EVALUATION OF TWO EQUILIBRIUM STILLS FOR MEASURING LOW-PRESSURE VAPOR-LIQUID EQUILIBRIA

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FOR MEASURING LOW-PRESSURE

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PREFACE

Two existing equilibrium stills were evaluated to compare their ease of operation and the accuracy of the data they produce. The objective is to establish a reliable method for obtaining thermodynamically consistent low-pressure vapor-liquid equilibrium (VLE) data. Vapor pressures for deionized water, methylcyclohexane, hexane, and toluene were measured in the range of 350 mm Hg to 760 mm Hg. VLE data were obtained for the isobaric systems methylcyclohexane + toluene and hexane + toluene and the isothermal system methylcyclohexane + toluene at 90°C. The vapor-pressure data were precise but not accurate in comparison to literature sources. In comparison, the VLE data were thermodynamically consistent and consistent with much of the literature data.

I would like to express my gratitude to and admiration for my advisors on this project, Dr. Robert L. Robinson Jr. and Dr. Khaled A. M. Gasem. Advisors of better quality could not be found; their guidance has made me a better researcher and engineer. I would also like to thank Dr. Martin High for serving on my advisory committee.

I would also like to recognize my family; without their love and support this journey would have been much more difficult. My husband and best friend, Brett, has been my supporter, my editor, and bringer-of-coffee during all-night data collection. My parents, Dan and Janis, have provided me with guidance and financial support throughout

the years and without them I would not have achieved this much. My grandparents, Lee and Lois Graham, have provided me with a Christian foundation and financial support. My sisters, Mindy and Kami, have provided me with love and support.

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LIST OF SYMBOLS

B	Second virial coefficient
f	Fugacity
G	Gibb's energy
H	Enthalpy
i,j	Chemical species i or j
m	Number of components in system
n	Number of moles
P	Pressure
P^s	Saturation vapor pressure
R	Gas constant
S	Entropy
T	Temperature
U	Internal energy
V	Volume
v	Molar volume
x	Liquid mole fraction
y	Vapor mole fraction
Z	Compressibility factor
α,β	Phase of component

γ	Activity coefficient
Δ	Difference
Λ	Model parameter
μ	Chemical potential
Φ	Fugacity coefficient
Φ^s	Fugacity coefficient at saturation conditions

Chapter 1

Introduction

"The separation of components in a chemical stream constitutes a major portion of all processes in the chemical and petroleum industries. For the design engineer trying to size equipment, predict operating costs, or design control schemes for new and existing separation processes, knowledge of the thermodynamic behavior of the system becomes invaluable." (Gess, Danner et al. 1991)

Vapor-liquid equilibrium (VLE) data are used to design separation equipment, derive new mathematical models, and check existing models. Therefore, a large, accurate database and the capability of producing additional accurate data are necessary. "The direct measurement of VLE remains an important source of information concerning the equilibrium properties of fluid mixtures. This is a consequence mainly of the dubious reliability of existing literature data, which may in addition cover pressure and temperature ranges different from those desired." (Malonowski 1982) Sometimes the literature does not contain data for the system to be studied and therefore, "high-accuracy VLE data are indispensable, and in most cases new, reliable and accurate, measurements should be made." (Malonowski 1982)

The purpose of this study is to evaluate two existing equilibrium stills and determine the reliability and ease of use of each and, most importantly, the accuracy of the data they produce. One of the equilibrium stills was used in a previous study by Sura (Sura 1991); however, the systems containing methylcyclohexane deviated seriously from literature data at high concentrations of methylcyclohexane. Since

methylcyclohexane is highly hygroscopic and was not given special consideration in the previous study. one reason for deviation could be the adsorption of water from the atmosphere. This possible source of error was eliminated in the current study by only opening methylcyclohexane under a nitrogen blanket. The objective is to establish a reliable facility for obtaining thermodynamically consistent low-pressure vapor liquid equilibrium data. Evaluation of the equilibrium stills involved measuring vapor pressures, isobaric VLE data, and isothermal VLE data. Vapor-pressure measurements were taken in the range of 350 mmHg to 760 mmHg for deionized water, hexane, toluene, and methylcyclohexane. The binary data consisted of the following systems: methylcyclohexane + toluene at 760 mmHg, methylcyclohexane + toluene at 90°C, and hexane + toluene at 760 mmHg. These systems were chosen due to the large number of existing data sets available for comparison and the availability of high purity chemicals; in addition, their refractive indices were sufficiently different that analysis by refractometry was acceptable.

The VLE data were subjected to consistency tests to determine the quality. These "consistency" tests included instrumental, internal, external, and thermodynamic consistency tests. Data that do not satisfy any consistency test may be discarded with the knowledge they are incorrect. If data are deemed consistent with all tests performed, then the data are probably correct. However, it is possible that "data can pass a thermodynamic consistency test and still be erroneous. For example, a systematic error in the temperature calibrations would go undetected in most, if not all, thermodynamic consistency tests when applied to an isothermal data set" (Jackson and Wilsak 1995). The following chapters detail the equipment, experimental method, and the evaluation

methods for the two existing equilibrium stills in the School of Chemical Engineering at Oklahoma State University.

Chapter 2

Background

Thermodynamics of Phase Behavior

The internal energy of a closed, homogeneous system is a function of entropy and volume and can be expressed as (Gess, Danner et al. 1991):

$$dU = TdS - PdV \tag{2-1}$$

where U = internal energy

S = entropy

V = volume

T = temperature

P = pressure

For a system to be at equilibrium, the internal energy must be at a minimum at constant entropy and constant volume. Equation 2-1 requires entropy and volume data which are not readily available or easy to obtain experimentally; therefore, an equivalent expression with experimentally available variables is desirable. An expression explicit in temperature and pressure can be obtained in the following manner. Define enthalpy, H, as

$$H = U + PV \tag{2-2}$$

Now, differentiation and substitution into Equation 2-1 results in the following

$$dH = TdS + VdP \tag{2-3}$$

The Gibbs energy is defined as

$$G = H - TS \tag{2-4}$$

and differentiation of the Gibbs energy yields

$$dG = dH - TdS - SdT \tag{2-5}$$

Now, substitution of Equation 2-3 into Equation 2-5 gives the following equation explicit in temperature and pressure

$$dG = -SdT + VdP \tag{2-6}$$

If a system is at equilibrium, the temperature and pressure do not change and the Gibbs energy must be at a minimum (Gess, Danner et al. 1991).

$$dG_{T,P} = 0 \tag{2-7}$$

For a system with more than one component, internal energy is also a function of the number of moles of each component present (Gess, Danner et al. 1991).

$$U = f(S, V, n_1, n_2, \ldots, n_m) \tag{2-8}$$

where m is the number of components in the system.

In 1875, J. Willard Gibbs defined chemical potential, μ. The concept of chemical potential is used to describe a system at equilibrium. (Prausnitz, Lichtenthaler et al. 1986)

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j} \tag{2-9}$$

Equation (2-1) becomes

$$dU = TdS - PdV + \sum \mu_i dn_i \tag{2-10}$$

Following the same development used to obtain Equation 2-6 (Prausnitz, Lichtenthaler et al. 1986),

$$dG = -SdT + VdP + \sum \mu_i dn_i \tag{2-11}$$

and

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} \tag{2-12}$$

For a system at equilibrium, the chemical potential of each component, i, must be the same in every phase (α,β,etc). (Prausnitz, Lichtenthaler et al. 1986)

$$\mu_i^{\alpha} = \mu_i^{\beta} \tag{2-13}$$

The chemical potential must be related to physically meaningful quantities in order to analyze phase behavior. G.N. Lewis defined fugacity, f_i, which provides a means to relate thermodynamic variables to physically measurable variables.

$$\mu_i - \mu_i^{\circ} = \mathrm{RT}\ln\frac{\hat{f}_i}{\hat{f}_i^{\circ}} \tag{2-14}$$

where $^{\circ}$ = a reference state for the quantity

"Fugacity is a corrected pressure which for a component in a mixture of ideal gases is equal to the partial pressure of that component." (Prausnitz, Lichtenthaler et al. 1986) For a real mixture, fugacity may be treated as a partial pressure corrected for non-ideal behavior. Fugacity may be related to the fundamental equilibrium relation in Equation 2-13 by writing Equation 2-14 for the number of phases present and substituting into Equation 2-13. For two phases α and β, the following equation is obtained:

$$\mu_i^{o,\alpha} + \mathrm{RT}\ln\frac{\hat{f}_i^{\alpha}}{\hat{f}_i^{o,\alpha}} = \mu_i^{o,\beta} + \mathrm{RT}\ln\frac{\hat{f}_i^{\beta}}{\hat{f}_i^{o,\beta}} \tag{2-15}$$

From this equation, a new fundamental equilibrium relation is developed which is more useful to the physical study of phase behavior. Whether the reference states are chosen to be the same or the relationship between them is known, the following equation results:

$$\hat{f}_i^{\alpha} = \hat{f}_i^{\beta} \tag{2-16}$$

The fugacities are related to physically measurable quantities through the fugacity coefficient, ϕ, and activity coefficient, γ. If the fugacity coefficient is used to relate the vapor-phase fugacity to the mole fraction and the activity coefficient to relate the liquid-phase fugacity to the mole fraction and a standard state fugacity, the following equation results:

$$\phi_i = \frac{\hat{f}_i^{V}}{y_i P} \tag{2-17}$$

$$\gamma_i = \frac{\hat{f}_i^{L}}{x_i \hat{f}_i^{oL}} \tag{2-18}$$

Now, Equations 2-17 and 2-18 may be substituted into Equation 2-16 to obtain the working equation for this study.

$$\phi_i y_i P = \gamma_i x_i \hat{f}_i^{oL} \tag{2-19}$$

The relations of the fugacity and activity coefficients to experimentally accessible information are discussed in the following sections.

Fugacity Coefficient

The vapor-phase fugacity is usually related to volumetric properties through an equation of state. The virial equation, truncated after the second term, is appropriate for low-pressure systems such as the ones in this study.

$$z = \frac{Pv}{RT} = 1 + \frac{B}{v} \tag{2-20}$$

where z = compressibility factor

P = total pressure

v = molar volume

R = gas constant

T = absolute temperature

B = second virial coefficient

The virial coefficients are dependent on temperature and composition but are independent of pressure. One of the important advantages of the virial equation of state is its direct extension to mixtures, which requires no arbitrary assumptions. "The composition dependence of all virial coefficients is given by a generalization of the statistical-mechanical derivation used to derive the virial equation for pure gases." (Prausnitz, Lichtenthaler et al. 1986) The second virial coefficient for a mixture is determined as follows:

$$B_{mixture} = \sum_{i=1}^{m} \sum_{j=1}^{m} y_i y_j B_{ij} \tag{2-21}$$

Therefore, the virial equation for a mixture, truncated after the second term is:

$$z_{mixture} = 1 + \frac{B_{mixture}}{v} \tag{2-22}$$

The fugacity coefficient in terms of independent variables V and T is as follows (Prausnitz, Lichtenthaler et al. 1986):

$$RT \ln \phi_i = \int_V^{\infty} \left[\left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_j} - \frac{RT}{V} \right] dV - RT \ln z \tag{2-23}$$

Substituting and performing the necessary differentiations and integrations for a binary mixture:

$$\ln \phi_1 = \frac{2}{v}(y_1 B_{11} + y_2 B_{12}) - \ln z_{mixture} \tag{2-24}$$

$$\ln \phi_2 = \frac{2}{v}(y_2 B_{22} + y_1 B_{12}) - \ln z_{mixture} \tag{2-25}$$

The second virial coefficient can be estimated using a variety of correlations (e.g. Tsonopoulos (Tsonopoulos and Heidman 1990)).

Activity Coefficient

The calculation of liquid-phase fugacity is often done by defining an ideal solution and determining deviations from ideal behavior in terms of excess functions (Prausnitz, Lichtenthaler et al. 1986). Activity coefficients may be related to the excess Gibbs energy by the following relation:

$$g^E = RT\sum_i x_i \ln \gamma_i \tag{2-26}$$

The excess Gibbs energy can be represented as a function of mole fraction by a number of available models. A model should be chosen based on the type of system studied. In this study, several models were tested, but only the Wilson model will be discussed in this section. The Wilson model is based on molecular considerations and the expression for the excess Gibbs energy for a binary solution is as follows:

$$\frac{g^E}{RT} = -x_1 \ln(x_1 + \Lambda_{12} x_2) - x_2 \ln(x_2 + \Lambda_{21} x_1) \tag{2-27}$$

Therefore, the activity coefficients can be expressed by the Wilson equation as follows:

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12} x_2) + x_2\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2}\right] \tag{2-28}$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) - x_1\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right] \qquad (2\text{-}29)$$

The model parameters Λ_{12} and Λ_{21} can be regressed using experimental P, T, x, y data for each system studied.

Now, in order to solve for the liquid-phase fugacity in Equation 2-18, a reference or standard state fugacity must be specified, since "at any composition, the activity coefficient depends on the choice of standard state and the numerical value of γ_i has no significance unless the numerical value of f_i^0 is also specified" (Prausnitz, Lichtenthaler et al. 1986). For low or moderate pressures, the standard state fugacity is often chosen as the fugacity of the pure liquid i at the system temperature and pressure, f_i^{oL}, as in the following equation:

$$f_i^{oL} = P_i^s \phi_i^s \exp\left(\int_{P_i^s}^{P} \frac{v_i^L dP}{RT}\right) \qquad (2\text{-}30)$$

where P_i^s = saturation vapor pressure

ϕ_i^s = fugacity coefficient at saturation conditions

v_i^L = molar volume of pure liquid component i

P = system pressure

T = system temperature

R = gas constant

At low pressures, the exponential term, or Poynting correction, becomes negligible and ϕ_i^s is very close to one, leaving the standard state fugacity equal to its saturation vapor pressure at system temperature.

Consistency Tests

Consistency tests provide a means to evaluate the "correctness" of experimental data. The four types of consistency tests used to evaluate experimental data are:

- Instrumental
- Internal
- External
- Thermodynamic

If the data satisfy these four tests, then the data are probably good. If the data do not satisfy one or more of these tests, then the data are probably incorrect.

Instrumental consistency is achieved when repeated measurements from each instrument are reproduced accurately within the claimed precision of certifiable calibrations traceable to the National Institute of Standards and Technology. Internal consistency tests compare the repeatability of measurements at various operating conditions to the expected uncertainty obtained from the error propagation. The experimental data may be compared to data from outside sources, if available, to determine if the data are externally consistent. Since the quality of data in the literature varies greatly, discretion must be used when applying external consistency tests. Thermodynamic consistency tests, as described below, are necessary when evaluating vapor-liquid equilibrium data to provide a check that the data obey the governing laws of thermodynamics.

The following sections provide a more detailed description of external and thermodynamic consistency tests.

External Consistency Tests

A valuable tool in evaluating experimental data is to use previous researchers' experimental data, if available, for comparison. However, one should exercise discretion since previous works will vary in magnitude of experimental error and data quality. One method employed in this study was to use GEOS, a Fortran-based computer program developed at Oklahoma State University by Dr. Khaled A. M. Gasem (Gasem 1997). GEOS contains several equations of state and activity coefficient models to allow the user to test the validity of various models for the system studied. This also allows easier comparison of numerous sets of experimental data. Comparison with previous experimental data is not a guarantee that current data are accurate, it is just another test to support the conclusion as to the quality of data. There will be a scatter of previous researchers' experimental data and if the current data do not show serious deviations from the bulk of previous data then it is a fair assumption that the data are externally consistent. External consistency is particularly likely if the data sets are from measurements which use different experimental techniques. If the data are externally consistent then Thermodynamic consistency tests must be performed to make a decision regarding the quality of data.

Thermodynamic Consistency Tests

The Gibbs-Duhem equation provides a means to test the thermodynamic consistency of vapor-liquid equilibrium data. This is possible because "the Gibbs-Duhem equation interrelates activity coefficients of all components in a mixture. Therefore, if data are available for all of the activity coefficients, these data should obey the Gibbs-

Duhem equation; if they do not, they cannot be correct. If they do obey the Gibbs-Duhem equation, the data are probably, although not necessarily, correct; it is conceivable that a given set of incorrect data may fortuitously satisfy the Gibbs-Duhem equation, but this is not likely." (Prausnitz, Lichtenthaler et al. 1986)

There are three commonly used methods to test data: the differential (slope) test, the integral (area) test, and the predictive test. The differential and integral tests are both simple and may be used to detect serious errors, but have disadvantages that exclude them from providing stringent tests for thermodynamic consistency. The predictive test is the test utilized in this study and has been called "the only meaningful way to check thermodynamic consistency of experimental data." (Prausnitz, Lichtenthaler et al. 1986) A brief discussion of the former tests and a more detailed discussion of the latter test are in the following sections.

Differential (Slope) Test

This test utilizes the following form of the Gibbs-Duhem equation:

$$x_1 \frac{d \ln \gamma_1}{dx_1} = x_2 \frac{d \ln \gamma_2}{dx_2} \tag{2-31}$$

To perform this test, plots are constructed for $\ln \gamma_1$ vs. x_1 and $\ln \gamma_2$ vs. x_2 and slopes are measured at various compositions. The slopes are used in Equation 2-31 to see if the Gibbs-Duhem equation is satisfied. This test is simple, but since it is difficult to measure the slopes with sufficient accuracy, this test only provides a means to detect serious errors in equilibrium data.

Integral (Area) Test

The basis of the integral test is the following simplified equation (Prausnitz, Lichtenthaler et al. 1986):

$$\int_0^1 \ln \frac{\gamma_1}{\gamma_2} dx_1 = 0 \qquad (2\text{-}32)$$

In this case, a plot of ln (γ_1/γ_2) vs. x_1 is prepared. The net area in the plot must be zero if the requirement of thermodynamic consistency is met. However, since a ratio of activity coefficients is used, the only data needed are x, y, and a ratio of pure-component vapor pressures. Thus, this test will check the relationship between the data used, but will not indicate an error in pressure since pressure data are not necessary for this test.

Predictive Test

This test provides a more complete check of thermodynamic consistency since P, T, x, and y data are all used. The equilibrium relation, Equation 2-19

$$\phi_i y_i P = \gamma_i x_i \hat{f}_i^{o\ell}$$

is used with the relations for fugacity and activity coefficients as discussed in previous sections. Since the activity coefficient models are based on the Gibbs-Duhem equation, the equilibrium relation satisfies the Gibbs-Duhem equation. The procedure for performing the predictive test is as follows:

- Obtain experimental data (P, T, x, y)
- Use three of the experimental values to obtain the fourth using the equilibrium relation

- Compare the fourth experimental value to the predicted value to obtain differences (i.e., ΔP, ΔT, etc.)
- Each difference should be evaluated using one or both of the following
  - Comparing the root mean square error to the experimental error
  - Plot ΔP (or Δy) vs. x, if the deviations are small and show random scatter uniformly about zero then the data are probably good since they agree with a thermodynamically consistent model. If the data do not agree with the chosen model, then either the data are not thermodynamically consistent or the chosen model is not appropriate for the system of interest.

Methods of Vapor-Liquid Equilibrium Data Collection

Vapor-liquid equilibrium (VLE) data may be classified as either low pressure or high pressure. Since this work focuses on low-pressure vapor-liquid equilibrium, only these methods will be discussed. "Most of the contemporary low pressure VLE measurements are done on two types of equipment, dynamic (circulation) stills and static equilibrium cells." (Rogalski and Malanowski 1980)

"On the basis of the literature on VLE data, it can be stated that the highest accuracy of measurement is obtained by means of static cell, i.e., a method in which the liquid and vapour phases are in the equilibrium state and boiling does not occur. The long time necessary for equilibration, the necessity for thorough degassing of samples, and the expensive auxiliary equipment needed are the most important drawbacks of this method. The dynamic stills, working in the stationary state of boiling under the pressure of an inert gas, are considerably simpler in operation, but are usually less accurate."

(Rogalski and Malanowski 1980) Due to the previously mentioned drawbacks of the static method, the dynamic method has been chosen. The focus of this work is to determine the accuracy of two existing circulation stills.

Chapter 3

Experimental Apparatus

Two glass equilibrium stills were evaluated in this study to determine the accuracy and reliability of each. The general setup was the same for both systems and the stills could be interchanged to allow ongoing studies of each still. For convenience, the stills will be referred to as Still #1 and Still #2. Still #1 was used in a previous study and is a modification by Sura (Sura 1991) of the ebulliometer of Rogalski and Malanowski (Rogalski and Malanowski 1980). Still #2 is a slight modification of the improved Labodest still from the work of Stage and Fischer (Stage and Fischer 1968) which is widely used in VLE studies. Both stills were fabricated at Oklahoma State University by the campus glass blower. A description of the general experimental setup and of the equipment used is contained in this chapter.

General Setup

A diagram of the overall experimental setup is shown in Figure 1. An aluminum frame was used to support the still, condenser, and manifold. The still was clamped to the frame and then connected to the condenser using an o-ring and a clamp to form a tight seal. The condenser was connected to the manifold in the same manner. The water in the condenser was cooled using a refrigerated circulating bath. The temperature probe was inserted into the equilibrium still and was sealed using an o-ring and a threaded plug. The temperature probe was connected to the Hart thermometer which was connected to a computer for data-logging.

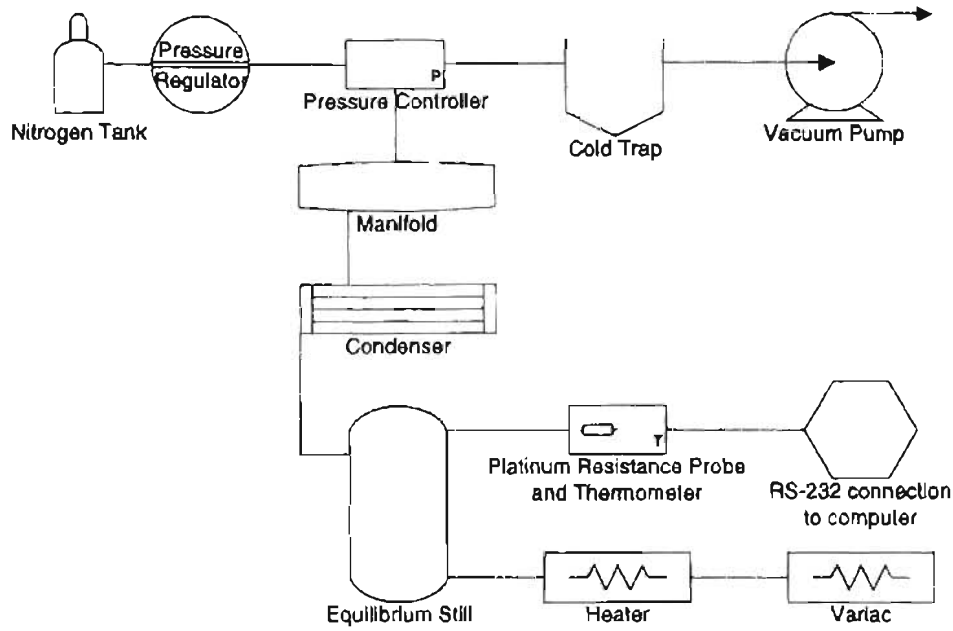

Figure 1. Overall Experimental Setup

The manifold was connected to the pressure controller using thick-walled Tygon tubing. The pressure controller was also connected to the pressure regulator and nitrogen tank through the pressure supply port and the ice trap and vacuum pump through the vacuum port.

Each still has a different type of heat source. Still #1 uses a heating tape wound around the boiling chamber, which is an external heat source. Still#2 has a heating rod inserted into the boiling chamber, which is an internal heat source. The heat source for the still was plugged into a variac to control the amount of heat input.

Still #1 has magnetic stir bars placed inside the feed chamber and the vapor sample chamber while Still #2 has a magnetic stir bar only in the feed chamber. A

magnetic stirrer was placed under the chamber(s) to eliminate fluctuations in composition and provide more accurate samples. The vapor sample chamber in Still #2 has a very small volume and does not require mixing since the turnover rate is high.

A detailed description of each piece of equipment is contained in the following sections.

Equilibrium Still #1

This still, Figure 2, was designed and constructed for a previous study by Sura (Sura 1991). The modifications made to the ebulliometer of Rogalski and Malanowski (Rogalski and Malanowski 1980) to arrive at the present design are detailed in Sura's work. The features of Still #1, Figure 2, are described in the following paragraph.

The boiling chamber, BC, requires an external heat source. In this work, a one-inch diameter heat tape was wound around the boiling chamber. The boiling chamber contains crushed glass sintered on the inner wall to provide nucleation sites which facilitate smooth boiling. When the liquid in the ebulliometer is heated, it partially vaporizes and a mixture of vapor and superheated liquid is carried up the Cottrell pump, CP, into the equilibrium chamber, EC. The platinum resistance probe is placed directly in the equilibrium chamber so an accurate temperature may be obtained. A threaded Teflon plug and o-ring were used to seal the connection, TC, between the probe, TP, and the still. As the vapor and liquid separate, they pass through a small opening, O, which forces the mixture to remain in contact until the phases separate in the separation cup, SC. The vapor travels around the splash guard, SG, and bathes the outside of the equilibrium chamber then exits and travels into the condenser, C. The condensed vapor

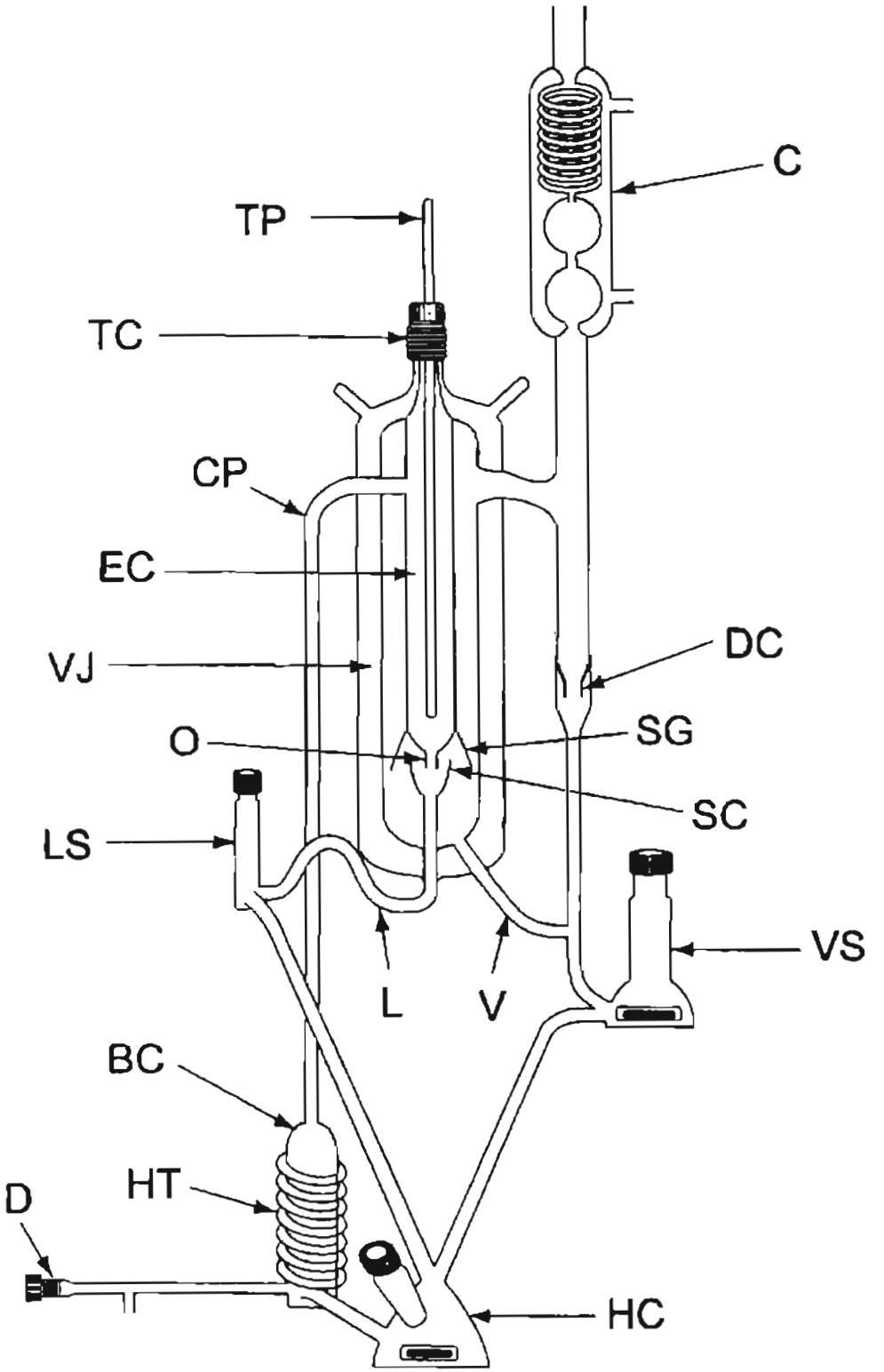

Figure 2. Equilibrium Still #1

falls through a drop rate counter, DC, which assists in monitoring steady state measurements. Any vapor that condenses on the outer walls of the separation chamber is prevented from entering the liquid by the splash guard and exits through tube V to join the condensed vapor before sampling. The vapor sample chamber, VS, was equipped with a magnetic stir bar to ensure uniform mixing of the condensed vapor from C and V. The liquid exits through tube L to the liquid sample chamber, LS. Both sample chambers have sampling ports that are sealed with Teflon septa and threaded lids. A vacuum jacket, VJ, surrounds the equilibrium chamber and separation area to minimize heat loss. The vapor and liquid streams and are recombined in the holding chamber, HC, where they are mixed before re-entering the boiling chamber. This mixing results in smoother boiling by reducing any composition fluctuations in the stream fed to the boiling chamber. The still was equipped with a drain plug, D, for easy cleanup.

