H^* - H)_V = L$ where L is the latent heat of vaporization and in this case the temperature term in the original equation of Clausius should be adjusted.

Finally, when the modified Clausius equation of state yields poor prediction of heat of mixing than the original unmodified equation, this may be due to erroneous derivatives of the parameters with temperature.

3. 4. 3 Comparison of Volume of Mixing with Literature Data

Volumes of mixing were calculated for the following systems

1) Oxygen-Argon at 83. 82°K(41)
2) Oxygen-Nitrogen at 83. 82°K(41)
3) Argon-Nitrogen at 83.78°K(42)

Using both of the proposed approaches. The results are shown in Figures (3. 3. 1) to (3. 3. 3) and Tables A. 4. 1 to A. 4. 3.

Excellent agreement between the experimental and calculated values was observed. The results are comparable for both approaches. The average deviation is less than 2%. For the system argon-nitrogen, the vapor pressure data of Prausnitz and Sprow(50) were used which were smooth and easy to interpolate. Moreover, whenever there is a difference in the reported values for the molal volume of the pure components, the value given in connection with the system under study were used.

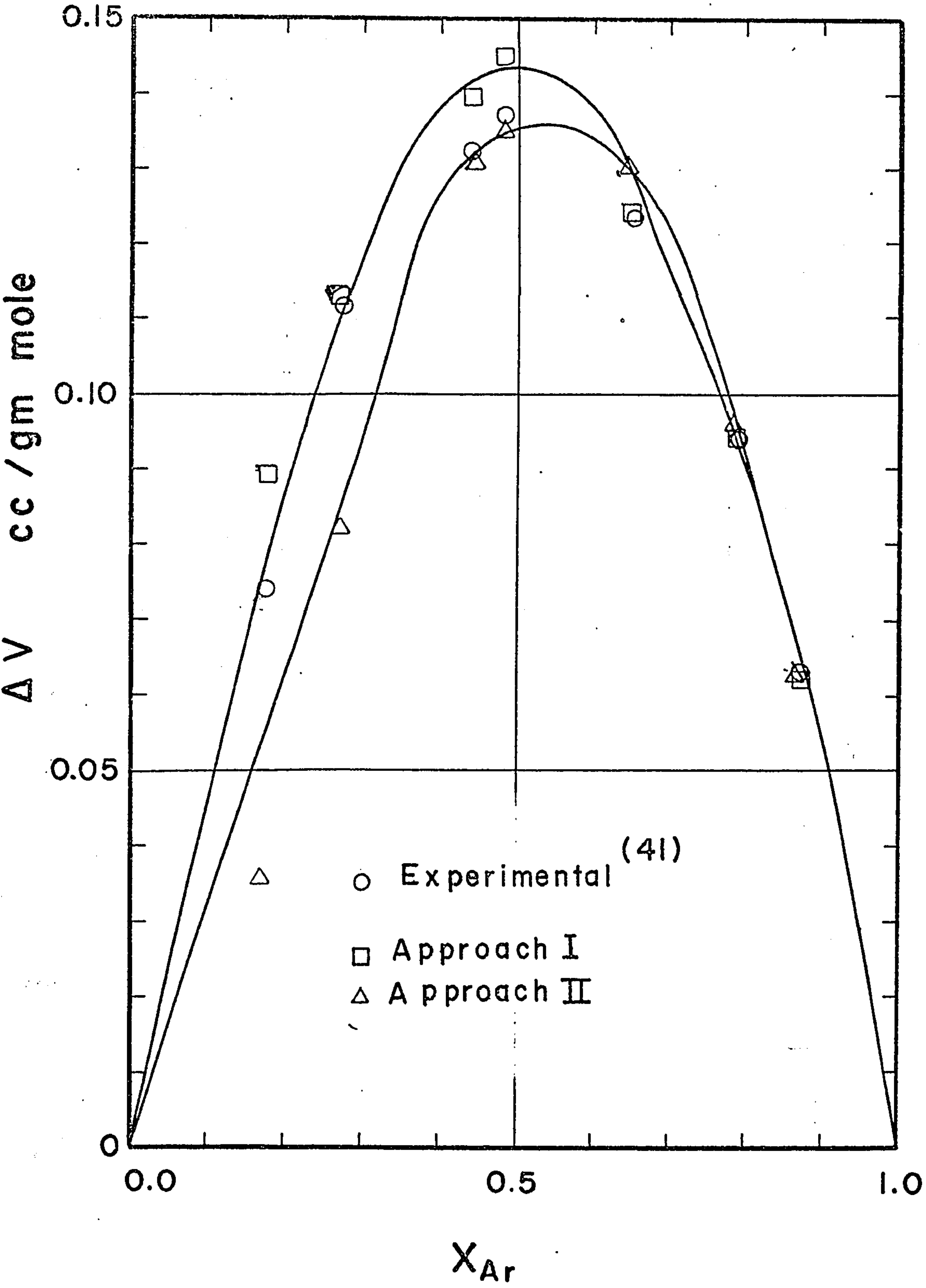

Fig. 3.3.1 Comparison of calculated and literature values of volume of mixing for oxygen-argon at 83.82°K.

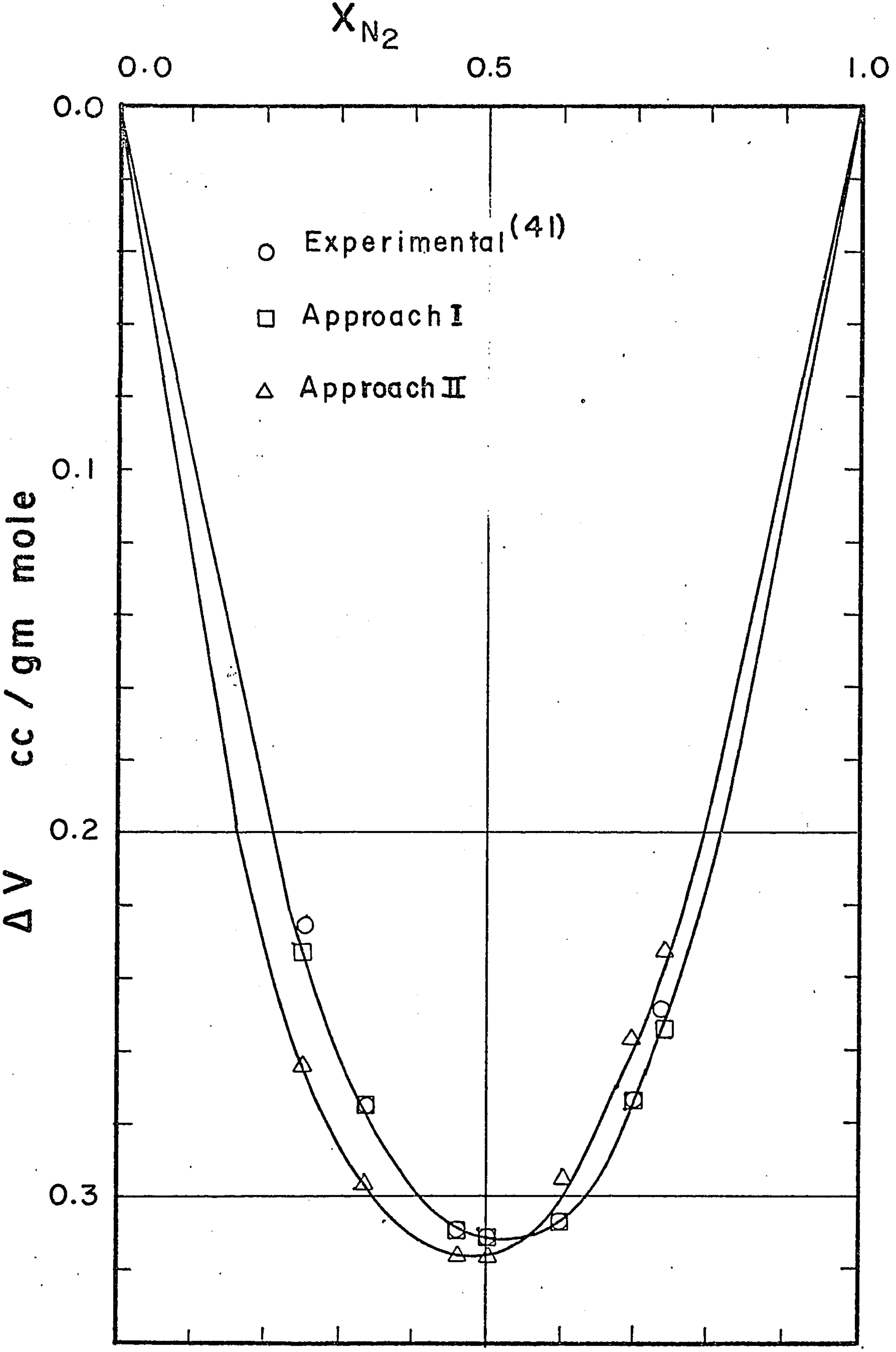

Fig. 3. 3. 2 Comparison of calculated and literature values of volume of mixing for oxygen-nitrogen at 83. 82°K.

