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ABSTRACT

Isothermal vapor-liquid equilibrium values for the system cyclohexane (1) - methyl methacrylate (2) were measured at 318.12, 333.13 and 348.14 K using a modified Dvorak and Boublik recirculating still. A binary azeotrope was found to exist at all three temperatures.

The experimental excess Gibbs free energy was calculated and correlated using the Wilson, the Non-Random Two Liquid, NRTL, and the Redlich-Kister equations and the results were compared to determine which equation gave the best fit.

Theoretically, the NRTL and the Redlich-Kister equations fitted the experimental data best as they gave the best fit of the excess Gibbs free energy. The NRTL equation gave the best fit at both 318.12 and 333.13 K, whereas the Redlich-Kister equation fitted the data best at 348.14 K. However, the Wilson equation gave the best fit of both the vapor composition and the total pressure at all three temperatures, and so it would be preferred from a practical viewpoint.

ACKNOWLEDGEMENTS

The author wishes to express gratitude to Dr. Benjamin C.-Y. Lu, under whose guidence and supervision this work was performed. Special thanks to Mr J.-M. Yu for his help with the computation and Mr. G. Gasperetti for his technical assistance.

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a	Parameter of Polar Contribution Term, $f^{(2)}(T_r)$; see equation (2-14)
A_{12}, A_{21}	Parameters in the Wilson Equation; see equations (2-26a) and (2-26b)
B	Second Virial Coefficient, cm^3/mol
B_{12}	Cross Second Virial Coefficient, cm^3/mol
BB, CC, DD	Adjustable Parameters in the Redlich-Kister Equation
C	Third Virial Coefficient, $(cm^3/mol)^2$
f	Fugacity
f^o	Standard-State Fugacity
$f^{(0)}$, $f^{(1)}$	Dimensionless Terms in the Pitzer-Curl and Tsonopoulos Correlations of the Second Virial Coefficient
$f^{(2)}$	Dimensionless Term in the Tsonopoulos Correlation of the Second Virial Coefficient
Δg_{12}, Δg_{21}	Adjustable Parameters in the NRTL Equation
G_{12}, G_{21}	Parameters in the NRTL Equation; see equations (2-29c) and (2-29d)
G^E	Excess Gibbs Free Energy, J/mol
k_{ij}	Characteristic Binary Constant; see equation (2-8)
N	Number of Experimental Data Points
p^o	Vapor Pressure, Torr
P	Total Pressure, Torr
P_c	Critical Pressure, atm
P^{SAT}	Saturated Vapor Pressure
R	Gas Constant

T	Absolute Temperature, K
T_c	Critical Temperature, K
T_r	Reduced Temperature equal to T/T_c
v^o	Molar Volume, cm^3/mol
v_c	Critical Volume, cm^3/mol
x	Mole Fraction in Liquid Phase
y	Mole Fraction in Vapor Phase
z	Compressibility Factor
α_{12}	Constant in the NRTL Equation, Characteristic of the Binary Components
γ	Liquid Activity Coefficient
δ_{12}	$= 2B_{12}-B_{11}-B_{22}$; see equation (2-22), cm^3/mol
$\Delta\lambda_{12}$, $\Delta\lambda_{21}$	Adjustable Parameters in the Wilson Equation
μ	Dipole Moment, Debye
μ_r	Reduced Dipole Moment; see equation (2-16)
ν	Molal Volume
τ_{12}, τ_{21}	Parameters in the NRTL Equation; see equations (2-29a) and (2-29b)
ϕ	Fugacity Coefficient
ω	Acentric Factor

SUPERSCRIPTS

E	Excess Property
ℓ	Liquid Phase
v	Vapor Phase
SAT	Saturated Property

SUBSCRIPTS

az	Azeotropic Condition
c	Critical Property
calc	Calculated Value
expt	Experimental Value
r	Reduced Property
i, j	Component Identification
1, 2	Component Identification
12	Mixture Identification

CHAPTER 1

INTRODUCTION

Polymers of methyl methacrylate were first used commercially for various coating and adhesive applications. More recently, these polymers have been used in emulsions for such diversified products as paints, floor polishes and finishes for textiles, leather and paper. These applications have made methyl methacrylate polymers the largest individual group of products in the acrylic field.

Methyl methacrylate is commercially manufactured by reacting acetone cyanohydrin, obtained from acetone and cyanide, with sulfuric acid to produce methacrylamide sulfate (α-sulfoisobutyramide), which is not isolated but is hydrolyzed and esterified in a single continuous process. Modification of the last stage can give methacrylic acid as the major product. If methacrylic acid is the major product, methyl methacrylate is then produced by direct esterification with an excess amount of methanol. The methyl methacrylate and methanol are then separated by distillation.

Hydrocarbons, such as cyclohexane, are frequently added for the azeotropic removal of the water liberated during the esterification, and provide the ester in excellent yield and purity (5). However, the methyl methacrylate may still contain some cyclohexane and may be further purified by distillation. Vapor-liquid equilibrium data for the system cyclohexane - methyl methacrylate, useful in the design of fractionating columns, has yet to be reported in the literature. The purpose of the present work, is to establish vapor-liquid

equilibrium data for mixtures of cyclohexane and methyl methacrylate at three isothermal conditions, by means of a modified Dvorak and Boublik (1) recirculating still.

In order to correlate the isothermal vapor-liquid equilibrium data, vapor and liquid phase non-idealities must be taken into account. At low and moderate pressures (up to several bars), the second virial coefficients may be used to reliably calculate vapor phase imperfections. The empirical correlation of Tsonopoulos (6), applicable to non-polar and polar gases as well as their mixtures, was used to calculate the second virial and cross second virial coefficients. These second virial coefficients are needed in the calculation of the experimental liquid activity coefficients, which are subsequently used to calculate the experimental excess Gibbs free energy.

Three equations were used to correlate the excess Gibbs free energy and the results were compared to determine which equation fit the experimental data best. The three equations that were used to fit the data were: 1- The Wilson Equation (2), 2- The Non-Random Two Liquid, NRTL, Equation (3), and, 3- The Redlich-Kister Equation (4).

CHAPTER 2

LITERATURE SURVEY

Many industrial processes, such as distillation and extraction, involve phase-contacting operations. In the design of distillation columns it is necessary to know the equilibrium composition of both the vapor and liquid phases.

The complete description of a vapor-liquid equilibrium system includes the equilibrium temperature and pressure as well as the concentration of the components in both phases. Vapor-liquid equilibrium data can be measured either under isobaric or isothermal conditions. From a design viewpoint, isobaric vapor-liquid equilibrium data are preferred as most distillation columns are operated at constant pressure. However, from a theoretical viewpoint, it is preferable to measure vapor-liquid equilibrium data under isothermal conditions. Therefore, there is a need for high quality experimental data which may be fitted to a suitable equation and used confidently for both interpolation and extrapolation.

This chapter gives a brief review of the different types of experimental equipment that may be used to measure vapor-liquid equilibrium data followed by a discussion of the correlations used to calculate vapor and liquid phase non-idealities.

2.1 Experimental Methods

There are many different types of equipment that may be used to measure vapor-liquid equilibrium data. The direct experimental determination usually involves the separation of

the vapor and liquid phases, which are in equilibrium, from which samples may be withdrawn for analytical analysis.

Hala et al. (7) have described the methods of direct determination of equilibrium data and classified them into the following groups:

1- Distillation Method

2- Circulation Method

3- Static Method

4- Dew and Bubble Point Method

5- Flow Method

2.1-1 Distillation Method

This is the oldest method for determining vapor-liquid equilibrium and is seldom used today. It is a very simple method, but it requires a large liquid charge of known concentration, from which a very small amount is distilled off. The condensate is then withdrawn for analysis. Large errors can result from condensation of the vapor on the cold walls of the distillation flask at the beginning of the experiment.

2.1-2 Circulation Method

This is the most widely used method as it can be used for both low and moderate pressures. The stills can differ significantly from one another in construction, but they are all based on the following principle. Vapors from a distillation flask pass through a vapor conduit where they are condensed and then collected in a receiver. When the

receiver is filled the condensate then flows back to the distillation flask through a liquid conduit. This process is continued until no change in composition in either flask is observed.

These stills can be classified into two groups; (a) stills with circulation of the vapor phase, and, (b) stills with circulation of both vapor and liquid phases.

The Othmer still is an example of the first group in which there is circulation of the vapor phase only. In this method liquid in the distillation flask is boiled and the vapors evolved are condensed and collected in a receiver. The overflow from the receiver is allowed to drain back into the boiling flask and the process is continued until there is no change in temperature. Samples of both the liquid and condensate can be removed for analysis at this point.

One disadvantage of this method is that the temperature is measured in the vapor phase and does not always correspond to the true boiling point. Also, inadequate mixing of the liquid in the boiling flask may occur due to the cold condensate that is returned to the flask and concentration gradients can arise. A modification to the Othmer still is the Jones still in which the condensate is completely vaporized before it is returned to the distillation flask. The vapor is then bubbled through the liquid in order to improve the mixing in the boiling flask.

The error in the temperature measurement using a still

with only circulation of the vapor phase can be eliminated through the use of the Cottrell pump in which a mixture of vapor carrying slugs of liquid are thrown onto the thermometer well. The conditions in the Cottrell pump are ideal for obtaining the desired equilibrium between the phases. Stills employing the Cottrell pump have circulation of both the vapor and liquid phases.

Gillespie introduced the first still of this type in which the vapor and liquid from the Cottrell pump spurt into the equilibrium chamber. They then flow to a separator where the vapor is separated from the liquid, and condensed before going to a receiver, while the liquid is returned directly to the boiling flask. Overflow from the condensate receiver is joined with the equilibrium liquid as it is returned to the boiling flask.

One drawback to the Gillespie still is that the liquid samples which are withdrawn from the boiling flask do not correspond to the liquid which is in equilibrium with the vapor.

Dvorak and Boublik modified the Gillespie still by the addition of a second receiver for the equilibrium liquid. In this still the liquid which is in equilibrium with the vapor, leaves the separator and is collected in a receiver before returning to the boiling flask. Samples taken from both the condensate and liquid reservoirs correspond to the vapor and liquid present in the equilibrium chamber. Dvorak and Boublik found that intense mixing is required in the two reservoirs,

so magnetic stirrers are added to both to prevent concentration gradients.

2.1-3 Static Method

In this method a solution is charged into a closed, evacuated cylinder which is agitated at constant temperature until equilibrium is established. Samples of the vapor and liquid are then removed for analysis. The disadvantage of this method is that at low pressures the amount of vapor required for analysis is of the same order as the total amount of vapor present. Removal of the vapor sample will cause a marked disturbance in the equilibrium.

2.1-4 Bubble and Dew Point Method

This method uses an apparatus similar to that used in the static method. The appartus is operated at constant temperature using a mixture of known composition. The equilibrium cell is evacuated before the liquid mixture is introduced and completely vaporized. The volume of the cell is decreased until condensation commences and is completed and the system pressure is recorded at these two points. These pressures are known respectively, as the dew and bubble points of the mixture. By repeating this procedure throughout the entire concentration range, saturation pressure curves for the vapor and liquid phases can be drawn as a function of composition. The main advantage of this method is that it is not necessary to withdraw samples of the two

phases for analysis. However, the dew and bubble points of most mixtures are generally not sharply defined so that highly precise equipment is required to detect the occurance of vapor or liquid sensitively.

2.1-5 Flow Method

This method is particularly useful as it can be used for systems of limited miscibility in the liquid phase. In the flow method, a steady-state stream of constant composition in either liquid or vapor phase or a combination of the two is fed continuously to the equilibrium cell. If the feed is in the vapor state, it is cooled in the equilibrium cell so that it partially condenses. Samples of the vapor, which are in equilibrium with the condensate are continuously removed and analyzed. The advantage of this method is that equilibrium is reached much faster than with the circulation method. However, feeding the equilibrium cell is difficult and complicated.

2.2 Empirical Correlation of the Second Virial Coefficient

Vapor phase non-idealities can be completely described through the use of the virial equation of state. The main advantage of the virial equation is that there is a theoretical relationship between the virial coefficients and the intermolecular potential (8). The virial equation of state is a power series in the reciprocal molar volume, ν,

$$z = 1 + \frac{B}{\nu} + \frac{C}{\nu^2} + \ldots \qquad (2\text{-}1)$$

where, z is the compressibility factor, B is the second virial coefficient and C is the third virial coefficient. For low and moderate pressures, the virial equation can be truncated after the second term (9).

Pitzer and Curl (10) proposed an empirical correlation to represent the second virial coefficient, which, in the reduced dimensionless form is,

$$\frac{B P_c}{R T_c} = f^{(0)}(T_r) + \omega f^{(1)}(T_r) \qquad (2\text{-}2)$$

where, P_c and T_c are the critical pressure and temperature, respectively, R is the gas constant, and T_r is the reduced temperature equal to T/T_c. The quantity, ω, is the acentric factor, suggested by Pitzer, as the macroscopic measure of the extent to which the force field around a molecule deviates from spherical symmetry (8). The acentric factor is defined by,

$$\omega = -\mathrm{Log}_{10}\left(\frac{P^{SAT}}{P_c}\right)_{T_r=0.7} - 1.000 \qquad (2\text{-}3)$$

where, P^{SAT} is the saturated vapor pressure. Noble gases, which are spherically symmetric, have acentric factors of zero.

The function $f^{(0)}$ gives the second virial coefficient for simple fluids (ω=0), while the function $f^{(1)}$ gives the effect of acentricity on the second virial coefficient. The functions $f^{(0)}(T_r)$ and $f^{(1)}(T_r)$ are;

$$f^{(0)}(T_r) = 0.1445 - 0.330(T_r)^{-1} - 0.1385(T_r)^{-2} - 0.0121(T_r)^{-3} \qquad (2\text{-}4)$$

$$f^{(1)}(T_r) = 0.073 + 0.46(T_r)^{-1} - 0.50(T_r)^{-2} - 0.097(T_r)^{-3} - 0.0073(T_r)^{-8} \qquad (2\text{-}5)$$

For pure compounds, the second virial coefficients are functions of temperature only. Another advantage of the virial equation of state is that it is easily extended to mixtures with no arbitrary assumptions. For mixtures, the second virial coefficient is,

$$B_{mixture} = \sum\sum_{ij} y_i y_j B_{ij} \qquad (2\text{-}6)$$

where, y_i is the mole fraction of component i in the vapor phase. For binary mixtures, equation (2-6) becomes,

$$B_{mixture} = y_1^2 B_{11} + 2 y_1 y_2 B_{12} + y_2^2 B_{22} \qquad (2\text{-}7)$$

where, B_{11} and B_{22} are the second virial coefficients of pure components 1 and 2, respectively, and account for interactions between the similar molecules of components 1 and 2. The quantity, B_{12}, is the cross second virial coefficient which accounts for interactions between the unlike molecules 1 and 2. The cross coefficient, B_{12}, like B_{11} and B_{22}, is dependent on temperature only, whereas, the second virial coefficient of the mixture $B_{mixture}$, is dependent upon the vapor composition as well as the temperature.

In order to evaluate the cross second virial coefficient, B_{12}, mixing rules must be established for the critical temperature, $T_{c_{12}}$, and pressure $P_{c_{12}}$, as well as for the acentric factor, ω_{12}. These were given by Tsonopoulos (6) as,

$$T_{c_{12}} = ((T_{c_1})(T_{c_2}))^{\frac{1}{2}} (1 - k_{12}) \qquad (2\text{-}8)$$

$$P_{c_{12}} = \frac{4\, T_{c_{12}} \left(P_{c_1} v_{c_1}/T_{c_1} + P_{c_2} v_{c_2}/T_{c_2}\right)}{\left(v_{c_1}^{1/3} + v_{c_2}^{1/3}\right)^3} \qquad (2\text{-}9)$$

$$\omega_{12} = 0.5(\omega_1 + \omega_2) \qquad (2\text{-}10)$$

The critical temperature has the greatest effect upon the accuracy of the cross second virial coefficient and the geometric mean approximation to the critical temperature appears to be an upper limit. In general, for mixtures which contain components that differ in molecular size, $T_{c_{12}}$, is usually somewhat smaller than the geometric mean (8). For this reason the correction factor, k_{12}, is introduced. It is characteristic of the 1-2 interaction, independent of temperature, density and composition and must be determined experimentally. The constant k_{12} is usually positive, although it can take on a negative value if there is hydrogen bonding between the molecules of the different species (6).

Tsonopoulos (6) modified the Pitzer-Curl correlation by the addition of an extra term to the function $f^{(0)}(T_r)$ and by eliminating the $(T_r)^{-1}$ term from the function $f^{(1)}(T_r)$. The functions in equations (2-4) and (2-5) thus become,

$$f^{(0)}(T_r) = f^{(0)}_{\text{Pitzer-Curl}} - 0.000607(T_r)^{-8} \qquad (2\text{-}11)$$

$$f^{(1)}(T_r) = 0.0637 + 0.331(T_r)^{-2} - 0.423(T_r)^{-3} - 0.008(T_r)^{-8} \qquad (2\text{-}12)$$

Tsonopoulos then extended the Pitzer-Curl correlation so

that it may also be applied to polar gases by the addition of the function $f^{(2)}(T_r)$ to equation (2-2),

$$\frac{B P_c}{R T_c} = f^{(0)}(T_r) + \omega f^{(1)}(T_r) + f^{(2)}(T_r) \qquad (2\text{-}13)$$

For non-hydrogen bonding polar compounds the function $f^{(2)}(T_r)$ is given by,

$$f^{(2)}(T_r) = a\, T_r^{-6} \qquad (2\text{-}14)$$

The coefficient a in equation (2-14) is dependent on the type of polar compound under consideration. For ketones, aldehydes, alkylnitriles and ethers the function a is given by,

$$a = -2.140\times10^{-4}\mu_r - 4.308\times10^{-21}(\mu_r)^8 \qquad (2\text{-}15)$$

where, μ_r is the reduced dipole moment defined as,

$$\mu_r = \frac{10^5 \mu P_c}{T_c} \qquad (2\text{-}16)$$

where, μ is the dipole moment of the polar molecule.

Tsonopoulos (11) suggested that esters of carboxylic acids are similar to ketones and may also be represented by equation (2-15).

For binary mixtures containing non-polar and non-hydrogen bonding compounds, such as hydrocarbons and esters, the cross-coefficient, a_{12}, may be assumed to be zero (6).

Tsonopoulos also suggested that for binary mixtures of this type, the value of k_{12} in equation (2-8) be assigned a value of 0.13.

2.3 Evaluation of Liquid Phase Activity Coefficients at Low and Moderate Pressures

For any system in vapor-liquid equilibrium, the equation of equilibrium which must be satified for all components in the system is of the form,

$$f_i^v = f_i^\ell \tag{2-17}$$

where, f_i^v and f_i^ℓ are the fugacities of component i in the vapor and liquid phases, respectively. For the vapor phase, the fugacity is related to the mole fraction of component i in the vapor, y_i, and the total pressure, P, by the fugacity coefficient, ϕ_i (9).

$$\phi_i \equiv \frac{f_i^v}{y_i P} \tag{2-18}$$

Similarly, the liquid phase fugacity is related to the mole fraction of component i in the liquid, x_i, and the standard-state fugacity, $f_i^{o\ell}$, through the liquid phase activity coefficient, γ_i, by,

$$\gamma_i \equiv \frac{f_i^\ell}{x_i f_i^{o\ell}} \tag{2-19}$$

By combining equations (2-18) and (2-19) the following equation of equilibrium is obtained,

$$\phi_i y_i P = \gamma_i x_i f_i^{o\ell} \tag{2-20}$$

At low or moderate pressures (up to several bars) and temperatures well below the critical, Van Ness (12) derived the following expression for evaluating experimental liquid

phase activity coefficients,

$$\ln\gamma_i = \ln\left(\frac{y_i P}{x_i p_i^o}\right) + \frac{(B_{ii}-v_i^o)(P-p_i^o)}{RT} + \frac{P(1-y_i)^2\delta_{ij}}{RT} \qquad (2\text{-}21)$$

where, p_i^o, B_{ii} and v_i^o are the vapor pressure, second virial coefficient and liquid molar volume of component i, respectively. The quantity R is the gas constant and T is the absolute temperature. The quantity δ_{ij} is defined by,

$$\delta_{ij} = 2\,B_{ij} - B_{ii} - B_{jj} \qquad (2\text{-}22)$$

where, B_{ij} is the cross second virial coefficient.