Equilibrium Still #2

Still #2, Figure 3, is a reproduction of the improved Labodest circulation apparatus found in the work of Stage and Fischer (Stage and Fischer 1968). The significant differences from Still #1 include: an internal heat source rather than external, a coiled Cottrell pump that sprays the vapor and liquid mixture up into the equilibrium chamber on the bottom tip of the temperature probe rather than entering at the top, splashing on the temperature probe near the middle and running down the probe, and the vapor sample chamber of Still #2 is smaller and does not have a magnetic stir bar. The features of Still #2 are detailed in the following paragraph.

A heating rod is placed inside the boiling chamber, BC, and the connection, HRC, is sealed using a threaded plug and o-ring seal. Crushed glass is sintered on the inner

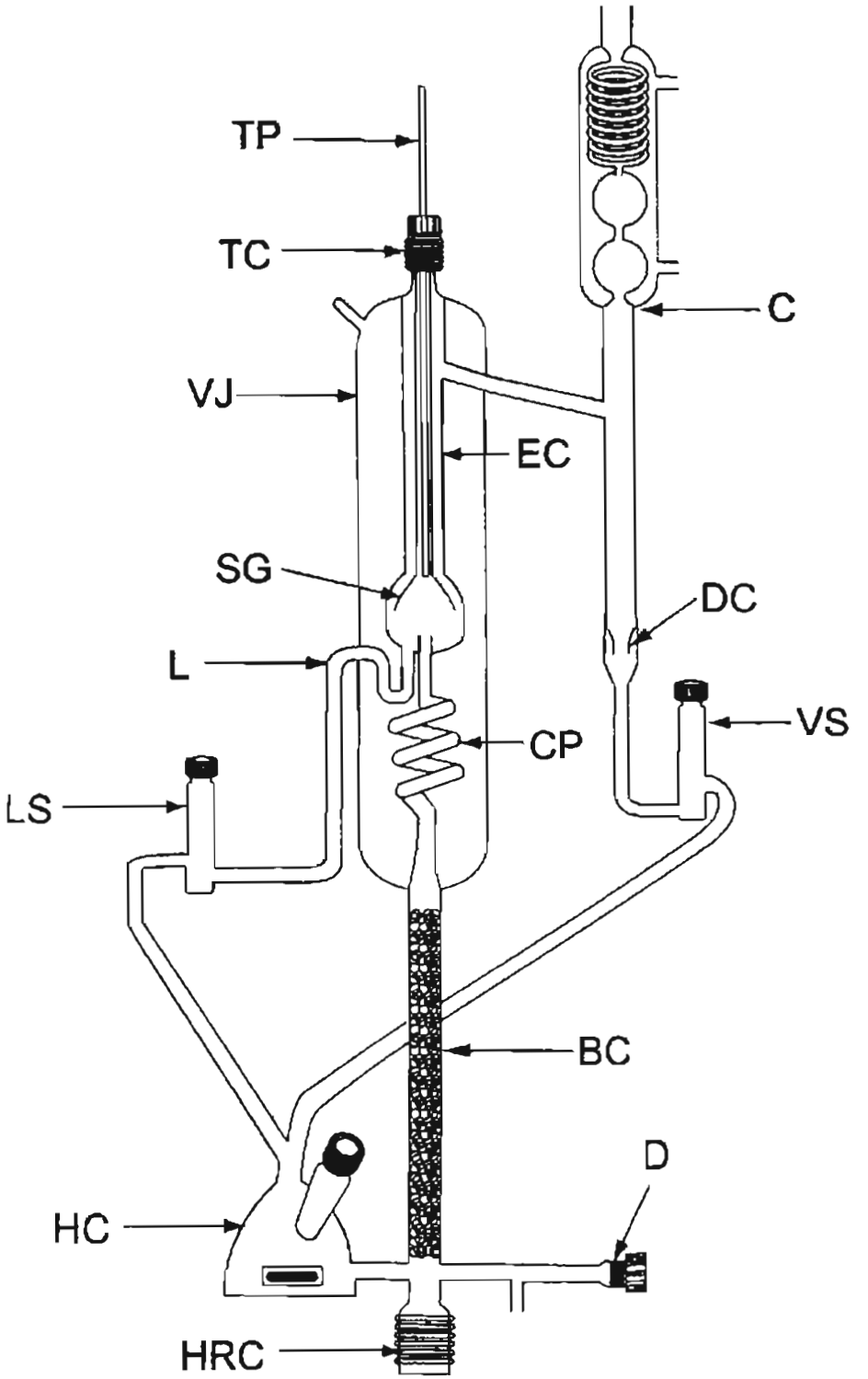

Figure 3. Equilibrium Still #2

walls of the boiling chamber to facilitate steady boiling. The heated vapor and liquid mixture travels up through the coiled Cottrell pump, CP, into the equilibrium chamber, EC. Sufficient heat is added so a "geyser" of vapor and liquid leaves CP and splashes onto the end of the platinum resistance probe, TP. The connection, TC, between the equilibrium still and temperature probe is sealed with a threaded Teflon plug and o-ring. A vacuum jacket, VJ, surrounds the equilibrium chamber and Cottrell pump to minimize heat loss. The liquid collects in the bottom of the equilibrium chamber and passes through a "liquid seal" U-shaped tube, L, to the liquid sample chamber, LS. The liquid seal formed by L prevents vapor carry-over into the liquid sampling chamber. The vapor travels around the splash guard, SG, and bathes the outside of the equilibrium chamber then exits into the condenser, C. The condensed vapor falls through the drop rate counter, DC, and into the vapor sample chamber, VS. Both sample chambers have a sample port that is sealed with a threaded lid and Teflon faced septa which is the same as still #1. The vapor and liquid are recombined in the holding chamber, HC, and mixed with a magnetic stir bar before reentry into the boiling chamber. The still has a drain plug, D, for easy cleanup.

Thermometer

A Hart Scientific Model 1006 Micro-Therm thermometer was used (this model has been renamed by Hart as Model 1506). This thermometer has two probe ports and is capable of measuring the temperature of either probe or the difference between two temperatures. The Mode switch selects the function to be displayed, where T_1 and T_2 indicate the probe port used, T_1-T_2 displays the temperature difference of the two probes, and T_{MIN}, T_{MAX}, and T_{CLR} display the minimum, maximum, spread between minimum

and maximum, or re-initializes the minima or maxima. The Scale switch allows the user to designate any of the following units: Celsius, Kelvin, Fahrenheit or Rankin temperatures, or Ohms resistance. The user may also select measurement intervals of one, five, ten, or one hundred seconds using the Resolution switch. The temperature probe used was a platinum resistance probe, serial number 319111. An important fact to note is that the probe coefficients for this probe are for specific ranges, i.e., –183°C to 0°C and 0°C to 480°C. These coefficients are programmed for different probe ports; the previously mentioned ranges are for Probe Port 2 and Probe Port 1, respectively. The thermometer was attached to a computer via an RS-232 connection. The program Hyperterminal was used to log the temperature readings so fluctuations could be recorded.

The system accuracy, using a platinum resistance probe, is guaranteed to be 0.040°C, but the typical accuracy is stated as 0.020°C.(1993)

Pressure Controller

A Ruska Model 7215*i* Digital Pressure Controller (DPC) was used to control the pressure in the equilibrium still. This DPC "uses a force-balanced, fused-quartz Bourdon tube technology to provide the precise measurement of pressure." (1999) The DPC operates in either Measure mode or Control mode. In Control mode, the pressure is simultaneously measured and controlled to allow the user to view the fluctuations from the setpoint. The Control mode was used in this study. The DPC is "calibrated per ANSI/NCSL Z-540-1-1994 using Ruska deadweight gauges that are directly traceable to the National Institute of Standards and Technology (NIST)" (1999). High-purity nitrogen was used as the pressure supply in this study. The user may choose instrumentation air or

nitrogen and the DPC will automatically make head corrections for either gas selected. Since some of the measurements were subatmospheric, a vacuum pump was connected to the vacuum supply/exhaust port.

The DPC has several options for display units. The user may choose a predefined standard unit or may program a user-defined unit. The unit used in this study was millimeters of mercury, mmHg.

The system precision is "defined as the combined effect of linearity, repeatability, and hysteresis throughout the operating temperature range."(1999) The system precision for the pressure range of 25 to 100% of full scale is 0.005% of the reading, and for the pressure range below 25% of full scale the precision is 0.005% of the reading at 25% of full scale. Therefore, since the full-scale reading of this DPC is 50 psi the range of precision is 0.032-0.038 mmHg for the operating range of 350-760 mmHg.

Mettler Toledo Model RA-510M Refractometer

Compositions were determined using a Mettler Toledo Model RA-510M Refractometer. Refractometry may be used to determine the composition of binary mixtures. The accuracy of the composition measurements increases as the difference in refractive index of the components increases. The refractive index of each component and mixtures of known composition were measured and calibration curves were prepared. An equation fit to the data may then be used to determine the composition of a sample for a given refractive index. The RA-510M measures solutions with an index in the range of 1.32000 to 1.56000 with a stated accuracy of ± 0.00005 and requires a minimum amount of 0.2 mL of the sample. The temperature of the sample is kept constant with a

thermostat control and may be specified by the user to allow comparison with literature sources. The temperature in this study was kept at 20.00°C since the literature sources for the pure components reported values at this temperature.

An automatic sampling unit may be added to the RA-510M to perform continuous measurements. Transfer of the experimental data to an attached computer is also possible. Addition of the autosampling unit and purchase of compatible computer software would allow simultaneous logging of pressure, temperature, and composition data. In this study only temperature data were logged to a computer.

Heat Sources

The two equilibrium stills used in this study had different types of heating sources, external and internal. The external heating source was a 2' x 1" Amtek heating tape wrapped around the boiling chamber. The internal heating source was a Glo-Quartz heating rod inserted directly into the boiling chamber. Both heating sources were connected to a variac in order to control the amount of heat produced.

Chemicals

The chemicals used in this study were purchased from Aldrich Chemical Company. The specifications were as follows:

Chemical	Reported Purity
hexane	99+%
methylcyclohexane	99+%
toluene	99.8%

No further purification of the chemicals was attempted.

Note: The methylcyclohexane is hygroscopic and was opened only under a nitrogen blanket.

Circulating Refrigerated Bath

An Endocal refrigerated circulating bath was used to provide cooling water for the condenser. The temperature was kept constant at 18°C, which was cool enough to condense any of the chemicals used in this study but not cold enough to cause excessive temperature gradients in the still.

Chapter 4

Experimental Procedure

General Experimental Procedure for VLE Data Collection

An outline of the procedure for collection of VLE data followed by a detailed description of each step is included in this section. The accuracy and reliability of the equipment was checked using standardized tests before collecting data. Ice point and triple point tests were used to determine the accuracy of the temperature equipment. Vapor-pressure measurements for the pure organics and deionized water provided a check of the temperature and pressure equipment. The accuracy of the refractometer was checked using high purity chemicals and deionized water.

Outline of Overall Procedure:

1) Prepare a calibration curve of refractive index versus mole fraction for the system to be studied, as discussed in the following section.
2) Rinse the still with acetone and thoroughly dry the still.
3) Rinse the condenser and the temperature probe with acetone and dry each thoroughly.
4) Rinse the still with about 30 to 40 mL of the pure component that will be used.
5) Rinse the condenser and the temperature probe with 20 mL of the pure component.
6) Fill the still with pure component 1, $x_1 = 1.0$. The amount of initial charge and the desired operating level of the liquid are discussed in the following section, Equilibrium Still.

7) Connect the still to the condenser.

8) Replace all o-rings and ensure that all clamps and plugs are tightly sealed.

9) Plug the heating source into the variac.

10) Turn on the pressure supply.

11) Turn on the vacuum pump.

12) Adjust the pressure controller to the desired pressure and allow it to stabilize. For isobaric runs the pressure controller is set to the desired value. For isothermal runs, a trial and error procedure must be used to obtain the desired temperature by adjusting the pressure setting.

13) Turn on the condenser.

14) Turn on the variac.

15) Begin taking measurements once the temperature has stabilized.

16) Adjust the composition and repeat measurements.

17) Repeat previous step until $x_1 = 0.4$. There should be an overlap in collected data near equimolar composition, therefore the next run will start with $x_1 = 0.0$ and continue to $x_1 = 0.6$.

18) Turn off the heat source and unplug it from the variac.

19) Allow the still to cool.

20) Adjust the pressure controller to near atmospheric pressure.

21) Turn off the pressure controller.

22) Turn off the vacuum pump.

23) Turn off the pressure supply.

24) After condensation no longer appears in the vapor arm, the condenser may be turned off.

25) Remove the still, drain and properly dispose of the chemicals.

26) Repeat the procedure beginning at step 1 starting with pure component 2, $x_2 = 1.0$ as the initial charge and repeat until $x_2 = 0.4$. The collected data should overlap near equimolar composition to confirm that the measurements are not dependent on the initial concentration.

Preparing a Calibration Curve

A calibration curve is necessary to determine the composition of samples taken from the equilibrium still. A calibration curve should be created for each mixture to be studied. Mixtures of known composition were prepared using Equations 4-1 and 4-2 to determine the volume needed of each component based on the desired mole fraction, the density of each component, and the molecular weight of each component.

$$V_1 = \frac{x_1 V \left(\frac{\rho_2}{M_2}\right)}{x_1\left(\frac{\rho_2}{M_2}\right) + x_2\left(\frac{\rho_1}{M_1}\right)} \tag{4-1}$$

$$V_2 = V - V_1 \tag{4-2}$$

where V = total volume desired for the mixture sample

V_i = volume of component i required

ρ_i = density of component i

M_i = molecular weight of component i

x_i = mole fraction of component i

These equations provided the volumes needed to prepare each composition, but since the volumes can only be measured to one or two decimal places a more precise measurement was needed to obtain an exact composition. The exact composition was determined using the weight of each component in the mixture. The components were placed in a 4 mL vial and sealed with a Teflon-faced septa and threaded lid. The vial was weighed empty and again after the addition of each component using a Mettler balance. The balance allowed weight measurements to the nearest 0.00001 g. The equations used to determine the mole fraction of component 1 in the mixture are as follows:

$$x_1 = \frac{W_A}{W_A + RW_B} \tag{4-3}$$

$$R = \frac{M_1}{M_2} \tag{4-4}$$

$$W_A = W_1 - W_0 \tag{4-5}$$

$$W_B = W_2 - W_1 \tag{4-6}$$

where W_0 = weight of empty bottle

W_1 = weight after component 1 added

W_2 = weight after component 2 added

The refractive index of each mixture was measured using a Mettler Toledo RA-510M refractometer. A plot was constructed for composition versus refractive index and the data were fit with a third-order polynomial trendline. The trendline equation was used to determine the composition of a sample using the refractive index. Appendix A contains the calibration curves for methylcyclohexane + toluene and hexane + toluene.

Procedure for the Mettler Toledo Model RA-510M Refractometer

1) Turn on the refractometer and allow it to warm up for at least 15 minutes.
2) Calibrate the refractometer before the initial use.
   a) Press the calibrate button, when "Prism Clear" appears press the Enter key.
   b) When "Set Water" appears, place 0.2 mL of deionized water in sample chamber and press Enter.
   c) If the calibration was successful, the message "Calib OK!" will appear. If the calibration was not successful then the message will state "Calib NG!" and step (a) should be repeated.
3) Wipe the sample chamber clean with a Kimwipe.
   a) Press the Reset button, if "No Sample" appears on the screen then proceed with sample measurements. If a reading appears, the sample chamber was not properly cleaned and must be dried before proceeding.
4) Place 0.2 mL of the sample in the sample chamber.
5) Press the Measure button and the refractive index will appear, the apparatus will beep once the temperature has stabilized and a reading has been made.
6) After each measurement, wipe the sample chamber with a Kimwipe then rinse with deionized water and wipe completely dry.
7) Press the Reset button to be sure all of the sample was removed. If the chamber is clean, "No Sample" will appear but if a reading appears then the chamber must be dried.

A problem encountered when sampling mixtures was evaporation of the sample. The components in the mixture did not evaporate at the same rate; therefore, the refractive

index continuously changed as the composition changed. The lid of the sample chamber did not form a tight seal so a vapor-proof lid was ordered from Mettler-Toledo to form a tight seal and inhibit vaporization, thus allowing accurate measurement of mixtures. There was still a small amount, about 1 mL, of space above the sample thus allowing a small amount of evaporation. Several tests were performed on the Mettler lid and two lids made by the Oklahoma State University Physics machine shop. The tests revealed that the Mettler lid provided the best results with little evaporation.

The refractive indices of high purity chemicals and deionized water were measured and compared to literature values as a check of the accuracy of the refractometer.

Equilibrium Still

The equilibrium still was rinsed with acetone and dried before each use. An aspirator was connected to the drain on the still and all but one opening was covered so air was pulled through the still at a high velocity. Air was pulled through each sampling chamber for several hours, sometimes overnight, to ensure all parts of the still were dry. The o-rings on the drain plug were replaced before each run. After the still was dry, it was rinsed with 30-40 mL of the pure component used in the study, filled with the pure component, and clamped to the aluminum frame. The initial charge for Still #1 was 115-125 cc and the initial charge for Still #2 was 105-115 cc depending on the component used. Once steady operation was achieved, an amount of the component was added or removed to achieve the optimum operating level. The desired operating level for Still #1 was to maintain the liquid level in tube L (see Figure 2) even with the bottom of the vacuum jacket. The desired operating level for Still #2 (see Figure 3) was to maintain a

liquid level in the separation chamber just below the spout from the Cottrell pump, CP, so that the equilibrium mixture did not pass through liquid when entering the separation chamber and so vapor would not flow into the liquid return tube L.

The condenser was rinsed with acetone and allowed to dry overnight. The o-rings on the condenser were changed before each run and the condenser was rinsed with the pure component.

Thermometer

Procedure for the Hart 1506 Micro-Therm Thermometer:

1) Plug the probe into the correct port for the temperature range to be measured, i.e., Port 1 has a range of 0°C to 480°C and Port 2 has a range of −183°C to 0°C.
2) Attach the RS-232 cable to the port on the back of the Hart and to the computer that will record the temperature measurements.
3) Insert the probe into the equilibrium still and tighten the plug so the o-ring makes a seal between the glass and the probe. The correct immersion depth for the probe is 2-7 inches from the tip immersed in the component to be measured. For this study, the probe was immersed 5-7 inches below TC in Figures 2 and 3.
4) Turn on the power supply.
5) Select the measurement options on the front panel under the display.
    a) Mode - in this study T_1 was the only mode used since probe port 1 was used for measurement
    b) Scale - Celsius was the preferred unit; therefore C was chosen
    c) Resolution - the sample time chosen for this study was 5 seconds

d) Analog - this changes the analog output scale and was not used in this study since digital output was recorded though the RS-232 connection

6) Open Hyperterminal in Windows (Start/Programs/Accessories/Communications/Hyperterminal) and connect it to the Hart. For this study the following port settings were used: Bits per second = 1200, Data bits = 8, Parity = None, Stop Bits = 1, Flow Control = None.

7) Send the collected measurements to a text file using the Capture Text command under the Transfer menu.

An ice-point test and triple point test were performed to check the accuracy of the thermometer.

Procedure for the ice-point test

An ice bath was prepared with crushed ice cubes made from deionized water and enough deionized water to cover the ice. The temperature probe was inserted into the ice bath taking care not to let the probe touch the bottom or the sides of the container. The ice bath was stirred periodically to ensure a uniform temperature. A reading of 0.000°C should have been obtained for the freezing point of water. The ice point test revealed a consistent reading of 0.047°C, which was accounted for by subtracting 0.047°C from the observed temperature readings during the subsequent vapor-pressure and VLE measurements.

Procedure for the triple-point test

The triple point test was performed as a second check of the offset determined from the ice point test. An Equiphase triple point cell was used as follows. Powdered

dry ice was used to create an ice mantle in the cell and the remaining dry ice was removed. Ethyl alcohol was poured in the sampling chamber to serve as a medium for measurement. If the ice mantle did not dislodge from the outside of the sampling chamber when the ethyl alcohol is added, then a metal rod was inserted until the ice mantle dislodged. The temperature probe was inserted into the ethyl alcohol to take a measurement. The result from the triple point test was about 0.057°C which confirmed the reading error of 0.047°C, since the correct reading should have been 0.010°C.

Pressure Controller

Procedure for the Ruska Model 7215i Digital Pressure Controller:

The pressure controller was allowed to warm up for three hours prior to initial use. To eliminate the warm-up period, the pressure controller was left in screen saver mode when not in use. The pressure controller was used to measure or control pressure. The control mode was used in this study. The procedure for operating the pressure controller in control mode is as follows:

1) Check to be sure the following connections are made and secured
    a) Pressure supply port to nitrogen tank
    b) Exhaust port to ice trap
    c) Ice trap to vacuum pump
    d) Test port to equilibrium still
    e) Reference port to exhaust port line
2) Fill the ice trap with ice
3) Turn the pressure supply on to 100% of full scale plus 15 psi, which is approximately 50 psig in this study

4) Turn on the vacuum pump and check that the oil level is in the acceptable operating range. If it is not, then either add or remove oil so the level is acceptable.
5) Set the pressure controller to the desired regulated pressure
6) Press the 'Control' key and 'Enter' to confirm entry into the control mode

Note: Do not use helium or any standard shop grade gas as the pressure supply. This will ruin the Bourdon capsule since helium will diffuse through the quartz and affect the permanent vacuum on the sealed side of the tube.

Equilibrium Measurements

This section describes the procedure for taking equilibrium measurements using Still #1. Still #2 was not used for equilibrium measurements (see Chapter 5, Results and Discussion, for an explanation.)

For isobaric runs, the pressure controller was set to the desired pressure. After the pressure stabilizes, the condenser and variac were turned on and the heat input was slowly increased until boiling began. The heat input was adjusted to maintain 60 to 80 drops per minute from the drop rate counter for the methylcyclohexane/toluene mixture and 80 to 120 drops per minute for the hexane/toluene mixture.

The drop ranges given above corresponded to a steady state as determined from measurements taken from this still. Measurements of drop rate versus measured temperatures were analyzed. The steady state range was determined to be the range where increasing drop rate made the least difference in observed temperature.

The temperature was monitored for at least one hour after the drop rate steadied. Small fluctuations in temperature occurred even after a steady state was achieved. These fluctuations were approximately 0.01°C for the pure components and the

methylcyclohexane/toluene mixture, but were as much as 0.1°C for the hexane/toluene mixture. The larger fluctuation in the hexane/toluene mixture may have been due to the larger difference in boiling points of the two chemicals and the higher drop rate required for this mixture. When the vapor and liquid streams are recombined in the holding chamber, HC, there may be slight fluctuations in the concentration of the mixture fed to the boiling chamber thus causing fluctuations in the boiling temperature. The larger difference in boiling points would cause more obvious the fluctuations and the higher drop rate would cause faster turnover and less mixing time in the holding chamber. The stir bar was adjusted to different rates of stirring and the fluctuations were still present. One possible solution is to redesign the still with a larger holding chamber so the concentration would not fluctuate as much with input from the vapor and liquid streams.

One observation of this researcher was that ambient temperature had an effect on drop rate and necessary heat input. Another concern was air from the heating and air conditioning system blowing past the still. A plastic sheet was secured to the support frame to keep air from blowing directly on the still.

Equilibrium measurements were taken once the pressure and temperature had stabilized. Measurements such as temperature, drop rate, level of fluctuation in the vapor arm, and liquid level in tube L (see Figure 2) were recorded. Then liquid and vapor samples were taken, in that sequence since the liquid-sampling chamber has a faster turnover than the vapor-sampling chamber. The syringes were inserted in the sampling chambers and were flushed by pumping three or four times to be certain no residue remained in the syringe from the previous sample. Next, 0.2 mL samples were withdrawn from each sampling chamber for analysis in the refractometer. Once the

samples were removed, they were placed on a wet paper towel with ice underneath and covered with another wet paper towel. The samples were cooled to lessen vaporization in the refractometer.

The samples were injected on the refractometer plate once they were cool. The sample was covered with the vapor-proof lid and a measurement taken. The samples were wiped away with a Kimwipe tissue and the plate was rinsed with deionized water and wiped again with a Kimwipe.

Isothermal runs were performed in the same manner except a trial-and-error procedure was used to obtain the desired temperature. The pressure was set at an estimated value using literature sources and smooth boiling was obtained, then the pressure was slowly adjusted until the desired temperature reading was obtained.

Each set of equilibrium measurements was obtained in two runs, starting with each pure component and moving past an equimolar mixture allowing for an overlap in measurements near equimolar, as previously mentioned. Each run took eighteen to twenty four hours and about twenty four hours before runs for cleaning and drying of the still. Therefore, each set of binary system data required at least four days to obtain.

The procedure for pure-component vapor-pressure measurements was similar to that of mixtures except sampling of the vapor and liquid was not necessary at every pressure and temperature. Sampling was only done to check the purity of the component, i.e., if the vapor and liquid samples had a refractive index that was different by more than the experimental uncertainty then it was checked again after thirty minutes. If the refractive index of the vapor and liquid was still different, then the component was

determined to be impure. None of the components in this study were determined to be impure.