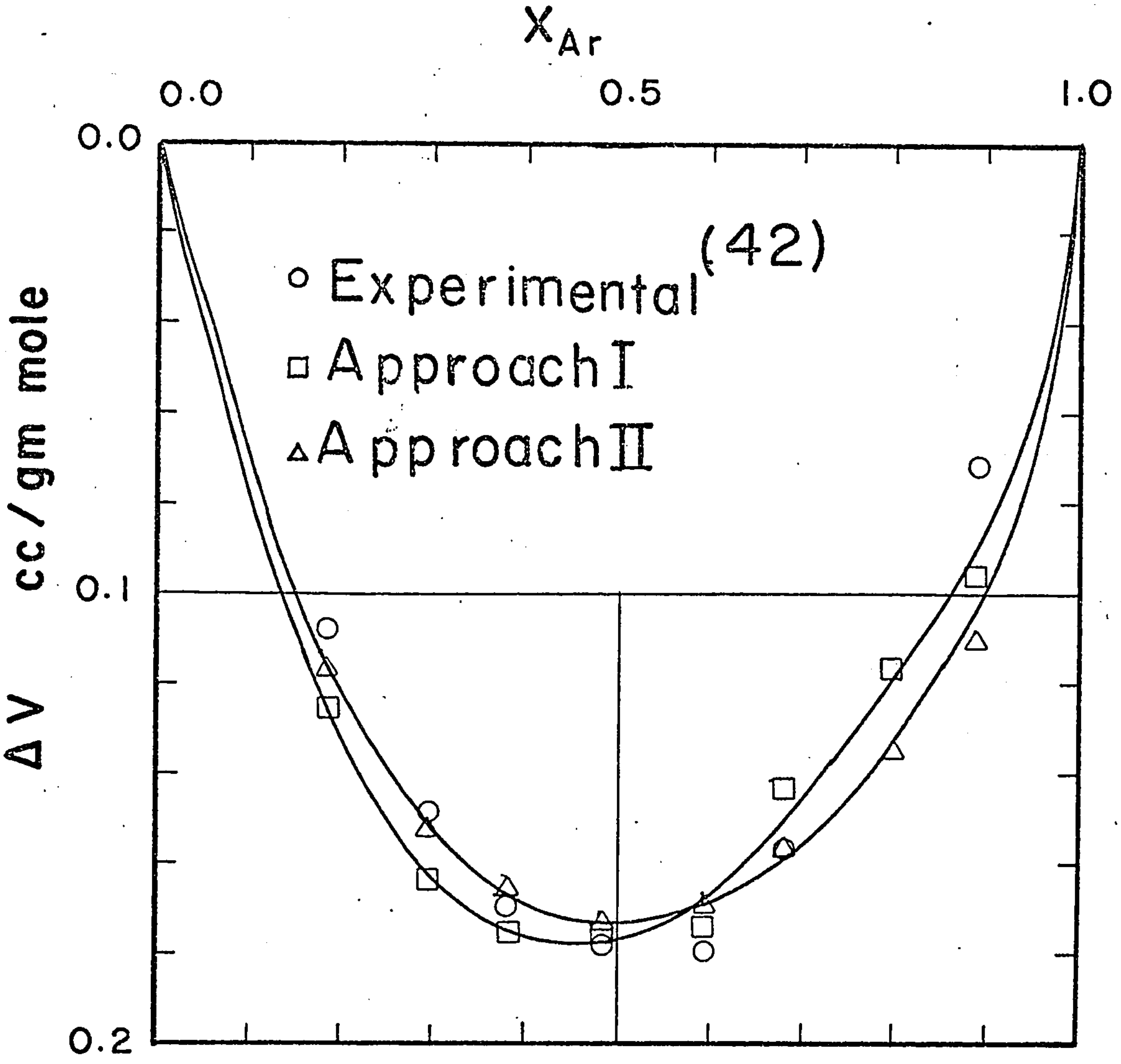

Fig. 3.3.3 Comparison of calculated and literature values of volume of mixing for argon-nitrogen at 83.78°K.

In the same way as in the heat of mixing calculations, the k_{ij} was assumed to be independent of temperature, pressure and composition. It was determined, in the same way, such that the sum of the absolute differences between the experimental and calculated values are minimum. The reported k_{ij}'s differ from the values reported in the literature and differ from those derived from the heat of mixing calculation.

3.4.4 Comparison of the Calculated Compressibility Factor Values For Pure Liquids With Literature Data

Comparison of the different proposed methods was obtained by using oxygen(57) and heptane(19). Satisfactory compressibility factors for pure liquids were obtained and are shown in Tables A.5.1, A.5.2 and A.5.3.

The results, thus far, indicated the superiority of the Redlich-Kwong equation of state over all the proposed methods. However, when the three parameters of the Clausius equation are treated as temperature dependent it was capable of predicting acceptable results although it was unable to do as well as the Redlich-Kwong equation.

The Clausius equation with two temperature dependent parameters produced results that could be compared to the three temperature dependent parameter approach only at low pressure. The results obtained are generally lower than the experimental ones.

In fact, presuming the applicability of the three parameter approach to calculate the compressibility factors, a further modification would be by adjusting the cohesive pressure term $\frac{a}{T\,(V+c)^2}$. In other words, a search for the right power to which the temperature should be raised might involve satisfying another condition which is $(H^* - H)_L - (H^* - H)_V = L$ where L is the latent heat of vaporization.

CHAPTER 4

DISCUSSIONS AND CONCLUSION

The objectives of this work were (i) to investigate the applicability of the latest modification of the Clausius equation of state, by considering the three parameters temperature dependent, to the calculation of the heat and the volume of mixing, and (ii) to investigate a proper variation of the parameters with temperature in the liquid region.

Perhaps the most important conclusions from this study are: (1) Although several theoretical and practical considerations led to the development of the Clausius equation of state, the reasoning is circumstantial and by no means rigorous.

When the k_{ij} values for a given binary system varies with the properties it derives from, this may be attributed to certain potential function which could be derived but which would not be completely satisfactory to describe the intermolecular forces. Such a conclusion could only be reached if the data are of unusually high accuracy and were measured over a wide range of temperatures. Therefore, it may not be feasible to use k_{ij} values obtained from one property of mixing for the prediction of other properties of mixing. It should be noted that for a better prediction of thermodynamic properties of mixing k_{ij} values may be treated as temperature and composition dependent. Hence, it is necessary to have enough experimentally determined data points to correlate k_{ij} with temperature and composition.

(2) The proposed method is very sensitive to the values of the derivatives of Ω_{ai}, Ω_{bi} and Ω_{ci} with temperature. Such phenomena

do not take place in vapor-liquid equilibrium calculations or volume of mixing which do not involve the derivatives of Ω_a, Ω_b and Ω_c. Enthalpy calculations may be adversely affected. However, study is required for establishing a reliable and rapid technique to determine the derivatives of Ω_{ai}, Ω_{bi} and Ω_{ci} for accurate results.

In brief, while the Clausius equation is attractive because of its simplicity and satisfies the three necessary conditions at equilibrium, the form of Equation (3. 24) has a serious disadvantage for performing accurate calculations of heat of mixing, the two terms on the right hand side of this Equation are large and nearly equal, a small error in either term can lead to a large error in the calculated heat of mixing. The main sources of error could be improper mixing rules for the mixture properties and erroneous derivatives of the parameters with temperature.

In the second proposed approach, Ω_a and Ω_b are treated as temperature dependent while Ω_c is constant with the expectation that the derivative of Ω_a and Ω_b with temperature will be easy and accurate to perform. For the systems examined, the variations of Ω_a and Ω_b with temperature have a specific trend. The derivatives do not change rapidly with temperature and are not difficult to establish.

(3) In the Berthelot(49) equation $\left(P + \frac{a}{TV^2}\right)(V - b) = RT$, the introduction of temperature in the cohesive pressure term offers no advantage over the van der Waals equation of state, while the Clausius equation embodies a certain definite improvement which may be attributed largely to the introduction of the quantity (V + c) in the cohesive pressure term. The modified van der Waals equation, i. e., Clausius equation, responds properly to the c parameter effect rather than T. So, in Clausius equation if we fix c, which

takes care of the linear shift necessary for the critical isotherm to a value assigned by the original equation of Clausius and proper adjustment of the other two parameters might produce an improved equation of state applying better in the liquid region and specifically in the calculation of heat of mixing.

Moreover, in the Berthelot equation, which is a modified form of van der Waals equation, the parameter a was treated as temperature dependent but it does not improve its predictive ability. This suggested that the temperature dependency of the cohesive pressure term of the Clausius equation of state $(a/T(V+c)^2)$ still is in much greater need of modification.

(4) It is suggested that the modified Clausius equation of state gives a reasonably accurate enthalpy of mixing when the parameters Ω_a and Ω_b are treated as temperature dependent and c is assigned a positive value to adjust the cohesive pressure term. Hence, when fitting PVT data at saturation to the Clausius equation, if a negative value of c is obtained, one may conclude that the data may not be reliable or the model still is in greater need for modification.

(5) It should be noted that a logical goal in equation of state development is to define adequately the temperature density and composition dependence of the Helmholtz free energy(16, 51, 39) for use as the generating function for the various other thermodynamic properties. Since the pressure is directly related to the density derivatives of the Helmholtz free energy, i. e. $\left(\frac{\partial A}{\partial \rho}\right)_T = \frac{P}{\rho^2}$, PVT data provide more information concerning the density dependence of the Holmholtz free energy than its temperature dependence. On the other hand, enthalpy is related to the temperature derivative of the Holmholtz free energy, i. e.,

$$\left(\frac{\partial G}{\partial T}\right)_{P, n_i} = \left(\frac{\partial A}{\partial T}\right)_{V, n_i}$$

$$H = G - T\left(\frac{\partial G}{\partial T}\right)_{P, n_i}$$

$$H = G - T\left(\frac{\partial A}{\partial T}\right)_{V, n_i}$$

or it may be written in the well known form of the Gibb's - Helmholtz equation

$$\Delta H^M = \Delta G^M - T\left(\frac{\partial \Delta G^M}{\partial T}\right)_{P, n_i}$$

where M designates the property of mixing. So, the enthalpy data should provide the information concerning the temperature dependence of the Holmholtz free energy. When an equation of state developed from PVT data, e. g., Clausius equation of state, yields poor predictions of enthalpy departure $(H - H^*)$ and consequently heat of mixing while predicting accurate densities, one has implicit proof that the temperature dependence of the Holmholtz free energy is inadequate.

The fact that the enthalpy departure from ideal behaviour $(H - H^*)$ was predicted much less accurately than densities when the three parameters of the Clausius equation of state were considered temperature dependent implies that the temperature dependence of the equation is in much greater need of modification than its density dependence. Because of the sensitivity of enthalpy to temperature dependence, enthalpy data could be used initially in seeking a modification to the temperature dependence of the Clausius equation of state.