The first term in equation (2-21) gives the activity coefficient for a liquid that is in equilibrium with an ideal vapor. While the second and third terms correct for the non-ideal behavior of the vapor phase.

Equation (2-21) is valid at low and moderate pressures provided the following assumptions are satisfied:

(1) The non-idealities of the vapor phase, both of the mixture and of the pure components, are adequately described by the virial equation of state truncated after the second term, i.e., $z=1+\frac{BP}{RT}$, where z is the compressibility factor.

(2) For isothermal vapor-liquid equilibrium, the liquid molar volumes of the pure components are incompressible over the pressure range in question.

(3) The temperature and pressure at which the standard-state fugacities are evaluated are the same as the equilibrium temperature and pressure of the mixture.

2.4 Correlation of Experimental Excess Gibbs Free Energy

Excess functions are thermodynamic properties of solutions which are in excess of those of an ideal solution at the same temperature, pressure and composition. For vapor-liquid equilibrium the most useful excess function is the excess Gibbs free energy, G^E, defined as,

$$G^E \equiv G_{\substack{\text{(actual solution} \\ \text{at T, P and } x_i)}} - G_{\substack{\text{(ideal solution} \\ \text{at T, P and } x_i)}} \qquad (2\text{-}23)$$

The excess Gibbs free energy is directly related to the liquid phase activity coefficient, γ_i, by,

$$G^E/RT = \sum_i x_i \ln\gamma_i \qquad (2\text{-}24)$$

From this equation the activity coefficient may then be defined as the partial molar Gibbs free energy,

$$\ln\gamma_i \equiv \left(\frac{\partial(n_T G^E/RT)}{\partial n_i}\right)_{T,P,n_{j(j\neq i)}} \qquad (2\text{-}25)$$

A number of models have been proposed for correlating the excess Gibbs free energy with the liquid composition, x_i, through the evaluation of two or more temperature dependent parameters. All equations must satisfy the condition that $G^E=0$ at $x_1=0$ and $x_1=1.0$. The primary purpose of expressing experimental data through model equations is to obtain a reliable representation which may then be used for extrapolation (9). The models used in the evaluation of data should introduce errors well below experimental errors. The perfectly adaptable model will translate experimental data into a set of

parameters without loss of accuracy. Parameters for the models are usually obtained by reduction of experimental data using the technique of least-squares fitting (13).

Exact agreement between the model and experiment is never achieved due to random and systematic errors in the data and to inadequacies in the model (9). In general, the test of models for physical significance is to compare average deviations between measured and calculated values (13). Since deviations can arise from both scatter of the data and inadequacies in the model, only comparison of deviations obtained from different equations on the same data set can give an indication of the merit of the different equations (3).

In general, models with fewer parameters giving the same deviations are the most suitable (13). The usual empirical models with two or three parameters at a given temperature can represent strong deviations from ideality. Three such equations are the Wilson equation, the Non-Random Two Liquid (NRTL) equation and the Redlich-Kister equation which are described below.

2.4-1 The Wilson Equation

Wilson (2) proposed an equation for correlating excess Gibbs free energy of liquid mixtures. The equation is based on the concept of local composition and contains only two adjustable parameters, $\Delta\lambda_{12}$ and $\Delta\lambda_{21}$. The parameters are positive if the deviation from ideality is positive and negative if the deviation is negative. The equation has the advantage

that it can represent excess Gibbs free energy of a wide variety of liquid mixtures including strongly non-ideal solutions (14).

The expression for the excess Gibbs free energy for binary mixtures is (15),

$$G^E/RT = -x_1 \ln(x_1+A_{12}x_2) - x_2 \ln(x_2+A_{21}x_1) \qquad (2\text{-}26)$$

where,

$$A_{12} = \frac{v_2^o}{v_1^o} \exp(\frac{-\Delta\lambda_{12}}{RT}) \qquad (2\text{-}26a)$$

$$A_{21} = \frac{v_1^o}{v_2^o} \exp(\frac{-\Delta\lambda_{21}}{RT}) \qquad (2\text{-}26b)$$

The quantities v_1^o and v_2^o are the liquid molar volumes of components 1 and 2, respectively, R is the gas constant and T is the absolute temperature.

Another advantage of the Wilson equation is that it can give accurate prediction of multicomponent properties from binary data alone. The only disadvantage is that it is not suitable for partially miscible systems, as it is unable to predict separation of the two liquid phases. This inadequacy may be removed if the right-hand side of equation (2-26) is multiplied by a constant, which is dependent on the binary system (2).

Expressions for the liquid activity coefficients may be obtained by the partial differentiation of equation (2-26) with respect to the liquid composition (15),

$$\ln\gamma_1 = -\ln(x_1+A_{12}x_2) + x_2(\frac{A_{12}}{x_1+A_{12}x_2} - \frac{A_{21}}{A_{21}x_1+x_2}) \qquad (2\text{-}27)$$

$$\ln\gamma_2 = -\ln(x_2+A_{21}x_1) - x_1\left(\frac{A_{12}}{x_1+A_{12}x_2} - \frac{A_{21}}{A_{21}x_1+x_2}\right) \qquad (2\text{-}28)$$

2.4-2 The Non-Random Two Liquid Equation

The basic idea in Wilson's derivation for the excess Gibbs free energy follows from the concept of local composition and was also used by Renon in his derivation of the non-random two liquid, NRTL, equation (8). The NRTL equation has the advantage over Wilson's equation that it is applicable to partially miscible, as well as completely miscible systems.

The NRTL equation uses only two adjustable parameters, Δg_{12} and Δg_{21}, but it contains a third constant, α_{12}, selected according to the chemical characteristics of the components of the mixture to provide flexibility required for representing the shape of the excess Gibbs free energy curve (3). The expression for binary mixtures is (15):

$$G^E/RT = x_1x_2\left(\frac{\tau_{21}G_{21}}{x_1+x_2G_{21}} + \frac{\tau_{12}G_{12}}{x_2+x_1G_{12}}\right) \qquad (2\text{-}29)$$

where,

$$\tau_{12} = \frac{\Delta g_{12}}{RT} \qquad (2\text{-}29a)$$

$$\tau_{21} = \frac{\Delta g_{21}}{RT} \qquad (2\text{-}29b)$$

and,

$$\ln G_{12} = -\alpha_{12}\tau_{12} \qquad (2\text{-}29c)$$

$$\ln G_{21} = -\alpha_{12}\tau_{21} \qquad (2\text{-}29d)$$

The constant α_{12} is positive, characteristic of the non-randomness of the mixture and is of the order of 0.1 to 0.3. It is an empirical constant, indepehdent of temperature (3). Like the Wilson equation, the NRTL equation can represent a wide variety of liquid mixtures, particularly those containing one or more polar components. It, too, can be used to represent multicomponent systems using only the binary parameters.

The expressions for the liquid activity coefficients follow from equation (2-25),

$$\ln\gamma_1 = x_2^2\left(\tau_{21}\frac{(G_{21})^2}{(x_1+x_2G_{21})^2} + \frac{\tau_{12}G_{12}}{(x_2+x_1G_{12})^2}\right) \qquad (2\text{-}30)$$

$$\ln\gamma_2 = x_1^2\left(\tau_{12}\frac{(G_{12})^2}{(x_2+x_1G_{12})^2} + \frac{\tau_{21}G_{21}}{(x_1+x_2G_{21})^2}\right) \qquad (2\text{-}31)$$

2.4-3 The Redlich-Kister Equation

The Redlich-Kister expansion (4) provides a flexible algebraic expression for representing the excess Gibbs free energy of liquid mixtures. It is usually represented by a power series of the liquid composition with three temperature dependent parameters, BB, CC and DD. For binary mixtures, the excess Gibbs free energy is given by,

$$G^E/RT = x_1x_2\ (BB + CC(x_1-x_2) + DD(x_1-x_2)^2) \qquad (2\text{-}32)$$

The Redlich-Kister equation provides a means of classifying different types of binary solutions (16). For perfect liquid solutions all parameters will be zero. For systems whose components are not associated, have nearly equal molal

volumes and moderate interaction, only the first term is required (CC=DD=0). For solutions that exhibit large deviations from ideality the three terms, BB, CC and DD, are required to represent the excess Gibbs free energy.

The liquid phase activity coefficients are again given by equation (2-25),

$$\ln\gamma_1 = x_2^2 \, (BB + CC(3x_1-x_2) + DD(x_1-x_2)(5x_1-x_2)) \qquad (2\text{-}33)$$

$$\ln\gamma_2 = x_1^2 \, (BB + CC(x_1-3x_2) + DD(x_1-x_2)(x_1-5x_2)) \qquad (2\text{-}34)$$

2.5 Data Reduction Methods for Parameter Estimation

Many methods for parameter estimation have been proposed, some of which are more effective than others. One commonly used method is that of least-squares fitting, which minimizes the sum of squares between experimental and calculated values through the adjustment of the parameters to be fitted.

Frequently, when the least-squares method is used as a fitting criterion, vapor composition and total pressure are calculated at a given temperature and liquid composition, i.e. those values that were measured experimentally. This assumes that no error exists in these measured values and that all the error lies in the measured values of the pressure and vapor composition. The least-squares method also gives no measure of the uncertainty in the parameter estimates (17).

Another method of parameter estimation is based on the

principle of maximum likelihood which gives values of the parameters that make the experimental observations appear most likely when taken as a whole. An important advantage of the maximum likelihood principle is that it assumes there is error in all the measured data, temperature, pressure, liquid and vapor compositions and uses all the data in the parameter estimation. It also gives an estimate of the uncertainty associated with the parameters.

However, for typical vapor-liquid equilibrium calculations, the technique used for binary data reduction is of some, but not major importance (9). When a perfect data set is used, the same parameters will be obtained regardless of the method used for data reduction. However, with a real data set there are likely to be discrepencies. The parameters depend on the fitting procedure as does the quality of the fit (18).

When using the least-squares method of data reduction, one generally minimizes the sum of squares between measured values of the liquid phase activity coefficients, $\ln(\gamma_1/\gamma_2)$, calculated using equation (2-21), and those calculated using an appropriate correlation (Wilson, NRTL, etc.). A disadvantage of fitting $\ln(\gamma_1/\gamma_2)$ is that it makes no use of the measured values of the total pressure (19).

Another popular method is to minimize the sum of squares between the calculated and experimental excess Gibbs free energy. This method is preferable when compared to fitting the activity coefficients, as it uses all the measured

data.

Van Ness et al. (20) suggested that from a practical viewpoint, the pressure be fitted rather than the excess Gibbs free energy, as it is the pressure-liquid composition curve that is to be approximated as closely as possible. Also, when the total pressure is fitted, errors in the pressure measurements tend to result in minimal errors in the estimation of the vapor composition. However, from a theoretical viewpoint, one wants the best representation of the excess Gibbs free energy (20).

Regardless of the method used for data reduction, an important factor influencing the quality of the fit is the values used for the vapor pressures of the pure components, p_1^o and p_2^o. It is essential that the vapor pressures be measured with the same apparatus and lots of materials as were used in the other measurements so that the vapor pressures are an integral part of the data set. Otherwise, severe error may be introduced to the calculated thermodynamic properties (19).

Finally, there is no 'best' procedure for fitting vapor-liquid equilibrium data as the choice will be influenced by many factors. These factors include the extent and quality of the data, the nature and flexibility of the model used and subjective judgement which conditions the selection (21). However, there is no method of data reduction which can be a substitute for reliable experimental data.

2.6 Thermodynamic Consistency Test of the Vapor-Liquid Equilibrium Data

The thermodynamic consistency of a set of vapor-liquid equilibrium data may be tested using the Gibbs-Duhem equation. At constant temperature and pressure it is given by:

$$\int_0^1 \ln(\gamma_1/\gamma_2)\, dx_1 = 0 \quad (T,P) \tag{2-35}$$

Equation (2-35) is commonly known as the area test. However, from the phase rule, vapor-liquid equilibrium for a binary system cannot be both isothermal and isobaric. For isothermal data the Gibbs-Duhem equation is,

$$\int_0^1 \ln(\gamma_1/\gamma_2)\, dx_1 = -\int_{x_1=0}^{x_1=1} \left(\frac{v^E}{RT}\right) dP \tag{2-36}$$

where, v^E is the excess molal volume. In most cases there is insufficient data to evaluate the integral on the right-hand side of equation (2-36) and at low pressures its value is extremely small, so the simplest approximation is to set it equal to zero (8).

In performing the area test on real data, the integral in equation (2-35) will not be exactly zero. Prausnitz (8) proposed a guide to test the thermodynamic consistency of real data,

$$0.02 > \left|\frac{\text{Area above x-axis - Area below x-axis}}{\text{Area above x-axis + Area below x-axis}}\right| \tag{2-37}$$

where all areas in equation (2-37) are taken as positive.

CHAPTER 3

EXPERIMENTAL DETAILS

3.1 Materials

Phillips 66 Research Grade cyclohexane and Aldrich analysis grade methyl methacrylate, containing 65 ppm hydroquinone, were used without further purification. The purity of the cyclohexane and methyl methacrylate were 99.99 and 99 mol per cent, respectively. Physical constants of both materials along with their critical properties, acentric factors, ω, and dipole moments, μ, are given in Table 3-1. It should be noted that the acentric factor that was used for the methyl methacrylate was that of its homomorph, 2-methylhexane. Also, the vapor pressure data of Stull (25) for pure methyl methacrylate were not in good agreement with those measured experimentally. Boublik's data (26) were in better agreement, although his values were slightly higher than the experimental. This could be due to the fact that Boublik extrapolated the vapor pressures to zero concentration of the inhibitor, hydroquinone, and it is these values that were reported. The experimental vapor pressures were measured using methyl methacrylate which contained 65 ppm hydroquinone. This would indicate that the presence of the inhibitor did have a definite effect upon the vapor pressure, and for this reason, the vapor pressures that were measured experimentally were preferred.

3.2 Apparatus

The equilibrium still along with the accessory equipment

Table 3-1:

PHYSICAL PROPERTIES OF THE PURE COMPONENTS

	Density (g/ml)		Molar Volume (cm^3/gmol)		
	288.15 K		318.12 K	333.13 K	348.14 K
	Exp.	Lit.			
Cyclohexane	0.7832	0.78315[22]	111.57[22]	113.78[22]	116.08[22]
Methyl Methacrylate	0.9491	0.9488[23]	109.49[23]	111.67[23]	114.00[23]

	Vapor Pressure (Torr)					
	318.12 K		333.13 K		348.14 K	
	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
Cyclohexane	224.24	224.62[24]	388.86	388.91[24]	637.32	637.32[24]
Methyl Methacrylate	94.74	90.9[25]	180.59	178.6[25]	322.89	316.3[25]
		95.29[26]		181.37[26]		323.13[26]

	T_c (K)	P_c (atm)	v_c (cm^3/gmol)	ω	μ (Debye)
Cyclohexane	553.4[15]	40.2[15]	308.0[15]	0.213[15]	0.3[15]
Methyl Methacrylate	554.75[27]	35.8[27]	332.9[27]	0.330[27]	1.675[27]

that was used to measure the temperature, pressure and vapor and liquid compositions are described below in the following sections:

3.2-1 The Equilibrium Still

The apparatus that was used to study the vapor-liquid equilibria was the modified Dvorak and Boublik still. This still, which originated from the Gillespie family of circulation stills, has been previously described by Boublikova and Lu (1). A schematic diagram of the still appears in Figure 3-1. The still was made entirely of pyrex glass.

Equilibrium was achieved through the use of the Cottrell pump (K) together with the circulation loop. The boiling vessel (A) was heated by an electric heater, which was inserted into the well (J). The equilibrium temperature was measured by a thermometer (described below) inserted into the thermometer well (E). The vapor, after being separated from the liquid in chamber (C), was condensed and both the liquid and condensed vapor were collected in reservoirs (B) and (G), respectively. Magnetic stirrers were placed in both reservoirs to ensure density gradients did not occur. Run-off from both reservoirs were mixed (H) before returning to the boiling vessel. The total amount of liquid required in the still is about 110 ml.

3.2-2 Temperature Measurement

The temperature of the equilibrium mixture was measured

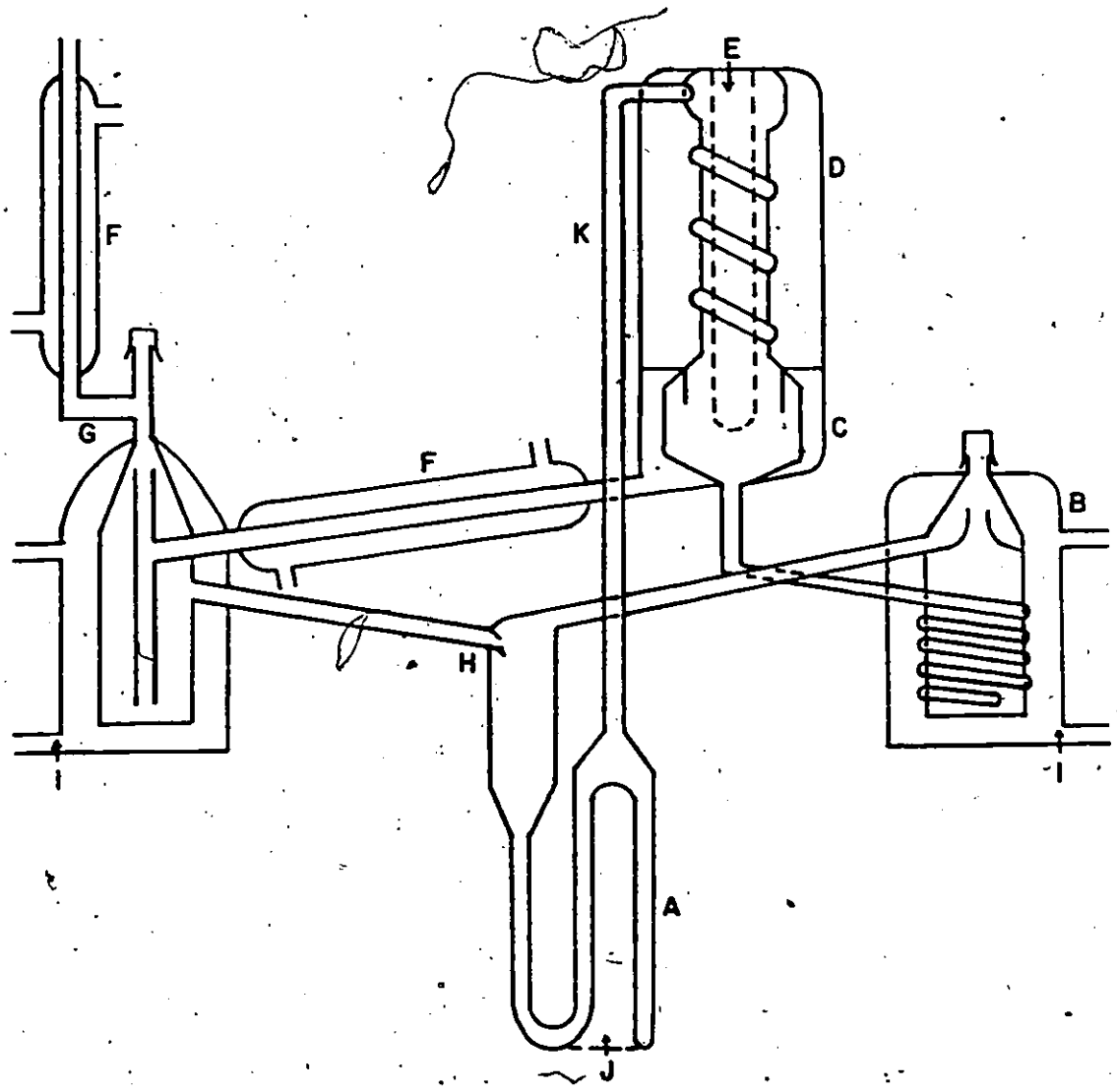

Figure 3-1: Schematic Diagram of the Modified Dvorak and Boublik Still

A- boiling vessel, B- liquid reservoir, C- vapor and liquid separator, D- evacuated chamber, E- thermometer well, F- condenser, G- condensate reservoir, H- mixing vessel, I- cooling jacket, J- heater well, K- Cottrell pump

using a Hewlett-Packard, model 2801A, quartz thermometer, which was checked at the triple point of water. The accuracy of the temperature measurements is estimated to be ±0.01 K. There was a correction factor which had to be subtracted from each of the temperature readings. These were 0.025, 0.020 and 0.005 at 318.15, 333.15 and 348.15 K, respectively.