Chapter 5

Results and Discussion

This chapter contains the results of the pure-component vapor-pressure data for deionized water, methylcyclohexane, hexane, and toluene, as well as vapor liquid equilibrium data for the isobaric systems methylcyclohexane + toluene and hexane + toluene and the isothermal system methylcyclohexane + toluene. The results are compared to available literature sources for external consistency and subjected to thermodynamic consistency tests. A discussion of each system studied is included in this chapter. All experimental temperatures listed in this study were corrected by subtracting 0.047°C from the observed temperature reading as discussed previously.

Pure-Component Vapor-Pressure Data

Pure-component vapor-pressure data were measured in both equilibrium stills for deionized water, methylcyclohexane, hexane, and toluene. A pressure range of 350 to 760 mmHg was chosen for these measurements. Since the goal of this study was to obtain a reliable method for measuring low-pressure VLE data, all measurements were taken at or below one atmosphere. To determine the lower limit of the experimental apparatus, the two stills were observed at decreasing pressures. The stability of operation was determined by observing the smoothness of boiling, the amount of fluctuation in the condensed vapor tube, the fluctuation in temperature, and whether the integrity of the seals was maintained. At pressures below 350 mmHg, air was pulled into the still around

or through the septa which caused fluctuations in temperature and in the level of condensed vapor.

Deionized water

The experimental vapor-pressure data for deionized water are listed in Table 1.

Table 1. Deionized Water Vapor Pressure

Still #1		Still #2	
Temperature (°C)	**Pressure (mmHg)**	**Temperature (°C)**	**Pressure (mmHg)**
100.04	760	100.03	760
99.29	740	99.29	740
98.53	720	98.53	720
97.75	700	97.75	700
96.75	675	96.75	675
95.72	650	95.71	650
93.55	600	93.55	600
91.23	550	91.22	550
91.23	550	88.71	500
88.73	500	85.98	450
86.00	450	84.54	425
83.02	400	83.00	400
81.41	375	81.39	375
79.70	350	79.68	350

The vapor-pressure data produced with the two equilibrium stills are in agreement within their experimental uncertainties. The guaranteed accuracy of the thermometer is 0.04°C and the largest temperature difference is 0.021°C which occurs at 450 mmHg. The data were compared to the work of Osborn and Douslin (Osborn and Douslin 1974). The literature data were regressed to obtain Antoine constants using the Fortran program Pure-Fluid Properties (PFP) developed by Dr. Khaled A. M. Gasem(Gasem). The

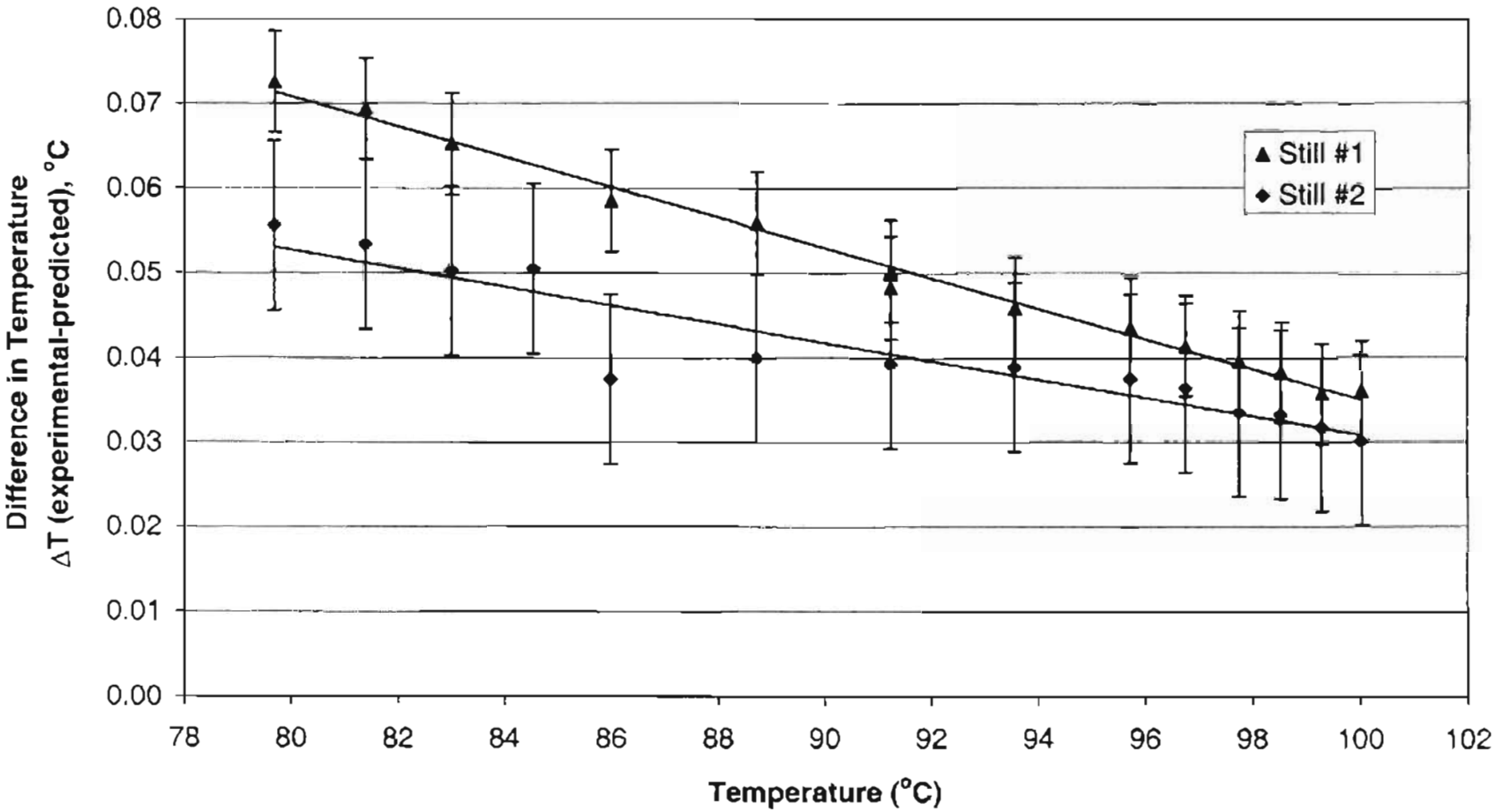

Figure 4. Deionized Water Vapor Pressure Compared to Osborn & Douslin: Temperature Differences

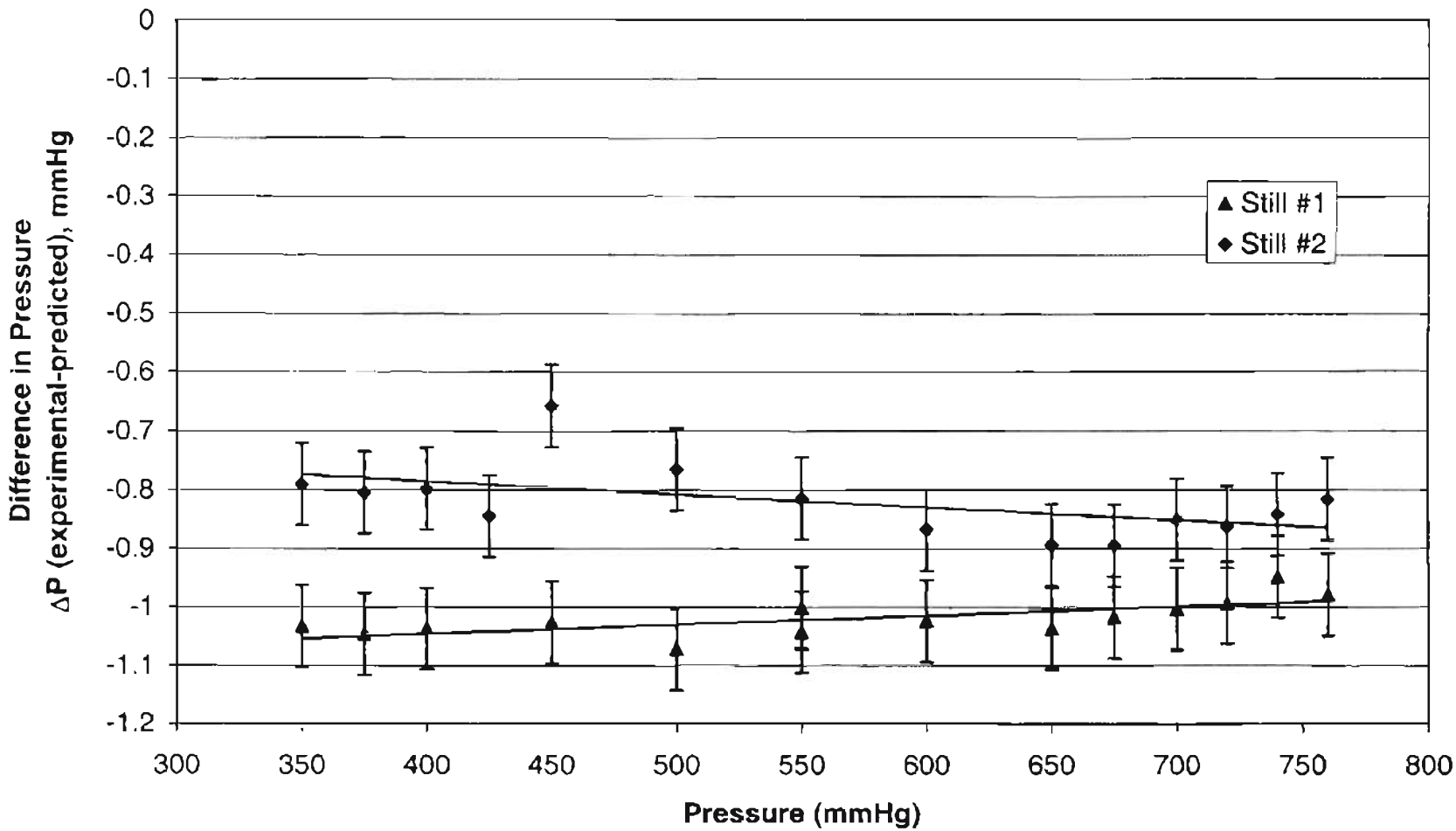

Figure 5. Deionized Water Vapor Pressure Compared to Osborn & Douslin: Pressure Differences

Antoine constants were used to predict temperature using experimental pressure and then the deviations in temperature were plotted. The same procedure was followed to obtain a plot of pressure deviation. Figures 4 and 5 show the deviations in temperature and pressure, respectively. The error bars on the plots are based on fluctuations of temperature and pressure measurements observed during operation of each still.

As the temperature decreases, the temperature difference between the experimental and calculated values increases. The data from Still #2 agree with Osborn and Douslin within the experimental uncertainty of 0.04°C at temperatures above about 90°C, but the data from Still #1 agree only at temperatures above about 96°C. The difference between the trendlines for Still #1 and Still #2 also increases as temperature decreases. The pressure deviations, Figure 5, for Still #1 and Still #2 show different trends. As pressure decreases, Still #1 shows an increasing pressure difference while Still #2 shows a decreasing pressure difference and as with temperature the two stills disagree most at lower pressure. For an experimental uncertainty of about 0.04 mmHg, neither still agrees with Osborn and Douslin.

Methylcyclohexane

The experimental vapor-pressure data from Still #1 and Still #2 for methylcyclohexane are listed in Table 2.

Table 2. Methylcyclohexane Vapor Pressure

Still #1 – Run 1		Still #1 – Run 2		Still #2	
Temperature (°C)	Pressure (mmHg)	Temperature (°C)	Pressure (mmHg)	Temperature (°C)	Pressure (mmHg)
100.95	760	100.98	760	100.99	760
100.01	740	100.04	740	100.04	740
99.05	720	99.08	720	99.07	720
98.07	700	98.09	700	98.10	700
96.82	675	96.83	675	96.85	675
95.52	650	95.54	650	95.55	650
92.81	600	92.82	600	92.83	600
89.91	550	89.92	550	89.93	550
89.91	550	89.92	550	89.92	550
86.79	500	86.80	500	86.81	500
83.42	450	83.43	450	83.44	450
79.74	400	79.74	400	79.75	400
77.76	375	77.77	375	77.77	375
75.68	350	75.68	350	75.68	350

The data were compared to the work of the Engineering Sciences Data Unit (ESDU) #82016(1982) in the same manner as described for deionized water. ESDU is a compilation of selected literature data, including the work of Willingham et al. (Willingham, Taylor et al. 1945). A Wagner equation was "fitted to the experimental data that had been selected and weighted in accordance with a critical assessment of all the data" (1982). Tabulated values are reported for a range of pressures and temperatures. Figures 6 and 7 show the temperature and pressure differences, respectively.

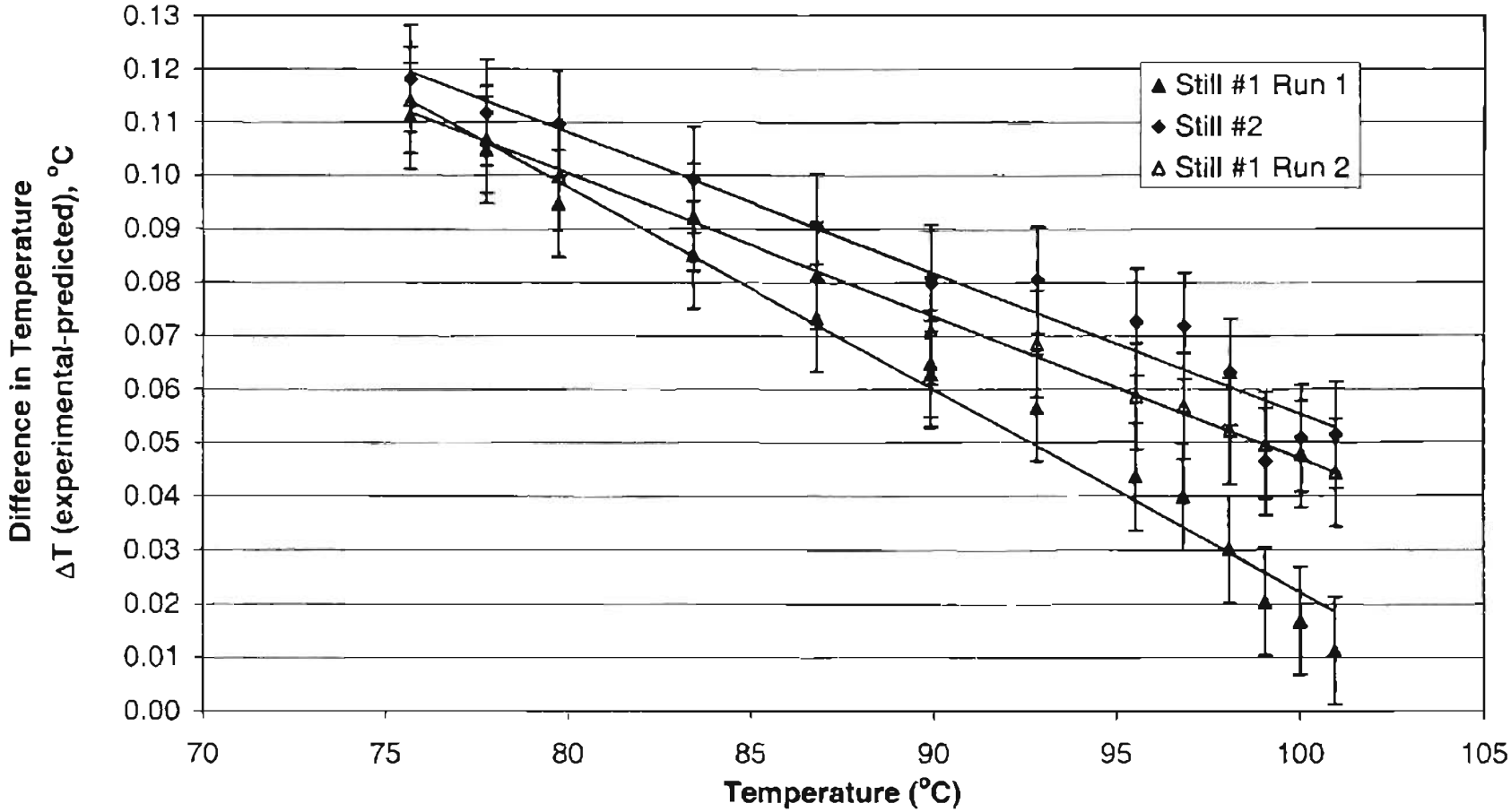

Figure 6. Methylcyclohexane Vapor Pressure Compared to ESDU #82016: Temperature Differences

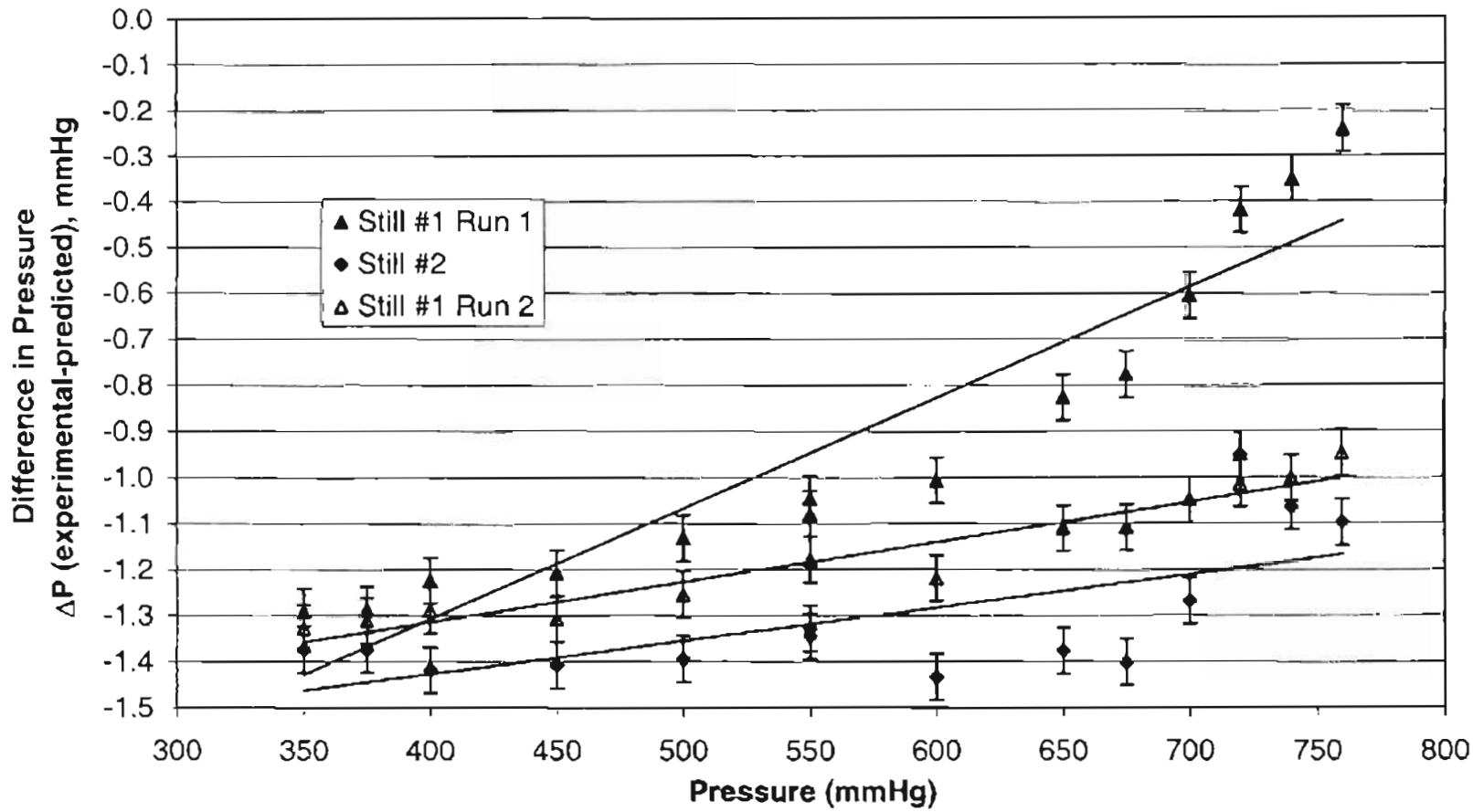

Figure 7. Methylcyclohexane Vapor Pressure Compared to ESDU #82016: Pressure Differences

The data from Still #1 (run 2) and Still #2 agree well as seen in Figures 6 and 7. The temperature difference between Still #1 (run 2) and Still #2 remains fairly constant around 0.01°C and the pressure difference is less than 0.2 mmHg. However, the data from Still #1 (run 1) agree with the other runs at low temperatures and pressures but deviate as the pressures increases to atmospheric pressure. Figure 6 shows that the temperature difference between Still #1 (run 1) and the other runs varies from zero at 75°C to about -0.04°C at 101°C which is at the limit of the experimental uncertainty. Although the stills produce data that are consistent with each other, the data do not agree well with ESDU. Only Still #1 run 1 agrees within experimental uncertainty with the ESDU data at temperatures greater than about 95°C. The pressure difference increases linearly from 350 to 600 mmHg as seen in Figure 7, then increases exponentially to 760 mmHg to a difference of about +0.8 mmHg. Again, as with water, the pressure differences from literature data exceed the experimental uncertainty. Although corrections were made to account for offset in temperature readings since the last calibration, it would be beneficial to calibrate the equipment more often and ensure more accurate measurements.

Figure 8 shows methylcyclohexane vapor-pressure data from this work and available literature sources. However, the differences in the data cannot be seen on this plot. Therefore, all of the data were regressed to obtain Antoine constants using the PFP program previously described (see Appendix B for the Antoine constants from this work and Appendix C for a sample printout of PFP results). Plots were then constructed using

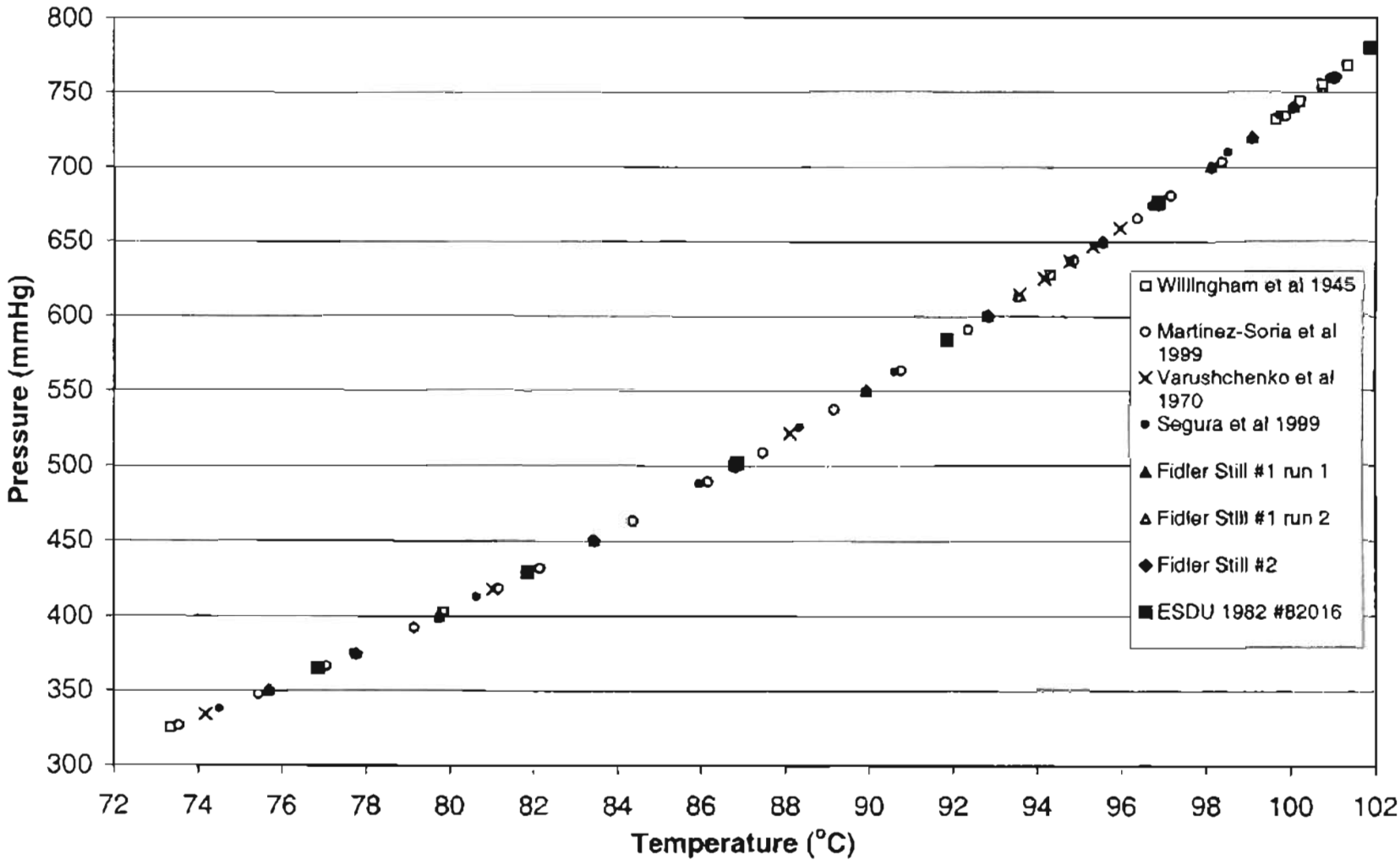

Figure 8. Methylcyclohexane Vapor Pressure

these constants to obtain 'smoothed' differences in pressure and temperature compared to Still #1 (run 1), as shown in Figures 9 and 10. The following procedure was used to obtain smoothed temperature differences: write Antoine equations for Still #1 (run 1) and the reference data, set the pressures equal, pick a temperature for Still #1 (run 1), solve for the reference temperature, then take the difference between the two temperatures. The following equation was used:

$$T_{ref} = \frac{B_{ref}}{A_{ref} - A_1 + \frac{B_1}{T_1 + C_1}} - C_{ref} \tag{5-1}$$

The temperatures picked for Still #1 (run 1) span the operating range at intervals of 0.25°C. A similar procedure was used to obtain smoothed pressure differences by setting the temperatures in the Antoine equations equal, picking a pressure for Still #1 (run 1), solving for the reference pressure and taking the difference. The following equation was used:

$$P_{ref} = \exp\left(A_{ref} - \frac{B_{ref}}{\frac{B_1}{A_1 - \ln P_1} - C_1 + C_{ref}} \right) \tag{5-2}$$

Similarly, the pressures picked for Still #1 (run 1) spanned the pressure range at intervals of 5 mmHg.