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TABLE A. 1. 1

Calculated Values of Ω_a, Ω_b and Ω_c of the Clausius Equation

Component	T°K	All Parameters are Considered Temperature Dependent			Two Parameters are Considered Temperature Dependent**	
		Ω_a	Ω_b	Ω_c	Ω_a	Ω_b
Nitrogen(18)	63.15	0.020218	0.624940	-0.1452	0.358479	0.480205
	65.89	0.024169	0.633595	-0.1458	0.367198	0.477779
	68.41	0.108932	0.615400	-0.09411	0.374735	0.475211
	71.91	0.267517	0.545015	0.0224	0.383655	0.468347
	74.45	0.320832	0.514556	0.06245	0.389933	0.463588
	76.00	0.331618	0.508809	0.06852	0.393545	0.46068
	77.00	0.333521	0.508661	0.06800	0.395821	0.458774
	77.35	0.333466	0.509165	0.06718	0.396610	0.458102
	78.00	0.332923	0.510458	0.06527	0.398062	0.456832
	83.80	0.368482	0.486082	0.08532	0.410039	0.444127
	84.00	0.371510	0.48326	0.08776	0.410404	0.443634
	88.04	0.362823	0.494589	0.07243	0.416516	0.432760
	94.09	0.333147	0.536810	0.03358	0.423870	0.413843
	98.60	0.336236	0.546058	0.02724	0.428607	0.398951
	103.88	0.348174	0.543743	0.02866	-	-
	110.57	0.377842	0.499872	0.05027	-	-
	115.80	0.393259	0.459221	0.06437	-	-
	120.13	0.402919	0.413063	0.07762	-	-
	126.2*	0.372942	0.106298	0.125	0.372942	0.106298
Argon(18)	83.78	0.231370	0.557711	0.0005	0.367232	0.467514
	84.00	0.226771	0.560974	-0.0039	0.367774	0.467331
	85.00	0.221321	0.566772	-0.0106	0.370223	0.466399
	86.00	0.226679	0.566178	-0.0081	0.372603	0.465336
	87.00	0.237279	0.562116	-0.0011	0.374907	0.464108
	87.29	0.240325	0.560890	0.00092	0.375562	0.463736
	94.43	0.271295	0.552972	0.01413	0.389848	0.451003
	99.20	0.294476	0.541368	0.62615	0.397726	0.440063
	105.97	0.327487	0.521664	0.04408	0.407991	0.424865
	110.98	0.343103	0.513511	0.04985	0.414798	0.413166
	116.81	0.364609	0.488641	0.06295	-	-
	124.22	0.380482	0.468711	0.06934	-	-
	130.03	0.395673	0.437145	0.08659	-	-
	134.86	0.403061	0.422495	0.08389	-	-
	139.06	0.407610	0.410802	0.085423	-	-
	150.72*	0.368896	0.094709	0.125	0.368896	0.094709

TABLE A. 1. 1 (. . . cont. . .)

Component	T°K	All Parameters are Considered Temperature Dependent			Two Parameters are Considered Temperature Dependent**	
		Ω_a	Ω_b	Ω_c	Ω_a	Ω_b
Oxygen(57)	66	0. 219392	0. 581846	0. 0282	0. 326089	0. 531155
	70	0. 264742	0. 566221	0. 0588	0. 338291	0. 527658
	72	0. 372613	0. 509568	0. 1511	0. 344222	0. 525951
	74	0. 325148	0. 538167	0. 1028	0. 349756	0. 523741
	76	0. 325145	0. 540125	0. 09800	0. 355234	0. 521754
	77	0. 274521	0. 570849	0. 0516	0. 357864	0. 520539
	78	0. 337939	0. 533748	0. 1048	0. 360460	0. 619310
	80	0. 340261	0. 533734	0. 1024	0. 365519	0. 516824
	82	0. 340520	0. 535177	0. 0983	0. 370424	0. 514285
	84	0. 344559	0. 533833	0. 0977	0. 375130	0. 511476
	86	0. 347361	0. 533258	0. 0962	0. 379685	0. 508592
	88	0. 349734	0. 532893	0. 0943	0. 384029	0. 505410
	92	0. 354061	0. 532326	0. 0906	0. 392254	0. 498713
	96	0. 358927	0. 530903	0. 0878	0. 399797	0. 491263
	100	0. 363485	0. 529159	0. 08516	0. 466633	0. 482917
	104	0. 368251	0. 526645	0. 0831	0. 412779	0. 473701
	108	0. 372672	0. 523924	0. 08111	0. 418232	0. 463594
	116	0. 381035	0. 516610	0. 07791	0. 426919	0. 440085
	124	0. 38817	0. 505747	0. 07597	-	-
	132	0. 395961	0. 489919	0. 07551	-	-
	140	0. 402634	0. 464522	0. 077617	-	-
	144	0. 405921	0. 444951	0. 08044	-	-
	148	0. 409483	0. 414552	0. 086037	-	-
	152	0. 414678	0. 356968	0. 09872	-	-
	154	0. 417832	0. 296487	0. 1127	-	-
	154. 576*	0. 365781	0. 067209	0. 125	0. 365781	0. 067209
Benzene(54)	273. 16	0. 182038	1. 248785	-0. 019279	0. 439895	1. 035789
	283. 16	0. 187539	1. 257176	-0. 01931	0. 446348	1. 029428
	293. 16	1. 111731	0. 158946	0. 5598	0. 452249	1. 02127
	298. 16	1. 0837	0. 165788	0. 54008	0. 455266	1. 018314
	303. 16	1. 063037	0. 156606	0. 5272	0. 457462	1. 013759
	313. 16	1. 023791	0. 142286	0. 501905	0. 462206	1. 00491
	323. 16	0. 981878	0. 136072	0. 4750	0. 466441	0. 995111

TABLE A. 1. 1 (. . . cont. . .)

Component	T°K	All Parameters are Considered Temperature Dependent			Two Parameters are Considered Temperature Dependent**	
		Ω_a	Ω_b	Ω_c	Ω_a	Ω_b
Heptane(54)	273.16	1.325451	0.130774	0.59498	0.48534	1.556948
	283.16	0.217521	2.085443	-0.01048	0.506158	1.702384
	293.16	1.294768	0.131754	0.5612	0.510322	1.687618
	298.16	1.25829	1.339	0.5420	0.51222	1.677183
	303.16	0.227515	2.111687	-0.0106	0.51433	1.676565
	313.16	1.16190	0.137723	0.49151	0.51801	1.652746
	323.16	0.237618	2.138622	-0.010819	0.52068	1.632181
	333.16	1.051143	0.121302	0.4359	0.522867	1.609913
	343.16	0.541678	1.540835	0.13445	0.524115	1.584694
	353.16	0.418658	1.827833	0.06886	0.524787	1.557248
	363.16	0.405045	1.858446	0.06064	0.524802	1.527090
	373.16	0.425978	1.796923	0.0705	0.524312	1.493871
	383.16	0.475303	1.631319	0.0967	0.524145	1.459753
	393.16	0.468454	1.629567	0.09285	0.522397	1.420509
	403.16	0.482291	1.54558	0.10130	0.520465	1.379050
	413.16	0.463781	1.588562	0.09083	0.517193	1.33210
	423.16	0.465022	1.546953	0.09227	0.514077	1.282661
	433.16	0.453073	1.566687	0.08567	0.509734	1.226688
	443.16	0.446033	1.567628	0.08184	0.505522	1.167985
	453.16	0.438063	1.576881	0.07729	0.560768	1.104089
	463.16	0.434601	1.576724	0.075103	0.496560	1.04597
	473.16	0.436415	1.483092	0.07934	0.489318	0.959582
	483.16	0.432974	1.441424	0.07923	-	-
	493.16	0.432757	1.351652	0.08264	-	-
	583.16	0.431019	1.25722	0.08566	-	-
	513.16	0.425611	1.175936	0.086815	-	-
Hexane(54)	293.16	1.096981	0.137482	0.485198	0.499524	1.434158
	298.16	1.067131	0.138861	0.468667	0.501254	1.424705
	303.16	1.038129	0.141052	0.45266	0.502837	1.414949
	313.16	1.024683	0.015573	0.451	0.505634	1.394288
	323.16	0.681028	0.932882	0.2281	0.507824	1.371435

* Critical temperature

** $\Omega_c = 0.125$

TABLE A.1.2

Constant Values of Ω_a, Ω_b and Ω_c of the Clausius Equation

Component	Ω_a	Ω_b	Ω_c	Range °K
Benzene	1.845109	0.148491	0.515976	293.16 - 323.16
Hexane	1.0674	0.139132	0.468242	293.16 - 323.16
Heptane	0.765277	1.22651	0.269133	273.16 - 323.16

TABLE A. 1. 3

Values of Ω_a and Ω_b of the Redlich-Kwong Equation of State

Component	T°K	Ω_a	Ω_b
Heptane	283.16	0.446856	0.075626
	303.16	0.446456	0.075946
	323.16	0.445634	0.076201
	373.16	0.438349	0.076424
	423.16	0.426966	0.076165
	473.16	0.411183	0.075206
Oxygen	76	0.396972	0.08667
	84	0.404208	0.086614

TABLE A. 2

Binary Interaction Constant k_{ij}

System	Temperature	The Three Parameters Temperature-Dependent		The Parameter Temperature-Dependent		Original Equation	Average Value
		From ΔH^E	From ΔV^E	From ΔH^E	From ΔV^E	From ΔH^E	From ΔH^E
Oxygen-Nitrogen	77°K	+ 0.005		0.0018			
		0.01					
	83.82°K		0.005		0.0135		
Argon-Nitrogen	84°K	-0.0136		0.0048			
		+ -0.0114					
	83.78°K		0.027		0.168		
Oxygen-Argon	84°K	+ 0.0664		0.0076			
		0.0696					
	86°K	0.0072			0.0158		
	83.82°K		0.0144				
Benzene-Hexane	25°	0.0062		0.0038			
	20°	0.0212		0.0032		-0.0152	-0.0004
Benzene-Heptane	50°C	o 0.0212		0.005		-0.0124	+0.0232
		oo 0.0124					
	25°C	o 0.02		0.0043		-0.014	0.0224
		oo 0.0068					
Heptane-Hexane	20°	o -0.006		-0.008		-0.0082	-0.0119
		oo -0.0078					

oo Based on smoothed values for the whole range, from the vicinity of the triple point to the critical point.

o Based on a limited range least square fit for the parameter.