For isothermal operation of the equilibrium still, the desired temperatures of 318.12, 333.13 and 348.14 K were obtained and regulated by adjusting the total pressure of the system.

3.2-3 Pressure Measurement

The pressure in the equilibrium still was measured using a Texas Instruments, model 144-01, Pressure Gauge, together with a Bourdon Capsule (0 to 174 kPa). The gauge was calibrated by measuring the vapor pressure of demineralized and distilled water in a Swietoslawski type ebulliometer, and checked by a mercury manometer in conjunction with a cathetometer. The system pressure was controlled by a two-liquid manostat. The accuracy of the pressure measurements is estimated to be ±0.05 Torr.

3.2-4 Equipment for Quantitative Analysis

An Anton-Paar K.G. digital densimeter (model DMA 02A) was used to measure the densities of the condensed vapor and liquid samples. A calibration curve was drawn by measuring the densities of mixtures of cyclohexane and methyl methacryl-

ate of known composition. The calibration values for the entire concentration range along with the calibration curve are reported in Appendix I. All measurements were taken at 288.15 K. The accuracy of the determined compositions is estimated to be ±0.002 mole fraction.

3.3 Experimental Procedure

The still was filled with the more volatile component, cyclohexane, and the vapor pressures were measured from 318.12 to 348.14 K. The results were in good agreement with those calculated using the Antoine equation (24).

The binary mixture was then prepared by removing 9.2 ml from both the liquid and condensed vapor reservoirs and replacing them with an equal amount of methyl methacrylate. The mixture was then heated to boiling and the pressure was adjusted manually until the desired temperature in the equilibrium chamber was obtained.

The mixture was left to boil at this temperature for approximately two hours to ensure equilibrium had been attained. The equilibrium temperature was maintained within ±0.005 K for solutions rich in cyclohexane and within ±0.01 K for those rich in methyl methacrylate. The higher fluctuations for the methyl methacrylate-rich solutions were due to the large change in the pressure with liquid phase composition in the lower cyclohexane concentration range.

After recording the system pressure and temperature the boiling was stopped by a sudden increase in the pressure to

atmospheric. Samples of approximately 5 ml were withdrawn from both the liquid and condensate reservoirs for analysis. The densities of both samples were then measured twice to ensure consistency.

Cyclohexane and methyl methacrylate were added to both the liquid and condensate reservoirs in specific amounts so that the desired concentration for the next run would be obtained.

It should be noted that when the vapor pressure of the pure methyl methacrylate was measured, its density was also measured before and after boiling, with no change observed. This indicates that no polymerization of the methyl methacrylate had occured. Therefore, the inhibitor, hydroquinone, present in the methyl methacrylate was adequate for preventing its polymerization in the condensed vapor.

3.4 Reduction of the Experimental Data

Once the experimental vapor-liquid equilibrium data were collected, they were then correlated using the Wilson, the NRTL and the Redlich-Kister equations. The three equations were fitted by minimizing the sum of squares between the experimental and calculated excess Gibbs free energy. Both the Wilson and the NRTL equations are non-linear and were fitted using the subroutine ZXMIN from the International Mathematical and Statistical Library (IMSL).

Once the optimum parameters were determined for each of the three equations, values of the total pressure, P, and the

vapor composition, y_1, were calculated using the correlations in conjunction with equation (2-21) by means of the Newton-Raphson method of iteration (28). (A detailed description of the Newton-Raphson method is presented in Appendix II).

A listing of the computer programme that was used appears in Appendix III.

CHAPTER 4

RESULTS AND DISCUSSION

The vapor-liquid equilibrium data for the system cyclohexane (1) and methyl methacrylate (2) were measured at three isothermal temperatures of 318.12, 333.13 and 348.14 K. The data included the total pressure, P, and the liquid and vapor compositions, x_1 and y_1, respectively. Second virial coefficients, B_{11} and B_{22}, and cross second virial coefficients, B_{12}, were calculated using the correlation of Tsonopoulos, equation (2-13). As had been stated previously, Tsonopoulos had suggested that the value of the correction, k_{12}, on the critical temperature in the cross second virial coefficient, $T_{c_{12}}$, (equation (2-8)) be given a value of 0.13 for hydrocarbon/ester mixtures. However, this value of k_{12} should only be used as an approximation if the actual value is unknown. The cross second virial coefficients were calculated with k_{12} equal to 0.13, and with different values in order to determine the exact value of k_{12} for cyclohexane - methyl methacrylate mixtures. The best value for k_{12} was found to be zero. Values of the cross second virial coefficients calculated with k_{12} equal to zero along with the second virial coefficients, B_{11} and B_{22}, are presented in Table 4-1.

The experimental liquid activity coefficients, γ_1 and γ_2, and the excess Gibbs free energy, G^E, were calculated using equations (2-21) and (2-24), respectively. These values along with the measured pressure, P, and liquid and vapor compositions, x_1 and y_1, are shown for the three isothermal temperatures in Table 4-2.

The experimental data at the three temperatures were fitted to three correlations, the Wilson, the NRTL and the Redlich-Kister equations, by minimizing the sum of squares of the residual excess Gibbs free energy, $\Sigma(G^E_{expt}-G^E_{calc})^2$. Both the Wilson and the NRTL equations contain two temperature dependent parameters, while the Redlich-Kister equation was fitted with three. However, the NRTL equation also contains a third constant, α_{12}, which is characteristic of the binary mixture, but independent of temperature. The value of α_{12} was found by fitting the two temperature dependent parameters in the NRTL equation at the three temperatures for different values of α_{12}. The sum of squares of the residual excess Gibbs free energy were compared at the three temperatures to find which value of α_{12} gave the smallest values. For the cyclohexane/methyl methacrylate mixture, the value of α_{12} was found to be 0.14. The values of the parameters for the three equations at the three temperatures are shown in Table 4-3.

The sum of squares of the residual excess Gibbs free energy for the three equations were compared at each temperature to determine which equation gave the best fit. Based on this criterion, it can be seen from Table 4-4 that the NRTL equation fitted the data best at 318.12 and 333.13 K, whereas the Redlich-Kister equation gave the best fit at 348.14 K. Values for the excess Gibbs free energy calculated by the Wilson, the NRTL and the Redlich-Kister equations (equations (2-26), (2-29) and (2-32), respectively) at the three temperatures are

listed in Table 4-5. Table 4-6 shows the average absolute deviations of the excess Gibbs free energy, $\Sigma|G^E_{expt}-G^E_{calc}|/N$, calculated by the three equations. (The quantity N is the number of experimental data points). Comparison of the average absolute deviations shows the NRTL equation to give the best fit at all three temperatures. However, based on the least-squares criterion, the NRTL equation gave the best fit only at 318.12 and 333.13 K and it was the Redlich-Kister equation which fit the data best at 348.14 K. For this reason, when the excess Gibbs free energy was plotted as a function of the liquid composition in Figures 4-1 to 4-3, the excess Gibbs free energy values that were calculated by the Redlich-Kister equation were plotted at 348.14 K rather than those that were calculated by the NRTL equation. The reason why only one equation was represented in each of the graphs was that although the values calculated by the three equations were different, these differences were not significant enough to be shown on the graphs and so only the equation which gave the best fit was depicted.

Once the parameters for each of the equations were known, the liquid activity coefficients, γ_1 and γ_2, were then calculated using the Wilson (equations (2-27) and (2-28)), the NRTL (equations (2-30) and (2-31)) and the Redlich-Kister (equations (2-33) and (2-34)) equations at the three temperatures. Average absolute deviations were calculated for both γ_1 and γ_2 and are compared in Table 4-7.

Except for γ_2 at 318.12 K, the Wilson equation gave the

smallest average absolute deviations of γ_1 and γ_2 at all three temperatures. The NRTL equation fit γ_2 best at 318.12 K. Values for the liquid activity coefficients calculated by the Wilson equation at the three temperatures are listed in Table 4-10. These calculated values were compared with the experimental liquid activity coefficients in Figures 4-4 to 4-6. Again, because the differences between the values calculated by the three equations were not significant, only the curve for the Wilson equation appears in each graph. The reason for this choice was that the Wilson equation had the smallest average absolute deviations in the liquid activity coefficients at the three temperatures.

Values of the vapor composition, y_1, and the total pressure, P, were calculated by means of the Newton-Raphson method of iteration, and average absolute deviations for y_1 and P were calculated for the three equations and are compared in Tables 4-8 and 4-9, respectively. Again, the Wilson equation gave the smallest average absolute deviations of both the vapor composition and the total pressure, at all three temperatures.

The values of the vapor composition calculated by the Wilson equation were in very good agreement with the experimental vapor compositions measured by the densimeter. The accuracy of the densimeter was estimated to be ±0.002 mole fraction, which was the same as the average absolute deviations for the Wilson equation at all three temperatures. The vapor compositions that were calculated by the NRTL equation

were also in good agreement with the experimental measurements. The total pressures that were calculated by the three equations were not in as good agreement with the experimental values as were the vapor compositions. For the Wilson equation the average absolute deviations were approximately 0.55 Torr, while the accuracy of the pressure gauge had been estimated to be ±0.05 Torr. This error in the total pressure could possibly be reduced by fitting the total pressure rather than the excess Gibbs free energy. This would not affect the calculated values of the vapor composition, but would be at the expense of the calculated excess Gibbs free energy, which theoretically, would not be desirable.

Again, because the Wilson equation had the smallest average absolute deviations in both the vapor composition and the total pressure at all temperatures, those values of y_1 and P that were calculated by the Wilson equation are presented in Table 4-10. These calculated values of y_1 and P were compared with the experimentally measured values in Figures 4-7 through 4-12.

There was an azeotrope present at all three temperatures. The values of the azeotropic compositions, x_{az}, and pressures P_{az}, calculated by the three equations, along with the experimental values are shown in Table 4-11. The three equations calculated the values of the azeotropic composition quite well at the three temperatures. However, the Wilson equation gave values that were closest to the experimental, particularly at 348.14 K where the NRTL and the Redlich-Kister compositions

were a little high. At the three temperatures, the values of the azeotropic pressure calculated by the Wilson equation were also superior to those calculated by the NRTL and the Redlich-Kister equations. The latter equations tended to give pressures that were a little low.

The thermodynamic consistency of the isothermal experimental data at 318.12, 333.13 and 348.14 K were tested by the area test, Figures 4-13 to 4-15. The isothermal data at 318.12 K were fitted using a fourth degree polynomial, while those at 333.13 and 348.14 K were fitted by a third degree polynomial. The results are shown in Table 4-12. The data at all three temperatures were judged to be thermodynamically consistent, based on the guide given by Prausnitz in equation (2-37).

Table 4-1:

SECOND VIRIAL AND CROSS SECOND VIRIAL COEFFICIENTS FOR CYCLOHEXANE (1) AND METHYL METHACRYLATE (2) AT 318.12, 333.13 AND 348.14 K.

B_{11} cm^3/mol	B_{22} cm^3/mol	B_{12} cm^3/mol	δ_{12}* cm^3/mol
	318.12 K		
-1529.0	-2260.0	-1757.7	273.6
	333.13 K		
-1333.3	-1915.8	-1520.3	208.5
	348.14 K		
-1178.2	-1650.0	-1333.6	160.9

*$\delta_{12} = 2\,B_{12} - B_{11} - B_{22}$

Table 4-2:

EXPERIMENTAL ISOTHERMAL VAPOR-LIQUID EQUILIBRIUM DATA FOR CYCLOHEXANE (1) AND METHYL METHACRYLATE (2) AT 318.12, 333.13 AND 348.14 K.

x_1	y_1	P	γ_1	γ_2	G^E
		Torr			J/mol
		318.12 K			
0.047	0.198	112.93	2.1434	1.0010	97.32
0.066	0.258	119.60	2.1050	1.0000	129.99
0.103	0.346	131.33	1.9842	1.0065	202.00
0.145	0.421	142.91	1.8642	1.0160	274.73
0.197	0.494	156.21	1.7577	1.0319	360.60
0.273	0.569	171.66	1.6032	1.0651	462.20
0.357	0.630	185.60	1.4658	1.1162	548.10
0.443	0.680	196.53	1.3488	1.1788	592.93
0.529	0.722	205.63	1.2538	1.2660	610.33
0.605	0.753	211.73	1.1766	1.3803	597.03
0.671	0.782	216.63	1.1266	1.4958	562.00
0.731	0.810	220.13	1.0883	1.6199	506.73
0.771	0.831	222.15	1.0681	1.7079	458.47
0.807	0.849	223.78	1.0500	1.8237	410.89
0.867	0.882	225.76	1.0241	2.0863	313.34
0.907	0.912	226.34	1.0148	2.2311	232.59
0.935	0.933	225.98	1.0055	2.4269	165.93
0.956	0.953	225.71	1.0033	2.5123	115.49
0.964	0.961	225.53	1.0025	2.5461	95.41
		333.13 K			
0.039	0.152	204.63	2.0806	0.9976	72.69
0.061	0.215	216.56	1.9893	0.9991	113.84
0.094	0.291	232.93	1.8769	1.0044	174.98

Table 4-2 con't.

x_1	y_1	P Torr	γ_1	γ_2	G^E J/mol
0.137	0.372	253.03	1.7855	1.0128	250.25
0.183	0.441	271.90	1.7003	1.0215	317.28
0.247	0.510	294.15	1.5734	1.0490	409.88
0.335	0.587	319.52	1.4476	1.0852	493.81
0.421	0.644	339.28	1.3399	1.1390	549.82
0.506	0.688	354.70	1.2436	1.2216	579.46
0.581	0.726	365.94	1.1781	1.3038	571.69
0.656	0.762	375.61	1.1233	1.4149	541.92
0.702	0.785	380.39	1.0947	1.4938	507.21
0.756	0.815	385.93	1.0703	1.5922	456.55
0.798	0.836	388.24	1.0461	1.7150	401.42
0.833	0.860	390.31	1.0362	1.7802	348.90
0.893	0.900	391.87	1.0155	1.9928	242.32
0.937	0.933	391.50	1.0023	2.2662	148.78
0.963	0.958	390.75	0.9995	2.4148	89.07
		348.14 K			
0.058	0.183	372.68	1.8777	0.9970	97.54
0.084	0.245	393.26	1.8292	0.9983	142.34
0.132	0.333	426.37	1.7115	1.0065	221.71
0.168	0.393	451.79	1.6789	1.0107	277.55
0.227	0.460	482.33	1.5495	1.0309	355.74
0.311	0.537	521.63	1.4242	1.0694	452.11
0.399	0.604	554.20	1.3238	1.1115	507.82
0.483	0.658	581.20	1.2472	1.1681	541.34
0.562	0.700	599.83	1.1754	1.2467	542.48
0.631	0.735	613.38	1.1230	1.3356	521.08
0.689	0.768	623.62	1.0919	1.4098	484.40
0.746	0.801	631.84	1.0651	1.4995	433.95
0.786	0.824	636.53	1.0472	1.5855	390.54
0.824	0.849	639.92	1.0345	1.6629	339.91

Table 4-2 con't.

x_1	y_1	P Torr	γ_1	γ_2	G^E J/mol
0.882	0.888	643.16	1.0157	1.8489	249.78
0.927	0.924	642.38	1.0044	2.0263	161.01
0.967	0.963	640.00	0.9999	2.1753	73.95

Table 4-3:

THE WILSON, THE NRTL AND THE REDLICH-KISTER PARAMETERS AT 318.12, 333.13 AND 348.14 K.

	318.12 K	333.13 K	348.14 K
	Wilson		
Λ_{12}	158.08	128.41	110.36
Λ_{21}	542.19	525.30	495.65
	NRTL		
Δg_{12}	874.28	883.25	853.95
Δg_{21}	-201.94	-243.37	-254.35
	Redlich-Kister		
BB	0.9244	0.8414	0.7577
CC	0.1925	0.1061	0.1005
DD	0.0029	-0.0307	-0.0421

Table 4-4:

SUM OF SQUARES OF RESIDUAL EXCESS GIBBS FREE ENERGY, $\Sigma(G^{E}_{expt}-G^{E}_{calc})^2$, (J^2/mol^2), FOR THE WILSON, THE NRTL AND THE REDLICH-KISTER EQUATIONS AT 318.12, 333.13 AND 348.14 K.

Wilson	NRTL	Redlich-Kister
	318.12 K	
237.91	181.81	240.19
	333.13 K	
253.16	147.39	251.28
	348.14 K	
471.13	350.11	330.66

Table 4-5:

THE EXCESS GIBBS FREE ENERGY, G^E, CALCULATED BY THE WILSON, THE NRTL AND THE REDLICH-KISTER EQUATIONS AT 318.12, 333.13 AND 348.14 K.

x_1 expt	G^E J/mol expt	G^E J/mol Wilson	G^E J/mol NRTL	G^E J/mol R-K
		318.12 K		
0.047	97.32	99.82	98.21	96.54
0.066	129.99	137.79	135.76	133.59
0.103	202.00	207.72	205.22	202.38
0.145	274.73	280.66	278.06	274.84
0.197	360.60	361.33	359.14	355.90
0.273	462.20	459.67	458.72	456.14
0.357	548.10	540.53	541.30	539.95
0.443	592.93	591.84	594.07	594.14
0.529	610.33	609.73	612.64	613.93
0.605	597.03	596.17	598.79	600.77
0.671	562.00	560.72	562.39	564.62
0.731	506.73	508.26	508.63	510.79
0.771	458.47	462.02	461.39	463.35
0.807	410.89	412.30	410.80	412.51
0.867	313.34	311.53	308.91	310.06
0.907	232.59	231.20	228.35	229.10
0.935	165.93	168.34	165.75	166.22
0.956	115.49	117.46	115.36	115.65
0.964	95.41	97.22	95.37	95.60
		333.13 K		
0.039	72.69	78.56	77.44	74.47
0.061	113.84	120.50	118.96	114.94
0.094	174.98	180.18	178.23	173.36

Table 4-5 con't.

x_1 expt	G^E J/mol expt	G^E J/mol Wilson	G^E J/mol NRTL	G^E J/mol R-K
0.137	250.25	252.04	249.94	244.99
0.183	317.28	321.40	319.50	315.45
0.247	409.88	404.72	403.54	401.72
0.335	493.81	493.45	493.66	495.48
0.421	549.82	550.08	551.56	556.21
0.506	579.46	575.34	577.55	583.38
0.581	571.69	570.87	573.07	578.34
0.656	541.92	539.85	541.35	544.70
0.702	507.21	506.96	507.75	509.43
0.756	456.55	454.18	453.96	453.50
0.798	401.42	402.06	401.02	399.00
0.833	348.90	350.88	349.24	346.15
0.893	242.32	245.92	243.68	239.71
0.937	148.78	154.32	152.30	148.89
0.963	89.07	94.04	92.57	90.13
		348.14 K		
0.058	97.54	108.61	107.45	100.58
0.084	142.34	153.63	152.19	143.65
0.132	221.71	230.67	229.05	219.20
0.168	277.55	283.21	281.67	272.06
0.227	355.74	359.41	358.31	350.62
0.311	452.11	446.06	445.93	442.69
0.399	507.82	508.26	509.18	510.67
0.483	541.34	539.03	540.63	545.20
0.562	542.48	541.15	542.87	548.33
0.631	521.05	520.59	521.94	526.50
0.689	484.43	486.29	487.03	489.83
0.746	433.95	436.67	436.61	437.15
0.786	390.54	392.00	391.35	390.23

Table 4-5 con't.

x_1 expt	G^E J/mol expt	G^E J/mol Wilson	G^E J/mol NRTL	G^E J/mol R-K
0.824	339.91	341.72	340.56	338.02
0.882	249.78	249.58	247.90	244.02
0.927	161.01	164.61	162.99	159.23
0.967	73.95	78.65	77.63	75.28

Table 4-6:

AVERAGE ABSOLUTE DEVIATIONS OF THE EXCESS GIBBS ENERGY, $\Sigma|G^E_{expt}-G^E_{calc}|/N$, (J/mol).