Figure 9 shows that at low temperatures, up to about 93°C, the work of Martinez-Soria et al. (Martinez-Soria, Pena et al. 1999) agrees with this work within experimental uncertainty. At higher temperatures, above 95°C, Willingham et al. (Willingham, Taylor et al. 1945), Varushchenko et al. (Varushchenko, Belikova et al. 1970), and ESDU

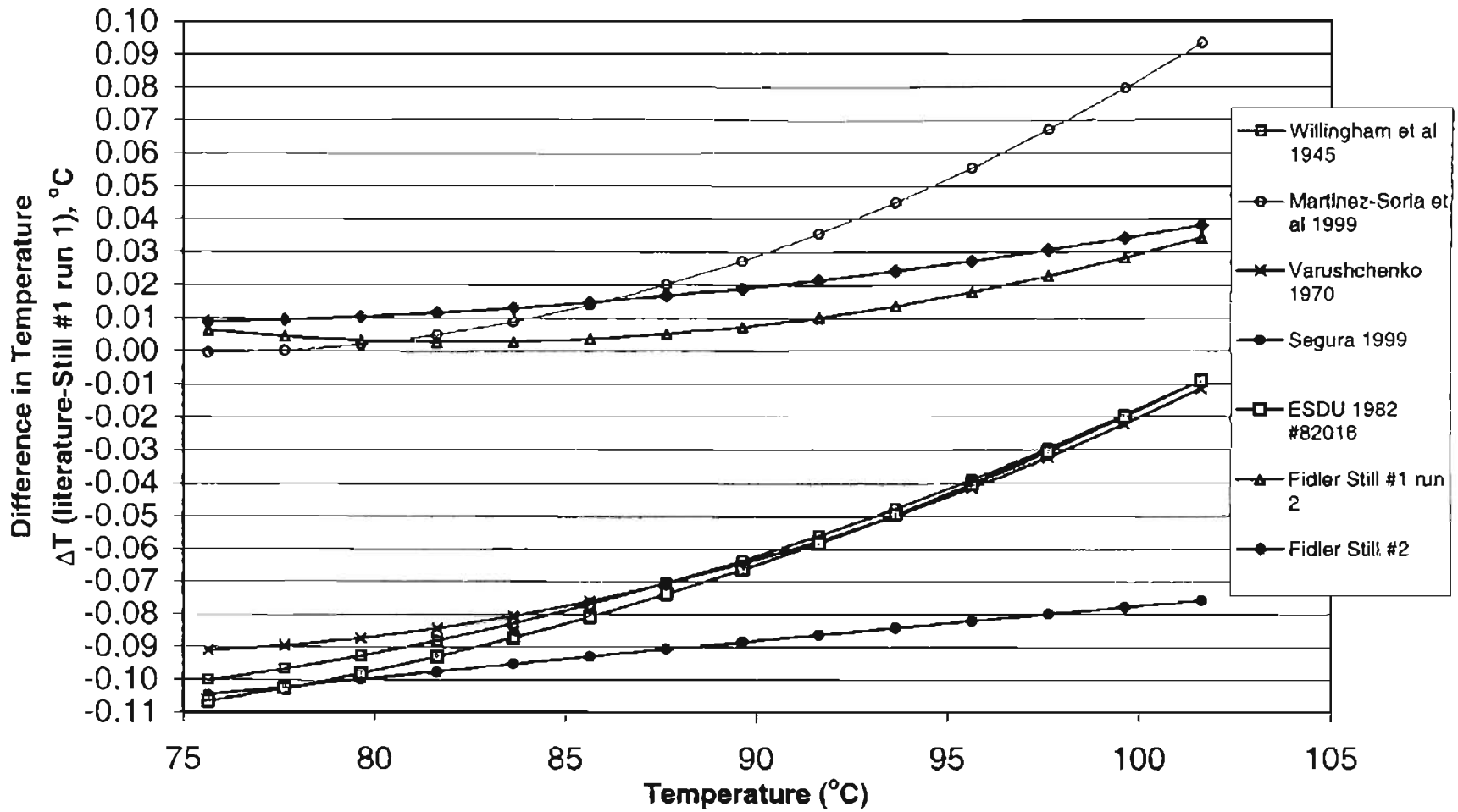

Figure 9. Smoothed Comparison of Temperature Differences in Methylcyclohexane to Still #1 Run 1

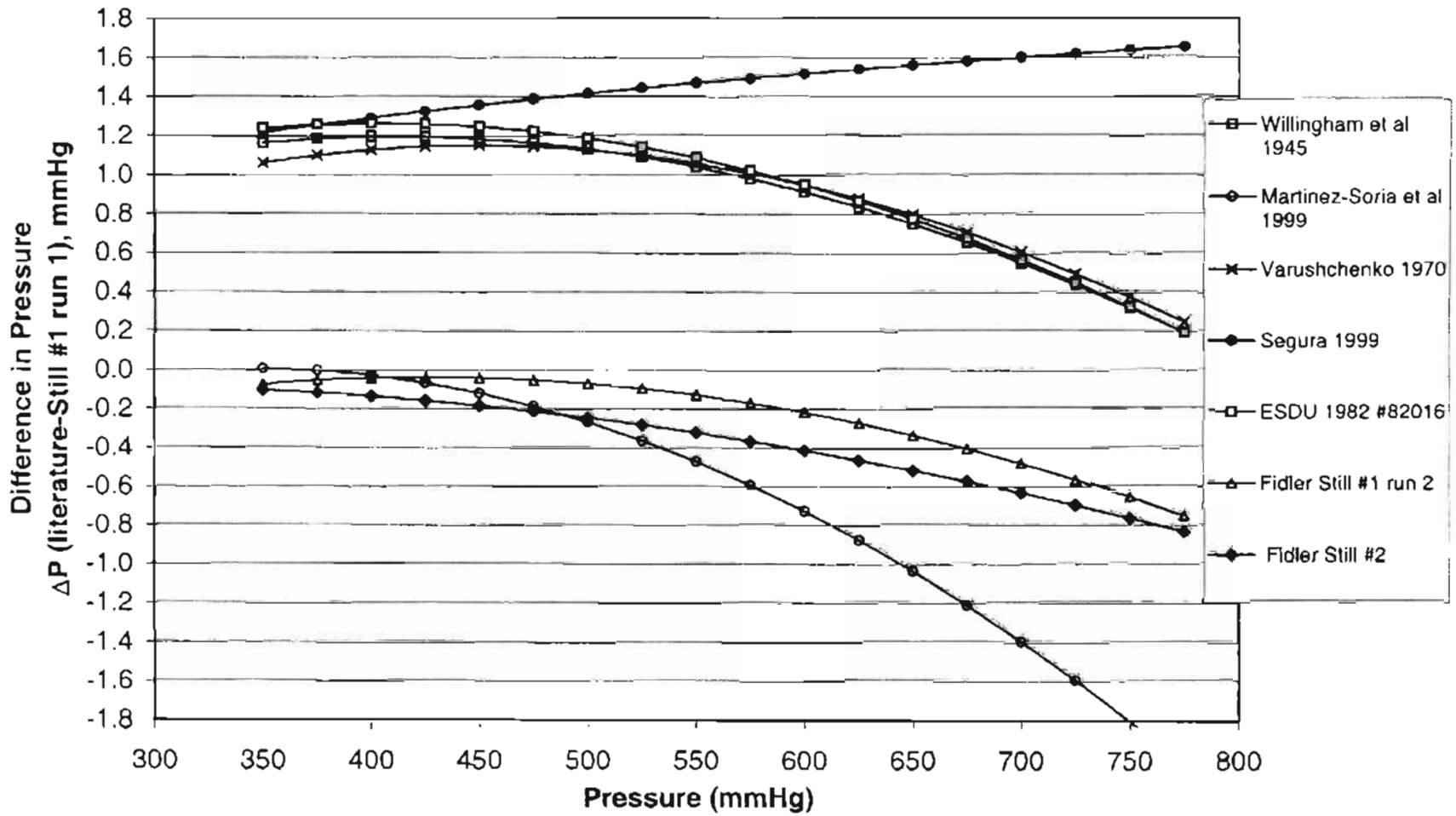

Figure 10. Smoothed Comparison of Pressure Differences in Methylcyclohexane to Still #1 Run 1

#82016(1982) agree with this work with experimental uncertainty. One interesting note is that the work of Martinez-Soria et al. seems to have an offset of +0.10°C from the data of Willingham et al., Varushchenko et al., and ESDU.

Figure 10 also shows agreement with Martinez-Soria et al. at low pressures and with Willingham et al., Varushchenko et al., and ESDU at higher pressures. However, only Martinez-Soria et al. is within experimental uncertainty at pressures lower than 410 mmHg. Again, the work of Martinez-Soria et al. seems to have an offset from Willingham et al., Varushchenko et al., and ESDU.

Hexane

The experimental vapor-pressure data for hexane are presented in Table 3.

Table 3. Hexane Vapor Pressure

Still #1		Still #2	
Temperature (°C)	Pressure (mmHg)	Temperature (°C)	Pressure (mmHg)
68.75	760	68.75	760
67.91	740	67.91	740
67.04	720	67.05	720
66.16	700	66.16	700
65.03	675	65.03	675
63.86	650	63.87	650
61.43	600	61.43	600
58.82	550	58.82	550
58.82	550	58.82	550
56.02	500	56.02	500
52.99	450	52.99	450
49.68	400	49.68	400
47.90	375	47.91	375
46.03	350	46.03	350

The temperature differences between the data collected on Stills #1 and #2 and the Engineering Sciences Data Unit (ESDU) #84022(1984) are shown in Figure 11. The data collected on the two stills are in very good agreement with one another and the maximum deviation from the literature data is +0.075°C at low temperatures. The data are within experimental uncertainty at temperatures above 58°C, roughly about half of the operating range. Figure 12 shows the pressure difference of the experimental data and the literature data. Once again, the data from the two stills are in very good agreement with one another, but the pressure differences from literature data exceed experimental uncertainty

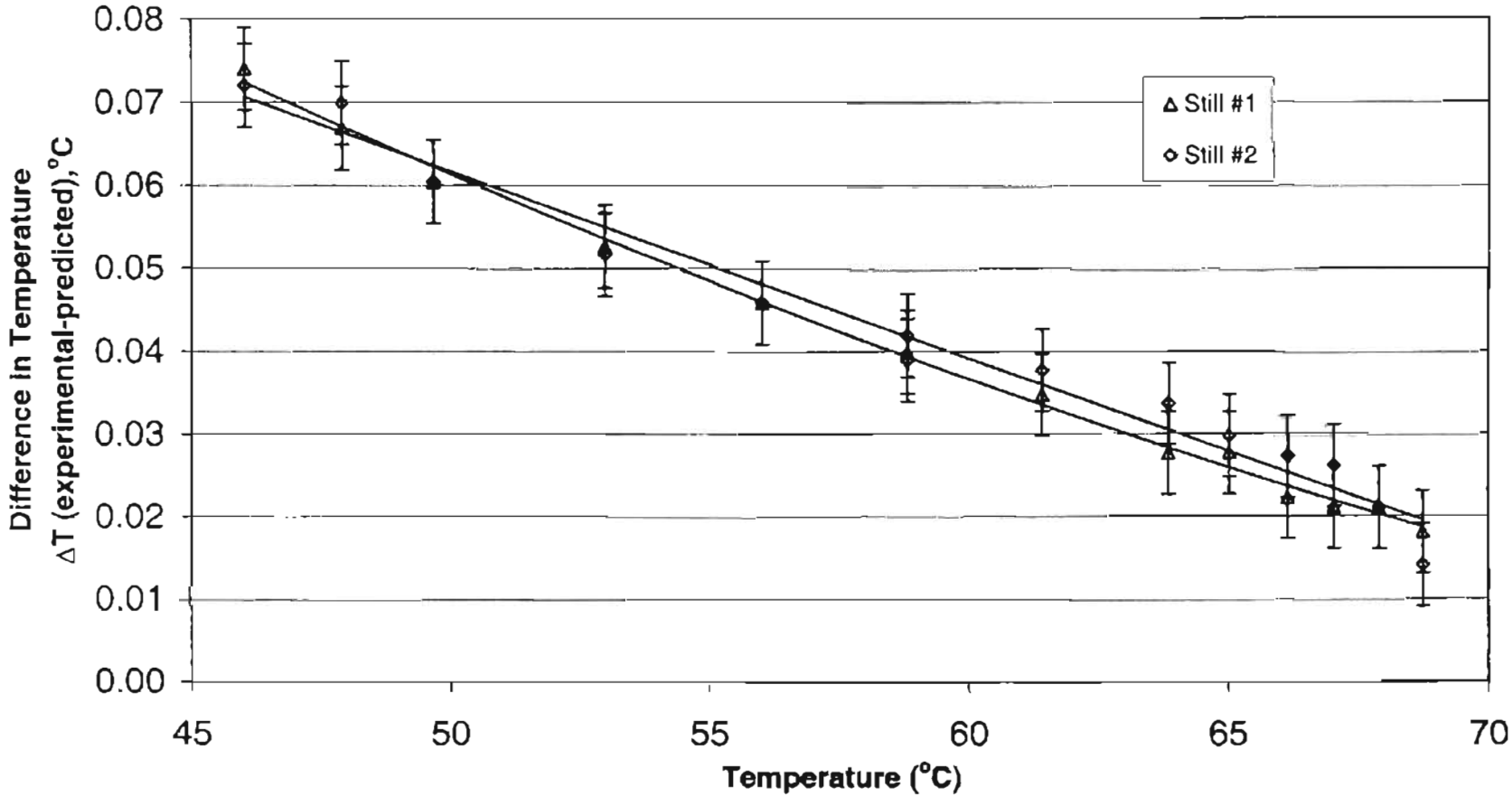

Figure 11. Hexane Vapor Pressure compared to ESDU #84022: Temperature Differences

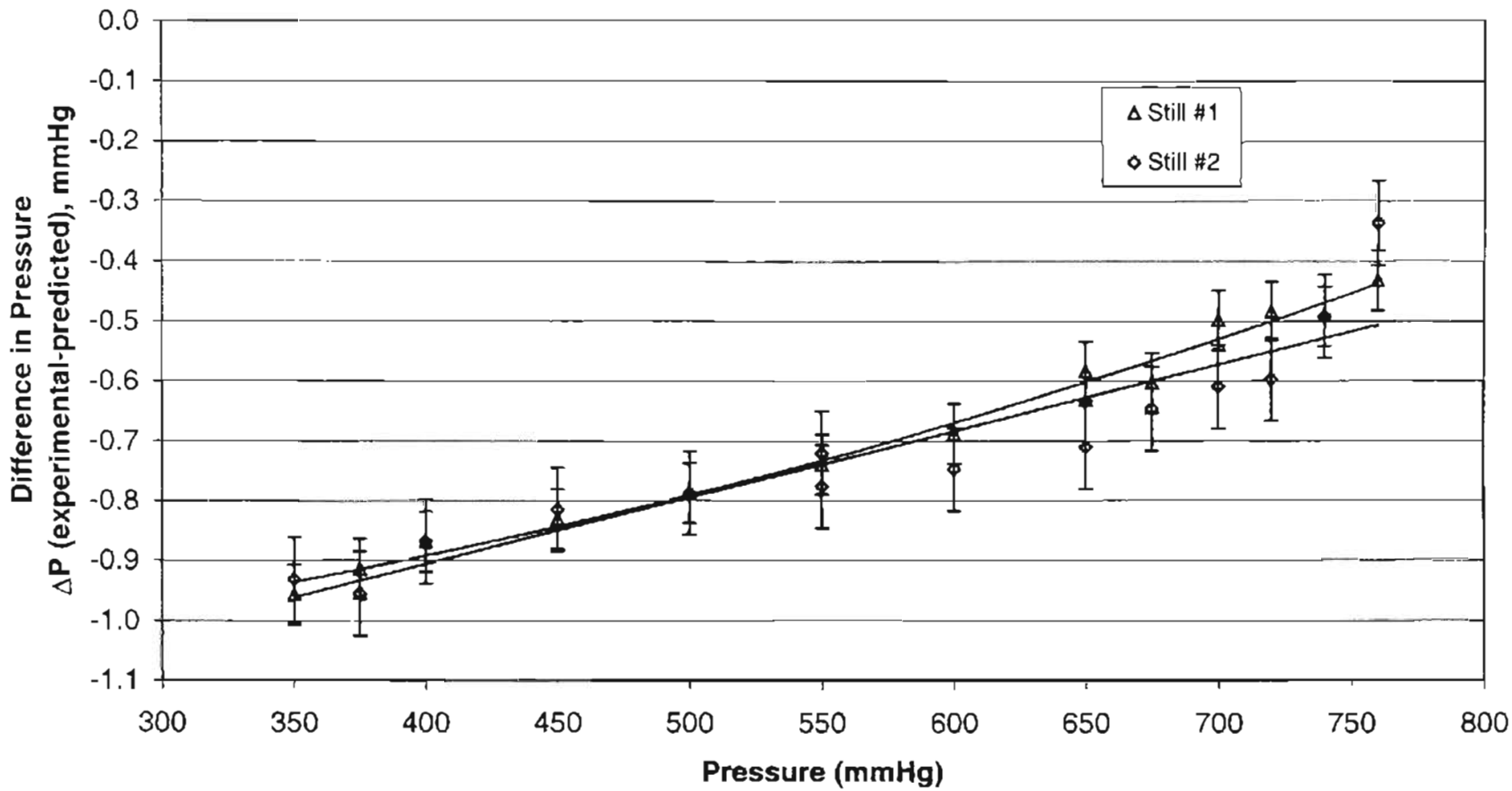

Figure 12. Hexane Vapor Pressure Compared to ESDU #84022: Pressure Differences

over the entire operating range. The maximum deviation from the literature data is about –0.95 mmHg at low pressures.

Figure 13 shows temperature versus pressure data for this work and available literature sources. Only extremely deviant data are apparent on this plot, one data point from Ringel and one point from Oscarson et al. are obviously different from the bulk of data. The previously described procedure was again used to create smoothed comparisons of the data. The data from Oscarson et al. only contained three data points in the range of interest and were not used in the smooth comparison since an Antoine fit with only three data points was not helpful. The data from Ringel were also omitted. This data only contained four data points in the range of interest and one of those was extremely deviant from the bulk of data. Therefore, the Antoine fit obtained for Ringel's work produced errors of magnitude greater than 300 mmHg for the smoothed pressure difference and greater than 250°C for the smoothed temperature difference.

The smoothed temperature differences in Figure 14 have the same general appearance as those for methylcyclohexane (Figure 9). Near the normal boiling point, Still #1 is about 0.01-0.02°C higher than Willingham et al. (Willingham, Taylor et al. 1945) and ESDU(1984),(1972), again ESDU was calculated using data from Willingham et al. (Willingham, Taylor et al. 1945). At lower temperatures, Still #1 is 0.06-0.08°C higher which exceeds experimental uncertainty. The temperature differences for methylcyclohexane compared to Willingham et al. (Willingham, Taylor et al. 1945) and ESDU(1982) were also about –0.01°C near the normal boiling point, but increased to -0.10°C at the lower temperatures.

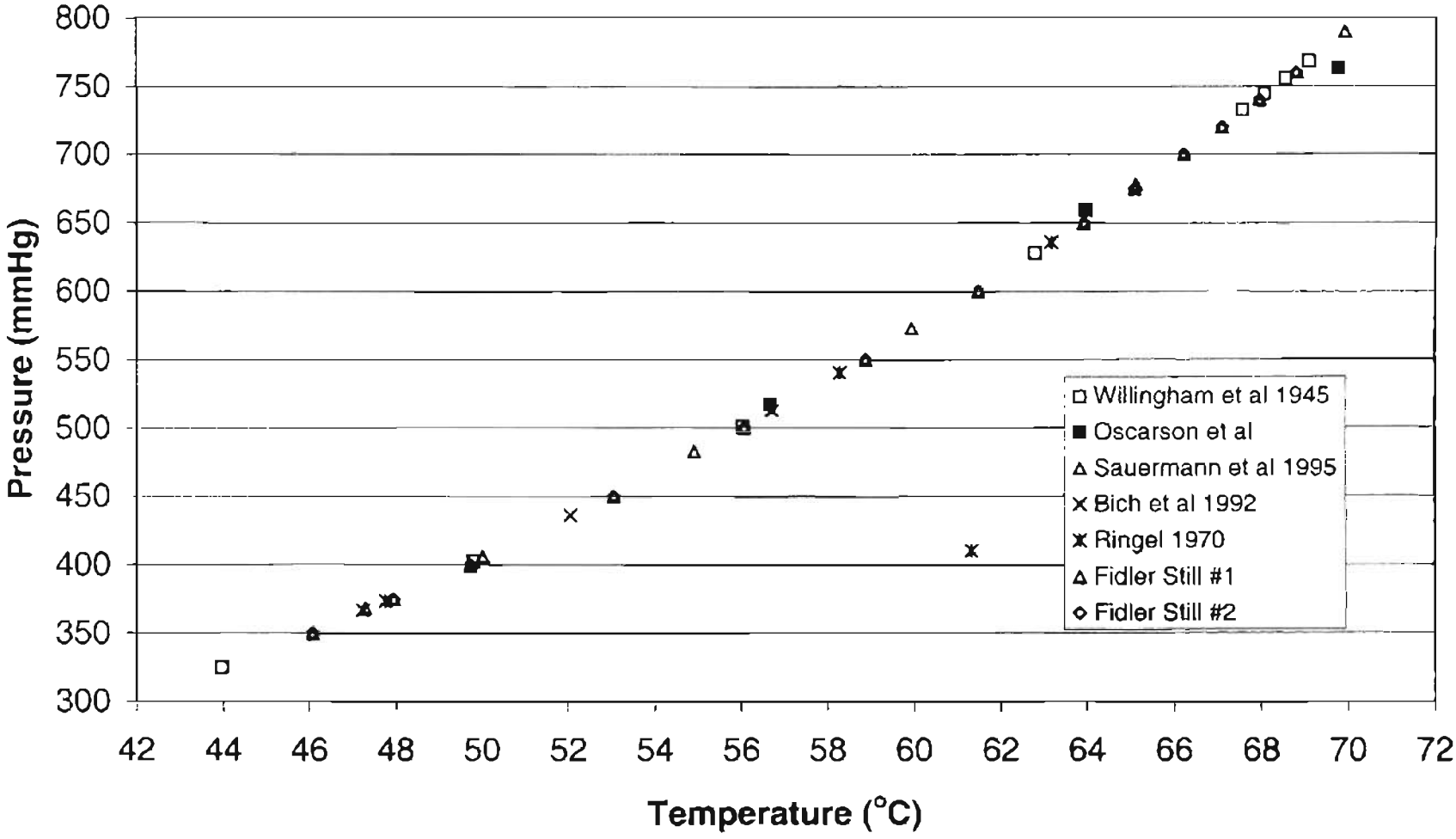

Figure 13. Hexane Vapor Pressure

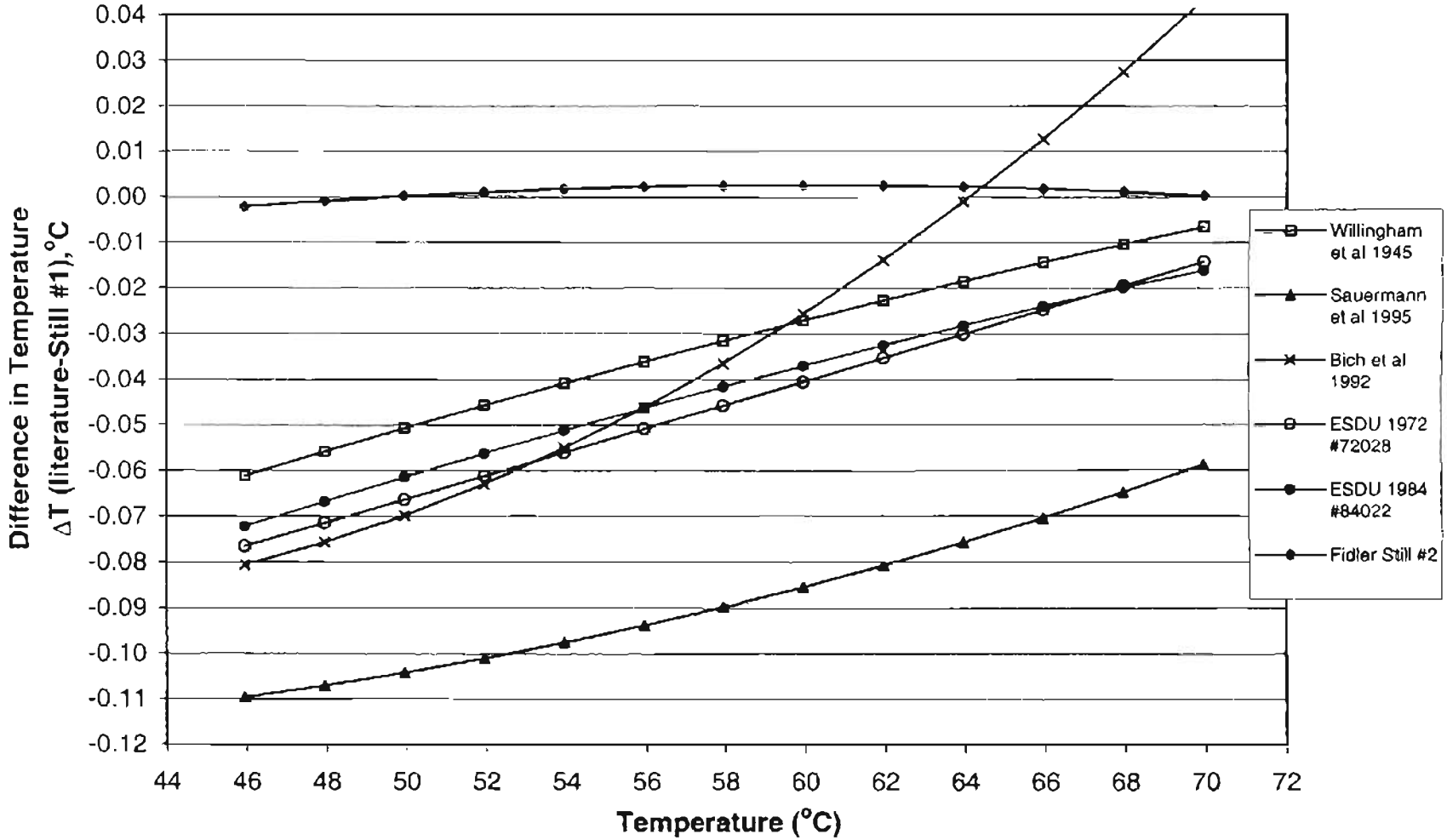

Figure 14. Smoothed Comparison of Temperature Differences in Hexane to Still #1

Figure 15 shows the smoothed pressure differences for hexane compared to Still #1. At 760 mmHg, Willingham et al. (Willingham, Taylor et al. 1945) is 0.2 mmHg higher and increases to 0.8 mmHg higher at 350 mmHg. ESDU(1984),(1972) is 0.4 mmHg higher at 760 mmHg and 0.9-1.0 higher at 350 mmHg. All of these errors exceed the experimental uncertainty of approximately 0.04 mmHg. The works of Bich et al. (Bich, Lober et al. 1992) and Sauermann et al. (Sauermann, Holzapfel et al.) disagree greatly with this work.