\+ Based on smoothed values for the derivative and unsmoothed one for the parameter.

TABLE A. 3. 1

Comparison of the Calculated and Literature Values(28) of Heat of Mixing for the System Oxygen-Nitrogen at 77°K (cal/gm mole)

		Approach I		Approach II
		$k_{ij} = 0.005$	$k_{ij} = 0.01$	$k_{ij} = 0.0018$
x_{N_2}	H^E_{exp}	+ H^E_{calc}	++ H^E_{calc}	H^E_{calc}
0.86	5.4	5.9	6.4	5.3
0.86	5.5	5.9	6.4	5.3
0.62	10.0	11.4	11.9	11.0
0.62	9.3	11.4	11.9	11.0
0.51	10.0	12.	12.4	12.1
0.35	10.9	10.7	10.9	11.4
0.26	10.2	8.9	9.1	9.9
0.26	10.0	8.9	9.1	9.9
0.26	9.9	8.9	9.1	9.9
0.08	4.7	3.3	3.4	4.
0.08	4.4	3.3	3.4	4.

\+ The unsmoothed values of the parameters were used with the smoothed values of the derivatives computed from the polynomial curve fit

++ The smoothed values of the parameters were used with the smoothed values of the derivatives computed from the polynomial curve fit

TABLE A. 3. 2

Comparison of the Calculated and Literature Values(41) of Heat of Mixing for the System Argon-Nitrogen at 84°K* (cal/gm mole)

		Approach I		Approach II
		++ k_{ij} = -0.0136	+ k_{ij} = -0.0114	k_{ij} = 0.0048
x_{N_2}	H^E_{exp}	H^E_{calc}	H^E_{calc}	H^E_{calc}
0.794	10.0	5.9	4.5	6.9
0.677	12.1	8.8	7.4	9.6
0.595	11.7	10.4	9.5	10.8
0.514	11.4	11.5	11.3	11.5
0.508	11.6	11.6	11.4	11.5
0.484	10.6	11.8	11.9	11.6
0.394	11.3	12.2	13.3	11.4
0.304	10.5	11.6	13.9	10.4
0.181	5.9	9.0	12.	7.5

* See Footnote on page 62

TABLE A. 3. 3

Comparison of the Calculated and Literature Values[(41)] of Heat of Mixing for the System Oxygen-Argon at 84°K* (cal/gm mole)

		Approach I				Approach II
		Best fit for the Polynomial		First Order fit		
x_{O_2}	H^E_{exp}	++ k_{ij} = 0.0696 H^E_{calc}	+ k_{ij} = 0.0664 H^E_{calc}	++ k_{ij} = 0.0104 H^E_{calc}	+ k_{ij} = 0.0146 H^E_{calc}	k_{ij} = 0.0076 H^E_{calc}
0.74	10.7	13.4	14.1	15.2	16.4	11.3
0.673	11.4	14.3	15.1	15.9	16.8	12.8
0.529	12.5	14.6	15.3	15.8	16.5	13.6
0.578	13.9	14.5	15.3	15.4	15.8	14.2
0.533	14.1	14.2	15.26	14.8	15.	14.4
0.532	13.6	14.2	14.95	14.8	14.9	14.4
0.505	14.6	13.9	14.7	14.3	14.3	14.5
0.501	14.6	13.86	14.6	14.2	14.2	14.5
0.496	14.2	13.8	14.5	14.1	14.1	14.5
0.475	14.5	13.5	14.2	13.7	13.6	14.4
0.460	14.7	13.3	14.0	13.4	13.2	14.35
0.438	14.6	12.9	13.6	12.9	12.6	14.2
0.384	13.9	11.8	12.5	11.5	11.	13.6
0.321	12.8	10.3	10.9	9.7	9.1	12.5

* See Footnote on page 62

TABLE A. 3. 4

Comparison of the Calculated and Literature Values(28) of Heat of Mixing for the System Oxygen-Argon at 86°K (cal/gm mole)

		Approach I	
		Best fit for the Polynomial $k_{ij} = 0.046$	First Order fit $k_{ij} = 0.0072$
x_{N_2}	H^E_{exp}	H^E_{calc}	H^E_{calc}
0.73	7.6	19.0	12.8
0.63	11.0	15.9	13.3
0.56	12.4	12.7	12.8
0.56	12.6	12.7	12.8
0.49	13.6	9.1	11.5
0.42	13.0	5.6	10.5
0.34	10.5	2.1	8.8
0.24	7.5	- 1.1	6.3

TABLE A. 3. 5

Comparison of the Calculated and Literature Values(27) of Heat of Mixing for the System Benzene-Hexane at 25°C (cal/gm mole)

		Approach I	Approach II
		k_{ij} = 0.0062	k_{ij} = 0.0038
x_{Hex}	H^E_{exp}	H^E_{calc}	H^E_{calc}
0.8481	102.9	96.38	95.52
0.7864	129.8	128.7	127.7
0.6425	185.5	185.8	184.5
0.5322	209.7	210.1	208.9
0.4758	213.5	215.1	214.0
0.3573	207.5	207.6	207.0
0.3505	205.2	206.3	205.8
0.3043	196.1	195.6	195.2
0.2789	189.3	187.8	187.5
0.1925	155.3	150.4	150.5
0.0843	82.8	78.05	78.4

TABLE A. 3. 6

Comparison of the Calculated and Literature Values[35] of Heat of Mixing for the System Benzene-Hexane at 20°C (Joule/gm mole)

		Approach I	Approach II	Average Value of the Parameter	Original Equation
		$k_{ij} = 0.0212$	$k_{ij} = 0.0032$	$k_{ij} = -0.0004$	$k_{ij} = -0.0152$
x_{Hexane}	H^E_{exp}	H^E_{calc}	H^E_{calc}	H^E_{calc}	H^E_{calc}
0.825	452.0	475.7	433.9	447.4	442.6
0.699	657	701.3	664.0	676.3	673.5
0.690	669	713.4	677.7	689.4	686.8
0.597	795	807.3	790.4	797.5	798.8
0.530	841	838.7	840.5	842.9	848.2
0.437	866	831.4	862.2	857.4	854.6
0.333	837	752.3	813.3	800.9	813.9
0.212	628	565.6	645.1	627.7	634.7
0.134	469	391.6	463.9	448.1	462.3

TABLE A. 3. 7

Comparison of the Calculated and Literature Values(57) of Heat of Mixing for the System

Benzene-Heptane at 50°C (Joule/gm mole)

		Approach I		Approach II	Average Value of the Parameter	Original Equation
		° $k_{ij} = 0.0212$	°° $k_{ij} = 0.0124$	$k_{ij} = 0.0054$	$k_{ij} = 0.0232$	$k_{ij} = -0.0124$
$x_{Heptane}$	H^E_{exp}	H^E_{calc}	H^E_{calc}	H^E_{calc}	H^E_{calc}	H^E_{calc}
0.7186	631.3	655.2	648.8	617.4	688.5	616.6
0.5609	821.3	835.6	828	814.9	851.5	811.2
0.4591	869.0	868.6	865	868.4	867.1	862.6
0.3893	861.0	849.5	841	865.2	835.8	858.0

° Limited range curve fit

°° Whole range up to the critical point curve fit

TABLE A. 3. 8

Comparison of the Calculated and Literature Values(48) of Heat of Mixing for the System Benzene-Heptane at 25°C (BTU/gm mole)

		Approach I		Approach II	Average Value of the Parameter	Original Equation
		$^{o}k_{ij} = 0.02$	$^{oo}k_{ij} = 0.0068$	$k_{ij} = 0.0043$	$k_{ij} = 0.0224$	$k_{ij} = -0.014$
$x_{Heptane}$	H^E_{exp}	H^E_{calc}	H^E_{calc}	H^E_{calc}	H^E_{calc}	H^E_{calc}
0. 95	100. 9	61. 82	59. 9	51. 5	70. 1	54. 7
0. 9	183. 9	118. 4	115. 2	101. 8	133. 4	105. 7
0. 7	370. 4	289. 3	285. 1	263. 3	317. 2	207. 1
0. 6	396.	338. 5	335. 9	316. 7	365. 9	324. 1
0. 5	387. 3	361. 2	361.	348. 3	384. 7	355. 5
0. 4	354.	355. 4	357. 8	353. 7	372. 8	360. 8
0. 3	296. 9	319. 0	323. 4	328. 3	329. 3	332. 4
0. 2	219. 2	249. 4	254. 7	266. 1	253. 2	269. 5
0. 1	104. 7	144. 1	148. 3	159. 6	143. 8	161. 7
0. 05	63. 52	77. 08	79. 6	86. 7	76. 3	88. 2

o Limited range curve fit

oo Whole range curve fit

TABLE A. 3. 9

Comparison of the Calculated and Literature Values$^{(40)}$ of Heat of Mixing for the System Heptane-Hexane at 20°C (Joule/gm mole)

		Approach I		Approach II	Average Value of the Parameter	Original Equation
x_{Hex}	H^E_{exp}	° $k_{ij} = -0.0078$ H^E_{calc}	°° $k_{ij} = -0.006$ H^E_{calc}	$k_{ij} = -0.008$ H^E_{calc}	$k_{ij} = -0.0082$ H^E_{calc}	$k_{ij} = -0.0119$ H^E_{calc}
0.604	15.5	14.0	15.1	11.3	14.0	15.
0.58	23.4	14.4	15.0	11.6	14.5	15.2
0.28	9.2	13.0	8.1	8.4	14.5	12.
0.179	5.0	9.7	4.8	5.0	11.2	8.7

° Limited range curve fit

°° Whole range curve fit

TABLE A. 4. 1

Comparison of the Calculated and Literature Values(41) of Volume of Mixing for the System Oxygen-Argon at 83. 82°K (ml/gm mole)