Wilson	NRTL	Redlich-Kister
	318.12 K	
2.7619	2.3408	2.7848
	333.13 K	
3.1005	2.2230	3.0772
	348.14 K	
3.7949	3.3865	3.7988

Table 4-7:

AVERAGE ABSOLUTE DEVIATIONS OF THE LIQUID ACTIVITY COEFFICIENTS OF CYCLOHEXANE (1) AND METHYL METHACRYLATE (2), $\Sigma|\gamma_{i_{expt}} - \gamma_{i_{calc}}|/N$.

	Wilson	NRTL	Redlich-Kister
		318.12 K	
γ_1	0.0095	0.0108	0.0131
γ_2	0.0184	0.0149	0.0180
		333.13 K	
γ_1	0.0113	0.0136	0.0209
γ_2	0.0124	0.0148	0.0212
		348.14 K	
γ_1	0.0081	0.0099	0.0191
γ_2	0.0083	0.0085	0.0151

Table 4-8:

AVERAGE ABSOLUTE DEVIATIONS OF THE VAPOR COMPOSITION, $\Sigma|y_{1_{expt}} - y_{1_{calc}}|/N$.

Wilson	NRTL	Redlich-Kister
	318.12 K	
0.0024	0.0026	0.0031
	333.13 K	
0.0023	0.0027	0.0039
	348.14 K	
0.0019	0.0022	0.0039

Table 4-9:

AVERAGE ABSOLUTE DEVIATIONS OF THE TOTAL PRESSURE, $\Sigma|P_{expt}-P_{calc}|/N$, (Torr).

Wilson	NRTL	Redlich-Kister
	318.12 K	
0.4203	0.4528	0.5148
	333.13 K	
0.5866	0.6640	1.0464
	348.14 K	
0.6641	0.7116	1.6035

Table 4-10:

VAPOR COMPOSITION, y_1, TOTAL PRESSURE, P, AND LIQUID ACTIVITY COEFFICIENTS, γ_1 AND γ_2, CALCULATED BY THE WILSON EQUATION AT 318.12, 333.13 AND 348.14 K.

x_1 expt	y_1	P Torr	γ_1	γ_2
		318.12 K		
0.047	0.199	113.17	2.1613	1.0016
0.066	0.257	119.89	2.1059	1.0032
0.103	0.348	131.90	2.0042	1.0077
0.145	0.426	143.99	1.8981	1.0155
0.197	0.498	156.95	1.7792	1.0292
0.273	0.574	172.62	1.6270	1.0579
0.357	0.636	186.32	1.4845	1.1035
0.443	0.684	197.34	1.3623	1.1686
0.529	0.724	206.08	1.2607	1.2576
0.605	0.757	212.34	1.1860	1.3625
0.671	0.785	216.87	1.1316	1.4803
0.731	0.811	220.33	1.0901	1.6159
0.771	0.829	222.29	1.0666	1.7259
0.807	0.848	223.80	1.0483	1.8414
0.867	0.882	225.61	1.0239	2.0790
0.907	0.910	226.20	1.0120	2.2778
0.935	0.933	226.19	1.0060	2.4418
0.956	0.952	225.90	1.0028	2.5811
0.964	0.960	225.72	1.0019	2.6384
		333.13 K		
0.039	0.148	204.32	2.0206	1.0010
0.061	0.213	216.60	1.9672	1.0024

Table 4-10 con't.

x_1 expt	y_1	P Torr	γ_1	γ_2
0.094	0.292	233.67	1.8912	1.0057
0.137	0.374	253.69	1.7991	1.0123
0.183	0.442	272.61	1.7085	1.0223
0.247	0.515	295.24	1.5951	1.0417
0.335	0.590	320.56	1.4600	1.0803
0.421	0.646	340.16	1.3484	1.1339
0.506	0.693	355.65	1.2555	1.2062
0.581	0.729	366.78	1.1863	1.2905
0.656	0.765	375.94	1.1282	1.4001
0.702	0.787	380.68	1.0978	1.4834
0.756	0.814	385.39	1.0672	1.6010
0.798	0.836	388.38	1.0470	1.7109
0.833	0.857	390.35	1.0328	1.8176
0.893	0.898	392.33	1.0140	2.0411
0.937	0.934	392.29	1.0050	2.2472
0.963	0.958	391.45	1.0018	2.3904
		348.14 K		
0.058	0.180	373.17	1.8502	1.0020
0.084	0.241	393.38	1.7986	1.0041
0.132	0.332	427.29	1.7094	1.0103
0.168	0.387	450.11	1.6474	1.0169
0.227	0.461	483.20	1.5539	1.0317
0.311	0.541	522.45	1.4369	1.0619
0.399	0.606	555.50	1.3321	1.1071
0.483	0.658	580.90	1.2472	1.1662
0.562	0.702	600.35	1.1796	1.2397
0.631	0.738	614.37	1.1296	1.3219
0.689	0.769	624.21	1.0937	1.4074
0.746	0.800	632.17	1.0639	1.5099
0.786	0.823	636.69	1.0462	1.5953

Table 4-10 con't.

x_1 expt	y_1	P Torr	γ_1	γ_2
0.824	0.847	640.05	1.0318	1.6888
0.882	0.887	643.09	1.0148	1.8605
0.927	0.924	643.21	1.0058	2.0204
0.967	0.963	641.11	1.0012	2.1977

Table 4-11:

AZEOTROPIC DATA FOR CYCLOHEXANE (1) AND METHYL METHACRYLATE (2) AT 318.12, 333.13 AND 348.14 K.

	Expt.	Wilson	NRTL	Redlich-Kister
		318.12 K		
x_{az}	0.921	0.921	0.922	0.921
P_{az}(Torr)	226.4	226.24	226.00	226.06
		333.13 K		
x_{az}	0.915	0.914	0.915	0.917
P_{az}(Torr)	392.5	392.50	392.18	391.62
		348.14 K		
x_{az}	0.906	0.907	0.908	0.909
P_{az}(Torr)	643.8	643.44	643.04	642.12

Table 4-12:

THERMODYNAMIC CONSISTENCY TEST OF THE EXPERIMENTAL DATA AT 318.12, 333.13 AND 348.14 K.

Area Above x-axis	Area Below x-axis	f(area)*
	318.12 K	
0.2223	0.2275	0.0116
	333.13 K	
0.2044	0.2081	0.0077
	348.14 K	
0.1889	0.1878	0.0024

*According to the guide proposed by Prausnitz

$$f(\text{area}) = \left|\frac{\text{Area above x-axis} - \text{Area below x-axis}}{\text{Area below x-axis} + \text{Area below x-axis}}\right| < 0.02$$

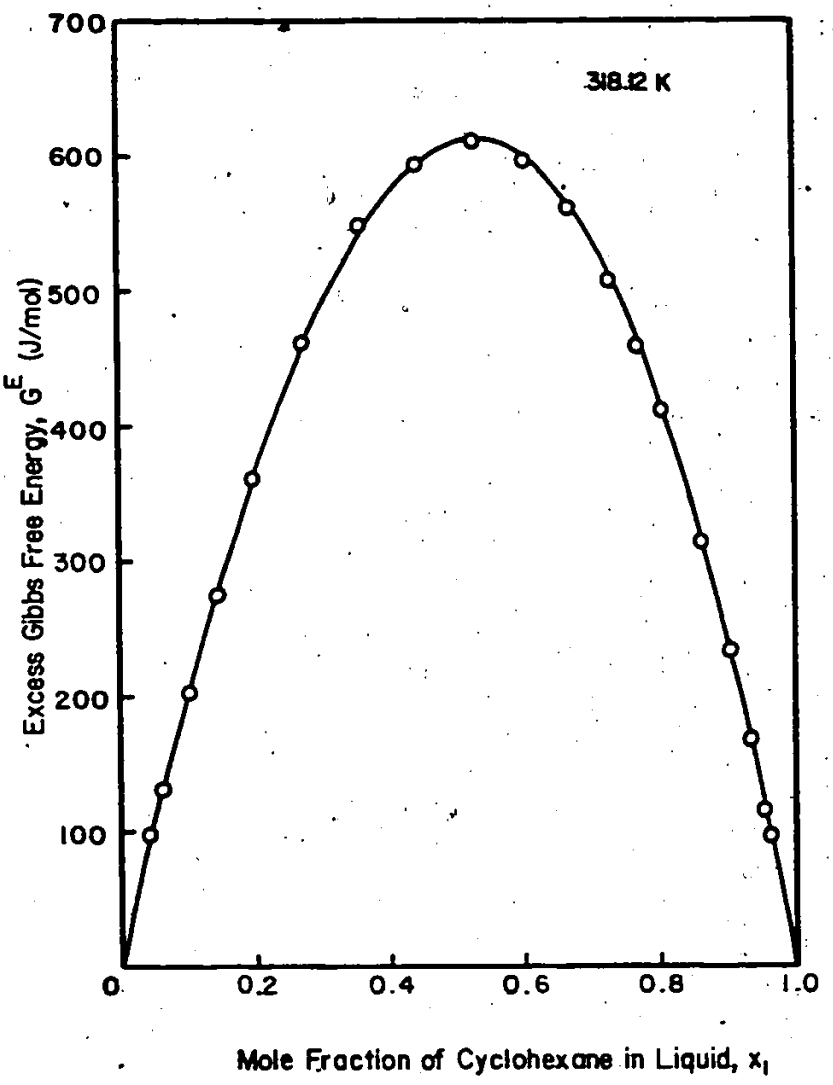

Figure 4-1: Excess Gibbs Free Energy for Mixtures of Cyclohexane (1) and Methyl Methacrylate (2) at 318.12 K. (O, Experimental, – Calculated by the NRTL Equation)

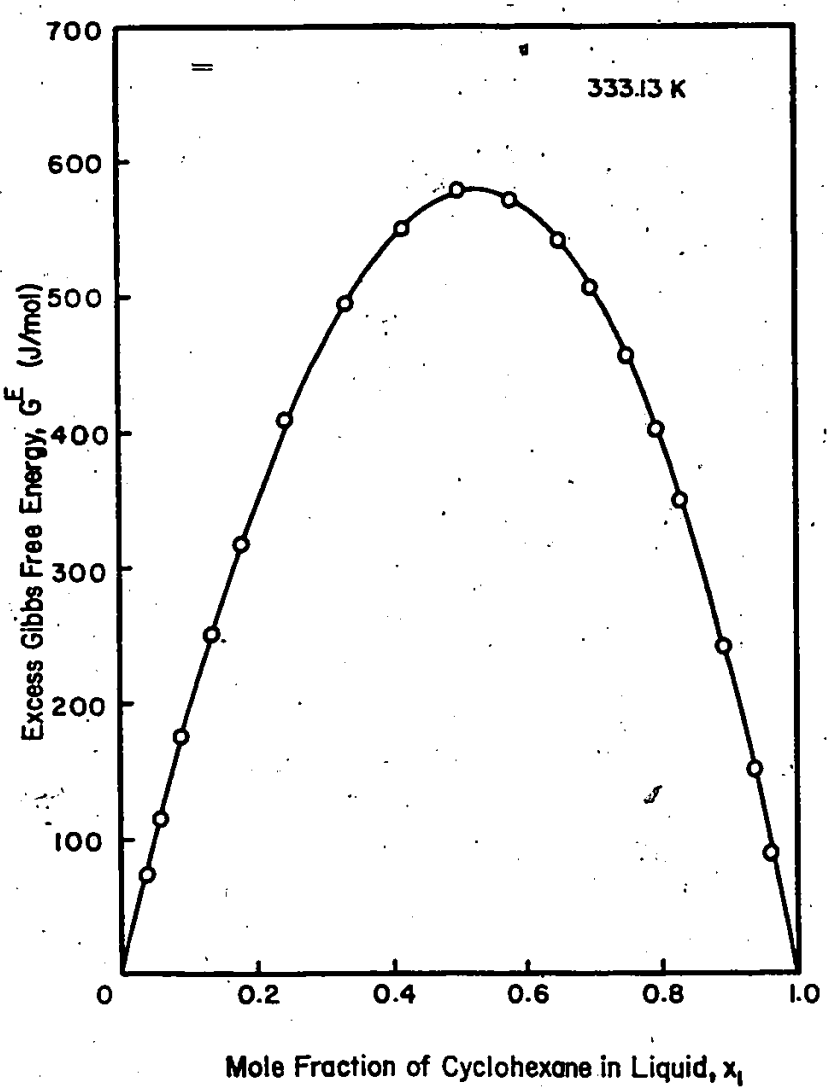

Figure 4-2: Excess Gibbs Free Energy for Mixtures of Cyclohexane (1) and Methyl Methacrylate (2) at 333.13 K. (O, Experimental, — Calculated by the NRTL Equation)

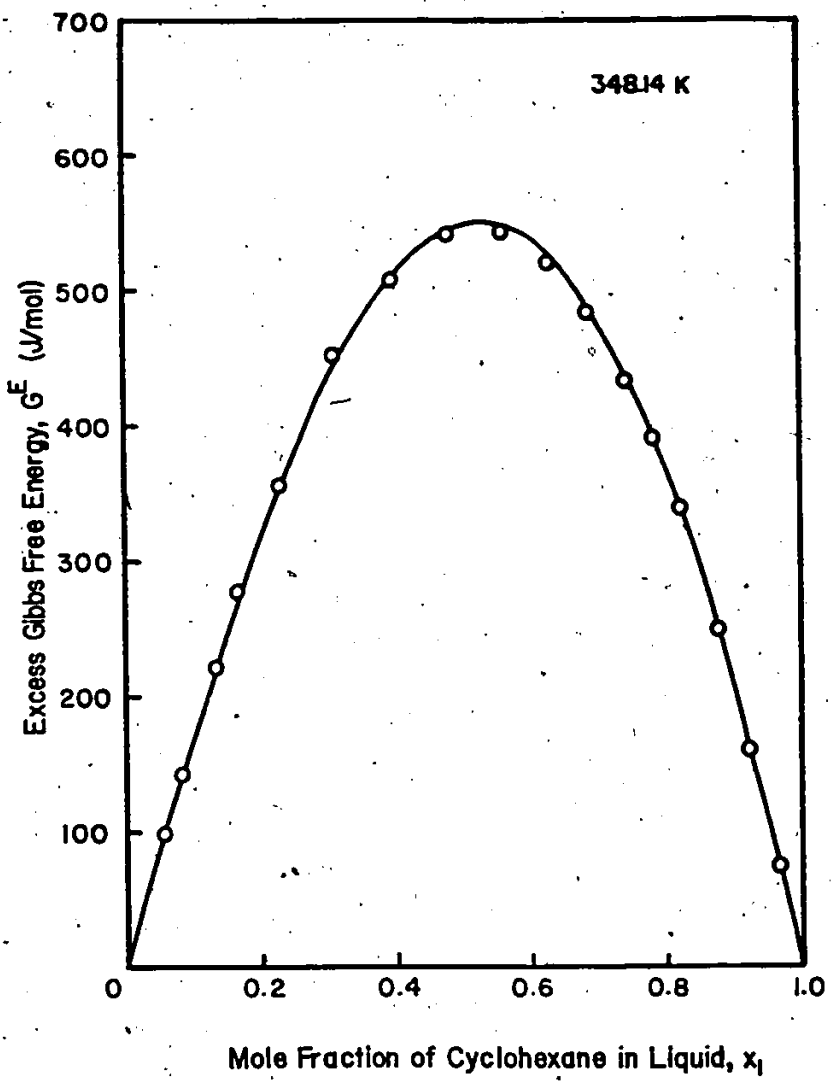

Figure 4-3: Excess Gibbs Free Energy for Mixtures of Cyclohexane (1) and Methyl Methacrylate (2) at 348.14 K. (O, Experimental, — Calculated by the Redlich-Kister Equation)

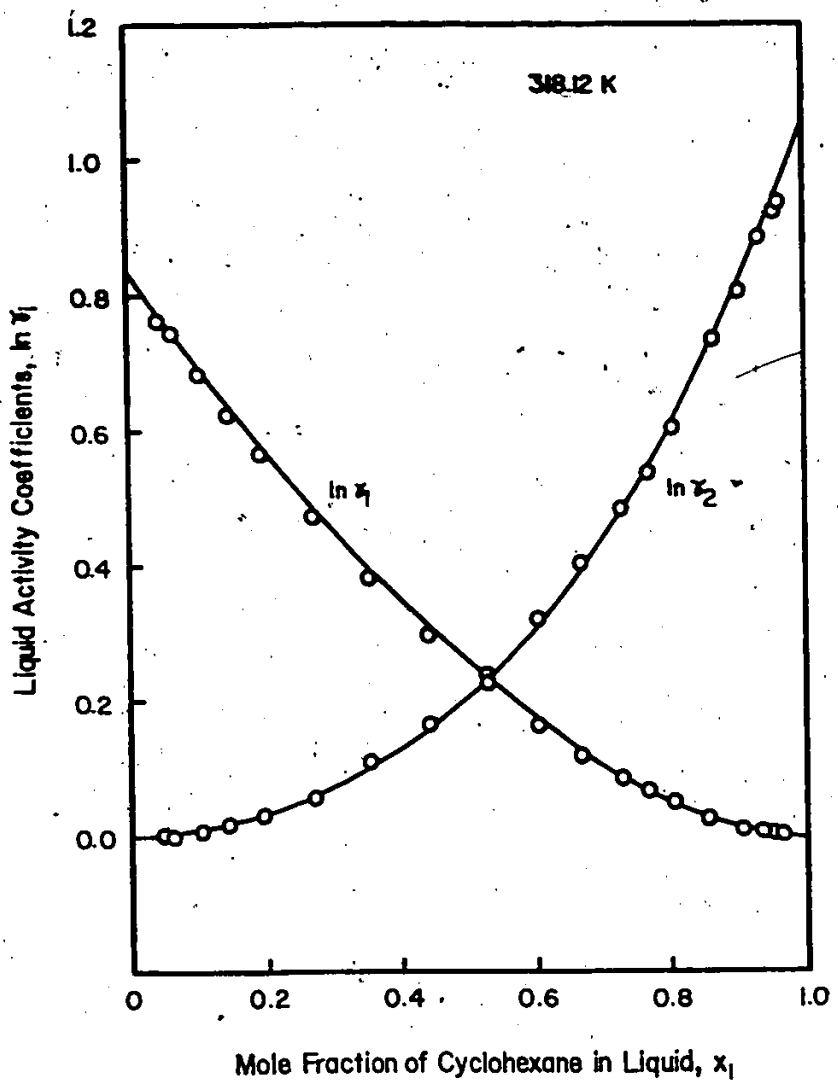

Figure 4-4: Comparison of Experimental and Calculated γ_i Values for Cyclohexane (1) and Methyl Methacrylate (2) at 318.12 K. (O, Experimental, — Calculated by the Wilson Equation)