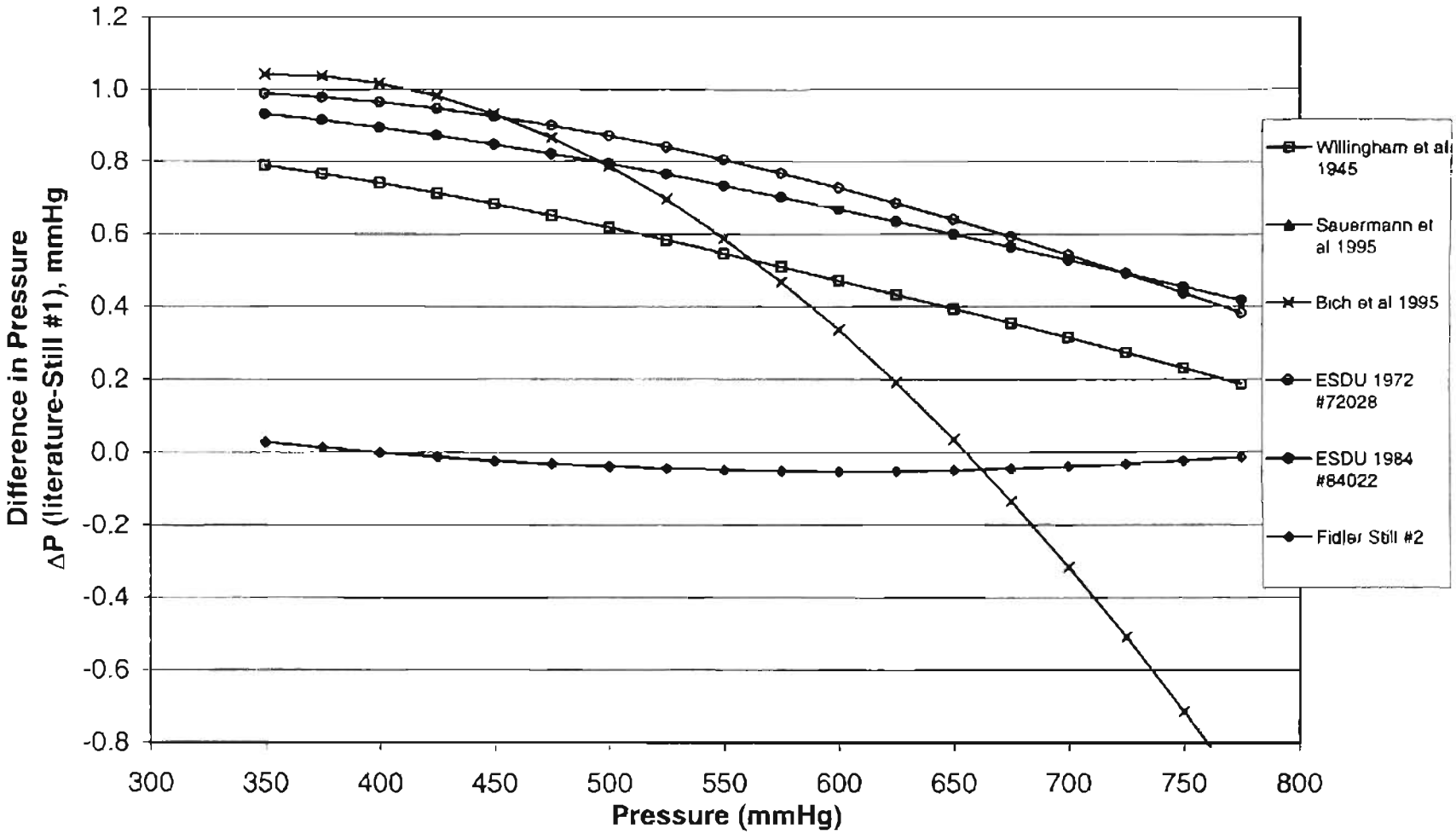

Figure 15. Smoothed Comparison of Pressure Differences in Hexane to Still #1

Toluene

The experimental toluene vapor-pressure data are listed in Table 4.

Table 4. Toluene Vapor Pressure

Still #1 – Run 1		Still #1 – Run 2		Still #2	
Temperature (°C)	Pressure (mmHg)	Temperature (°C)	Pressure (mmHg)	Temperature (°C)	Pressure (mmHg)
110.65	760	110.65	760	110.65	760
109.72	740	109.71	740	109.73	740
108.78	720	108.76	720	108.78	720
107.80	700	107.79	700	107.80	700
106.55	675	106.54	675	106.55	675
105.26	650	105.26	650	105.26	650
102.56	600	102.56	600	102.57	600
99.67	550	99.68	550	99.69	550
96.57	500	96.58	500	96.59	500
93.22	450	93.23	450	93.23	450
89.56	400	89.57	400	89.57	400
85.51	350	85.51	350	85.48	350
87.59	375	87.59	375	87.60	375
99.68	550	99.68	550	99.69	550

The data were compared to ESDU #86012(1986), which was compiled using the works of Willingham et al. (Willingham, Taylor et al. 1945) and Forziati et al. (Forziati, Norris et al. 1949). The temperature differences are shown in Figure 16. The three runs on the two stills agree within 0.01°C but vary from the literature data 0.015°C at the normal boiling point to 0.09°C at low pressures. Still #1 (run 1) and Still #2 only agree within experimental uncertainty above temperatures of about 108°C and Still #1 (run 2) agrees above temperatures of 105°C. Again, the stills produce precise but not consistent data over the entire operating range with the values from ESDU. The pressure differences are shown in Figure 17. The three runs differ from one another by more than the

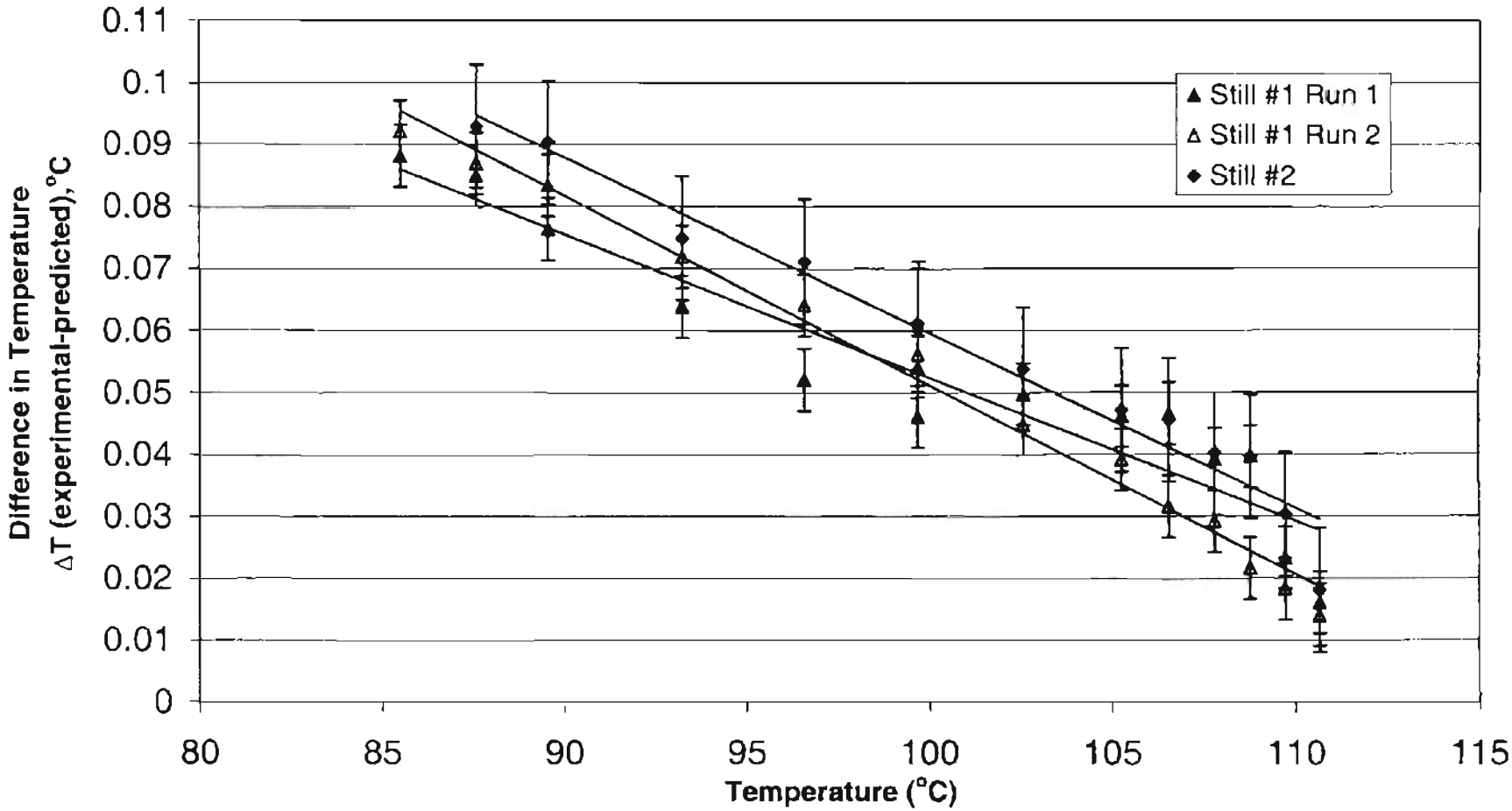

Figure 16. Toluene Vapor Pressure Compared to ESDU #86012: Temperature Differences

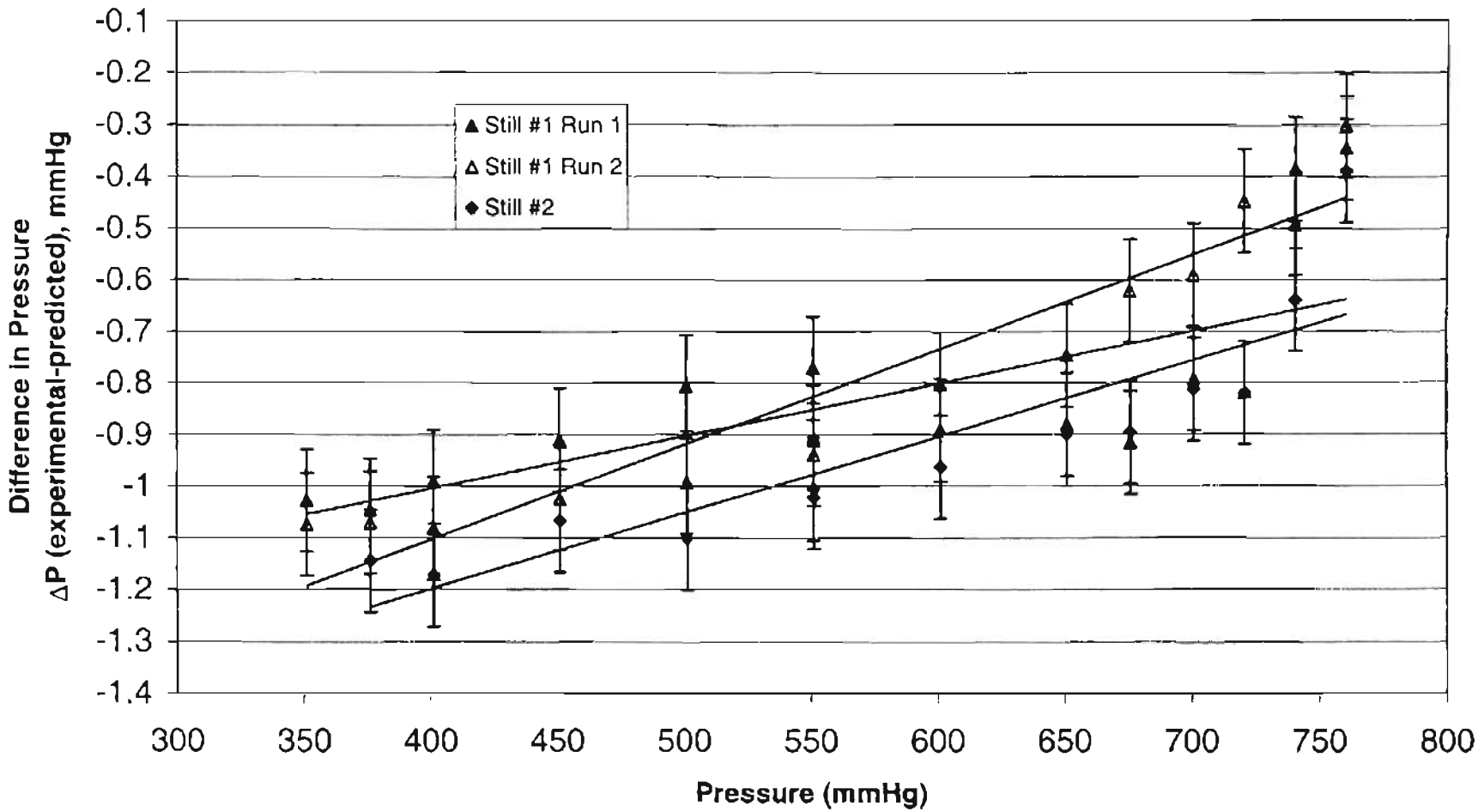

Figure 17. Toluene Vapor Pressure Compared to ESDU #86012: Pressure Differences

experimental uncertainty and differ from ESDU data by about –1.1 mmHg at low pressures.

The vapor-pressure data for this work and available literature sources are shown in Figure 18. There are no extremely deviant data evident on this plot.

Figure 19 shows the smoothed temperature differences compared to Still #1 run 2. All of the literature data except Reich et al. (Reich, Cartes et al. 1998) are in agreement within experimental uncertainty at the normal boiling point and most agree at temperatures above about 105°C.

The smoothed pressure differences are shown on Figure 20. The majority of the literature data varies from about 0.4 mmHg higher at atmospheric pressure to 1.1 mmHg higher at low pressures. The data from Willingham et al. (Willingham, Taylor et al. 1945), Forziati et al. (Forziati, Norris et al. 1949), ESDU #73029(1973), and ESDU #86012(1986) are within 0.2 mmHg over the operating range which exceeds the experimental uncertainty for this project. The reported uncertainty in pressure for the four literature sources are reported to be in the range of 0.04 to 0.08 mmHg which means these sources are in fairly good agreement with one another. The works of Martinez-Soria et al. (Martinez-Soria, Pena et al. 1999) and Reich et al. (Reich, Cartes et al. 1998) disagree with this work as well as the other literature sources.

Figures 21 and 22 show the temperature differences and pressure differences, respectively, compiled for the four pure components. A clear trend is not apparent for all four components that would allow further correction of temperature or pressure measurements; therefore, only the correction of 0.047°C previously discussed will be made for subsequent temperature measurements.

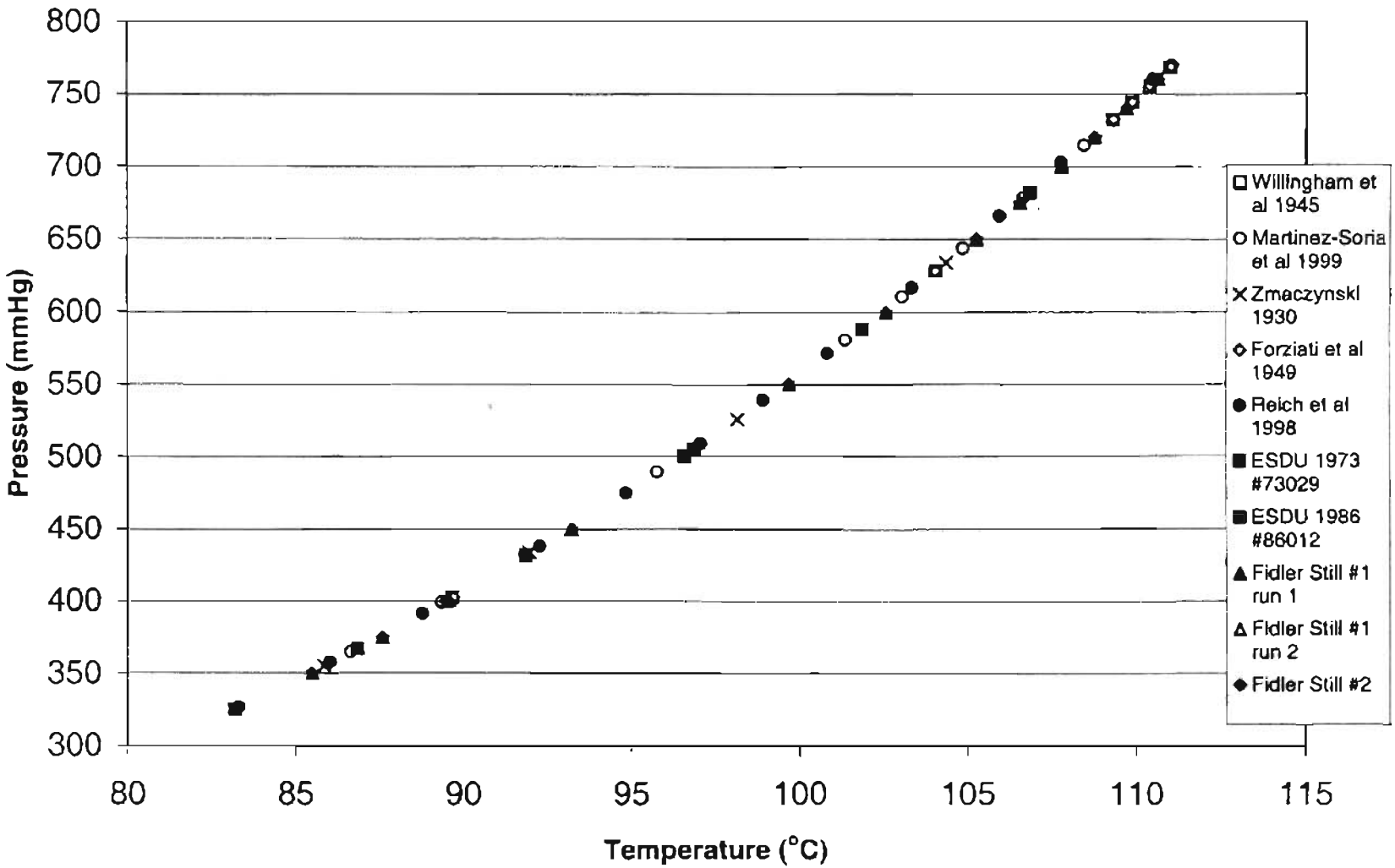

Figure 18. Toluene Vapor Pressure

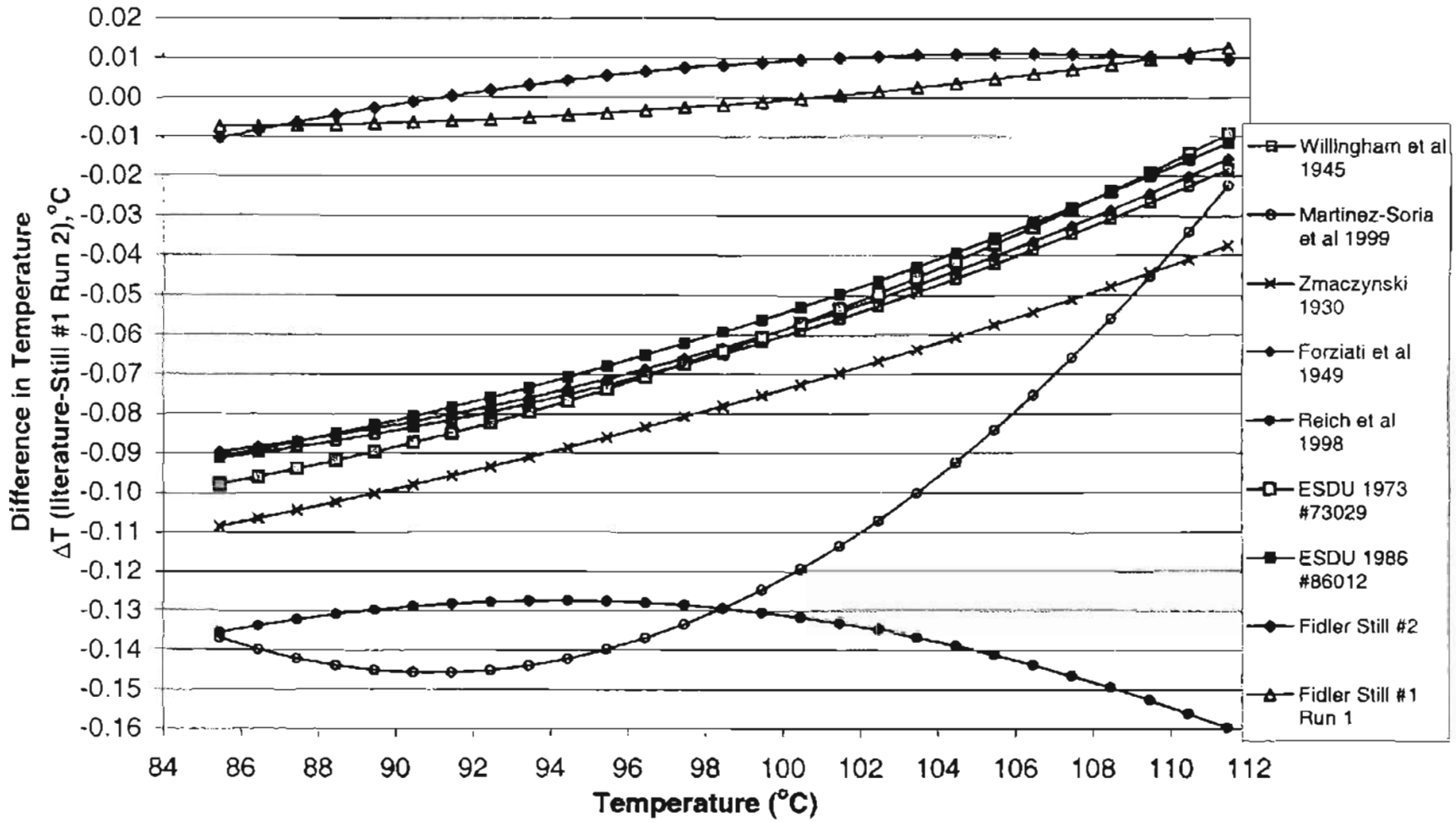

Figure 19. Smoothed Comparison of Temperature Differences in Toluene to Still #1 Run 2

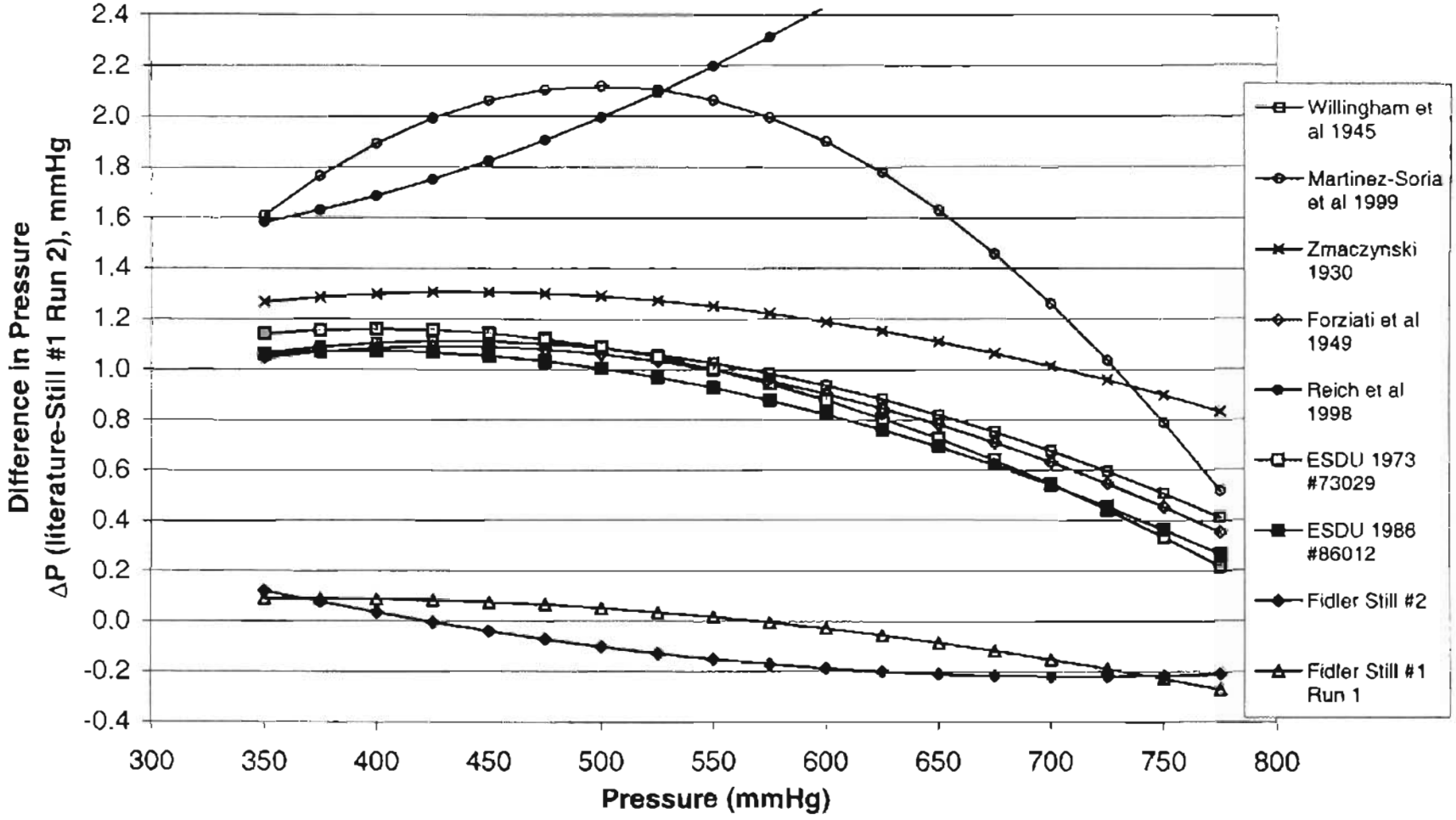

Figure 20. Smoothed Comparison of Pressure Differences in Toluene to Still #1 Run 2