		Approach I	Approach II
		k_{ij} = 0.0144	k_{ij} = 0.0158
x_{Ar}	V^E_{exp}	V^E_{calc}	V^E_{calc}
0.1673	0.0748	0.0897	0.0359
0.2701	0.1102	0.1134	0.0824
0.4438	0.1314	0.1395	0.1301
0.4779	0.1365	0.1450	0.1345
0.6493	0.1230	0.1236	0.1306
0.6620	0.1203	0.1230	0.1285
0.7838	0.0959	0.0924	0.0958
0.8614	0.0633	0.0631	0.0626

TABLE A. 4. 2

Comparison of the Calculated and Literature Values(41) of Volume of Mixing for the System Oxygen-Nitrogen at 83. 82°K (ml/gm mole)

		Approach I	Approach II
		k_{ij} = 0.005	k_{ij} = 0.0135
x_{N_2}	V^E_{exp}	V^E_{calc}	V^E_{calc}
0. 7381	-0. 2460	-0. 2536	-0. 2331
0. 6960	-0. 2733	-0. 2728	-0. 2572
0. 6037	-0. 3082	-0. 3063	-0. 2961
0. 5024	-0. 3132	-0. 3136	-0. 3164
0. 4567	-0. 3100	-0. 3098	-0. 3178
0. 3308	-0. 2756	-0. 2743	-0. 2963
0. 2513	-0. 2269	-0. 2327	-0. 2635

TABLE A. 4. 3

Comparison of the Calculated and Literature Values$^{(42)}$ of Volume of Mixing for the System Argon-Nitrogen at 83. 78°K (ml/gm mole

		Approach I	Approach II
		k_{ij} = 0.027	k_{ij} = 0.168
x_{N_2}	V^E_{exp}	V^E_{calc}	V^E_{calc}
0.888	-0.0713	-0.0977	-0.1111
0.7919	-0.1187	-0.1177	-0.1351
0.6782	-0.1571	-0.143	-0.1579
0.5894	-0.1741	-0.1606	-0.1698
0.4779	-0.1794	-0.1747	-0.1747
0.3791	-0.1691	-0.1747	-0.1671
0.2938	-0.1490	-0.1624	-0.1515
0.1844	-0.1079	-0.1243	-0.1163

TABLE A. 5. 1

Comparison of the Calculated and Experimental Values of Molar Volumes and Compressibility Factors for Oxygen(57)

Temp. °K	Pressure	Volume (Exp.)	Z_{exp}	Approach I	Approach II	The Redlich-Kwong Eq.	Z_{calc} Using Smoothed Values of the Parameters	V_{calc} Using Smoothed Values of the Parameters
84	0.497	27.32	0.0019699	0.0019624	0.001965	0.001963	0.001981	27.471
	1.0	27.32	0.00396	0.00396	0.00396	0.00396	0.003985	27.466
	9.8692	27.28	0.03906	0.03899	0.03896	0.03897	0.03921	27.38
	49.346	27.10	0.1940	0.19178	0.19259	0.1937	0.1935	27.035
	98.692	26.9	0.3851	0.38000	0.37713	0.38413	0.3817	26.661
	108.682	26.86	0.4235	0.4171	0.41401	0.4223	0.4193	26.59
	156.679	26.68	0.6065	0.5950	0.58862	0.60439	0.5975	26.285
	197.385	26.53	0.7597	0.7432	0.73379	0.7571	0.74608	26.054
	296.077	26.21	1.1258	1.09491	1.07696	1.1219	1.0986	25.576
76	0.1669	26.47	0.000708	0.0007086	0.000708	0.000684	0.000715	26.703
	1.0	26.46	0.000424	0.00424	0.00424	0.00411	0.00428	26.70
	9.8692	26.43	0.0418	0.04179	0.04176	0.0418	0.0422	26.639
	23.757	26.376	0.10048	0.10024	0.100085	0.10047	0.10113	26.54
	39.6131	26.328	0.1672	0.1665	0.1661	0.1671	0.1679	26.446
	49.348	26.28	0.208	0.20699	0.2063	0.2079	0.2088	26.38
	78.72	26.15	0.3301	0.3281	0.3265	0.33037	0.3309	26.215
	84.137	26.14	0.3527	0.35027	0.3485	0.3528	0.3533	26.185
	98.692	26.13	0.4135	0.40966	0.4073	0.4131	0.4131	26.106
	116.353	26.07	0.4864	0.4813	0.47815	0.48596	0.4854	26.015
	158.458	25.94	0.6591	0.65042	0.6450	0.6585	0.6558	25.81
	197.385	25.94	0.8172	0.8049	0.7971	0.8168	0.812	25.64
	209.678	25.787	0.8670	0.8534	0.8447	0.8665	0.860	25.589

TABLE A. 5. 2

Comparison of the Calculated PVT and Compressibility Factor of Heptane

Using the Smoothed Values of the Parameters

T = 303. 16°K

$P_{atm.}$	V_{exp}	V_{cal}^{o}	V_{calc}^{oo}	Z_{exp}	Z_{calc}^{o}	Z_{calc}^{oo}
0. 99669	148. 673	152. 138	157. 392	0.595708×10^{-2}	0.60959×10^{-2}	0.63064×10^{-2}
49. 341	147. 275	136. 087	143. 7777	0. 29213	0. 269939	0. 28519
98. 68	146. 283	125. 552	134. 563	0. 58032	0. 4980857	0. 5338
197. 36	144. 499	112. 339	127. 726	1. 1465	0. 89134	. 97375
296. 045	142. 936	104. 151	115. 243	1. 70116	1. 23955	1. 37157
493. 468	140. 282	94. 303	106. 095	2. 7826	1. 870577	2. 104478
986. 82	135. 303	83. 135	95. 514	5. 3677	3. 29809	3. 7892
1973. 634	128. 771	75. 282	87. 931	10. 2171	5. 97308	6. 97671
2960. 45	124. 33	72. 130	84. 85	14. 7975	8. 5845	10. 0984
4934. 08	118. 242	69. 355	82. 119	23. 4543	13. 7571	16. 2889

o Limited range fit

oo Whole range fit

TABLE A. 5. 3

Comparison of the Calculated Compressibility Factors and the Experimental of Pure Heptane Using Different Methods

T°K	P_{bars}	Z_{exp}	Approach I	Approach II	The mod. Redlich-Kwong Equation$^{(8)}$
303.16	50	0.29213	0.29085	0.28697	0.29178
	100	0.58032	0.57966	0.56067	0.57904
	200	1.1465	1.15211	1.0815	1.14296
	300	1.70116	1.71888	1.5792	1.69612
	500	2.7826	2.83942	2.53287	2.78
	1000	5.36767	5.59148	4.7999	5.41436
	2000	10.2171	10.9892	9.15812	10.54256
	3000	14.7975	16.3222	13.438	15.59678
	5000	23.4543	26.9086	21.92816	25.62304
323.16	50	0.2807	0.2821	0.2734	0.2790
	100	0.5570	0.5620	0.53159	0.55288
	200	1.09844	1.11612	1.01868	1.08865
	300	1.62305	1.66410	1.48080	1.61262
	500	2.65642	2.74625	2.36172	2.63657
	1000	5.1078	5.40014	4.4447	5.11772
	2000	9.69216	10.5989	8.4507	9.9371
	3000	14.01255	15.73233	12.34778	14.58215
	5000	22.16677	25.9196	20.10572	24.09182
373.16	50	0.25996	0.25512	0.24773	0.25866
	100	0.51366	0.49708	0.47310	0.509137
	200	1.00654	0.95609	0.88646	0.99319
	300	1.4844	1.3938	1.27056	1.46179
	500	2.4070	2.23196	1.99157	2.36997
	1000	4.58614	4.22171	3.671	4.5522
	2000	8.62856	8.0371	6.8566	8.76854
	3000	12.4207	11.7776	9.9676	12.9088
	5000	19.5518	19.1852	16.12629	21.11479
423.16	50	0.24868	0.25613	0.22769	0.24592
	100	0.48734	0.37741	0.42193	0.47865
	200	0.94011	0.87386	0.76448	0.92063
	300	1.38351	1.23799	1.07443	1.34319
	500	2.22371	1.91772	1.64509	2.15488
	1000	4.18946	3.4958	2.9487	4.08924

TABLE A. 5. 3 (. . . cont. . .)

T°K	P_{bars}	Z_{exp}	Approach I	Approach II	The mod. Redlich-Kwong Equation(8)
423.16	2000	7.80662	6.48545	5.38731	7.80942
	3000	11.18376	9.40422	7.7554	11.45178
	5000	17.5121	15.1808	12.43027	18.66873
473.16	50	0.24746	0.22847	0.2096	0.24173
	100	0.47635	0.42046	0.36798	0.46042
	200	0.90641	0.76168	0.63288	0.86598
	300	1.31393	1.07373	0.86409	1.24831
	500	2.08726	1.65403	1.27787	1.97627
	1000	3.88068	2.9939	2.19365	3.698
	2000	7.15634	5.55382	3.86386	6.9916
	3000	10.20212	7.96635	5.46622	10.21537
	5000	15.8945	12.80479	8.61189	16.5932

APPENDIX B

COMPUTER PROGRAMS

B-1	Evaluation of Ω_a, Ω_b, Ω_c of the Clausius equation of state
B-2	Calculation of volumes and heats of mixing of mixtures
B-3	Evaluation of the supporting properties (Subroutine Supt)