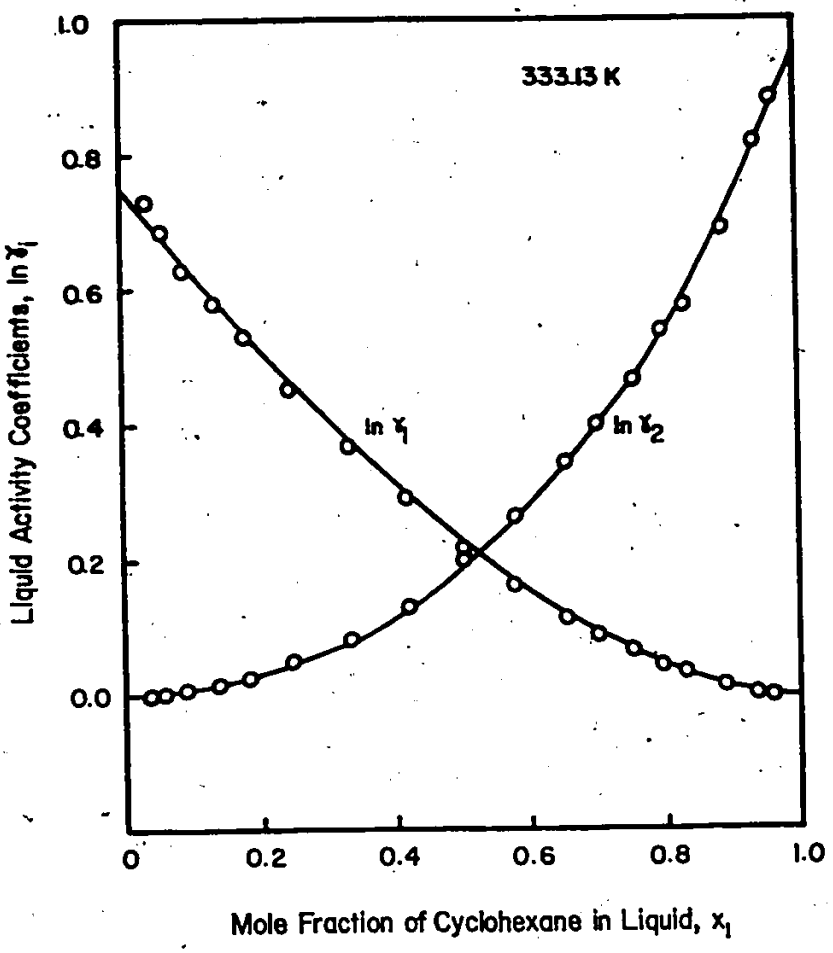

Figure 4-5: Comparison of Experimental and Calculated γ_i Values for Cyclohexane (1) and Methyl Methacrylate (2) at 333.13 K. (O, Experimental, — Calculated by the Wilson Equation)

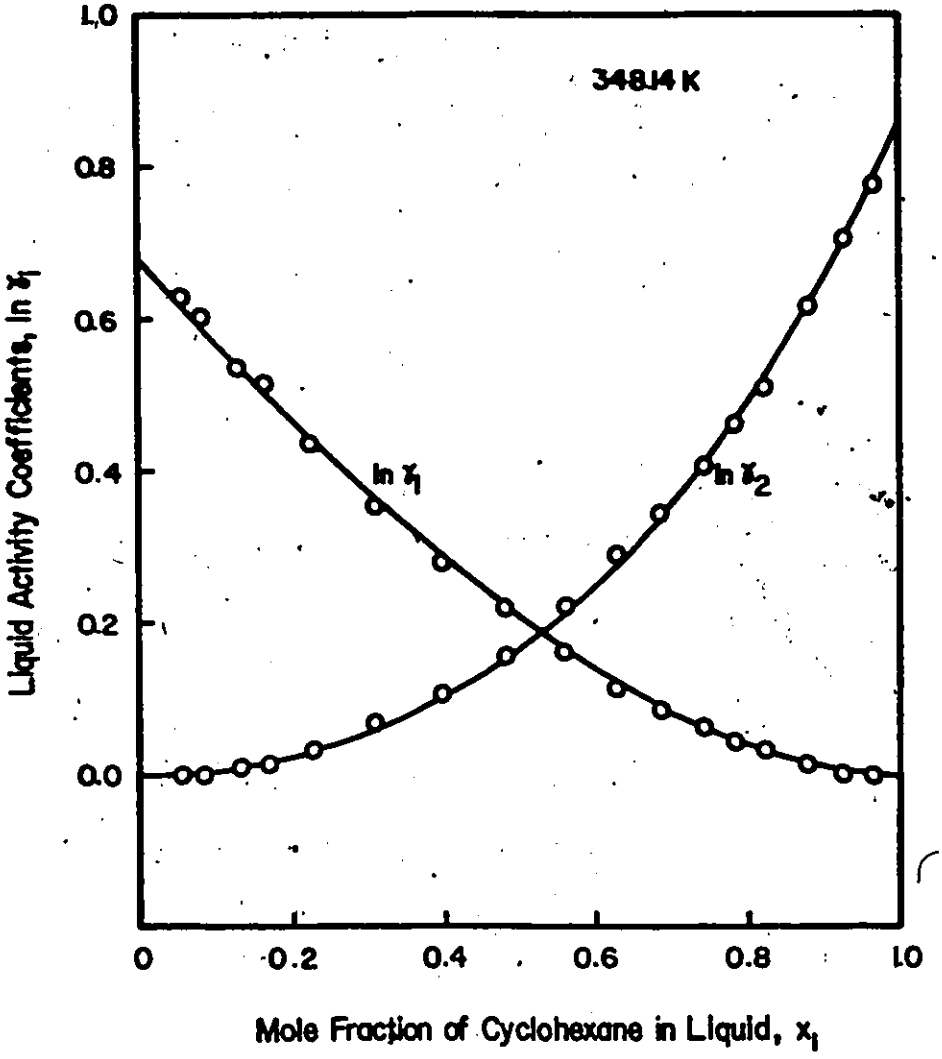

Figure 4-6: Comparison of Experimental and Calculated γ_i Values for Cyclohexane (1) and Methyl Methacrylate (2) at 348.14 K. (O, Experimental, — Calculated by the Wilson Equation)

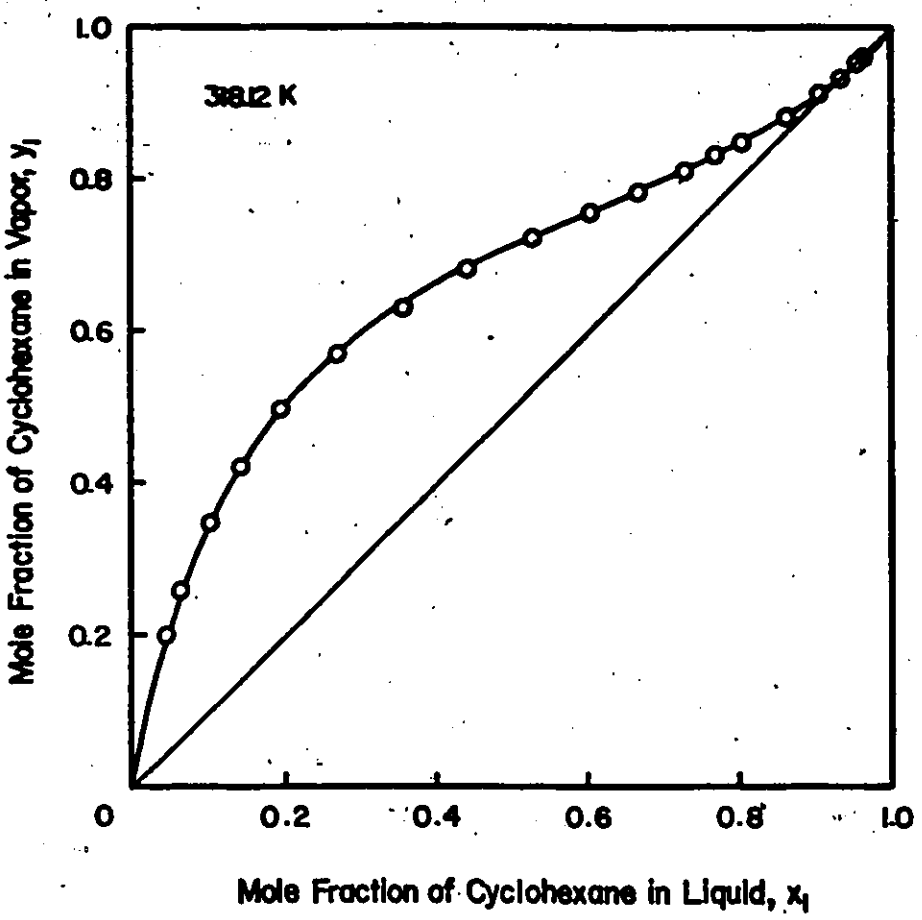

Figure 4-7: Comparison of Experimental and Calculated y_1 Values for Cyclohexane (1) and Methyl Methacrylate (2) at 318.12 K. (O, Experimental, — Calculated by the Wilson Equation)

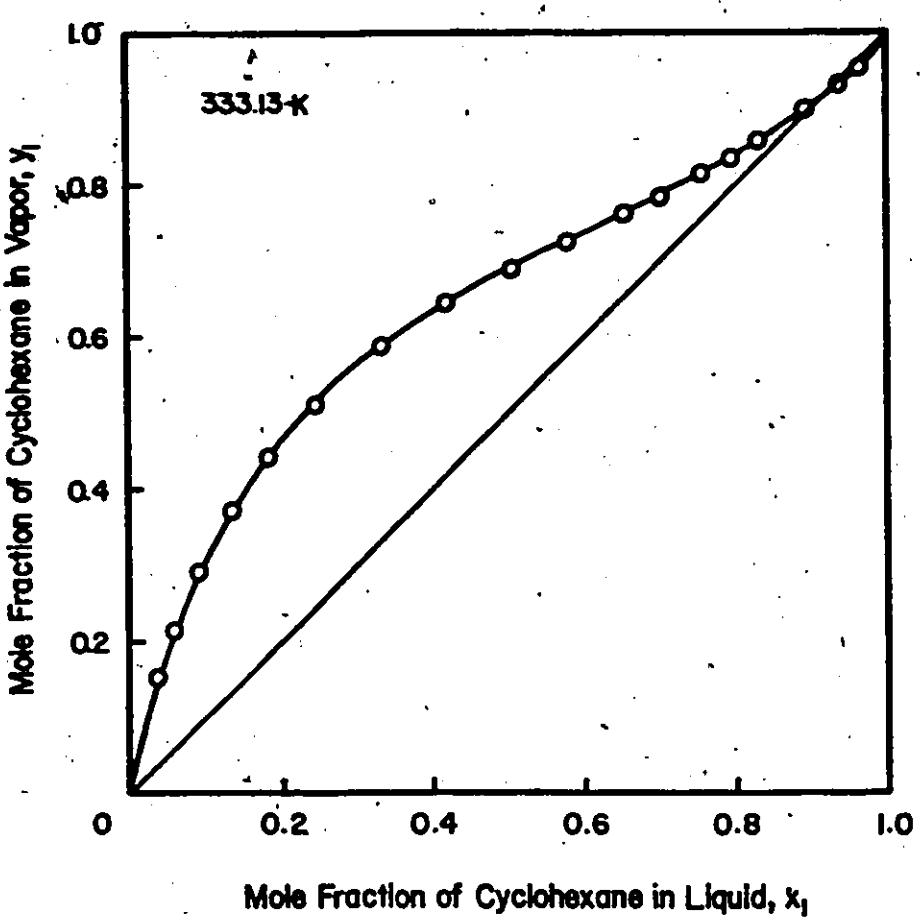

Figure 4-8: Comparison of Experimental and Calculated y_1 Values for Cyclohexane (1) and Methyl Methacrylate (2) at 333.13 K. (O, Experimental, — Calculated by the Wilson Equation)

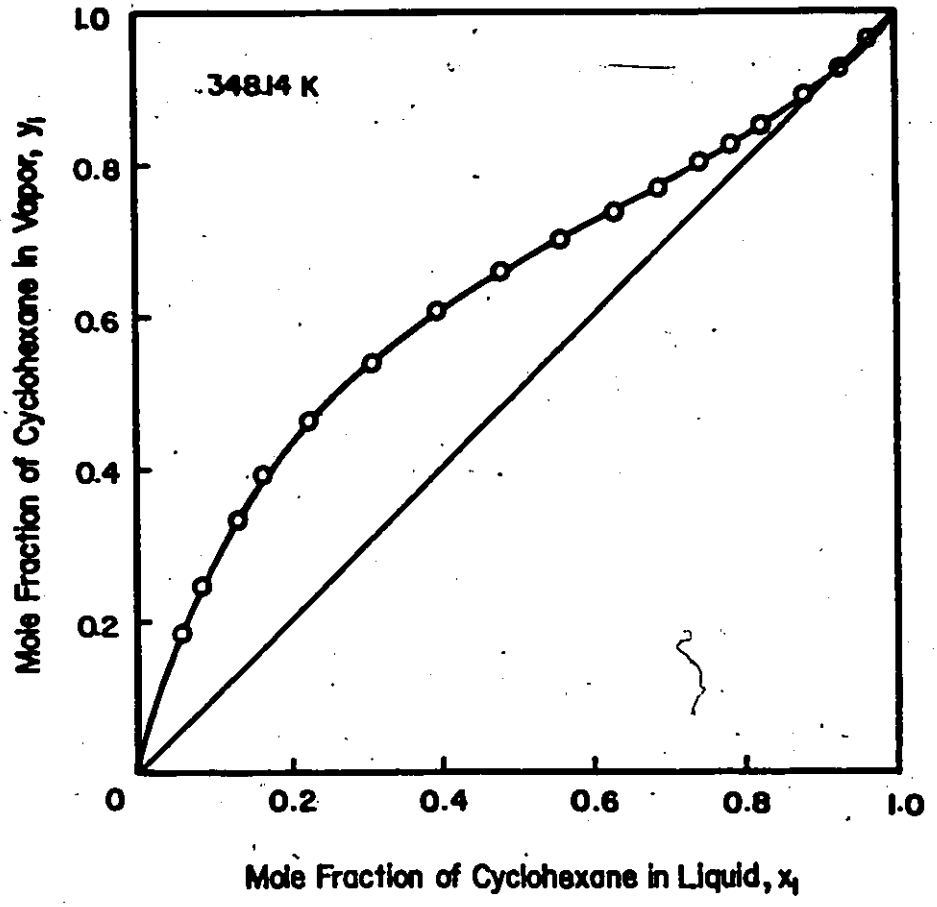

Figure 4-9: Comparison of Experimental and Calculated y_1 Values for Cyclohexane (1) and Methyl Methacrylate (2) at 348.14 K. (O, Experimental, — Calculated by the Wilson Equation)

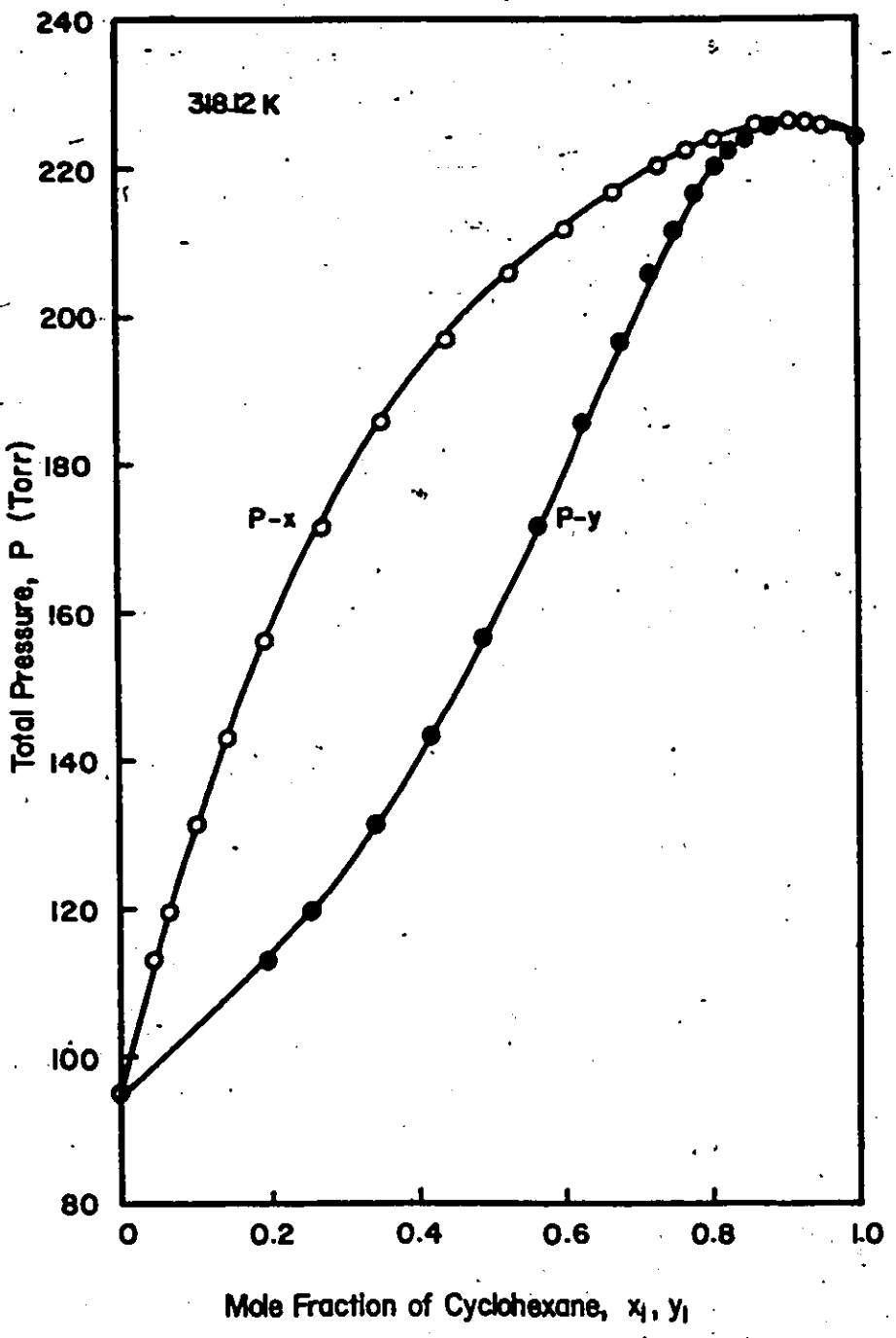

Figure 4-10: Comparison of Experimental and Calculated P and y_1 Values for Cyclohexane (1) and Methyl Methacrylate (2) at 318.12 K. (O,●, Experimental, — Calculated by the Wilson Equation)

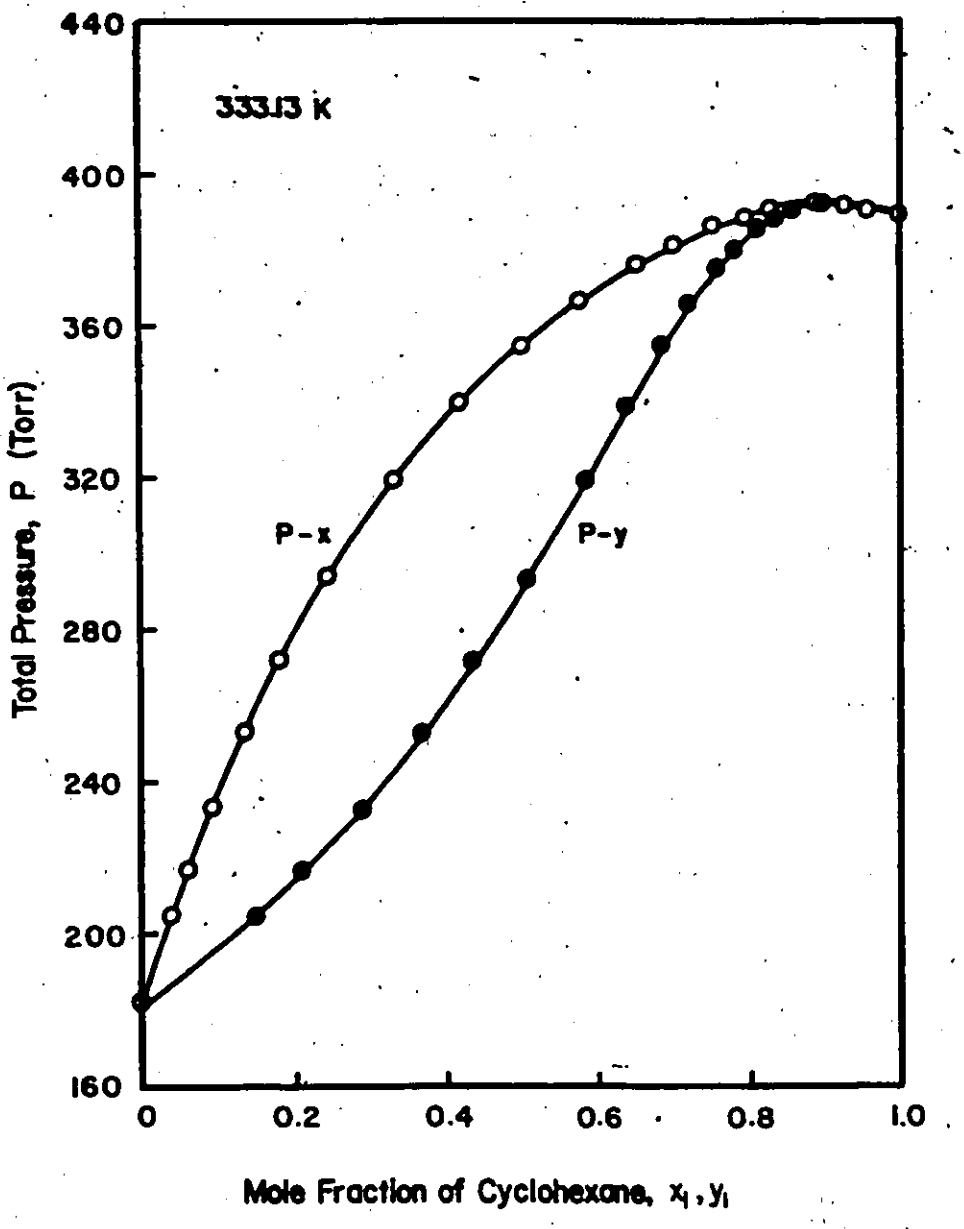

Figure 4-11: Comparison of Experimental and Calculated P and y_1 Values for Cyclohexane (1) and Methyl Methacrylate (2) at 333.13 K. (O,●, Experimental, — Calculated by the Wilson Equation)