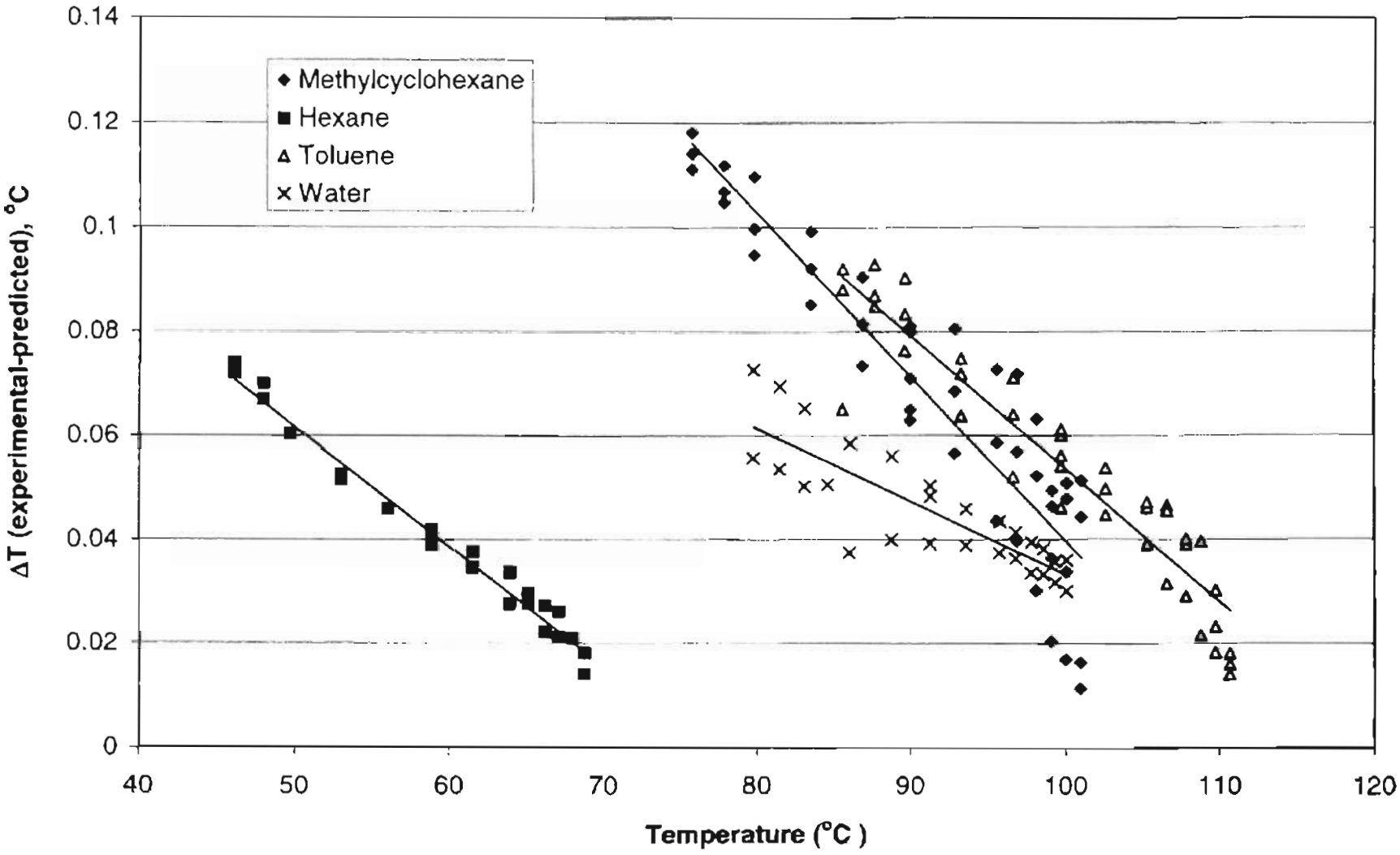

Figure 21. Temperature Difference for Pure Components

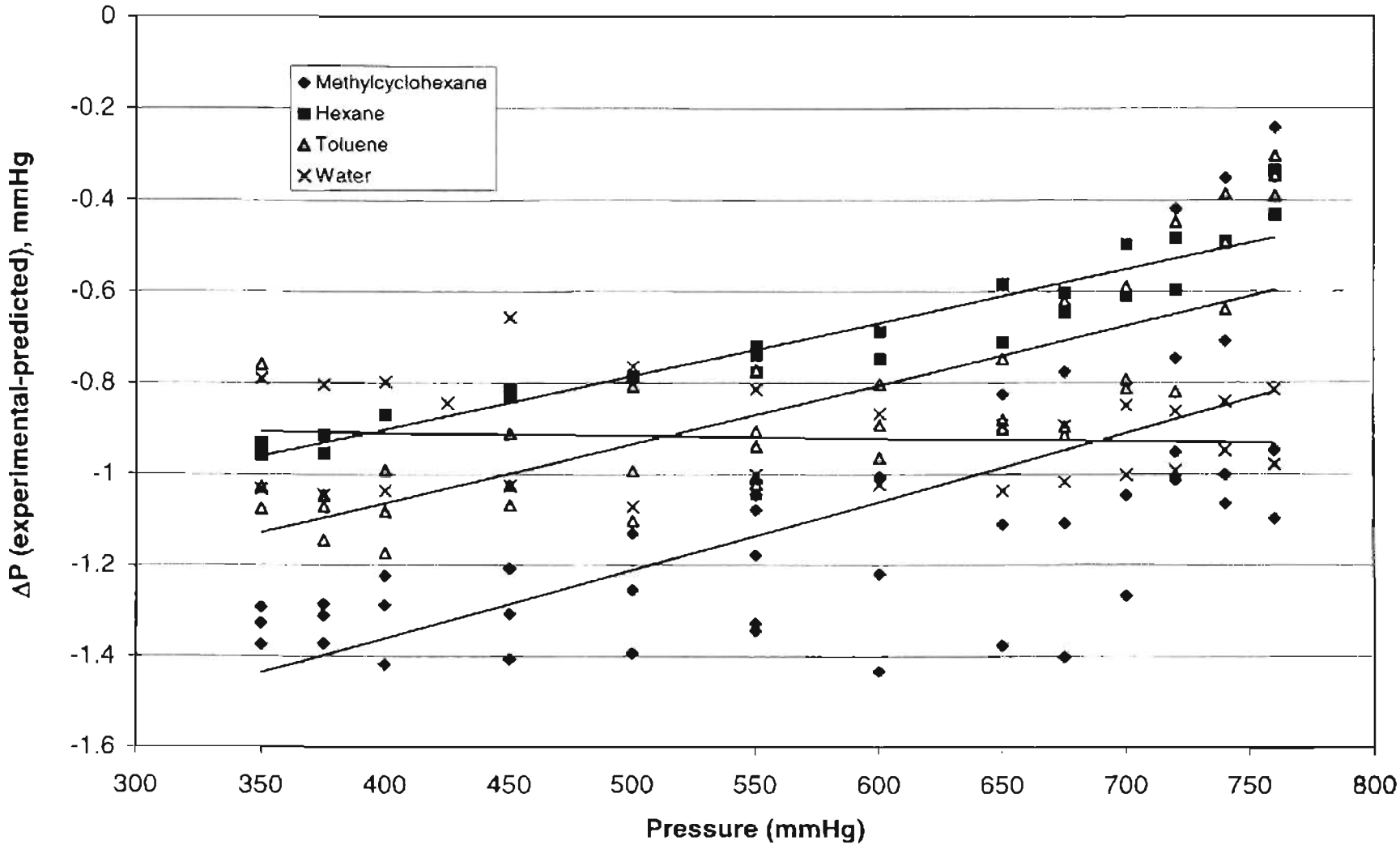

Figure 22. Pressure Difference for Pure Components

The main conclusions reached for pure-component vapor pressures is that the current stills produce data that are precise, but only accurate in the temperature differences compared to literature data at or near atmospheric pressure. The pressure differences exceed experimental uncertainty over the operating range for all pure components.

Vapor-Liquid Equilibrium Data

Methylcyclohexane + Toluene at 760 mmHg

This system was run in both equilibrium stills. Tables 5 and 6 contain the VLE data for the methylcyclohexane + toluene system at 760 mmHg from Still #1 and Table 7 contains data from Still #2. Ten literature sources (Quiggle and Fenske 1937; Garner and Hall 1955; Thijssen 1955; Smit and Ruyter 1960; Robinson Jr. 1962; Ellis and Contractor 1964; Ellis, Broughton et al. 1969; Tyminski and Klepanska 1977; Coca and Pis 1979; Sura 1991) were found for methylcyclohexane + toluene at 760 mmHg; however, two of the sources (Thijssen 1955; Smit and Ruyter 1960) did not include temperature data so they could not be included in the temperature versus composition or the temperature difference versus liquid mole fraction plots. They were included in the vapor mole fraction versus liquid mole fraction and vapor mole fraction difference versus liquid mole fraction plots which will follow. The data were plotted for temperature versus composition along with the literature sources to see if any gross errors were present, see Figure 23. The data from Still #1 were in agreement with the literature sources for most of the run, however the data from Still #2 were in very poor agreement with the literature. The observed temperature was about 2 to 3°C below the expected temperature at a given mole fraction and temperature readings were very unstable. The drop rate was increased from about 70 drops per minute to 200 drops per minute and the temperature was still almost 1°C lower than expected. An important note is that some of the literature data are not in good agreement in the methylcyclohexane-rich region. One possible reason is the contamination of methylcyclohexane with water from the surroundings if it is opened without a nitrogen blanket. The presence of water would lower the boiling point and

Table 5. Methylcyclohexane (1) + Toluene (2) at 760 mmHg, Still #1, Data Set 1

Run	Liquid Mole Fraction x_1	Vapor Mole Fraction y_1	Temperature (°C)
1	1.0000	1.0000	100.94
1	0.9556	0.9599	101.03
1	0.9085	0.9181	101.15
1	0.8733	0.8864	101.27
1	0.8373	0.8544	101.39
1	0.8057	0.8266	101.53
1	0.7667	0.7935	101.70
1	0.7208	0.7551	101.93
1	0.6859	0.7243	102.14
1	0.6464	0.6911	102.37
1	0.6086	0.6589	102.64
1	0.5622	0.6189	102.96
1	0.5250	0.5874	103.26
2	0.5082	0.5726	103.37
1	0.4923	0.5585	103.53
2	0.4744	0.5426	103.66
1	0.4592	0.5279	103.83
2	0.4358	0.5071	104.02
2	0.3972	0.4735	104.40
2	0.3622	0.4394	104.79
2	0.3212	0.4010	105.24
2	0.2915	0.3716	105.62
2	0.2582	0.3369	106.07
2	0.1905	0.2596	107.04
2	0.1644	0.2293	107.44
2	0.1384	0.1984	107.86
2	0.1149	0.1678	108.28
2	0.0887	0.1331	108.75
2	0.0628	0.0978	109.24
2	0.0000	0.0000	110.61

Table 6. Methylcyclohexane (1) + Toluene (2) at 760 mmHg, Still #1, Data Set 2

Run	Liquid Mole Fraction x_1	Vapor Mole Fraction y_1	Temperature (°C)
1	1.0000	1.0000	100.94
1	0.9556	0.9594	101.02
1	0.9139	0.9214	101.14
1	0.8735	0.8862	101.26
1	0.8358	0.8516	101.40
1	0.8030	0.8241	101.53

change the refractive index of the mixture. The methylcyclohexane in this study was opened only under a nitrogen blanket. Figure 24 shows vapor composition versus liquid composition. Gross errors can also be seen on this plot. One point from Thijssen (Thijssen 1955) deviated from the bulk, this point was removed and was believed to be a typographical error since the same vapor mole fraction was listed for liquid mole fractions of 0.30 and 0.35. At any given liquid mole fraction, the vapor mole fractions in Still #2 are about 0.05 higher than those from Still #1 and the literature data. Due to the instability and poor results, it was concluded that Still #2 should not be used for VLE measurements. No conclusive evidence was found to explain the poor behavior of Still #2.

The data were evaluated using consistency tests previously described. This section will detail the results of the external and thermodynamic consistency tests. The data were regressed using several activity coefficient models and equations of state using the previously described GEOS program (see Appendix D for a sample of GEOS output). The Antoine constants obtained from the pure-component vapor pressures were used and slightly adjusted if necessary to produce zero error at the pure-component ends. Data points which deviated two and one half times the root mean square deviation (RMSD)

Table 7. Methylcyclohexane (1) + Toluene (2) at 760 mmHg, Still #2

Run	Liquid Mole Fraction x_1	Vapor Mole Fraction y_1	Temperature (°C)	Drop Rate (drops/min)
1	0.0000	0.0000	110.66	64
1	0.0213	0.0465	107.91	64
1	0.0502	0.1020	106.85	76
2	0.0505	0.1043	106.78	72
2	0.0831	0.1596	105.98	72
2	0.1122	0.2036	105.35	88
3	0.1124	0.1992	105.44	88
3	0.1258	0.2253	105.14	80
3	0.1547	0.2745	104.49	62
3	0.1876	0.3166	103.97	68
3	0.2276	0.3571	103.49	76
3	0.2637	0.4091	103.15	60
3	0.3100	0.4530	102.72	80
4	0.3113	0.4087	104.64	200
4	0.3105	0.4091	104.64	200
4	0.3105	0.4082	104.61	200
4	0.3099	0.4237	103.98	130
4	0.3092	0.4242	103.91	135
5	0.3085	0.4329	103.68	110
5	0.3083	0.4339	104.79	100
5	0.3482	0.4704	104.46	120
6	1.0000	1.0000	100.94	100
6	0.9556	0.9594	101.02	100
6	0.9139	0.9214	101.14	110
6	0.8735	0.8862	101.26	96
6	0.8358	0.8516	101.40	85
6	0.8030	0.8241	101.53	108

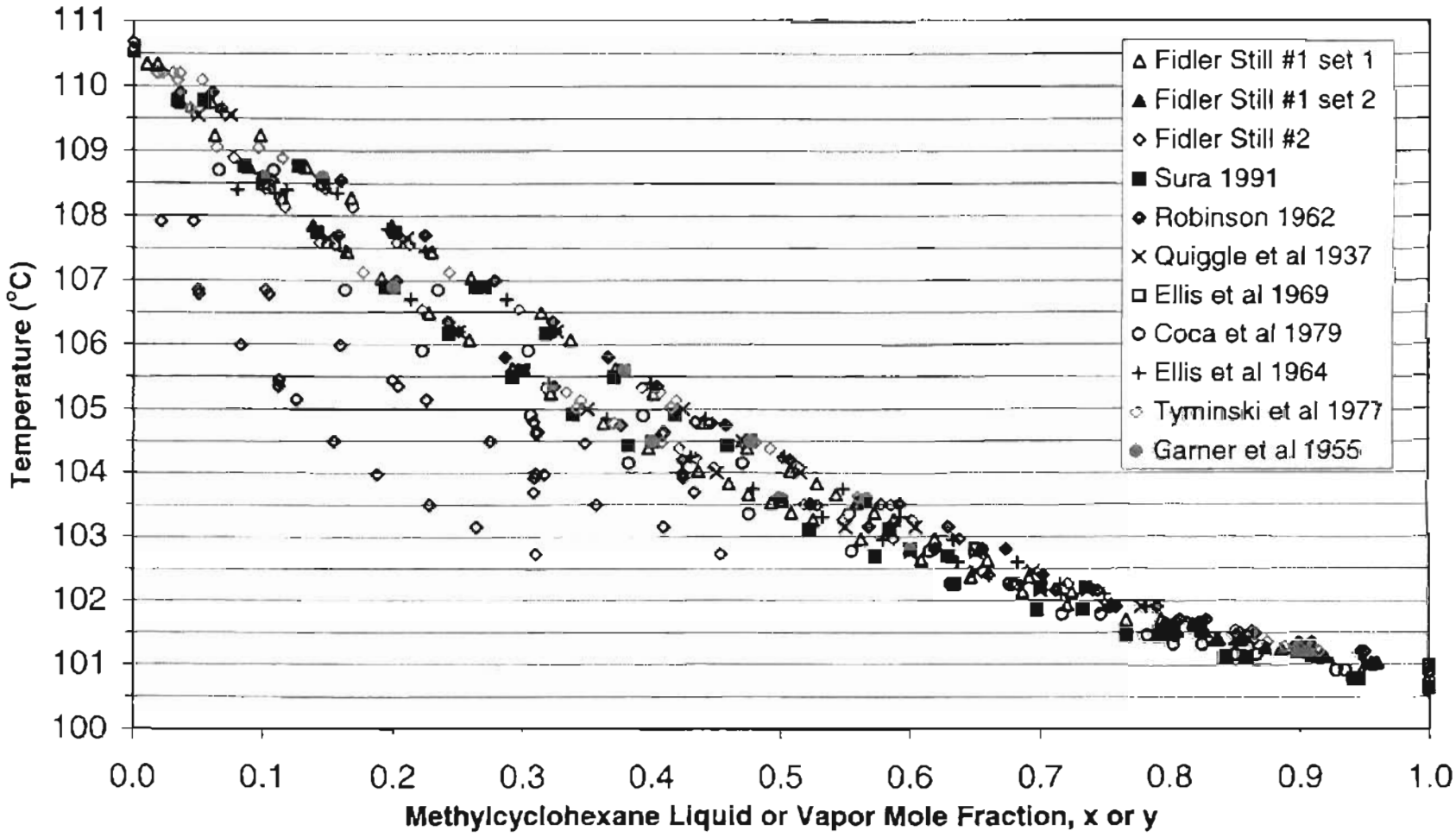

Figure 23. Methylcyclohexane + Toluene at 760 mmHg, Temperature versus Composition

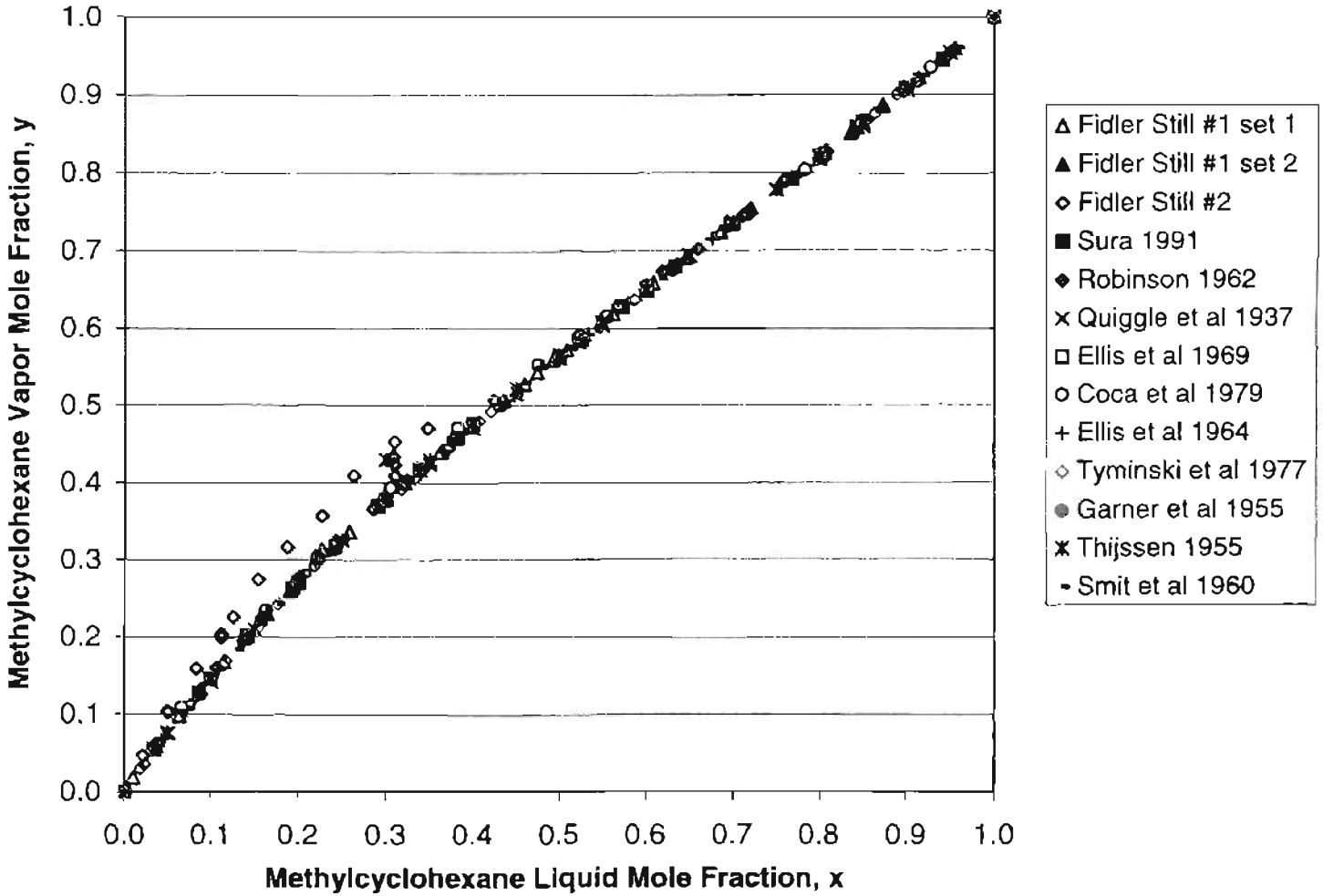

Figure 24. Methylcyclohexane + Toluene at 760 mmHg, Vapor Mole Fraction versus Liquid Mole Fraction

were deemed outliers and removed from the data set, as suggested in the literature (Shaver, Robinson Jr. et al. 2001). Model parameters were obtained by optimizing the data from Still #1 set 1 in GEOS. The optimized parameters were used to calculate values for the literature data to obtain differences for external consistency. The Wilson and Van Laar activity coefficient models were used, as well as the ideal and virial equations of state. Table 8 shows the root mean square deviations (RMSD) in temperature and vapor composition, as well as the binary model parameters for each of the model regressions.

Table 8. Results of Model Regression for Methylcyclohexane + Toluene at 760 mmHg, Still #1 set 1

Activity Coefficient Model	Equation of State	Root Mean Square Deviation (RMSD) T (°C)	y, Vapor Composition	Model Parameters Λ(1,2)	Λ(2,1)
Wilson	Ideal	0.0105	0.0028	0.86625	0.90236
Wilson	Virial	0.0106	0.0012	0.84787	0.92722
Van Laar	Ideal	0.0106	0.0028	0.24096	0.23623
Van Laar	Virial	0.0106	0.0012	0.23755	0.22746

The Wilson model and virial equation (truncated after the second term) were chosen for use in the predictive method of thermodynamic consistency tests and as a basis for the external consistency tests. Figure 25 shows the differences in experimental temperatures from those predicted using the Wilson model (fit to the data of this work) and virial

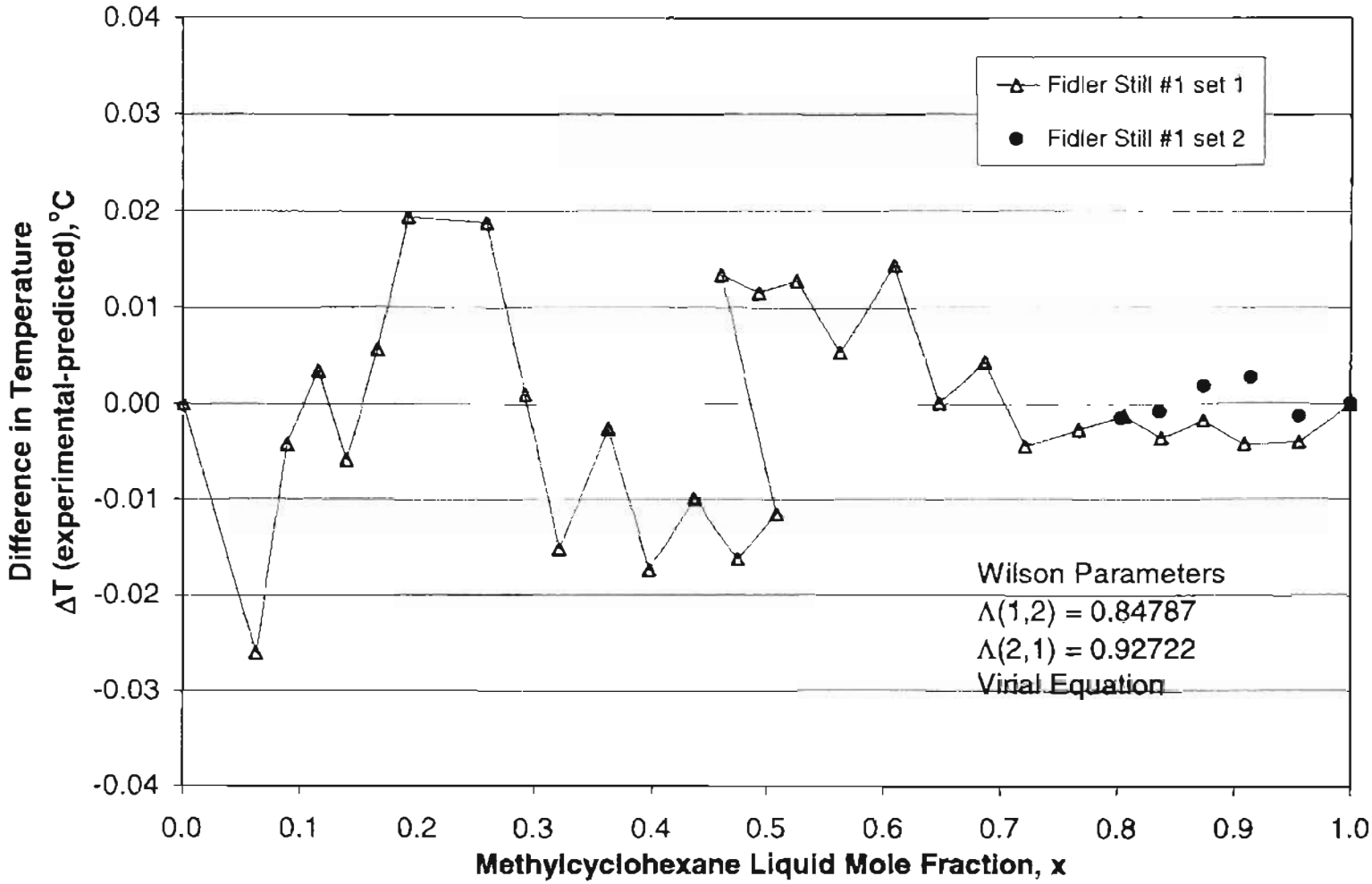

Figure 25. Deviation of Calculated Temperatures for Methylcyclohexane + Toluene at 760 mmHg

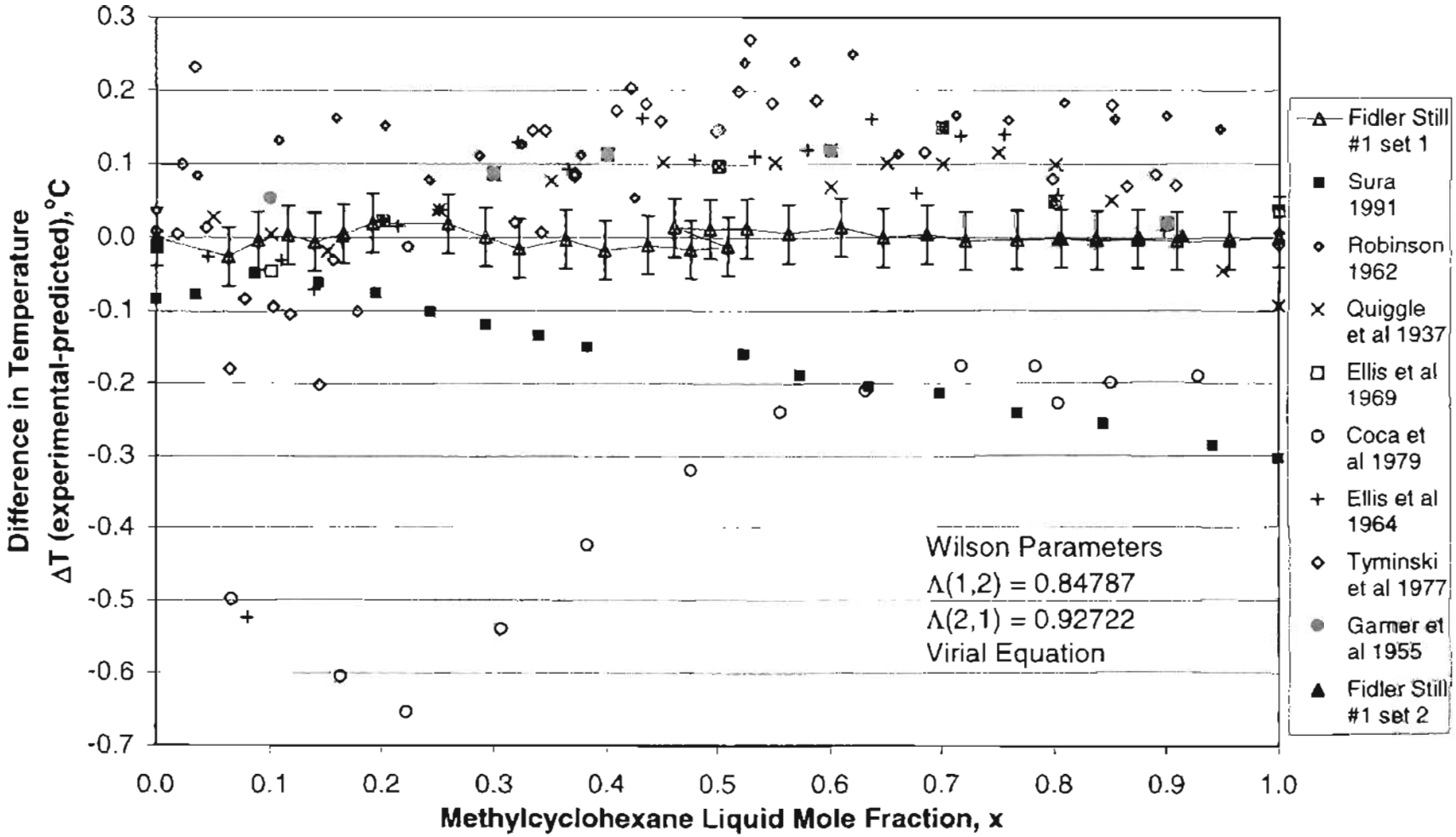

Figure 26. Comparison of Experimental Temperatures for Methylcyclohexane + Toluene at 760 mmHg

equation. This figure represents the predictive method of thermodynamic consistency for temperature. The differences are all within the experimental uncertainty. Figure 26 shows the available literature sources compared with the optimized model for Still #1 set 1. Since the data are fit to this study, the differences from zero only represent the difference from this work and the difference between data points of various researchers represent the difference in those works. There is a scatter of literature data around the current work, however the bulk of the data has a higher experimental temperature, most notably near equimolar mixtures. Some of the literature data (Quiggle and Fenske 1937; Garner and Hall 1955; Robinson Jr. 1962; Ellis and Contractor 1964) only claim accuracies on the order of ±0.1°C, therefore if the uncertainties of these data are considered they are in good agreement with the current work. Most of the pure-component boiling points are in good agreement with this work. As a second check, the Antoine constants were adjusted for each literature source to give zero error at the pure-component end points, see Figure 27. The work of Sura (Sura 1991) is in good agreement with this work. The works of Ellis et al. (Ellis and Contractor 1964; Ellis, Broughton et al. 1969) and Garner et al. (Garner and Hall 1955) claim uncertainties of 0.1 and 0.2°C, respectively, and are in good agreement near the pure-component ends, but differ by 0.1 and 0.15°C at near-equimolar compositions. The error bars for Ellis et al. (Ellis and Contractor 1964) were added to demonstrate that even in the equimolar region the data are in good agreement when the experimental uncertainties of the literature data are considered.