B-1 Evaluation of Ω_a, Ω_b, Ω_c of the Clausius equation of state

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C       EVALUATION OF THE ADJUSTABLE PARAMETERS OF THE CLAUSIUS EQN
C       OF STATE ,THE THREE PARAMETERS ARE TEMPERATURE DEPENDENT
C       ORIGINALLY WRITTEN BY I.M. ELSHAYAL
C       SUBROUTINE FUG IS REQUIRED.
        IMPLICIT REAL*8(A-H,O-Z)
        DIMENSION TITLE(20),X(8)
        DIMENSION TT(50)
      1 READ(1,300)(TITLE(I),I=1,15)
    300 FORMAT(20A4)
        WRITE(3,400)(TITLE(I),I=1,15)
    400 FORMAT(1H1,10X,' EVALUATION OF ADJUSTABLE PARAMETERS OF CLAUSIUS
       2 EQUATION FOR',15A4///)
        EL = 1.0D0
        LL = 1
        NOBS=3
     10 READ(1,100)PC,VC,TC,W,R,TOL
        IF(PC.LE.0.0D0) GO TO 800
    100 FORMAT(8F10.4)
        SDTHI=0.0D0
        SDZV=0.0D0
     20 READ(1,1111) P,V,T,VL
        PR=P/PC
        TR=T/TC
        BATA = (DLOG10(PR)-DLOG10(TR)*8.0D0/3.0D0-0.1832D0*(PR/TR/TR-
       2 1.0D0))/((1.0D0-TR)/TR+DLOG10(TR)*1.8D0)
        READ(1,1111) P,V,T,VL
   1111 FORMAT(4F10.0)
        TR=T/TC
        ALFA = (VC/VL-1.0D0-(1.0D0-TR)**(1./3.))/((1.0D0-TR)+(1.0D0-TR)
       2**(1./3.))
        READ(1,100) (TT(I),I=1,NOBS)
        READ(1,1111) WC ,DELWC
        WRITE(3,100)ALFA,BATA
    999 CONTINUE
        DO 30 I=1,NOBS
        T=TT(I)
        RT=R*T
        TR=T/TC
        CALL PFK(BATA,TR,PR)
        P=PR*PC
        VL = VC/(1.0D0+ALFA*(1.0D0-TR)+(1.0D0+ALFA)*(1.0D0-TR)**(1./3.))
        ZL=P*VL/R/T
        ZV=P*V/R/T

        SSS =(R*TC)/(PC*VC)
        EL2 = EL + 2.0D0
C       INITIAL GUESS OF WA,WB
        WA=.422
        WB=.250
        A2 = (WA*SSS**2*VC**2*TC**EL*PC)/
       2 (R**2=T**EL2)
        B = ((WB*VC)/(R*T))*(4.0D0 - SSS)
        CCC = (WC*VC*(3.0D0*SSS - 8.0D0)) / (R*T)
        H=B*P/ZL
        E=B*P/ZV
        HHL = CCC*P/ZL
        EEV = CCC * P/ZV
        CALL FUG(W,PR,TR,THI)
        THI = DEXP(2.302590D0*THI)
        ZLL=ZL
        ZVV=ZV
        THIL=THI
        THIV=THI
        HOLD=H
        IJK=0
     39 IJK=IJK+1
        IF(IJK.GE.30) GO TO 49
        J=0
     40 CONTINUE
```

```
      IH=0
   41 IF(H.LT.1.0D0) GO TO 42
      H = H - 0.05D0
      IH=IH+1
      IF(IH.LT.20) GO TO 41
   43 H = 0.98D0
   42 J=J+1
      FFH = DLOG(THIV*ZL) + DLOG(1.0D0 - H) -
     1 H/(1.0D0-H) + (HHL + 2.0D0) *
     2 ((1.0D0/(1.0D0-H)) - ZL)
      DFFH = (HHL+1.0D0)/(1.0D0-H)**2 -(1.0D0/(1.0D0-H))
      TEST=FFH/DFFH
      H=H-TEST
      IF(J.GT.40)GO TO 45
      IF(DABS(TEST/H).GT.TOL) GO TO 40
   45 B=H*ZL/P
      A2 = B*((1.0D0/(1.0D0-H)) - ZL)*(1.0D0+HHL)**2/H
      IJ=0

   47 IF(E.GT.0.0D0) GO TO 46
      E = E + 0.01D0
      IH=IH+1
      IF(IH.LT.20)GO TO 47
      E = 0.02D0
   46 IJ=IJ+1
      IH=0
      FE = -B*P/E+1./(1.-E)-(A2/B)*E/(1.+EEV)**2
      DFE = B*P/E**2 + 1./(1.-E)**2 - (A2/B)/(1.+EEV)**2
      TEST=FE/DFE
      E=E-TEST
      IF(IJ.GT.40)GO TO 48
      IF(DABS(TEST/E).GT.TOL) GO TO 47
   48 ZVV=B*P/E
      THIV = E/(1.0D0-E) - DLOG(ZVV) - DLOG(1.0D0-E) -
     2 (A2/B)*((2.0D0+EEV)/((1.0D0+EEV)**2)) *E
      THIV = DEXP(THIV)
      WRITE(3,501) J,IJ,IJK
  501 FORMAT(3I5)
      IF(DABS(H-HOLD)/H.LE.TOL*10.0D0) GO TO 49
C     WRITE(3,200)P,T,ZV,ZVV,VL,VLL,THIV,THIL,WA,WB,THI,H,E
      HOLD=H
      GO TO 39
   49 ZLL=B*P/H
      VLL=R*T*ZLL/P
      THIL = H/(1.0D0-H) - DLOG(ZLL) - DLOG(1.0D0-H) -
     2 (A2/B)*H*((2.0D0+HHL)/((1.0D0+HHL)**2))
      THIL = 1.0D0/DEXP(-THIL)
      WB = (3*R*T/VC)*(1.0D0/(4.0D0-SSS))
      WA = (A2*R**2*T**EL2) /(SSS**2*VC**2*TC**EL*PC)
      DTHI=THI-THIV
      DZV=ZV-ZVV
      SDTHI = SDTHI + DABS(DTHI)
      SDZV = SDZV + DABS(DZV)
   51 WRITE(3,200)P,T,ZV,ZVV,VL,VLL,THIV,THIL,WA,WB,THI,H,E
  200 FORMAT(1H ,D11.4,F8.2,6F9.5,2F10.6,2F8.4,D11.4)
   80 CONTINUE
      ADTHI=SDTHI/NOBS
      ADZV=SDZV/NOBS
      WRITE(3,311) ADTHI,ADZV
      WRITE(3,3111) WC
      TOLZV = 0.0000D0
      IF(ADZV.LE.TOLZV) GO TO 9999

      WC = WC - DELWC
      IF(LL.EQ.20) GO TO 9999
      LL = LL + 1
      SDTHI=0.0D0
      SDZV=0.0D0
      GO TO 999
 9999 GO TO 1
 3111 FORMAT(///25X,' WC = ',5X,D15.8)
  311 FORMAT(//20X,'AV. DEV. IN FUGACITY = ',D15.8
     1 ,'AV. DEV. IN ZV = ',D15.8/)
  800 STOP
      END
```

```
      SUBROUTINE FUG(W,PR,TR,THI)
C     GENERALIZED CORRELATION OF FUGACITY COEFFICIENT OF PURE
C     COMPONENTS AT SATURATION.
      IMPLICIT REAL*8(A-H,O-Z)
   10 IF(TR.GT.0.56D0) GO TO 20
      THI=(PR/2.303)*((.1445-(.330+(.1385+(.0121)/TR)/TR)/TR)/TR
     1+W*(.073+(.460-(.5+(.097+.0073/TR**5)/TR)/TR)/TR)/TR)
      RETURN
   20 IF(TR.GT.0.70D0) GO TO 30
      THI=(-.53746+(.58798-(.18226-.009499/TR)/TR)/TR)
     1+W*(.11821-(.006542+(.045992-.0115504/TR)/TR)/TR)
      RETURN
   30 IF(TR.GT.0.84D0) GO TO 40
      THI=(-.65625+(.47890+(.13943-.12157/TR)/TR)/TR)
     1+W*(-.47886+(.53604+(.08951-.14448/TR)/TR)/TR)
      RETURN
   40 THI=(-0.87471+(0.73459-(0.11130-(0.27772-0.20204/TR)/TR)/TR)/TR)
     1+W*(-1.15987+(1.25872-(.13670-(.35086-.34700/TR)/TR)/TR)/TR)
      RETURN
      END
```

```
      SUBROUTINE PFK(BATA,TR,PR)
      IMPLICIT REAL*8(A-H,O-Z)
      ITER=0
      TOL=0.00001D0
      PRC=-0.1832D0
   30 PR=BATA*(1.-TR)/TR+(1.8*BATA+8./3.)*DLOG10(TR)+PRC
      PRC=0.1832D0*(DEXP(PR*2.30259D0)/TR/TR-1.0D0)
      ITER=ITER+1
      IF(ITER.GT.20) GO TO 32
      IF(ITER.EQ.1) GO TO 31
      IF(DABS((PR-PROLD)/PR).LT.TOL) GO TO 32
   31 PROLD=PR
      GO TO 30
   32 PR = DEXP(PR*2.30259D0)
      RETURN
      END
```

B-2 Calculation of volumes and heats of mixing for mixtures

```
C     THIS PROGRAM CALCULATES HEAT AND VOLUME OF MIXING  USING CLAUSIUS
C    EQUATION OF STATE FROM PURE COMPONENT PROPERTIES
C   OF STATE FROM PURE COMPONENT PROPERTIES
C       THREE PARAMETERS ARE FUNCTION OF TEMP.
C      SALAH   HAMAM     ,CHEMICAL ENGINEERING DEPARTMENT
       IMPLICIT REAL*8(A-H,O-Z)
       DIMENSION PC(5),VC(5),TC(5),W(5),C1RKL(5),C2RKL(5),C3RKL(5),
     @D1CL(5),D2CL(5),D3CL(5),D1CLIJ(5,5),TITLE(20),CORRL(5,5),
     @PCO(5),VCO(5),TCO(5),VLO(5),PO(5),COMPA(5),COMPB(5),
     @A(4),Z(3),D(5),
     @PP(80),XX(80,5),VVL(80),HHL(80),PVOL(5)  ,  X(5),DBDT(5),DCDT(5)
      COMMON  /FIRST/ TC,PC,VCO,W ,T,P,R,VLO,PO,VLC,NCOMP
     1    /SECOND/ Z,A,MTYPE
  800 READ(1,5)(TITLE(I),I=1,19)
    6 FORMAT(1H1,19A4)
    5 FORMAT(      19A4)
      WRITE(3,6)(TITLE(I),I=1,19)
      READ(1,500)NCOMP,R
  500 FORMAT( I5,F10.5)
      IF(NCOMP.LE.0) GO TO 900
      WRITE(3,505)
  505 FORMAT(1H0,4X,2HPC,10X,2HVC,9X,2HTC,13X,1HW,9X,5HC1RKL,9X,5HC2RKL,
     @9X,5HC3RKL,10X,9HCOMPONENT//)
      DO 210 I=1,NCOMP
      READ(1,510)PCO(I),VCO(I),TCO(I),W(I),C1RKL(I),C2RKL(I),C3RKL(I),
     1                                  COMPA(I), COMPB(I)
  510 FORMAT(7F10.0,2X,2A4)
      READ(1,666)D1CL(I),D2CL(I),D3CL(I),VLO(I),PO(I)
      WRITE(3,515)D1CL(I),D2CL(I),D3CL(I),VLO(I),PO(I),COMPA(I),COMPB(I)
  210 WRITE(3,515)PCO(I),VCO(I),TCO(I),W(I),C1RKL(I),C2RKL(I),C3RKL(I),
     1                                  COMPA(I),COMPB(I)
  515 FORMAT(1H ,7E12.5,3X,2A4)
      CORRL(NCOMP,NCOMP)=0.0
      NCOMP1=NCOMP-1
      WRITE(3,519)
  519 FORMAT(/10X,12HINPUT DATA://4X,' P '  ,10X,'HM',5X,'X1','X2')
      DO 9 I=1,NCOMP1
      I1=I+1
      DO 9  J=I1,NCOMP
    9 READ(1,520)CORRL(I,J)
  520 FORMAT(8F10.0)
      READ(1,520) TTT
      I=0