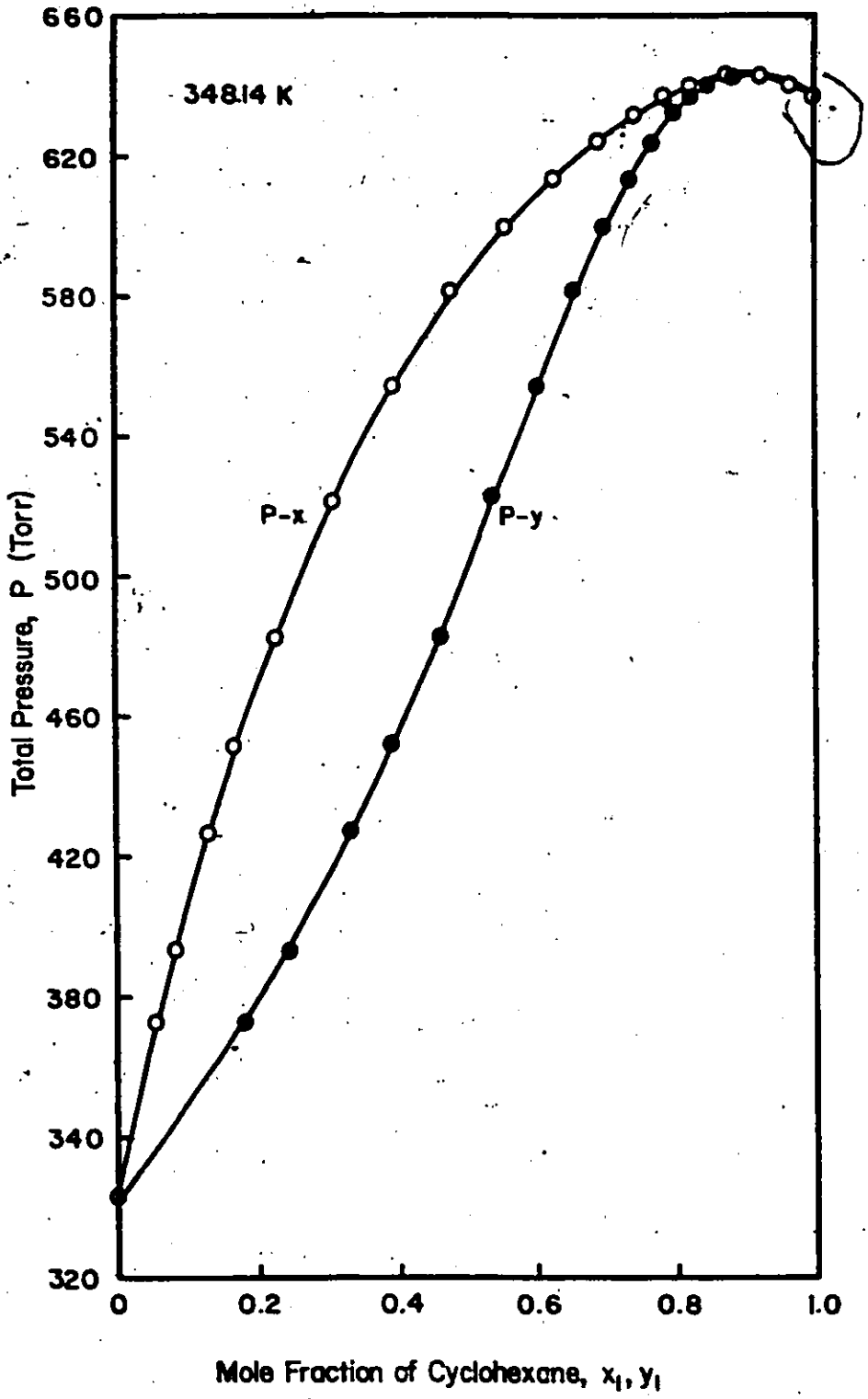

Figure 4-12: Comparison of Experimental and Calculated P and y_1 Values for Cyclohexane (1) and Methyl Methacrylate (2) at 348.14 K. (○,●, Experimental, — Calculated by the Wilson Equation)

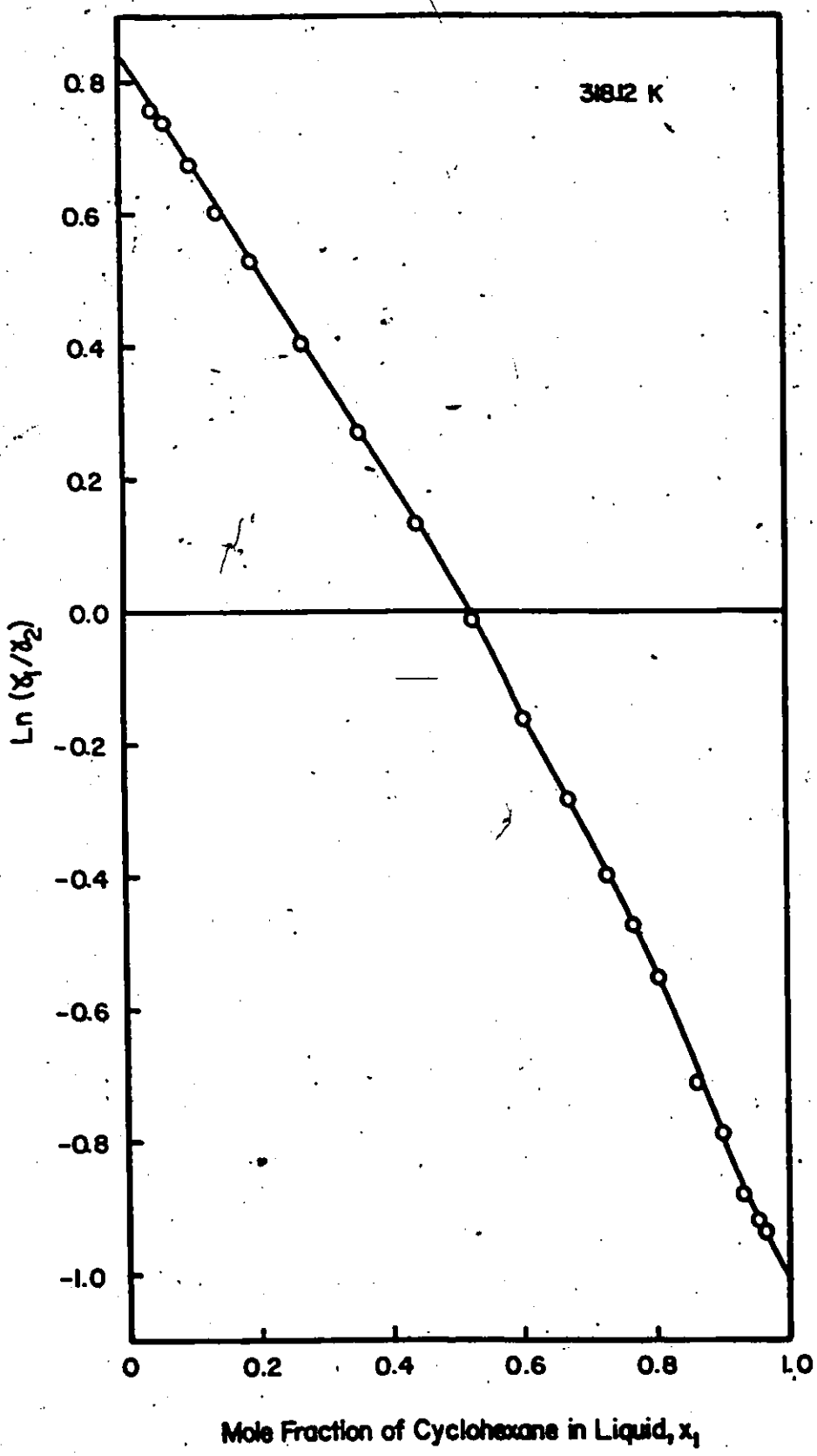

Figure 4-13: Thermodynamic Consistency Test of the Vapor-Liquid Equilibrium Data for Cyclohexane (1) and Methyl Methacrylate (2) at 318.12 K.

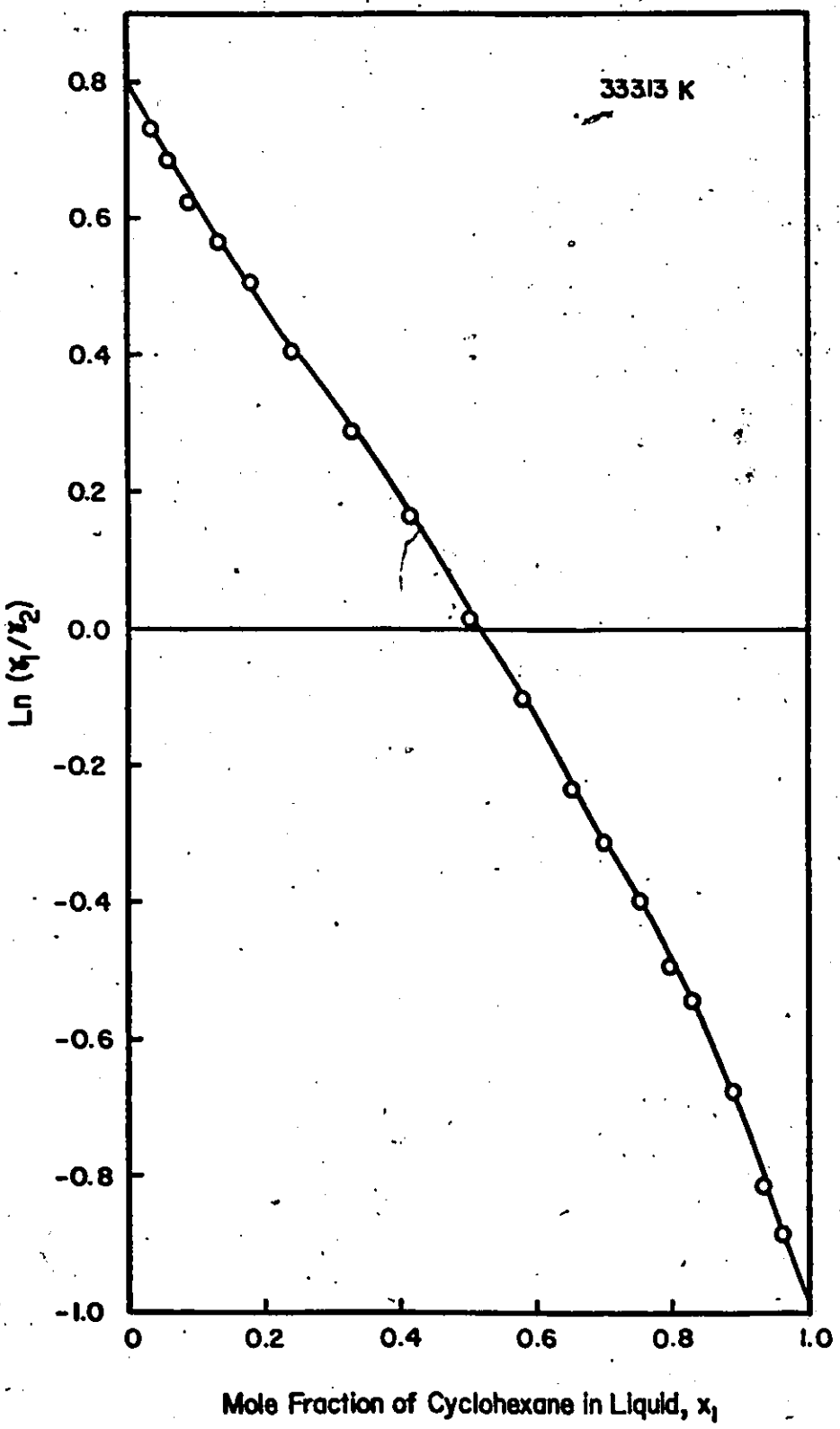

Figure 4-14: Thermodynamic Consistency Test of the Vapor-Liquid Equilibrium Data for Cyclohexane (1) and Methyl Methacrylate (2) at 333.13 K.

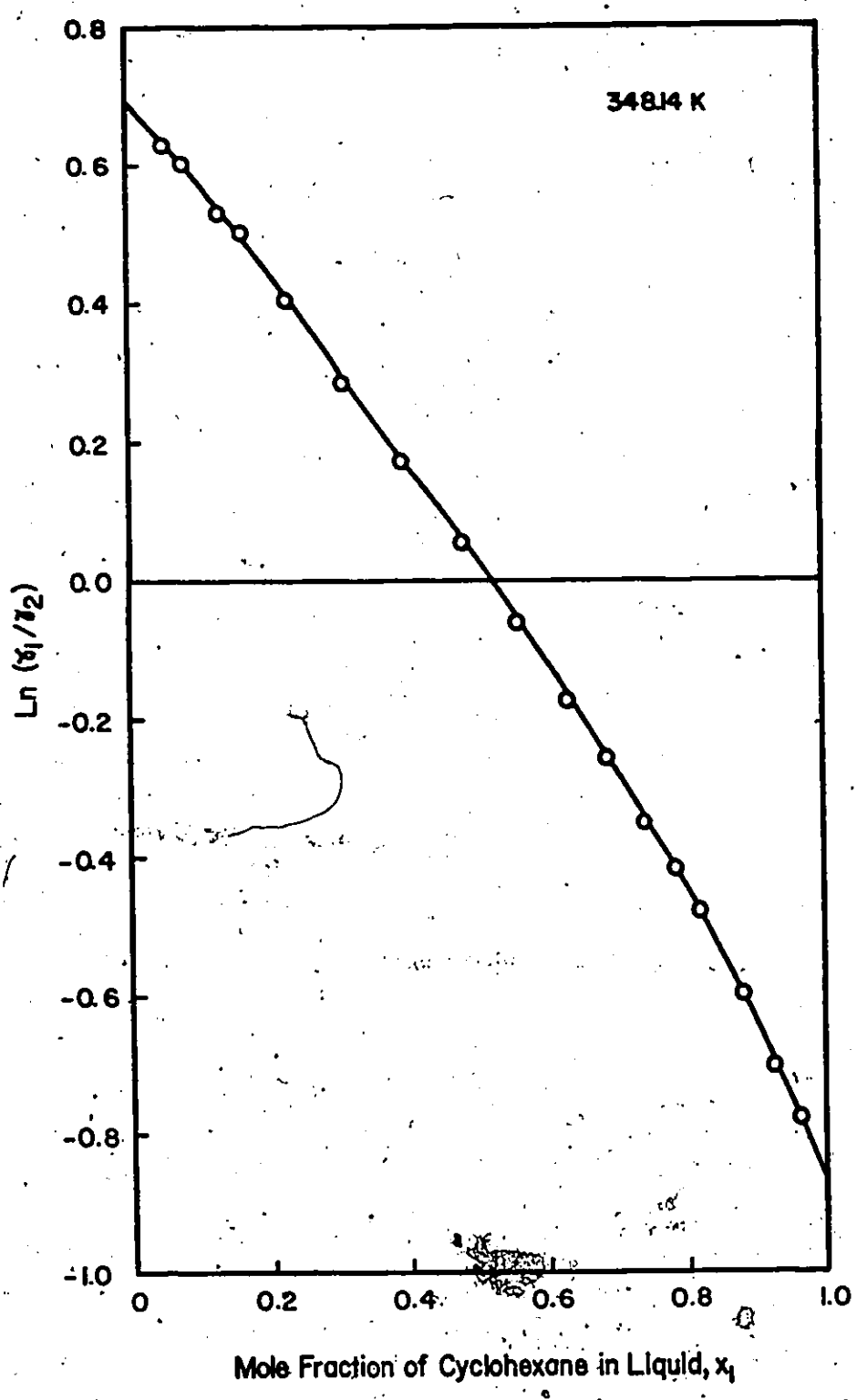

Figure 4-15: Thermodynamic Consistency Test of the Vapor-Liquid Equilibrium Data for Cyclohexane (1) and Methyl Methacrylate (2) at 348.14 K.

CHAPTER 5

CONCLUSIONS

Based upon the least-squares criterion for fitting the residual excess Gibbs free energy, the NRTL equation fitted the experimental data best at 318.12 and 333.13 K. At 348.14 K, it was the Redlich-Kister equation which gave the best fit of the data. However, it was the Wilson equation which had the smallest average absolute deviations for both the total pressure and vapor composition. And, from a practical viewpoint, it is the P-x curve that is to be approximated as closely as possible. Therefore, theoretically, the best fit was obtained from the NRTL and the Redlich-Kister equations, as they gave the best representation of the excess Gibbs free energy. However, practically, the Wilson equation fitted the data best.

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APPENDIX I

Table A1-1:

CALIBRATION OF COMPOSITION-DENSITY FOR THE SYSTEM CYCLOHEXANE (1) - METHYL METHACRYLATE (2) AT 288.15 K.

Mole Fraction Cyclohexane x_1	Density g/ml
0	0.9491
0.1055	0.9282
0.1482	0.9201
0.1911	0.9117
0.2650	0.8989
0.3345	0.8855
0.4067	0.8727
0.4841	0.8524
0.5695	0.8452
0.6669	0.8300
0.7686	0.8124
0.8081	0.8085
0.8824	0.7982
0.9277	0.7922
1.0000	0.7832

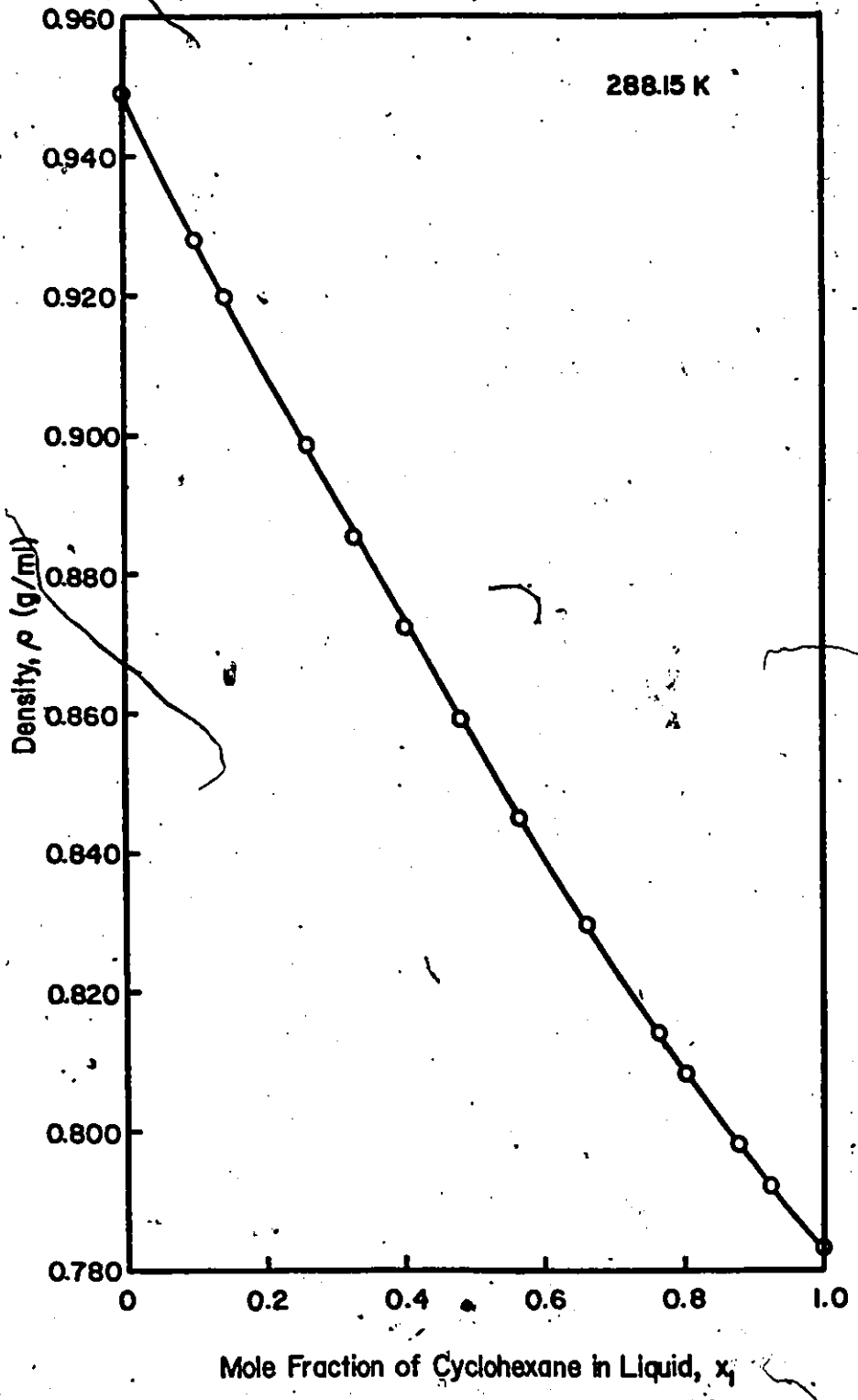

Figure A1-1: Calibration Curve of Density - Composition for Cyclohexane (1) and Methyl Methacrylate (2) at 288.15 K.