Figure 28 shows the deviation in calculated vapor compositions. The experimental uncertainty for mole fraction is ±0.0015 and is based on deviations from the

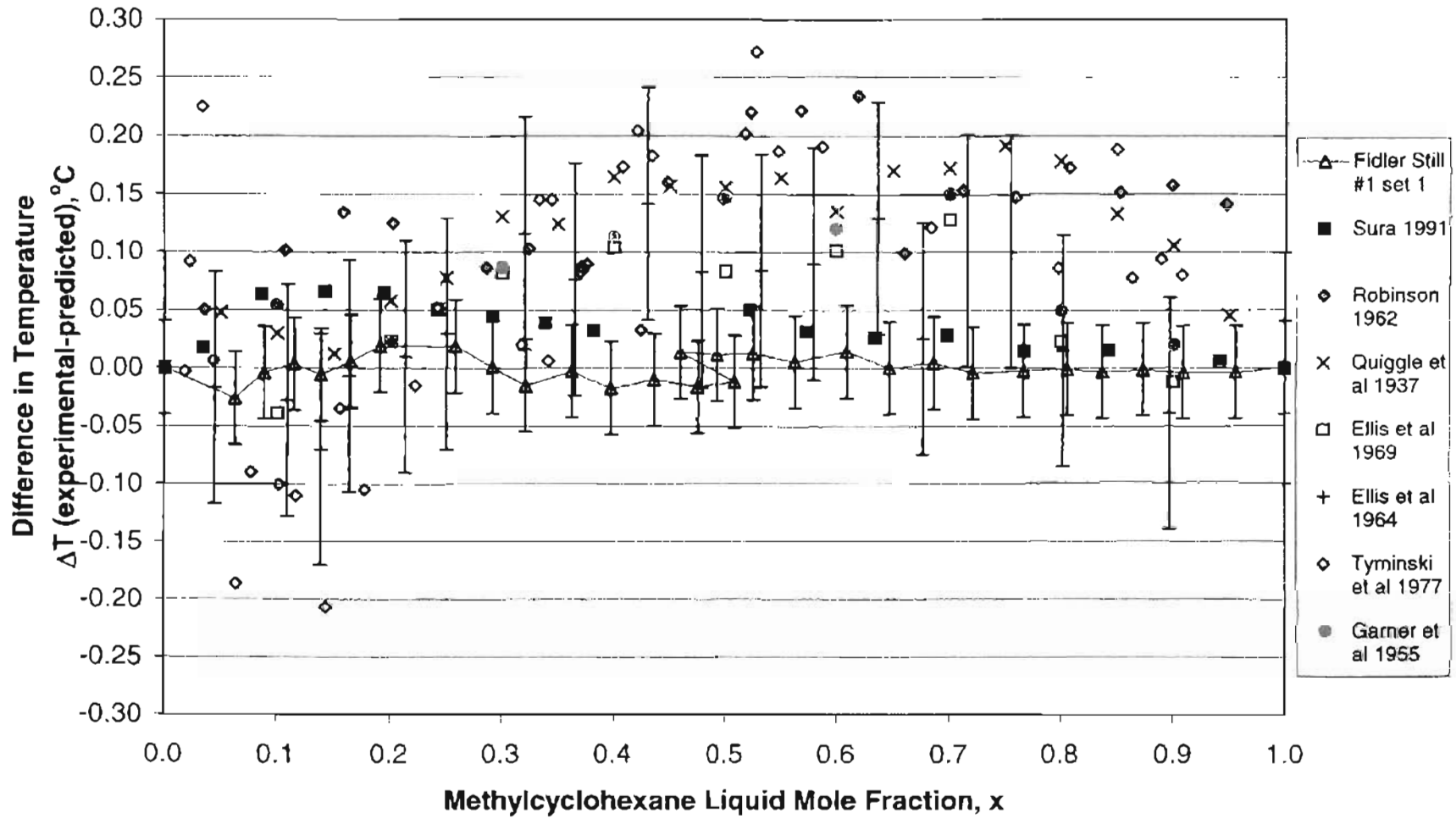

Figure 27. Detailed Comparison of Experimental Temperatures for Methylcyclohexane + Toluene at 760 mmHg

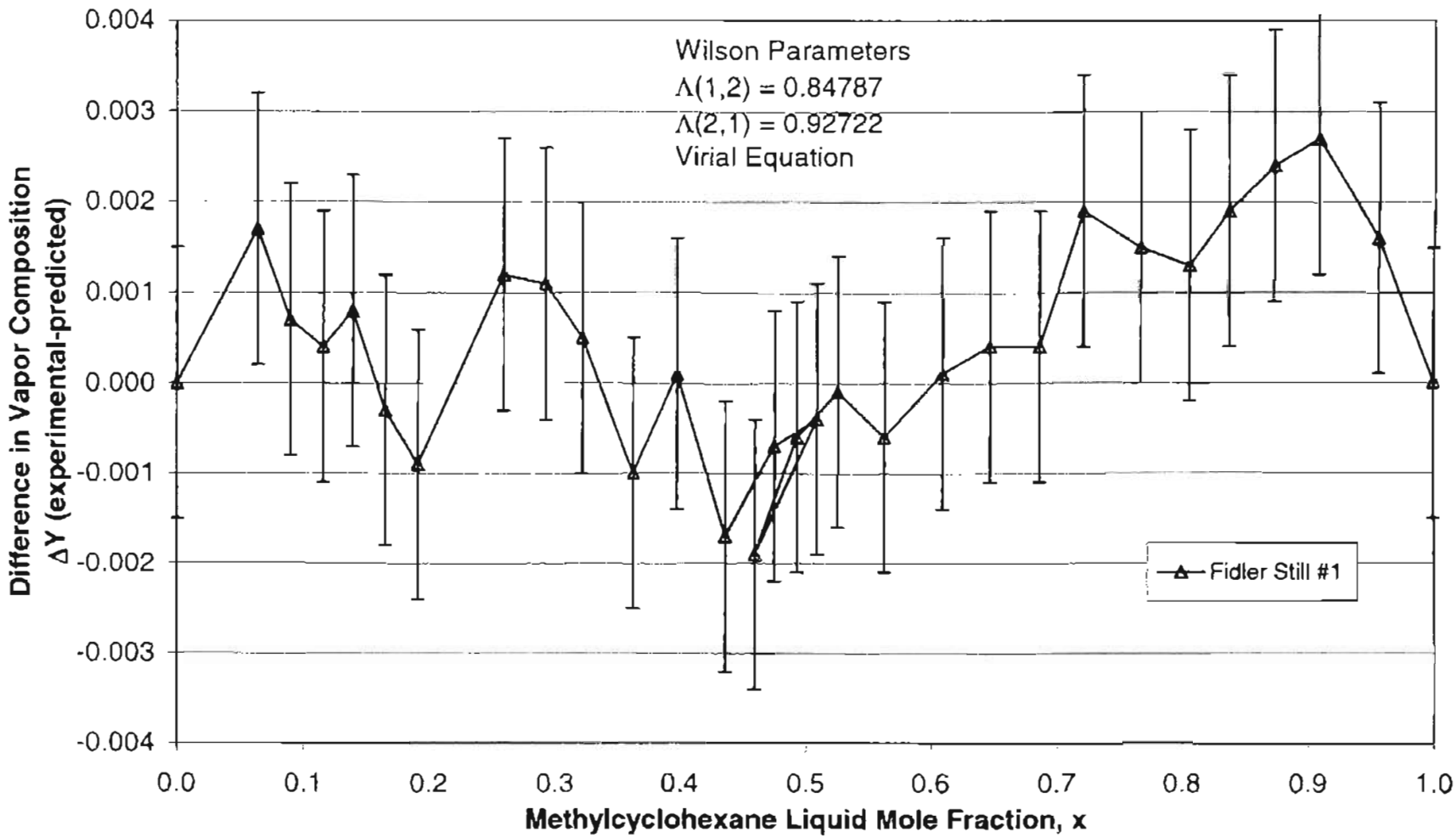

Figure 28. Deviation of Calculated Vapor Compositions for Methylcyclohexane + Toluene at 760 mmHg

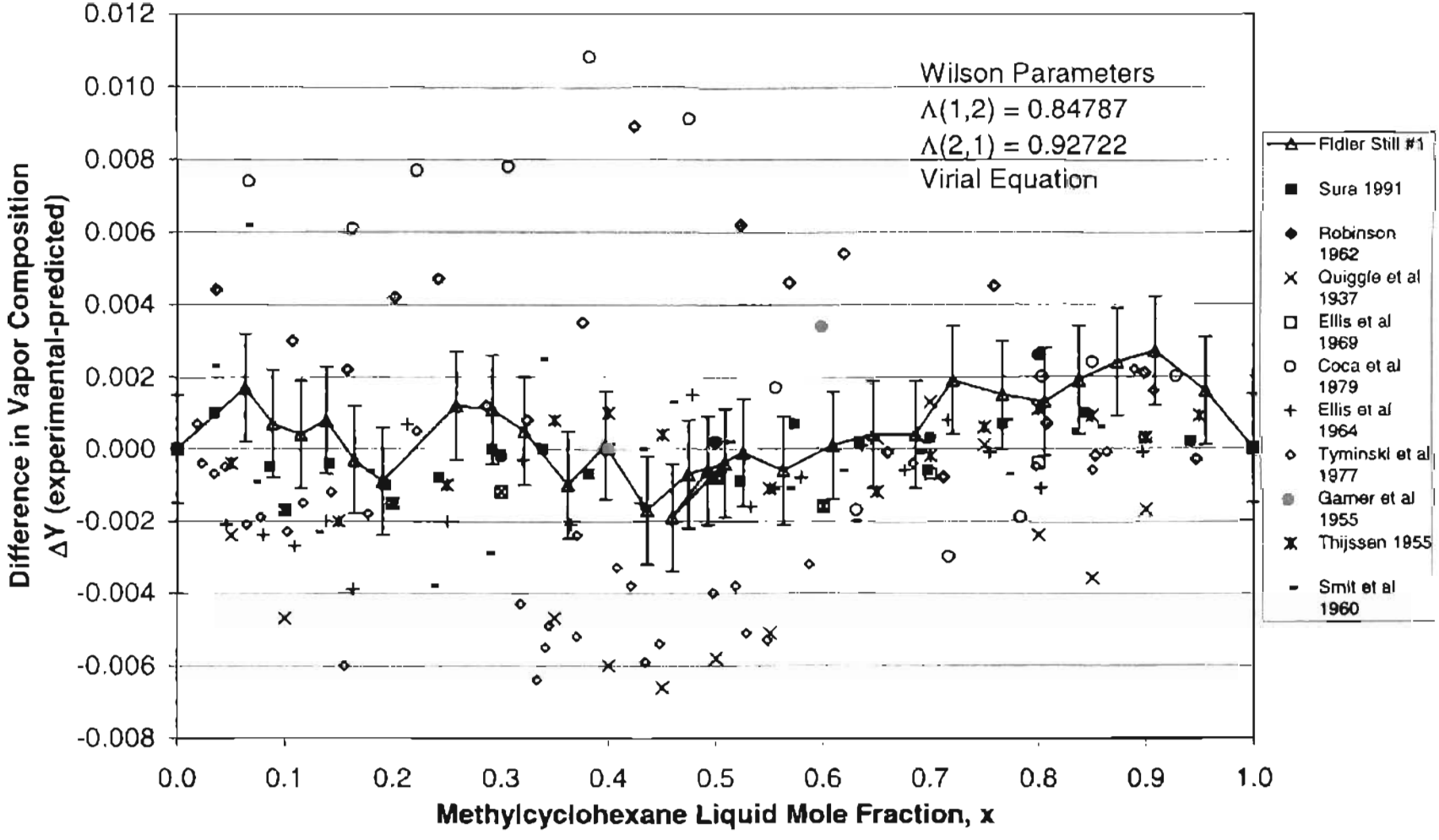

Figure 29. Comparison of Experimental Vapor Compositions for Methylcyclohexane + Toluene at 760 mmHg

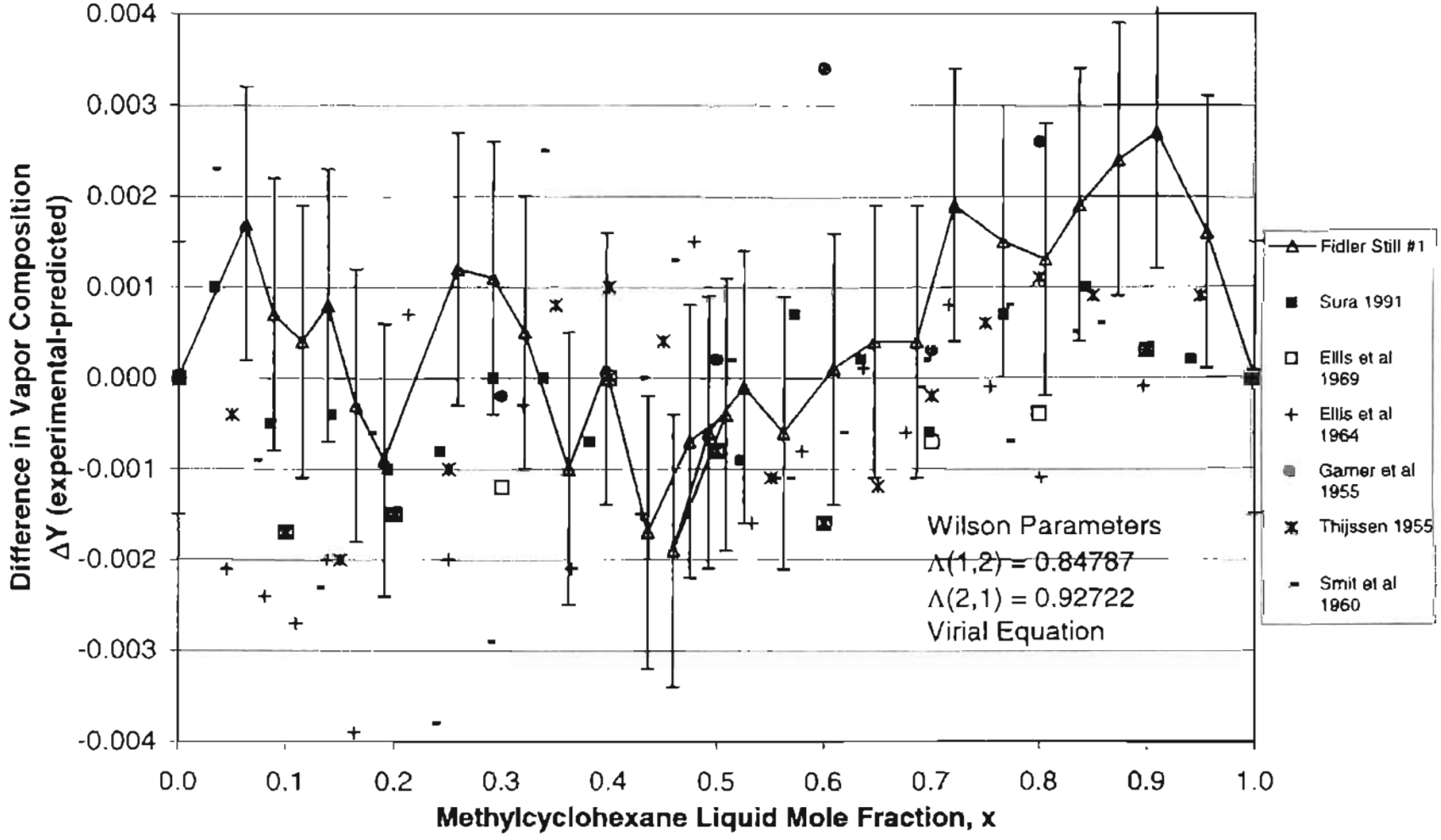

Figure 30. Detailed Comparison of Experimental Vapor Compositions for Methylcyclohexane + Toluene at 760 mmHg

calibration curve for this mixture. The majority of the points are within experimental uncertainty, however there are a few which exceed experimental uncertainty. A comparison of the literature vapor-phase compositions is shown on Figure 29. The bulk of the literature data are in agreement with this work. A more detailed comparison is shown on Figure 30. The experimental uncertainties of the literature data are on the same order of magnitude as this work. Even without considering the literature experimental uncertainties, the majority of the literature data are in agreement with this work. If the experimental uncertainties of the literature data were also considered, nearly all of the points would be in agreement with this work.

Another plot useful in evaluating thermodynamic consistency is activity coefficient versus liquid mole fraction. Both experimental and calculated activity coefficients are plotted to demonstrate the fit of the model to the experimental data. If a model satisfies the Gibbs-Duhem equation and that model fits the experimental data within its uncertainty, then the data are thermodynamically consistent. Since the Wilson model satisfies the Gibbs-Duhem equation it may be used. Figure 31 shows the activity coefficient versus methylcyclohexane liquid mole fraction. The error bars were obtained by propagation of experimental error, see Appendix E for details. Nearly all data points are within their experimental uncertainty, which strengthens the probability that the data are thermodynamically consistent.

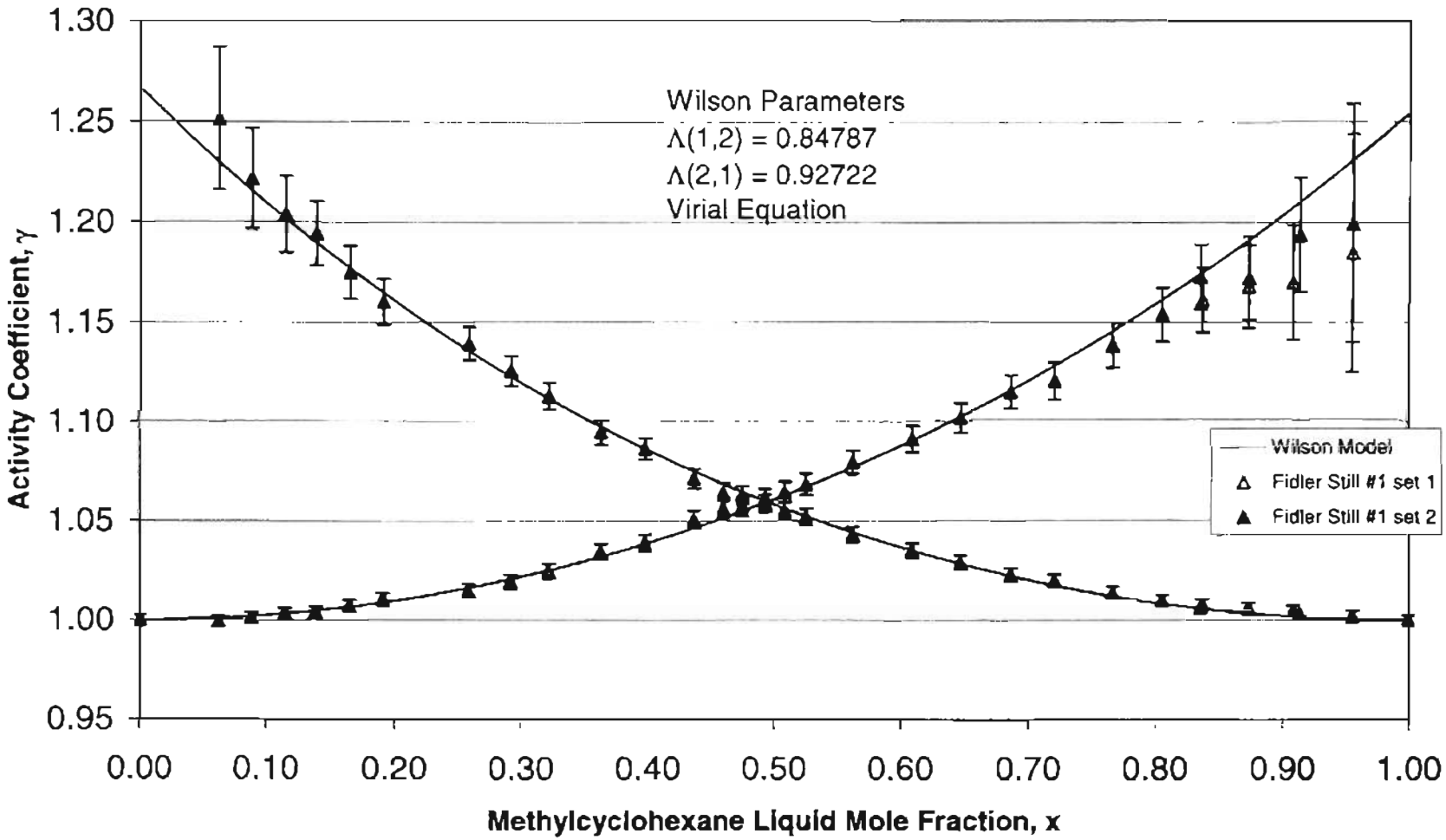

Figure 31. Activity Coefficients for Methylcyclohexane + Toluene at 760 mmHg

Hexane + Toluene at 760 mmHg

Two sets of isobaric data were obtained for the hexane + toluene mixture from Still #1. As previously mentioned, each set was obtained from two separate runs. Each run started with a pure component and the second component was added in sequential steps until a nearly equimolar mixture was obtained. The data from each run were overlapped near equimolar composition to show consistency between the two runs. Tables 9 and 10 present the VLE data for sets one and two, respectively.

Table 9. Hexane(1) + Toluene(2) at 760 mmHg, Data Set 1

Run	Liquid Mole Fraction x_1	Vapor Mole Fraction y_1	Temperature (°C)
1	0.0000	0.0000	110.62
1	0.0203	0.0840	108.31
1	0.0461	0.1676	105.73
1	0.0687	0.2286	103.61
1	0.0947	0.2976	101.45
1	0.1316	0.3853	98.65
1	0.1912	0.4897	94.73
1	0.2406	0.5522	91.85
2	0.2763	0.5963	89.79
1	0.3091	0.6237	88.39
2	0.3308	0.6481	87.48
2	0.3297	0.6447	87.46
2	0.3857	0.6935	85.23
1	0.3944	0.6998	84.76
2	0.4590	0.7454	82.55
2	0.5280	0.7886	80.29
2	0.6027	0.8296	78.08
2	0.6777	0.8679	76.02
2	0.7393	0.8947	74.49
2	0.8231	0.9306	72.50
2	0.9199	0.9690	70.38
2	1.0000	1.0000	68.71

Table 10. Hexane(1) + Toluene(2) at 760 mmHg, Data Set 2

Run	Liquid Mole Fraction x_1	Vapor Mole Fraction y_1	Temperature (°C)
2	0.0000	0.0000	110.60
2	0.0163	0.0699	108.64
2	0.0435	0.1620	105.89
2	0.0681	0.2314	103.66
2	0.0955	0.2936	101.38
2	0.0948	0.3013	101.35
2	0.1286	0.3711	98.79
2	0.1908	0.4896	94.67
2	0.2415	0.5586	91.75
1	0.2742	0.5927	89.89
2	0.3095	0.6276	88.22
1	0.3307	0.6472	87.42
1	0.3255	0.6472	87.42
1	0.3872	0.6967	85.06
2	0.4022	0.7109	84.40
1	0.4537	0.7467	82.66
1	0.5303	0.7933	80.23
1	0.6000	0.8299	78.16
1	0.6827	0.8706	75.93
1	0.7407	0.8953	74.47
1	0.8199	0.9285	72.61
1	0.9276	0.9713	70.22
1	1.0000	1.0000	68.70

Four literature sources (Sieg 1950; Robinson Jr. 1962; Michishita, Arai et al. 1971; Sura 1991) were available for this system. Figure 32 shows temperature versus composition. The data agree well except in the vapor phase near equimolar where there is some scatter among researchers. The scatter cannot be seen as well in the vapor mole fraction versus liquid mole fraction plot, Figure 33. The data were further analyzed as described