   10 I=I+1
      SX=0.0
C INPUT FOR MULTI COMPONENT SYSTEMS
C      READ(1,666)      PP(I),(XX(I,J),J=1,NCOMP),(YY(I,J),J=1,NCOMP)
C
C INPUT FOR BINARY SYSTEMS
       READ(1,666) PP(I),HHL(I),(XX(I,J),J=1,NCOMP1)
     1 ,VVL(I)
C
C      READ( 1,520) PP(I),(XX(I,J),J=1,NCOMP1),(YY(I,J),J=1,NCOMP1)
  565 FORMAT(8F10.0)
C      THIS STATEMENT TO GET THE SECOND COMPONENT MOLE FRACTION
      DO 15 J=1,NCOMP1
   15 SX=SX+ XX(I,J)
      XX(I,NCOMP)=1.0-SX
      IF(R.LT.11.0) GO TO 16
   16 WRITE(3,456)PP(I),HHL(I),(XX(I,J),J=1,NCOMP)
  456 FORMAT(4F10.5)
C     THIS STATEMENT TO END READING DATA
      IF(PP(I).GE.0) GO TO 10
   20 NOBS=I-1
      READ(1,525)      KIJ,CINI,CFIN
  525 FORMAT(I5,2F10.0)
   30 KIJ=KIJ+1
      IF(KIJ.GE.2) GO TO 800
      WRITE(3,526)KIJ,CINI,CFIN
  526 FORMAT(I5,2F10.4   )
```

```
      K=0
      KK=20

      KK=0
  280 CONTINUE
      WRITE(3,6)(TITLE(I),I=1,19)
      KK=KK+1
      WRITE(3,516)
  516 FORMAT(1H ,/1H,16X,3HKIJ)
      DO 220 I=1,NCOMP1
      CORRL(I,I)=0.0
      I1=I+1
      DO 220 J=I1,NCOMP
      IF(KK.GE.20) GO TO 214
      CORRL(I,J)=CINI+(KK-1)*(CFIN-CINI)/10.
  214 WRITE(3,530)I,J,CORRL(I,J)
  530 FORMAT(1H ,6X,2I2,F10.4,2F10.4)
      CORRL(J,I)=CORRL(I,J)
  220 CONTINUE
      K=0
      SDV=0.0
      SDH = 0.0
      DO 221 I=1,NCOMP
      PC(I)=PCO(I)
      VC(I)=VCO(I)
  221 TC(I)=TCO(I)
  120 T=TTT
      RT=R*T
  223 CONTINUE
      ITER=0
      K=K+1
      P=PP(K)
      WRITE(3,950) P
  950 FORMAT(//10X,' P TI ZI = ',F10.5)
      DO 40 J=1,NCOMP
   40 X(J)=XX(K,J)
   42 CALL SUPT(C1RKL,C2RKL,C3RKL,CORRL,D1CL,D2CL,D3CL,D1CLIJ,HL,X,
     a1,KIJ)
      ITER = ITER + 1
      WRITE(3,600) T,PP(K)
  600 FORMAT(3X,3HT= ,F8.2,5HP=   ,F10.4)
      DHL = HL - HHL(K)
      DVL=VLC-VVL(K)
      WRITE(3,610) COMPA(J),COMPB(J),X(J),HL,HHL(K),DHL
      WRITE(3,610)COMPA(J),COMPB(J),X(J),VVL(K),VLC,DVL
  610 FORMAT(10X,2A4,4E12.4)
      SDH = SDH +DABS(DHL)
      SDV=SDV+DABS(DVL)
      IF(K-NOBS)223,850,850
  850 CONTINUE
      WRITE(3,620) SDH
  620 FORMAT(/10X,'ACCUM. SUM OF DEV. IN HEAT OF MIXING = ',E14.8)
      WRITE(3,524)SDV
  524 FORMAT(//10X,'ACCUM. SUM OF DEV. IN VOL. OF MIXING=',E14.8)
      IF(KK-11) 280,30,30
  900 STOP
      END
```

B-3 Evaluation of the supporting properties (Subroutine Supt)

```
      SUBROUTINE SUPT(C1RKL,C2RKL,C3RKL,CORRL,D1CL,D2CL,D3CL,D1CLIJ,
     @HL,X,LV,KIJ)
C      EVALUTION OF SUPPORTING PROPERTIES,THE FUGACITY AND THE
C      PARTIAL MOLAL VOLUME OF FLUID MIXTURES.
       IMPLICIT REAL*8(A-H,O-Z)
       DIMENSION PC(5),VC(5),TC(5),W(5),C1RKL(5),C2RKL(5),C3RKL(5),
     @D1CL(5),D2CL(5),D3CL(5),D1CLIJ(5,5),TITLE(20),CORRL(5,5),
     @PCO(5),VCO(5),TCO(5),VLO(5),PO(5),COMPA(5),COMPB(5),
     @A(4),Z(3),D(5),
     @PP(80),XX(80,5),VVL(80),HHL(80),PVOL(5) , X(5),
     @WIJ(5,5),TCOIJ(5,5),TCIJ(5,5),
     @ARKL(5,5),BRKL(5),CRKL(5),
     @A2I(5),BI(5),AIRKL(5),CI(5),ZLL(5)   ,DBDT(5),DCDT(5)
      COMMON   /FIRST/ TC,PC,VCO,W ,T,P,R,VLO,PO,VLC,NCOMP
     1   /SECOND/ Z,A,MTYPE
C     LV=0, FOR VAPOR PHASE.
C     LV=1, FOR LIQUID PHASE.
C     KIJ=1, TCIJ=SQRT(TCI*TCJ)*(1.-KIJ)
C     KIJ=2, AIJ=SQRT(AI*AJ)*(1.-KIJ)
C     KIJ=3, AIJ=(AI*KIJ+(1.-KIJ)*AJ)/2.
      RT=R*T
   91 DO 100 I=1,NCOMP
      ZC = (PC(I)*VCO(I))/(R*TC(I))
      ARKL(I,I) = C1RKL(I)*(VCO(I)**2)*PC(I)*TC(I)/(ZC**2)
      BRKL(I) = C2RKL(I)*          (4.0 - (1.0/ZC))*VCO(I)
      CRKL(I) = C3RKL(I)*          ((3./ZC)-8.)*VCO(I)
      D1CLIJ(I,I)=ARKL(I,I)*((D1CL(I)+D1CL(I))/(C1RKL(I)+C1RKL(I)))
      DBDT(I)=D2CL(I)*(4.0-(1.0/ZC))*VCO(I)
      DCDT(I)=D3CL(I)*    ((3.0/ZC)-8.0)*VCO(I)
      IF(I.EQ.NCOMP)GOTO100
      I1=I+1
      DO 155 J=I1,NCOMP
      IF(KIJ.GT.1) GO TO 97
      TCIJ( I,J)=(TC(I)*TC(J))**0.5*(1.0-CORRL(I,J))
      TCIJ( J,I)=TCIJ( I,J)
      WIJ(I.,J)=(W(I)+W(J))*0.5
      ZCOIJ=0.291-0.08*WIJ(I,J)
   94 VCOIJ=(VCO(I)**(1./3.)+VCO(J)**(1./3.))**3/8.0
   96 PCOIJ=ZCOIJ* R    *TCIJ( I,J)/VCOIJ
      PCIJ=PCOIJ
   95 ARKL(I,J)=(C1RKL(I)+C1RKL(J))*0.5*
     2(VCOIJ)**2*PCOIJ*TCIJ(I,J)/((ZCOIJ)**2)
      D1CLIJ(I,J) = ARKL(I,J) * ((D1CL(I) + D1CL(J)) / (C1RKL(I) +
     @C1RKL(J)))
      GO TO 98
   97 IF(KIJ.GT.2) GO TO 99
      ARKL(I,J)=(ARKL(I,I)*ARKL(J,J))**0.5*(1.0-CORRL(I,J))
      GO TO 98
   99 ARKL(I,J)=(ARKL(I,I)*CORRL(I,J)+(1.-CORRL(I,J))*ARKL(J,J))
   98 ARKL(J,I)=ARKL(I,J)
      D1CLIJ(J,I)=D1CLIJ(I,J)
  155 CONTINUE
  100 CONTINUE
      AMRKL=0.0
      BMRKL=0.0
      CMRKL = 0.0
      DO 120 I=1,NCOMP
      A2I(I) = ARKL(I,I)/((R**2)*(T**3))
      BI(I)=BRKL(I)/RT
      CI(I) = CRKL(I)/RT
      BMRKL=BMRKL+X(I)*BRKL(I)
      CMRKL = CMRKL + X(I)*CRKL(I)
      AIRKL(I)=0.0
      DO 120 J=1,NCOMP
      AIRKL(I)=AIRKL(I)+X(J)*ARKL(I,J)
  120 AMRKL=AMRKL+X(I)*X(J)*ARKL(I,J)
```