APPENDIX II

The Newton-Raphson Method of Iteration

Values of the vapor composition, y_1, and the total pressure, P, were calculated at a given temperature, T, and liquid composition, x_1, through the use of equation (2-21) once the parameters in the Wilson, the NRTL and the Redlich-Kister equations were known. The y_1 and P values were calculated by means of the Newton-Raphson iterative method as described below:

For the binary components, there are two non-linear equations for the liquid activity coefficients. The relationship, $y_1 + y_2 = 1$, was introduced into the expression for $\ln \gamma_2$. Thus, equation (2-21) was written for the two components as,

$$\ln\gamma_1 = \ln\left(\frac{y_1 P}{x_1 p_1^o}\right) + \frac{(B_{11}-v_1^o)(P-p_1^o)}{RT} + \frac{P(1-y_1)^2\delta_{12}}{RT} \qquad \text{(A2-1)}$$

$$\ln\gamma_2 = \ln\left(\frac{(1-y_1)P}{(1-x_1)p_2^o}\right) + \frac{(B_{22}-v_2^o)(P-p_2^o)}{RT} + \frac{y_1^2\delta_{12}P}{RT} \qquad \text{(A2-2)}$$

The values of $\ln \gamma_1$ and $\ln \gamma_2$ in equations (A2-1) and (A2-2) were no longer the experimental values, but those that were calculated by the three equations. Thus, the only unknowns in these equations were y_1 and P, and so equations (A2-1) and (A2-2) were written as,

$$f_1(y_1,P) = 0 \qquad \text{(A2-3)}$$

$$f_2(y_1,P) = 0 \qquad \text{(A2-4)}$$

In the first approximation to the solution of the functions f_1 and f_2, the experimental values of y_1 and P were used as initial estimates. In order to get the next approximation, the following approach was established, and for simplification, y_1 was replaced by y.

At the (k+1)th approximation, the functions $f_1(y_{k+1},P_{k+1})$ and $f_2(y_{k+1},P_{k+1})$ were expanded into a two-term Taylor series about the point (y_k,P_k).

$$f_1(y_{k+1},P_{k+1}) = f_1(y_k,P_k) + (y_{k+1}-y_k)\frac{\partial f_1(y_k,P_k)}{\partial y_k} + (P_{k+1}-P_k)\frac{\partial f_1(y_k,P_k)}{\partial P_k} + \ldots \quad \text{(A2-5)}$$

$$f_2(y_{k+1},P_{k+1}) = f_2(y_k,P_k) + (y_{k+1}-y_k)\frac{\partial f_2(y_k,P_k)}{\partial y_k} + (P_{k+1}-P_k)\frac{\partial f_2(y_k,P_k)}{\partial P_k} + \ldots \quad \text{(A2-6)}$$

Assuming that the values of y_{k+1} and P_{k+1} were both very close to the actual roots, thereby making the values of the functions $f_1(y_{k+1},P_{k+1})$ and $f_2(y_{k+1},P_{k+1})$ approximately equal to zero, equations (A2-5) and (A2-6) were simplified as follows,

$$0 = f_1(y_k,P_k) + h\frac{\partial f_1(y_k,P_k)}{\partial y_k} + k\frac{\partial f_1(y_k,P_k)}{\partial P_k} \quad \text{(A2-7)}$$

$$0 = f_2(y_k,P_k) + h\frac{\partial f_2(y_k,P_k)}{\partial y_k} + k\frac{\partial f_2(y_k,P_k)}{\partial P_k} \quad \text{(A2-8)}$$

where,

$h = y_{k+1} - y_k$ and $k = P_{k+1} - P_k$

Thus, the (k+1)th approximation of y and P was obtained from the k-th by,

$$y_{k+1} = h + y_k \qquad \text{(A2-9)}$$

$$P_{k+1} = k + P_k \qquad \text{(A2-10)}$$

The values of h and k were calculated at each iteration by solving equations (A2-7) and (A2-8). Rearranging, the following two simultaneous equations were obtained,

$$h \frac{\partial f_1(y_k,P_k)}{\partial y_k} + k \frac{\partial f_1(y_k,P_k)}{\partial P_k} = -f_1(y_k,P_k) \qquad \text{(A2-11)}$$

$$h \frac{\partial f_2(y_k,P_k)}{\partial y_k} + k \frac{\partial f_2(y_k,P_k)}{\partial P_k} = -f_2(y_k,P_k) \qquad \text{(A2-12)}$$

These simultaneous equations were solved for h and k by determinants, provided that the determinant, J, was not zero, i.e.,

$$J = \begin{vmatrix} \frac{\partial f_1(y_k,P_k)}{\partial y_k} & \frac{\partial f_1(y_k,P_k)}{\partial P_k} \\ \frac{\partial f_2(y_k,P_k)}{\partial y_k} & \frac{\partial f_2(y_k,P_k)}{\partial P_k} \end{vmatrix} \neq 0 \qquad \text{(A2-13)}$$

Hence,

$$h = \frac{\begin{vmatrix} -f_1(y_k,P_k) & \frac{\partial f_1(y_k,P_k)}{\partial P_k} \\ -f_2(y_k,P_k) & \frac{\partial f_2(y_k,P_k)}{\partial P_k} \end{vmatrix}}{J} \qquad \text{(A2-14)}$$

$$k = \frac{\begin{vmatrix} \frac{\partial f_1(y_k, P_k)}{\partial y_k} & -f_1(y_k, P_k) \\ \frac{\partial f_2(y_k, P_k)}{\partial y_k} & -f_2(y_k, P_k) \end{vmatrix}}{J} \qquad \text{(A2-15)}$$

Having determined the values of h and k, equations (A2-9) and (A2-10) were then used to get the next approximation, and the calculations were repeated until the desired accuracy in the calculated values of y and P was achieved. The computer programme that was used to perform the calculations is presented in Appendix III.