```
      A2 = AMRKL/((R**2)*(T**3))
      B=BMRKL/RT
      C = CMRKL/RT
C THE FOLLOWING STEPS FOR CALC. OF ENTHALPY DEPART. FOR PURE COMP.
      HPP = 0.0
      DO 400 I=1,NCOMP
      PO(I)=P
      A(1)=1.0
      A(2)=(CI(I)*P*2   )-(BI(I)*P)-1.0
      A(3)=((CI(I)**2   )*(P**2.0)) -(2.0*CI(I)*BI(I)*(P**2.0))-(2.0
     @*CI(I)*P)+((A2I(I)/BI(I))*BI(I)*P)
      A(4)=(-BI(I)*(CI(I)**2)*(P**3))-((CI(I)**2   )*(P**2.0))-((A2I(I)
     @/BI(I))*(BI(I)**2   )*(P**2))
      CALL CUBEQN
      IF(MTYPE)215,240,240
 215  IF(LV.EQ.0)GOTO245
      ZL=DMIN1(Z(1),Z(2),Z(3))
      GOTO 965
 245  ZL=DMAX1 (Z(1),Z(2),Z(3))
      GO TO 965
 240  ZL=Z(1)
 965  ZLL(I)=ZL
      H=BI(I)*P/ZL
      HH=CI(I)*P/ZL
      VAR1=BI(I)
      VAR2=A2I(I)
      CALL EQNRK(VAR2,VAR1,P,H,HH,ZL,LV)
      ZLL(I)=ZL
      HHO = CI(I) * PO(I) / ZLL(I)
      HO=BI(I)*PO(I)/ZLL(I)
      H1=X(I)*RT*(1.-ZLL(I)+ (A2I(I)/BI(I))*
     @((2.0*HO/(1.0+HHO))
     1 + (HO/(1.0+HHO))**2 * (VCO(I) / (R*BI(I))) * ((3.0*R*TC(I)/(PC(I)
     @*VCO(I)))-8.0)*D3CL(I)))
      H2 = (VCO(I)/(R*BI(I))) * (4.0-(R*TC(I))/(PC(I)*VCO(I)))*
     1D2CL(I)*(HO/(1.-HO))
      H3 = (HHO/(1.0+HHO)) *D1CL(I)*(((R*TC(I)/PC(I))**2*PC(I)*TC(I)
     @)/(RT**2*CI(I)))
      H21=X(I)*RT*H2
      H31=X(I)*RT*H3
      HP=H1+H21-H31
      HPP = HPP + HP
      WRITE(3,957)PO(I)
 957  FORMAT(//10X,'  PO(I)',F10.5)
 400  CONTINUE
      A(1)=1.0
      A(2) = (C*P*2.0) - (B*P) - 1.0
      A(3) = ((C**2)*(P**2)) - (2.0*C*B*(P**2)) - (2.0*C*P)
     2 + ((A2/B)*B*P)
      A(4) = (-B*(C**2)*(P**3)) - ((C**2)*(P**2)) - ((A2/B)*(B**2)*(P**2
     2))
      CALL CUBEQN
      IF(MTYPE)115,140,140
 115  IF(LV.EQ.0) GO TO 145
      ZL=DMIN1(Z(1),Z(2),Z(3))
      GO TO 150
 145  ZL=DMAX1(Z(1),Z(2),Z(3))
      GO TO 150
 140  ZL=Z(1)
 150  H=B*P/ZL
      HH = C*P/ZL
 591  FORMAT(5X,6E12.4,I2)
      WRITE(3,591) H,HH,P,A2,B,ZL,LV
```

```
      CALL EQNRK(A2,B,P,H,HH,ZL,LV)
      VL=RT*B/H
 123  CONTINUE
      IF(LV.EQ.0) GO TO 135
      QD = T*(VL+CMRKL)**2
      QH = (2.0*AMRKL)/(T*(VL+CMRKL)**3)
      QK = RT/((VL-BMRKL)**2)
 135  DO 130 I=1,NCOMP
      IF(LV.EQ.0) GO TO 130
      QE1 = 0.0
      DO 125 J=1, NCOMP
 125  QE1 = QE1+ X(J)*ARKL(I,J)
      QE = 2.0* (QE1 - ((AMRKL*CRKL(I))/(VL+CMRKL)))
      QG = (RT/(VL-BMRKL)) * (1.0 + (BRKL(I)/(VL-BMRKL)))
      PVOL(I) = ((QE/QD) - QG) / (QH-QK)
      WRITE(3,997)PVOL(I)
 997  FORMAT(//10X,'PVOL(I)=',F10.5)
 130  CONTINUE
      VLC=0.0
      DO 211  I=1,NCOMP
 211  VLC=VLC+X(I)*(PVOL(I)-VLO(I))
      SUM1 = 0.0
      DO 500 I=1,NCOMP
 500  SUM1 = SUM1 + X(I) * D3CL(I)* (3.*((R*TC(I))/(PC(I)*VCO(I))) -
     @8.0) * VCO(I)
      SUM2 = 0.0
      DO 689 I=1,NCOMP
 689  SUM2 = SUM2 + X(I) * D2CL(I)*(4.0-((R*TC(I))/(PC(I)*VCO(I))))
     @*VCO(I)
      SUM3 = 0.0
      DO 700 I=1,NCOMP
      DO 800 J=1,NCOMP
      SUM3=SUM3+X(I)*X(J)*D1CLIJ(I,J)
 800  CONTINUE
 700  CONTINUE
      H11 = 1.0 - ZL + (A2/B)*((2.0*H/(1.0+HH)) +( H /(1.0+HH))**2
     @*SUM1*(1.0/(R*B)))
      H22 = (SUM2/(R*B))*(H/(1.0-H))
      H33 = (SUM3/(C*RT**2)) * (HH/(1.0+HH))
      HP1 = RT*(H11 + H22 - H33)
      HLP=HPP-HP1
      HL=.0242179*HLP
      HL=.0435631585*HLP

      HL =0.101325*HLP
 300  RETURN
      END
```

```
      SUBROUTINE CUBEQN(43)
C    SOLVES CUBIC EQUATION OF CLUAISUS EQUATION OF STATE FOR COMPRESSIBILITY
C    FACTORS
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION A(4),Z(3) ,B(3)
      COMMON /SECOND/ Z,A,MTYPE
    1 CONTINUE
      B(1)=A(2)/A(1)
      B1OV3=B(1)/3.0
      B(2)=A(3)/A(1)
      B(3)=A(4)/A(1)
      ALF=B(2)-B(1)*B1OV3
      BET=2.0*B1OV3**3  -B(2)*B1OV3+B(3)
      BETOV2=BET/2.0
      ALFOV3=ALF/3.0
      CUAOV3=ALFOV3**3
      SQBOV2=BETOV2**2
      DEL=SQBOV2+CUAOV3
      IF(DEL)40,20,30
   20 MTYPE=0.0
      GAM=DSQRT(-ALFOV3)
      IF(BET)22,22,21
   21 Z(1)=-2.0*GAM-B1OV3
      Z(2)=GAM-B1OV3
      Z(3)=Z(2)
      GO TO 50
   22 Z(1)=2.0*GAM-B1OV3
      Z(2)=-GAM-B1OV3
      Z(3)=Z(2)
      GO TO 50
   30 MTYPE=1
      EPS=DSQRT(DEL)
      TAU=-BETOV2
      RCU=TAU+EPS
      SCU=TAU-EPS
      SIR=1.0
      SIS=1.0
       IF(RCU)31,32,32
   31 SIR=-1.0
   32 IF(SCU)33,34,34
   33 SIS=-1.0
   34 R=SIR*(SIR*RCU)**0.33333333

      S=SIS*(SIS*SCU)**0.33333333
      Z(1)=R+S-B1OV3
      Z(2)=-(R+S)/2.0-B1OV3
      Z(3)=0.86602540*(R-S)
      GO TO 50
   40 MTYPE=-1
      QUOT=SQBOV2/CUAOV3
      ROOT=DSQRT(-QUOT)
      IF(BET)42,41,41
   41 PEI=(1.5707963+DATAN(ROOT/DSQRT(1.0-ROOT**2    )))/3.0
      GO TO 43
   42 PEI=DATAN(DSQRT(1.0-ROOT**2    )/ROOT)/3.0
   43 FACT=2.0*DSQRT(-ALFOV3)
      Z(1)=FACT*DCOS(PEI)-B1OV3
      PEI2=PEI+2.0943951
      Z(2)=FACT*DCOS(PEI2)-B1OV3
      PEI4=PEI+4.1887902
      Z(3)=FACT*DCOS(PEI4)-B1OV3
   50 RETURN
      END
```

```
      SUBROUTINE EQNRK(A2,B,P,E,EE,Z,LV)
      IMPLICIT REAL*8(A-H,O-Z)
      TOL=1.0E-6
      IH=0
      IJ=0
   45 IF(LV.LT.1) GO TO 47
      IF(E.LT.1.0) GO TO 46
      E=E-0.02
      IH=IH+1
      IF(IH.LT.20) GO TO 45
      E=0.98
      GO TO 46
   47 IF(E.GT.0.0) GO TO 46
      E=E+0.01
      IH=IH+1
      IF(IH.LT.20)GO TO 47
      E=0.02
   46 IJ=IJ+1
      FE=-B*P /E+1./(1.0-E)-(A2/B)*E/(1.+EE)**2
      DFE=B*P /E**2 +1./(1.-E)**2-(A2/B)/(1.+EE)**2
C     WRITE(3,592)E,FE,DFE,LV
C 592 FORMAT(20X,3E12.4,5X,I2)
C     IF(ABS(DFE).LT.1.0E-20) DFE=DFE/ABS(DFE)*1.0E-20
      TEST=FE/DFE
      E=E-TEST
      IF(IJ.GT.60)GO TO 48
      IF(DABS(TEST/E).GT.TOL) GO TO 45
   48 Z  =B*P/E
      RETURN
      END
```