APPENDIX III

```
C THIS IS MULTIFIL AS OF JANUARY 12,1983
//          ),'GCRD.SHI                ',MSGLEVEL=(2,0),
//          CLASS=J
// EXEC FRCC=IMSLS,REGION.GO=200K,TIME.GO=(5,0)
//FORT.SYSIN DD *                                    SOURCE DECK NEXT
C ***************************************************
C  DEPARTMENT OF CHEMICAL ENGINEERING
C
C    LADY DIANE
C
C    THIS PROGRAM IS USED FOR THE
C    EVALUATION AND CORRELATION OF LIQUID
C    PHASE ACTIVITY COEFFIENTS AND GIBBS FREE
C    ENERGIES, AT GIVEN TEMPERATURE AND LIQUID
C    COMPOSITION, TOTAL PRESSURE AND VAPOR
C    COMPOSITIONS ARE CALCULATED BY MEANS
C    OF THE NEWTON-RAPHSON METHOD OF ITERATION.
C
C ***************************************************************************
C    THIS PROGRAM IS DESIGNED BY MEANS OF A CURVE FITTING  OF GE VS X
C    INSTEAD OF USING A CURVE FITTING OF GAMMA VS X
C
C
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION TC(2),PC(2),VC(2),W(2),U(2),UR(2),TT(3),PPT(30),
     *F11(30),FF1(30),F12(30),F13(30),CAMAL1(30),CAMA1(30),X2(30),
     *Y2(30),F21(30),FF2(30),F22(30),F23(30),CAMAL2(30),CAMA2(30),
     *CAMLC1(30),CAMLC2(30),CAMAC1(30),CAMAC2(30),DIFF(30),SDIFF(30),
     *PEES(30),PECEN(30),CY1(30),CPT(30),DEGE(30),DEGEC(30),GAP(30),
     *VV1(3),VV2(3),Y1(30),PT(30),CMH(30),PPP1(3),PPP2(3),
     *PECEN1(30),CTF(30),CAML(30),CCCAML(30),YAC1(30),G1D2C(30),
     *PTT(30),DIFFF(30),PEESB(30),NAME(30),X1(30),Y(30),G1D2(30)
      EXTERNAL FUNCT
      INTEGER N,NSIG,MAXFN,IOPT,NDP
      REAL  X(2), H(3), G(2), W(6), F
      COMMON /NDPT/ NDP
      READ(5,600) (NAME(IJK),IJK=1,20)
  600 FORMAT(20A4)
      WRITE(6,500) (NAME(IJK),IJK=1,20)
  500 FORMAT('1',1H1///1X,20A4)
      READ (5,401) NNN
  401 FORMAT (I1)
      PRINT 501,NNN
  501 FORMAT(//2X,'NO. OF  ISOTHERMALS =',I2,2X//)
      WRITE (6,2001)
 2001 FORMAT (///1X,9HCOMPONENT,3X,6HTC (K),3X,8HPC (ATM),3X,12HVC (CC/G
     *MOL),3X,16HACCENTRIC FACTOR,3X,21HDIPOLE MOMENT (DEBYE),3X,10HREDU
     *CED CM//)
```

```
      DO 11 I=1,2
      READ (5,402) TC(I),PC(I),VC(I),WM(I),U(I)
  402 FORMAT (F8.2, F8.2, F7.1, F7.3, F7.3)
C ***********************************************
      PC(I) = PC(I)/760.
C ***********************************************
      UR(I)=PC(I)*(U(I)**2)*100000./TC(I)**2
      PRINT 502,I,TC(I),PC(I),VC(I),WM(I),U(I),UR(I)
  502 FORMAT(4X,I1,6X,F6.2,5X,F4.1,9X,F5.1,11X,F5.3,17X,F5.3,13X,F6.3/)
   11 CONTINUE
      DO 12 J=1,ANN
      READ (5,403) NDP
  403 FORMAT (I2)
      READ (5,404) TT(J),PPP1(J),PPP2(J),VV1(J),VV2(J)
  404 FORMAT (F7.3,F8.2,F8.2,F7.2,F7.2)
      PRINT 503,TT(J),PPP1(J),VV1(J),PPP2(J),VV2(J)
      READ (5,405) YA,PPA
  405 FORMAT (F7.2, F5.1)
      PA = PPA/760.0
  503 FORMAT(//1X,13HTEMPERATURE: ,F6.3,4H (C),//5X,7HPSAT1 =,F7.2,5H (M
     *M),5X,7HVMOL1 =,F7.2,10H (CC/GMOL)/5X,7HPSAT2 =,F7.2,5H (MM),5X,7H
     *VMOL2 =,F7.2,10H (CC/GMOL))
      PRINT 504,NDP
  504 FORMAT(//2X,' NO. OF DATA POINTS =',I3)
      T=TT(J)+273.15
      V1=VV1(J)
      V2=VV2(J)
      UR1=UR(1)
      UR2=UR(2)
      WM1=WM(1)
      WM2=WM(2)
      U1=U(1)
      U2=U(2)
      TR1=T/TC(1)
      TR2=T/TC(2)
      PP1=PPP1(J)/760.
      PP2=PPP2(J)/760.
      TC1=TC(1)
      TC2=TC(2)
      PC1=PC(1)
      PC2=PC(2)
      VC1=VC(1)
      VC2=VC(2)
      CALL SECOM1(T,TC1,TC2,PC1,PC2,WM1,WM2,SS1,SS2,U1,U2,VC1,VC2,UR1,
     *UR2,TR1,TR2,B1,B2,B12,DEL)
      R=82.057
      PRINT 98
   98 FORMAT('1'///2X,'EXPERIMENTAL GAMMA'//)
```

```
      DO 13 K=1,NOP
      READ (5,406) X1(K),Y1(K),PPT(K)
  406 FORMAT (F6.3, F6.3, F6.2)
      PT(K)=PPT(K)/760.
      F11(K)=Y1(K)*PT(K)/(X1(K)*PP1)
      FF1(K)=DLOG(F11(K))
      F12(K)=(PT(K)-PP1)*(B1-V1)/(R*T)
      F13(K)=PT(K)*DEL*((1.-Y1(K))**2)/(R*T)
      CAMAL1(K)=FF1(K)+F12(K)+F13(K)
      X2(K)=1.-X1(K)
      Y2(K)=1.-Y1(K)
      F21(K)=Y2(K)*PT(K)/(X2(K)*PP2)
      FF2(K)=DLOG(F21(K))
      F22(K)=(PT(K)-PP2)*(B2-V2)/(R*T)
      F23(K)=PT(K)*DEL*((1.-Y2(K))**2)/(R*T)
      CAMAL2(K)=FF2(K)+F22(K)+F23(K)
      CAMA1(K)=DEXP(CAMAL1(K))
      CAMA2(K)=DEXP(CAMAL2(K))
      TR = 8.3144
      DEGE(K) = (X1(K)*CAMAL1(K)+(1.-X1(K))*CAMAL2(K))*TR*T
      Y(K) = DEGE(K)
      IF (K.EQ.1) WRITE (6,2003)
 2003 FORMAT (6X,2HX1,7X,2HY1,5X,10HGAM1(EXPT),3X,10HGAM2(EXPT),3X,8HLN(
     *GAM1),3X,8HLN(GAM2),3X,11HGE/RT(EXPT)//)
      PRINT 6,K,X1(K),Y1(K),CAMA1(K),CAMA2(K),CAMAL1(K),CAMAL2(K),Y(K)
    6 FORMAT(1X,I2,2X,F5.3,4X,F5.3,5X,F6.4,7X,F6.4,6X,F6.4,5X,F6.4,5X,F8
     *.4)
   13 CONTINUE
      CDEL1=0.000
      PDEL1=0.000
      ZRMS1=0.000
      PDEL=0.000
      ZRMS=0.000
      CDEL=0.000
      CDEL2=0.0
      PDEL2=0.0
      ZRMS2=0.0
      N = 2
      NSIG = 4
      MAXFN = 500
      IOPT = 0
      X(1) = 0.75
      X(2) = 0.43
      CALL ZXMIN (FUNCT,N,NSIG,MAXFN,IOPT,X,H,G,F,W,IER)
      PAR1 = -1.987*T*DLOG(V1/V2*X(1))
      PAR2 = -1.987*T*DLOG(V2/V1*X(2))
      WRITE (6,2004)
 2004 FORMAT ('1',///2X,'THE PARAMETERS IN THE WILSON EQUATION ARE:'/)
```

```
      WRITE (6,1234) FAC1,FAC2
 1234 FORMAT (1CX,5HX(1)=,F7.2,3X,5HX(2)=,F7.2)
      F = F*((TR*T)**2)
      WRITE (6,2015) F
 2015 FORMAT (///2X,'THE SUM OF THE SQUARED DIFFERENCES BETWEEN EXPERIMEN
     *TAL AND CALCULATED EXCESS GIBBS FREE ENERGY IS: ',F7.2)
      OMS1=0.000
      OMS2=0.000
      OMS3=0.000
      DO 38 JJ=1,NDP
      A12 = X1(JJ) + X(1)*(1.-X1(JJ))
      A21 = (1.-X1(JJ)) + X(2)*X1(JJ)
      DEGEC(JJ) = (-X1(JJ)*DLOG(A12) - (1.-X1(JJ))*DLOG(A21))*TR*T
      GAP(JJ)=DEGE(JJ)-DEGEC(JJ)
      OMS1=OMS1+GAP(JJ)**2
      OMS2=OMS2+DABS(GAP(JJ))
      OMM(JJ)=GAP(JJ)*100/DEGE(JJ)
      OMS3=OMS3+DABS(OMM(JJ))
      IF (JJ.EQ.1) WRITE (6,2005)
 2005 FORMAT ('1',///1X,61HEXPERIMENTAL AND CALCULATED EXCESS GIBBS FREE
     * ENERGY (J/GMOL)//)
      IF (JJ.EQ.1) WRITE (6,2006)
 2006 FORMAT (6X,2HX1,5X,8HGE(EXPT),5X,8HGE(CALC),5X,5H% DEV/)
      PRINT 47,JJ,X1(JJ),DEGE(JJ),DEGEC(JJ),OMM(JJ)
   47 FORMAT(1X,I2,2X,F5.3,3X,F8.4,5X,F8.4,4X,F7.4)
   38 CONTINUE
      GSTAND=OMS1/(NDP-2)
      SGTAND=DSQRT(GSTAND)
      GCENTA=DABS(OMS2)/NDP
      CGENTA=GCENTA
      GAPECE=OMS3/NDP
      WRITE (6,2007)
 2007 FORMAT (//1X,'THE STANDARD DEVIATION, AVERAGE ABSOLUTE DIFFERENCE
     *AND THE ABSOLUTE % DEVIATION OF THE EXCESS GIBBS FREE ENERGY ARE:'
     *//)
      PRINT 49,SGTAND,CGENTA,GAPECE
   49 FORMAT(2X,3F20.4)
      DO 14 M=1,NDP
      A12 = X1(M) + X(1)*(1.-X1(M))
      A21 = (1.-X1(M)) + X(2)*X1(M)
      CAMLC1(M)=-DLOG(A12) + (1.-X1(M))*(X(1)/A12 - X(2)/A21)
      CAMLC2(M)=-DLOG(A21) - X1(M)*(X(1)/A12 - X(2)/A21)
      CCAML(M)=CAMAL1(M)-CAMAL2(M)
       CCCAML(M)=CAMLC1(M)-CAMLC2(M)
      CAMAC1(M)=DEXP(CAMLC1(M))
      CAMAC2(M)=DEXP(CAMLC2(M))
      DIFF(M)=CAMLC1(M)-CAMAL1(M)
      SDIFF(M)=DIFF(M)**2
```

```
      PERS(M)=DIFF(M)*100/CAMAL1(M)
      DIFF(M)=CAMLC2(M)-CAMAL2(M)
      PERSE(M)=DIFFE(M)*100./CAMAL2(M)
      CDEL=CDEL+CABS(DIFF(M))
      PDEL=PDEL+CABS(PERS(M))
      ZRMS=ZRMS+SDIFF(M)
      DIFF1=CAMAC1(M)-CAMA1(M)
      SDIFF1=DIFF1**2
      PERS1=DIFF1*100/CAMA1(M)
      CDEL1=CDEL1+DABS(DIFF1)
      PDEL1=PDEL1+DABS(PERS1)
      ZRMS1=ZRMS1+SDIFF1
      DIFF2=CAMAC2(M)-CAMA2(M)
      SDIFF2=DIFF2**2
      PERS2=DIFF2*100./CAMA2(M)
      CDEL2=CDEL2+DABS(DIFF2)
      PDEL2=PDEL2+CABS(PERS2)
      ZRMS2=ZRMS2+SDIFF2
      IF (M.EQ.1) WRITE (6,2008)
2008  FORMAT ('1',///6X,2HX1,7X,2HY1,6X,8HLN(GAM1),3X,8HLN(GAM1),3X,5HX
     *DEV,6X,8HLN(GAM2),3X,8HLN(GAM2),3X,5HX DEV)
      IF (M.EQ.1) WRITE (6,2009)
2009  FORMAT (24X,6H(EXPT),5X,6H(CALC),16X,6H(EXPT),5X,6H(CALC)//)
   14 PRINT 18,M,X1(M),Y1(M),CAMAL1(M),CAMLC1(M),PERS(M),CAMAL2(M),
     *CAMLC2(M),PERSE(M)
   18 FORMAT(1X,I2,2X,F5.3,4X,F5.3,4X,F7.5,4X,F7.5,4X,F6.2,5X,F7.5,4X,F7
     *.5,4X,F6.2)
      DRMS2=DABS(ZRMS2)/(NDP-2)
      RMS2=DSQRT(DRMS2)
      ABSPE2=PDEL2/NDP
      SDEL2=DABS(CDEL2)/NDP
      PERSE2=SDEL2
      DRMS1=DABS(ZRMS1)/(NDP-2)
      RMS1=DSQRT(DRMS1)
      ABSPE1=PDEL1/NDP
      SDEL1=DABS(CDEL1)/NDP
      PERSE1=SDEL1
      DRMS=DABS(ZRMS)/(NDP-2)
      RMS=DSQRT(DRMS)
      ABSPER=PDEL/NDP
      SDEL=DABS(CDEL)/NDP
      PERSE=SDEL
      WRITE (6,2010)
2010  FORMAT (//1X,'RMS, AVERAGE ABSOLUTE AND AVERAGE ABSOLUTE % DEVIATI
     *ON OF LN(GAMMA1)')
      PRINT 16,RMS,PERSE,ABSPER
   16 FORMAT(/3X,3F15.4)
      PRINT 229
```

```
      229 FORMAT(///1X,'RMS, AVERAGE ABSOLUTE AND AVERAGE ABSOLUTE % DEVIATIO
     *N OF GAMMA1')
          PRINT 227,RMS1,PERSE1,ABSPE1
      227 FORMAT(/3X,3F15.4)
          PRINT 230
      230 FORMAT(///1X,'RMS, AVERAGE ABSOLUTE AND AVERAGE ABSOLUTE % DEVIATIO
     *N OF GAMMA2')
          PRINT 231,RMS2,PERSE2,ABSPE2
      231 FORMAT(/3X,3F15.4)
          DO 1000 M=1,NDP
          G102(M) = CAMAL1(M) - CAMAL2(M)
          G102C(M) = CAMLC1(M) - CAMLC2(M)
          IF (M.EQ.1) WRITE (6,2012)
     2012 FORMAT ('1',///6X,2HX1,5X,13HLN(GAM1/GAM2),3X,13HLN(GAM1/GAM2))
          IF (M.EQ.1) WRITE (6,2013)
     2013 FORMAT (16X,6H(EXPT),10X,6H(CALC)//)
          WRITE (6,2014) M,X1(M),G102(M),G102C(M)
     2014 FORMAT(1X,I2,2X,F5.3,5X,F7.4,9X,F7.4)
     1000 CONTINUE
          CALL CALPY(NDP,V1,V2,PP1,PP2,PT,X1,Y1,DEL,B1,B2,T,CAMAC1,CAMAC2,
     *CY1,CPT)
          SUM1=0.000
          SUM=0.000
          SSUM1=0.000
          SSUM=0.000
          SSSUM1=0.000
          SSSUM=0.000
          DO 15 L=1,NDP
          DYY=Y1(L)-CY1(L)
          CPT(L) = CPT(L)*760.
          DPP=PPT(L)-CPT(L)
          PECEN(L)=(Y1(L)-CY1(L))*100/Y1(L)
          PECEN1(L)=(CPT(L)-PPT(L))*100/PPT(L)
          SUM=SUM+(Y1(L)-CY1(L))**2
          SUM1=SUM1+(PPT(L)-CPT(L))**2
          SSUM=SSUM+DABS(DYY)
          SSUM1=SSUM1+DABS(DPP)
          SSSUM=SSSUM+DABS(PECEN(L))
          SSSUM1=SSSUM1+DABS(PECEN1(L))
          IF (L.EQ.1) WRITE (6,2011)
     2011 FORMAT ('1',///6X,2HX1,5X,8HY1(EXPT),3X,8HY1(CALC),3X,5H% DEV,6X,1
     *1HP(MM)(EXPT),3X,11HP(MM)(CALC),3X,5H% DEV//)
       15 PRINT 41,L,X1(L),Y1(L),CY1(L),PECEN(L),PPT(L),CPT(L),PECEN1(L)
       41 FORMAT(1X,I2,2X,F5.3,5X,F5.3,5X,F5.3,5X,F5.2,6X,F6.2,8X,F6.2,6X,F5
     *.2)
          STAND=DABS(SUM)/(NDP-2)
          DSTAND=DSQRT(STAND)
          CENTA=DABS(SSUM)/NDP
```

```
238.            APECEN=SSSUM/NDP
239.            PSTAND=DABS(SUM1)/(NDP-2)
240.            PPSTAN=DSQRT(PSTAND)
241.            PPECEN=SSSUM1/NDP
242.            CENTAP=DABS(SSUM1)/NDP
243.            DCENTA=CENTA
244.            DCENTP=CENTAP
245.            PRINT 78
246.         78 FORMAT(//1X,'RMS, AVERAGE ABSOLUTE AND AVERAGE ABSOLUTE % DEVIATIO
246.1          *N OF Y1')
247.            PRINT 79,DSTAND,DCENTA,APECEN
248.         79 FORMAT(/3X,3F15.4)
249.            PRINT 54
250.         54 FORMAT(//1X,'RMS, AVERAGE ABSOLUTE AND AVERAGE ABSOLUTE % DEVIATIO
250.1          *N OF P')
251.            PRINT 59,PPSTAN,DCENTP,PPECEN
252.         59 FORMAT(/3X,3F15.4)
267.            IF(YA.LT. 0.0) GO TO 12
268.            CALL CALZXP(V1,V2,PP1,PP2,T,YA,PA,DEL,B1,B2,X,YYAC1,PCA)
269.         12 CONTINUE
271.            STOP
272.            END
273.      C ***************************************************************************
274.      C
275.      C
276.      C   PREDICTION OF THE SECOND VIRIAL COEFFICIENTS
277.      C   USING THE CORRELATION OF TSONOPOULOS
278.      C
279.      C
280.      C ***************************************************************************
281.            SUBROUTINE SECCN1(T,TC1,TC2,PC1,PC2,WH1,WH2,S61,SS2,U1,U2,VC1,
282.           *VC2,UR1,UR2,TF1,TR2,B1,B2,B12,DEL)
283.            IMPLICIT REAL*8(A-H,O-Z)
283.1           REAL KIJ
284.            R=82.057
285.            FBO1=0.1445-0.330/TR1-0.1385/TR1**2-0.0121/TR1**3-0.000807/TR1**8
286.            FB11=0.0637+0.331/TR1**2-0.423/TR1**3-0.008/TR1**8
287.            IF(UR1 .LT. 4.0) GO TO 420
288.            FU1=-5.23722C+5.6658C7*(DLOG(UR1))-2.13361**(DLOG(UR1)**2)
289.           *+0.2525373*(DLOG(UR1)**3)+(5.789770-6.181427*(DLOG(UR1))+2.283270*
290.           *(DLOG(UR1)**2)-0.2649074*(DLOG(UR1)**3))/TF1
291.            GO TO 421
292.        420 FU1 = T*0.0
293.        421 CONTINUE
295.            TOTL1=FBO1+WH1*FB11+FU1
296.            B1=R*TC1*TOTL1/PC1
297.            FBO2=0.1445-0.330/TR2-0.1385/TR2**2-0.0121/TR2**3-0.000807/TR2**8
298.            FB22=0.0637+0.331/TR2**2-0.423/TR2**3-0.008/TR2**8
```

```
299.            IF(UR2 .LT. 4.0) GO TO 422
300.            FU2=(-2.140E-4*UR2-4.308E-21*(UR2**8))/(TR2**6)
303.            GO TO 423
304.          422 FU2=T*0.0
305.          423 CONTINUE
307.            TOTL2=FBC2+WH2*FB22+FU2
308.            B2=R*TC2*TOTL2/PC2
309.      C
310.      C CROSS SECOND VIRIAL COEFFICIENTS
311.      C
312.            TTC12=TC1*TC2
312.1           KIJ = 0.00
313.            TC12=DSQRT(TTC12)*(1.- KIJ)
314.            WH12=(WH1+WH2)/2.
315.            PVC=PC1*VC1/TC1+PC2*VC2/TC2
316.            RS=1./3.
317.            VC12=((VC1**RS+VC2**RS)/2.)**3
318.            PC12=4*TC12*PVC/VC12
319.            UR12=10000.*U1*U2*PC12/TC12**2
321.            TR12=T/TC12
322.            FBC12=0.1445-0.330/TR12-0.1385/TR12**2-0.0121/TR12**3
322.1          *-0.000607/TR12**8
323.            FB12=0.0637+0.331/TR12**2-0.423/TR12**3-0.008/TR12**8
324.            IF(UR12 .LT. 400.0)  GO TO 424
325.            FU12=-5.237220+5.665807*(DLOG(UR12))-2.133816*(DLOG(UR12)**2)
326.           *+0.2525373*(DLOG(UR12)**3)+(5.769770-6.181427*(DLOG(UR12))+
327.           *2.283279*(DLOG(UR12)**2)-0.2649074*(DLOG(UR12)**3))/TR12
328.            GO TO 425
329.          424 FU12=TR12*0.0
330.          425 CONTINUE
332.            TOTL12=FBC12+WH12*FB12+FU12
333.            B12=R*TC12*TOTL12/PC12
334.            DEL=2*B12-B1-B2
334.1           WRITE (6,2002) KIJ
334.2        2002 FORMAT (//1X, 36HSECOND VIRIAL COEFFICIENTS (CC/GMOL),6X,6HKIJ =,
334.3          *F6.2,1H)/)
335.            PRINT 4,B1,B2,B12,DEL
336.          4 FORMAT(4X,3HB1=,F10.3,4X,3HB2=,F10.3,4X,4HB12=,F10.3,4X,4HDEL=,F9.
336.1          *3//)
337.            RETURN
338.            END
339.      C     ***********************************************************************
340.      C
341.      C FUNCT CALCULATES F WHICH IS THE SQUARE OF THE DIFFERENCE BETWEEN
342.      C       EXPERIMENTAL AND CALCULATED EXCESS GIBBS FREE ENERGY.
343.      C
344.      C     ***********************************************************************
345.      C
```

```
      SUBROUTINE FUNCT (N,X,F)
      INTEGER N, NDP
      REAL X(N),F,X1(30),Y(30),YC(30)
      COMMON /ACCPT/ NDP
      TR = 6.3144348.14
      X1(1) = C.C47
      X1(2) = 0.066
      X1(3) = 0.103
      X1(4) = 0.145
      X1(5) = 0.197
      X1(6) = 0.273
      X1(7) = 0.357
      X1(8) = 0.443
      X1(9) = C.529
      X1(10) = C.605
      X1(11) = C.671
      X1(12) = C.731
      X1(13) = C.771
      X1(14) = C.807
      X1(15) = C.867
      X1(16) = C.907
      X1(17) = 0.935
      X1(18) = 0.956
      X1(19) = 0.964
      Y(1) = 0.C3679
      Y(2) = 0.04915
      Y(3) = 0.07637
      Y(4) = 0.10387
      Y(5) = 0.13633
      Y(6) = 0.17474
      Y(7) = 0.20722
      Y(8) = 0.22417
      Y(9) = 0.23075
      Y(10) = 0.22572
      Y(11) = 0.21248
      Y(12) = 0.19158
      Y(13) = 0.17333
      Y(14) = C.15534
      Y(15) = 0.11847
      Y(16) = 0.08793
      Y(17) = C.06273
      Y(18) = C.04367
      Y(19) = 0.03607
      F = 0.0
      DO 340 I=1,NDP
      A12 = X1(I) + X(1)*(1.-X1(I))
      A21 = (1.-X1(I)) + X(2)*X1(I)
      YC(I) = -X1(I)*DLOG(A12) - (1.-X1(I))*DLOG(A21)
```

```
      F = F + (Y(I) - YC(I))**2
  340 CONTINUE
      RETURN
      END
C     ******************************************************************
C
C     CALCULATIONS OF VAPOR COMPOSITIONS
C     AND TOTAL PRESSURES BY MEANS OF
C     NEWTON-RAPHSON METHOD OF ITERATION
C
C     ******************************************************************
      SUBROUTINE CALPY(NN,V1,V2,PP1,PP2,PT,X1,Y1,DEL,B1,B2,T,CAMAC1,
     *CAMAC2,CY1,CPT)
      IMPLICIT REAL*8(A-H,O-Z)
        DIMENSION PT(30),X1(30),Y1(30),CAMAC1(30),CAMAC2(30),ZX1(30),
     *CY1(30),CPT(30),ZAMAC1(30),ZAMAC2(30),DECY1(50),DECPT(50)
        R=82.057
      DO 22 I=1,NN
      ZX1(I)=X1(I)
      ZAMAC1(I)=CAMAC1(I)
      ZAMAC2(I)=CAMAC2(I)
      CY1(I)=Y1(I)
      CPT(I)=PT(I)
      DO 23 J=1,50
      SF11=((CPT(I)-PP1)*(B1-V1))/(R*T)+(CPT(I)*DEL*((1.-CY1(I))**2))/
     *(T*R)
      SF1=DEXP(SF11)
      F1=SF1-ZAMAC1(I)*ZX1(I)*PP1/(CY1(I)*CPT(I))
      SF21=((CPT(I)-PP2)*(B2-V2))/(T*R)+(CPT(I)*DEL*(CY1(I)**2))/(T*R)
      SF2=DEXP(SF21)
      F2=SF2-ZAMAC2(I)*(1.-ZX1(I))*PP2/((1.-CY1(I))*CPT(I))
      FF1=-2*CPT(I)*DEL*(1.-CY1(I))*SF1/(R*T)+ZAMAC1(I)*ZX1(I)*PP1/
     *((CY1(I)**2)*CPT(I))
      FF2=(B1-V1)*SF1/(R*T)+ZAMAC1(I)*ZX1(I)*PP1/((CPT(I)**2)*CY1(I))
      G1=2*CY1(I)*CPT(I)*DEL*SF2/(R*T)-ZAMAC2(I)*(1.-ZX1(I))*PP2/
     *(((1.-CY1(I))**2)*CPT(I))
      G2=(B2-V2)*SF2/(T*R)+ZAMAC2(I)*(1.-ZX1(I))*PP2/((CPT(I)**2)*
     *(1.-CY1(I)))
      CCPIB=FF1*G2-FF2*G1
      C=-F1*G2+FF2*F2
      S=-F2*FF1+G1*F1
      DECY1(J)=C/CCPIB
      DECPT(J)=S/CCPIB
      IF(DABS(F1).LE.0.0000001.AND.DABS(F2).LE.0.0000001) GO TO 22
      IF(I.EQ.50) GO TO 707
      DEMAX1=CY1(I)*0.2
      DEMAX2=CPT(I)*0.2
      IF(DABS(DECY1(J)).GT.DEMAX1) DECY1(J)=DSIGN(DEMAX1,DECY1(J))
```

```
      IF(ABS(DECPT(J)).GT.DEMAX2) DECPT(J)=DSIGN(DEMAX2,DECPT(J))
      CY1(I)=CY1(I)+DECY1(J)
      CPT(I)=CPT(I)+DECPT(J)
      GO TO 23
  707 PRINT 505
  505 FORMAT('0','ITERATION NO IS OUT OF RANGE')
   23 CONTINUE
   22 CONTINUE
      RETURN
      END
C     ******************************************************************
C
C     THE CALCULATION OF AZEOTROPIC COMPOSITION AND PRESSURE
C
C     ******************************************************************
      SUBROUTINE CALAZP(V1,V2,PP1,PP2,T,YA,PA,DEL,B1,B2,X,
     *YYAC1,PCA)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION YAC1(90),YAC2(90),CAMLA1(90),CAMLA2(90),CAMAL1(90),
     *CAMAL2(90),PAC(90),DEYAC1(90),DEPAC(90)
      REAL X(2)
      R=82.057
      DO 25 I=1,90
      IF(I.EQ.1) PAC(I)=PA
      IF(I.EQ.1) YAC1(I)=YA
      YAC2(I)=1.-YAC1(I)
      A12 = YAC1(I) + YAC2(I)*X(1)
      A21 = YAC2(I) + YAC1(I)*X(2)
      CAMLA1(I)=-DLOG(A12) + YAC2(I)*(X(1)/A12-X(2)/A21)
      CAMLA2(I)=-DLOG(A21) - YAC1(I)*(X(1)/A12-X(2)/A21)
      CAMAL1(I)=DEXP(CAMLA1(I))
      CAMAL2(I)=DEXP(CAMLA2(I))
      SF11=((PAC(I)-PP1)*(B1-V1))/(R*T)+(PAC(I)*DEL*((1.-YAC1(I))**2))/
     *(T*R)
      SF1=DEXP(SF11)
      F1=SF1-CAMAL1(I)*YAC1(I)*PP1/(YAC1(I)*PAC(I))
      SF21=((PAC(I)-PP2)*(B2-V2))/(T*R)+(PAC(I)*DEL*(YAC1(I)**2))/
     *(T*R)
      SF2=DEXP(SF21)
      F2=SF2-CAMAL2(I)*(1.-YAC1(I))*PP2/((1.-YAC1(I))*PAC(I))
      FF1=-2*PAC(I)*DEL*(1.-YAC1(I))*SF1/(T*R)+CAMAL1(I)*YAC1(I)*PP1/
     *((YAC1(I)**2)*PAC(I))
      FF2=(B1-V1)*SF1/(T*R)*CAMAL1(I)*YAC1(I)*PP1/((PAC(I)**2)*YAC1(I))
      G1=2*YAC1(I)*PAC(I)*DEL*SF2/(R*T)-CAMLA2(I)*(1.-YAC1(I))*PP2/
     *(((1.-YAC1(I))**2)*PAC(I))
      G2=(B2-V2)*SF2/(T*R)+CAMAL2(I)*(1.-YAC1(I))*PP2/((PAC(I)**2)*(1.-
     *YAC1(I)))
```

```
            COMB=F1*G2-F2*G1
            G=-1.*G2*F1/F2
            S=-F2*F1+G1*F1
            DEYAC1(I)=G/COMBIN
            DEPAC(I)=S/COMBIN
            IF(DABS(F1).LE.0.0000001.AND.DABS(F2).LE.0.0000001) GO TO 22
            IF(I.EQ.20) GO TO 30
            DEMAX1=YAC1(I)*0.001
            DEMAX2=PAC(I)*0.01
            IF(DABS(DEYAC1(I)).GT.DEMAX1) DEYAC1(I)=DSIGN(DEMAX1,DEYAC1(I))
            IF(DABS(DEPAC(I)).GT.DEMAX2) DEPAC(I)=DSIGN(DEMAX2,DEPAC(I))
            YAC1(I+1)=YAC1(I)+DEYAC1(I)
            PAC(I+1)=PAC(I)+DEPAC(I)
            PCA=PAC(I+1)*760.
            YYAC1=YAC1(I+1)*1.
         25 CONTINUE
         22 PRINT 27
         27 FORMAT('1',///2X,'THE AZEOTROPIC COMPOSITION AND PRESSURE ARE:')
            PRINT 28,YYAC1,PCA
         28 FORMAT(//3X,4HXAZ=,F6.3,6X,4HPAZ=,F7.2)
            GO TO 32
         30 PRINT 31
         31 FORMAT('0','ITERATION NO IS OUT OF RANGE')
         32 RETURN
            END
   //GO.SYSIN DD *
```