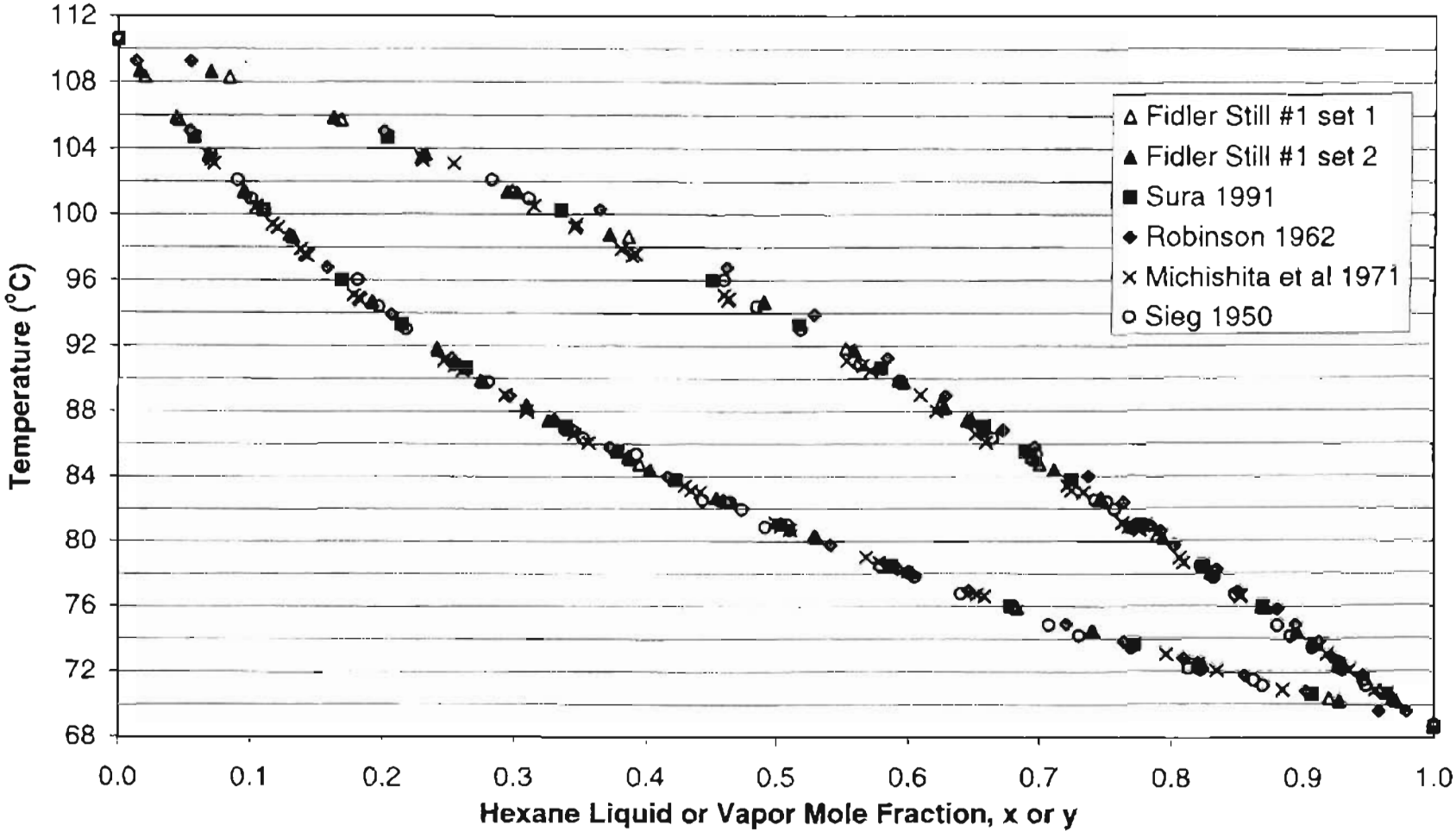

Figure 32. Hexane + Toluene at 760 mmHg, Temperature versus Composition

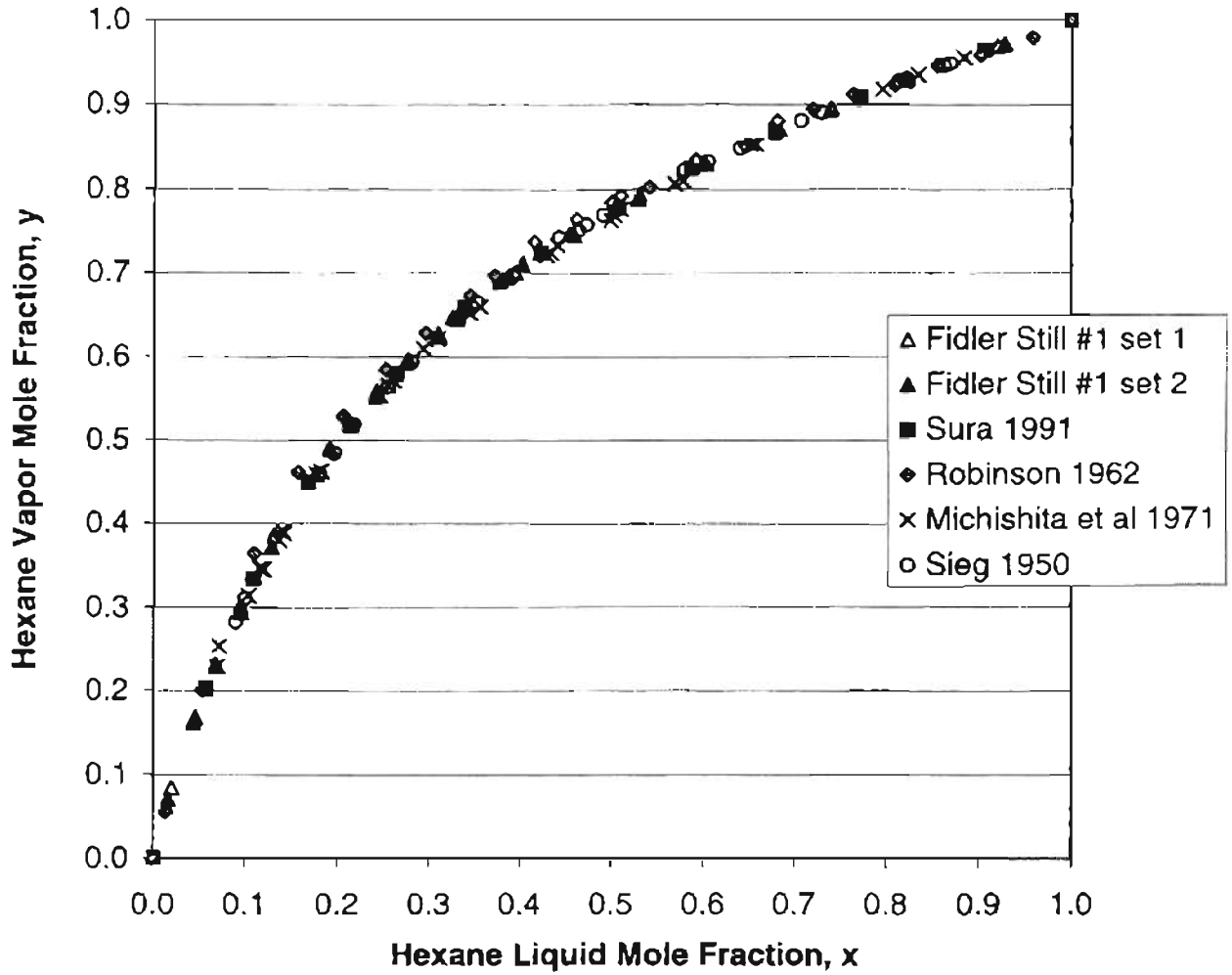

Figure 33. Hexane + Toluene at 760 mmHg, Vapor Mole Fraction versus Liquid Mole Fraction

previously by obtaining model parameters for Still #1 (set 1) and using those parameters to calculate values for the literature data. The Wilson and Van Laar models were used along with the virial and ideal equations of state. Table 11 shows the results of the model regression including the RMSD and model parameters.

Table 11. Results of Model Regression for Hexane + Toluene at 760 mmHg

Activity Coefficient Model	Equation of State	Root Mean Square Deviation (RMSD) T (°C)	y, Vapor Composition	Model Parameters Λ(1,2)	Λ(2,1)
Wilson	Ideal	0.048	0.0098	0.86771	0.83913
Wilson	Virial	0.050	0.0037	0.84412	0.83336
Van Laar	Ideal	0.048	0.0098	0.30228	0.30691
Van Laar	Virial	0.050	0.0037	0.33545	0.33716

The Wilson model and the virial equation truncated after the second term were chosen for further data analysis. Figure 34 shows the deviation of calculated temperatures from experimental temperatures for the two sets of data from Still #1. The error bars on this plot are based on observed fluctuations of temperature during the run. The fluctuations for this system were much larger than those of other systems, probably due to the large difference in pure-component boiling points. The difference in pure-component boiling points is almost 42°C for this system and less than 10°C for the methylcyclohexane + toluene system at 760 mmHg. Most of the points are within the uncertainty of the system fluctuations; however, the system fluctuations exceed the experimental uncertainty based on equipment accuracies. Figure 35 shows the comparison of experimental and calculated temperatures for the literature data as well. Robinson (Robinson Jr. 1962) and

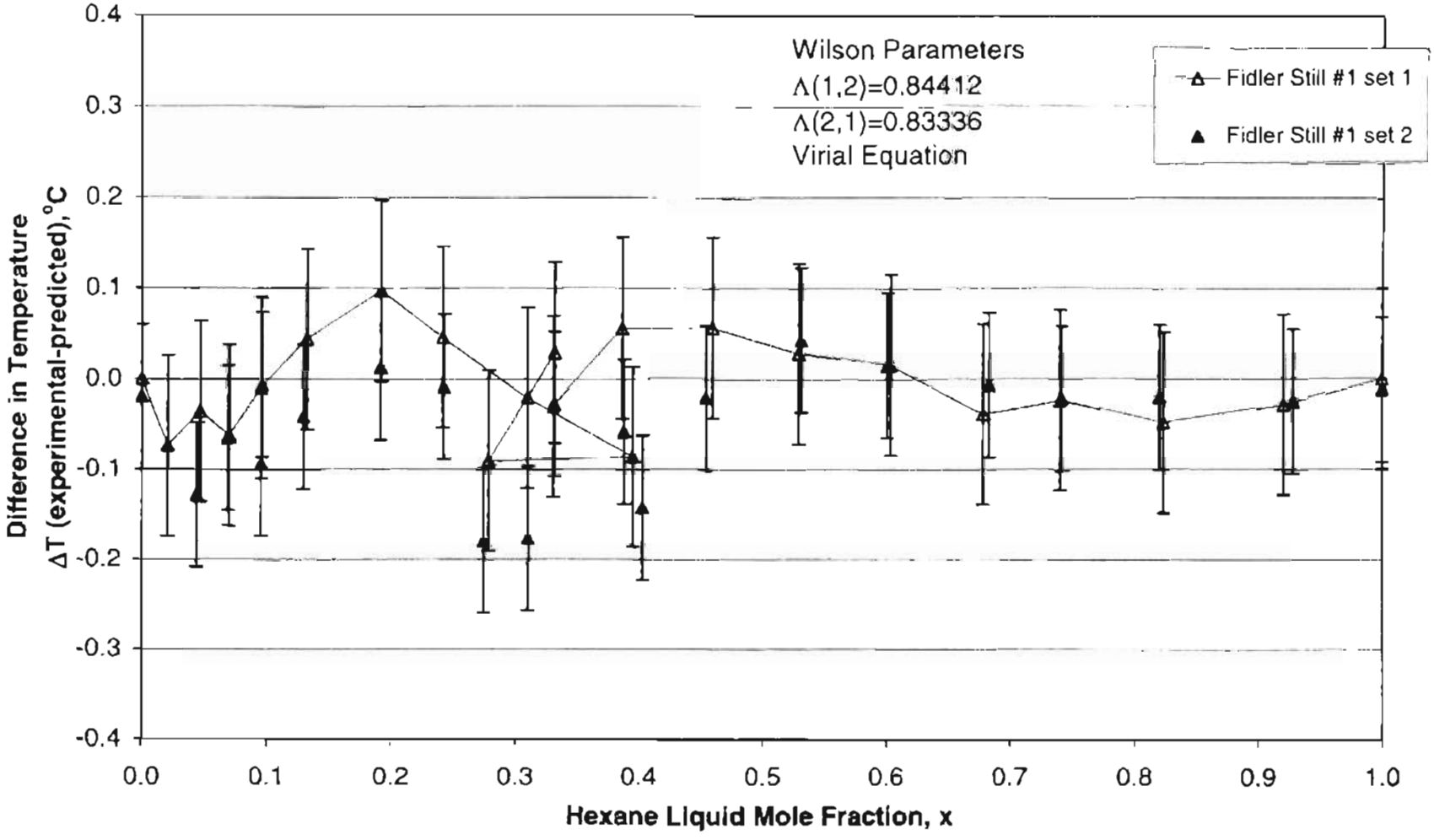

Figure 34. Deviation of Calculated Temperatures for Hexane + Toluene at 760 mmHg

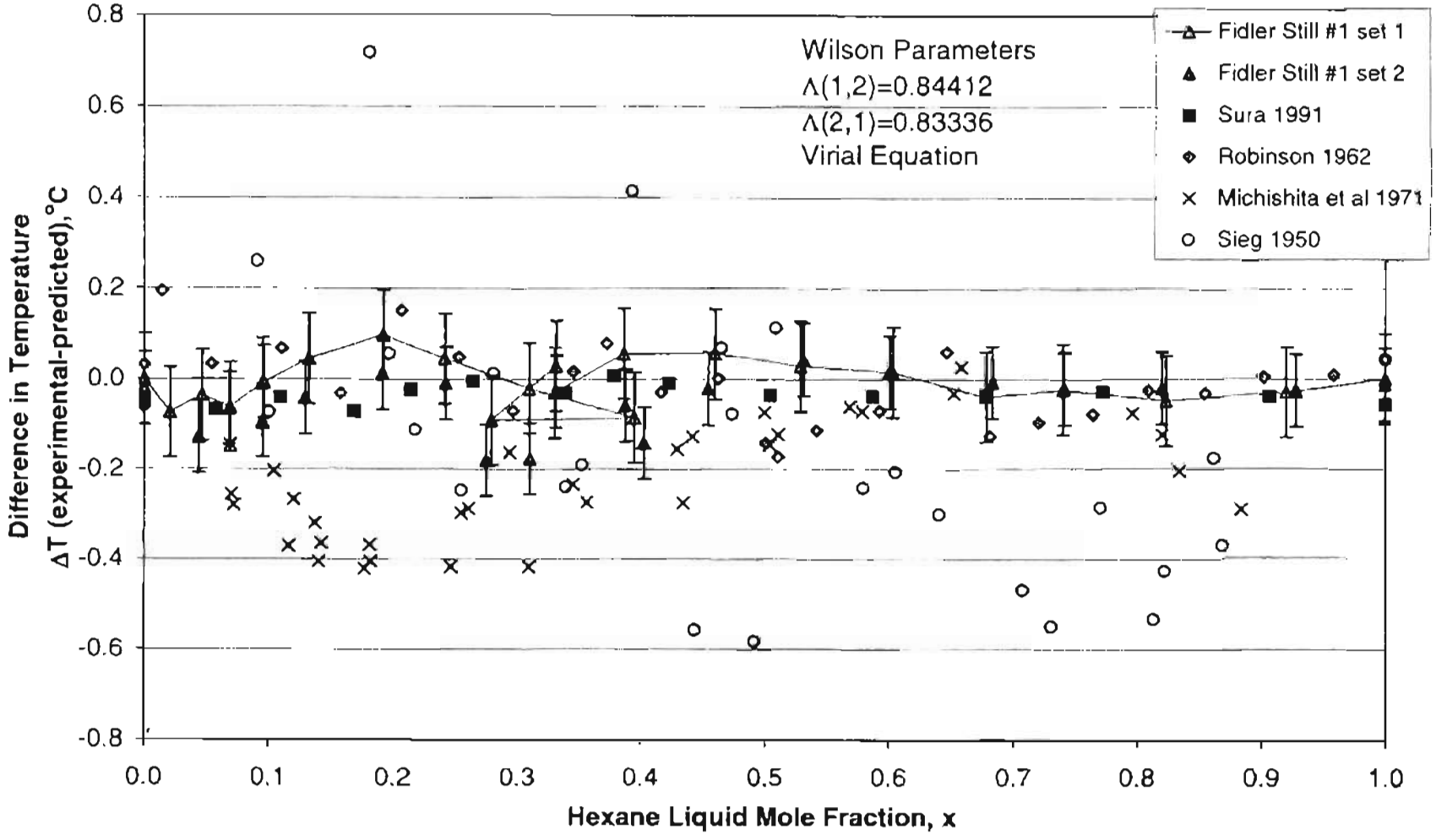

Figure 35. Comparison of Experimental Temperatures for Hexane + Toluene at 760 mmHg

Sura (Sura 1991) agree fairly well but Michishita et al. (Michishita, Arai et al. 1971) and Sieg (Sieg 1950) do not agree well with this work or each other. Figure 36 shows a more detailed comparison of temperature difference versus liquid mole fraction. The Antoine constants were adjusted for each study to give zero error for the pure components. The data agree within the system fluctuations except from 0.5 to 0.7 hexane liquid mole fraction, where Robinson (Robinson Jr. 1962) is lower than this work or the work of Sura (Sura 1991). The deviation of calculated vapor compositions from experimental vapor compositions is shown in Figure 37. The experimental uncertainty for mole fraction is 0.0037 and is based on the RMSD for vapor composition from GEOS. Many of the data points are within experimental uncertainty. Figure 38 shows the comparison of experimental vapor compositions with calculated vapor compositions for this work and the literature data. This plot shows significant scatter among the researchers. Figure 39 shows a more detailed comparison of this work with Sieg (Sieg 1950) and Sura (Sura 1991). Both agree fairly well with this work, with the exception of two points of Sieg near 0.2 hexane liquid mole fraction.

Activity coefficients for the hexane + toluene at 760 mmHg system are shown on Figure 40. Nearly all of the activity coefficients are within the uncertainty compared to the Wilson model. The method for calculating uncertainty is detailed in Appendix E and is based on propagation of experimental error.

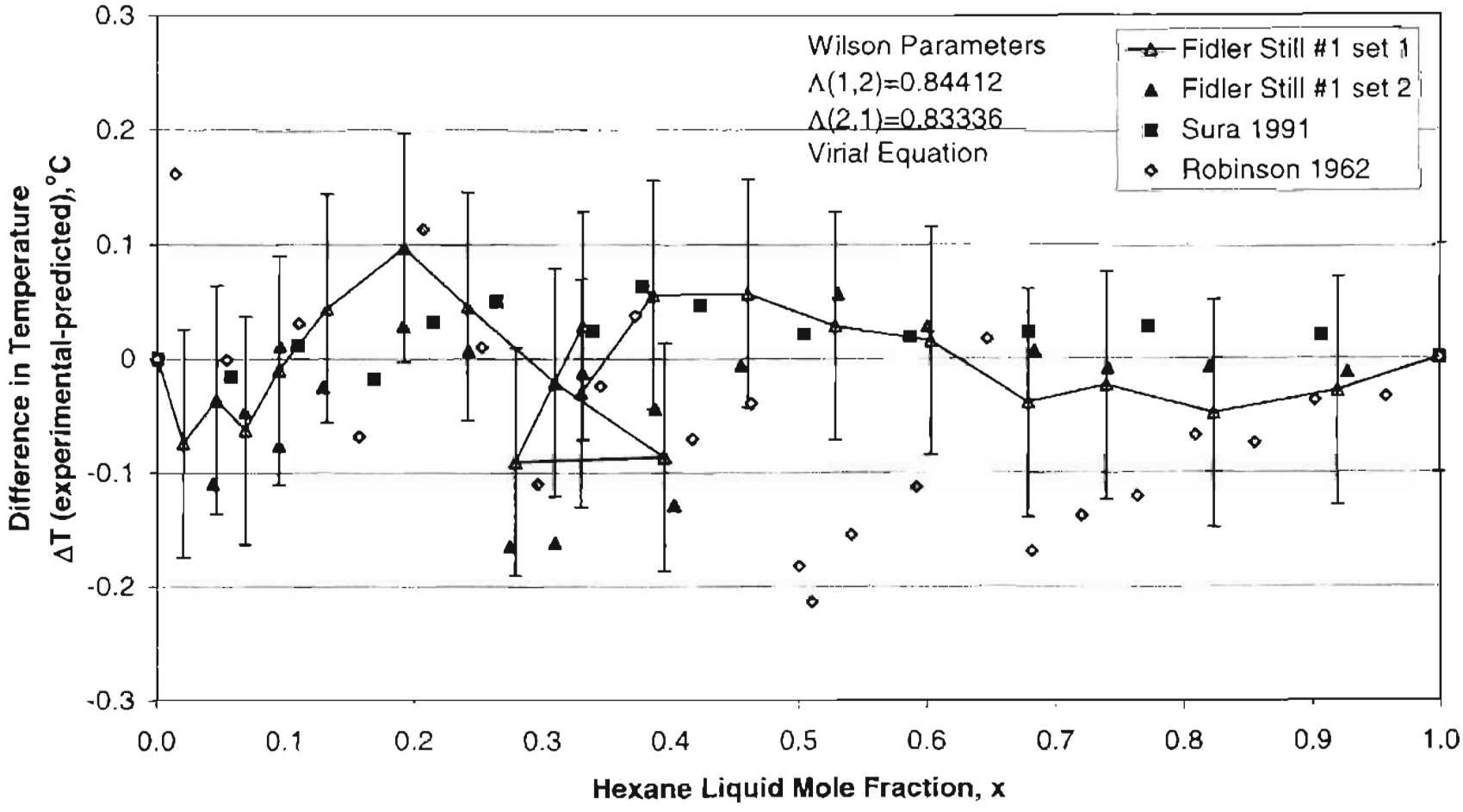

Figure 36. Detailed Comparison of Experimental Temperatures for Hexane + Toluene at 760 mmHg

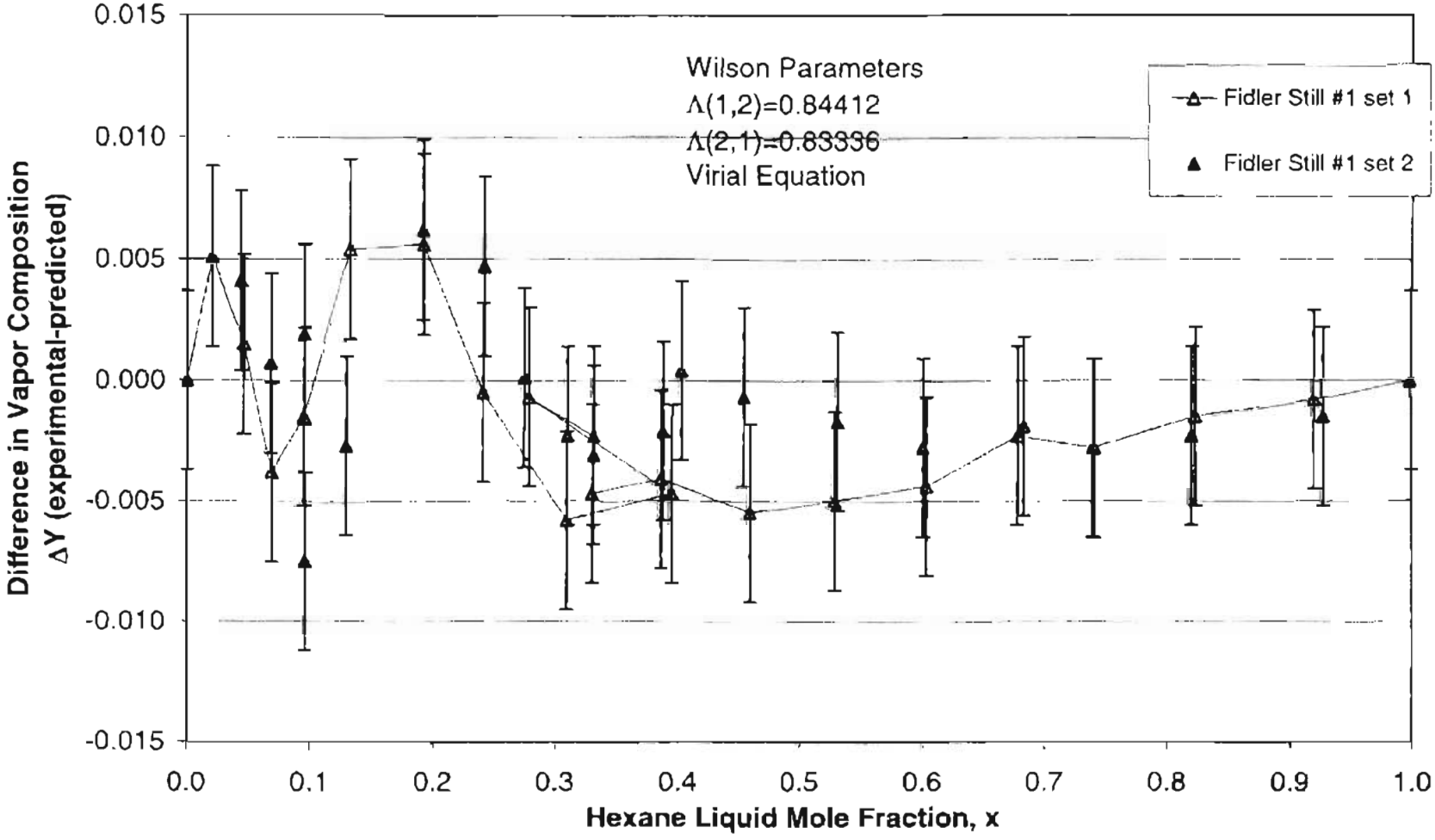

Figure 37. Deviation of Calculated Vapor Compositions for Hexane + Toluene at 760 mmHg

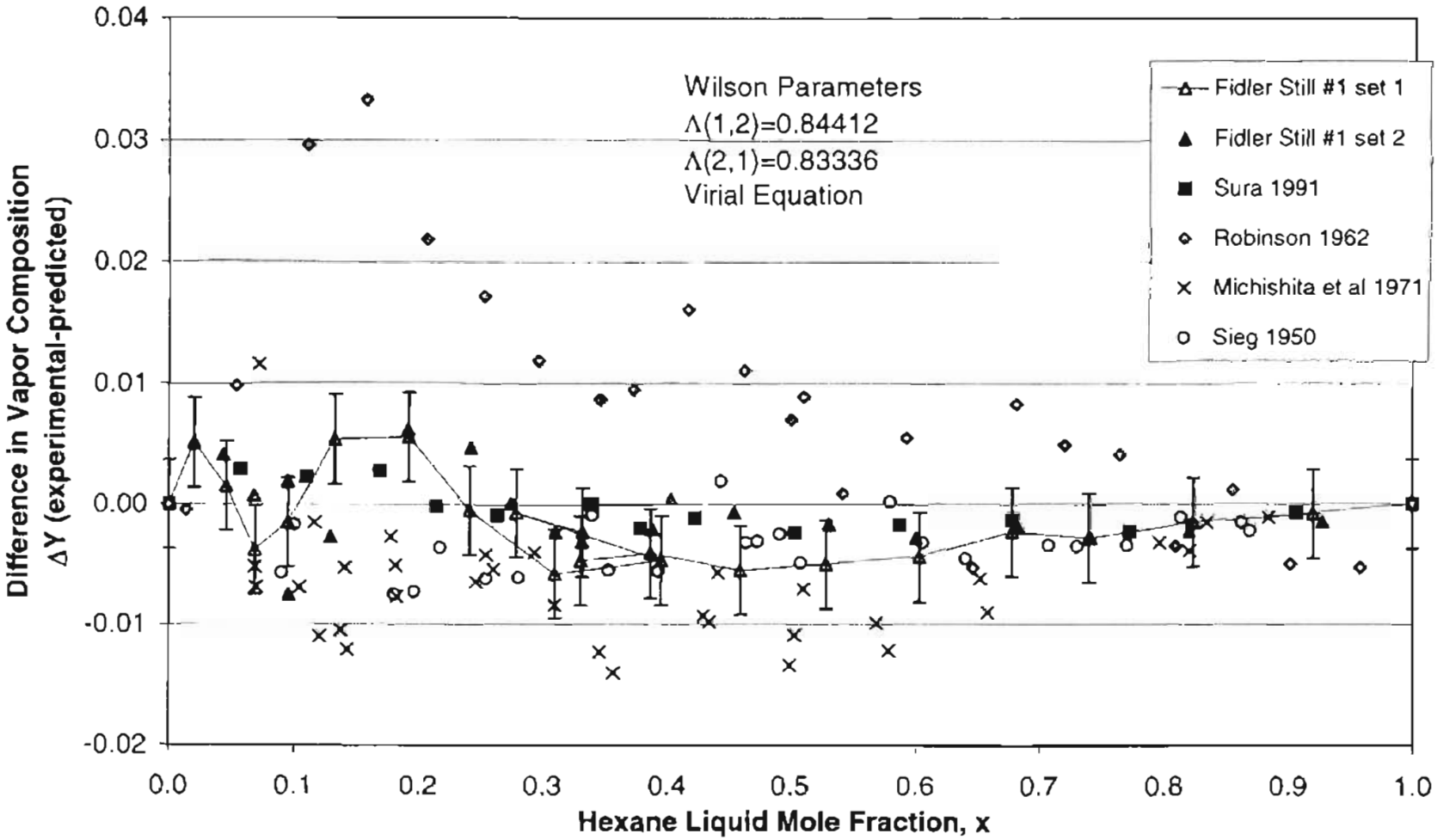

Figure 38. Comparison of Experimental Vapor Compositions for Hexane + Toluene at 760 mmHg

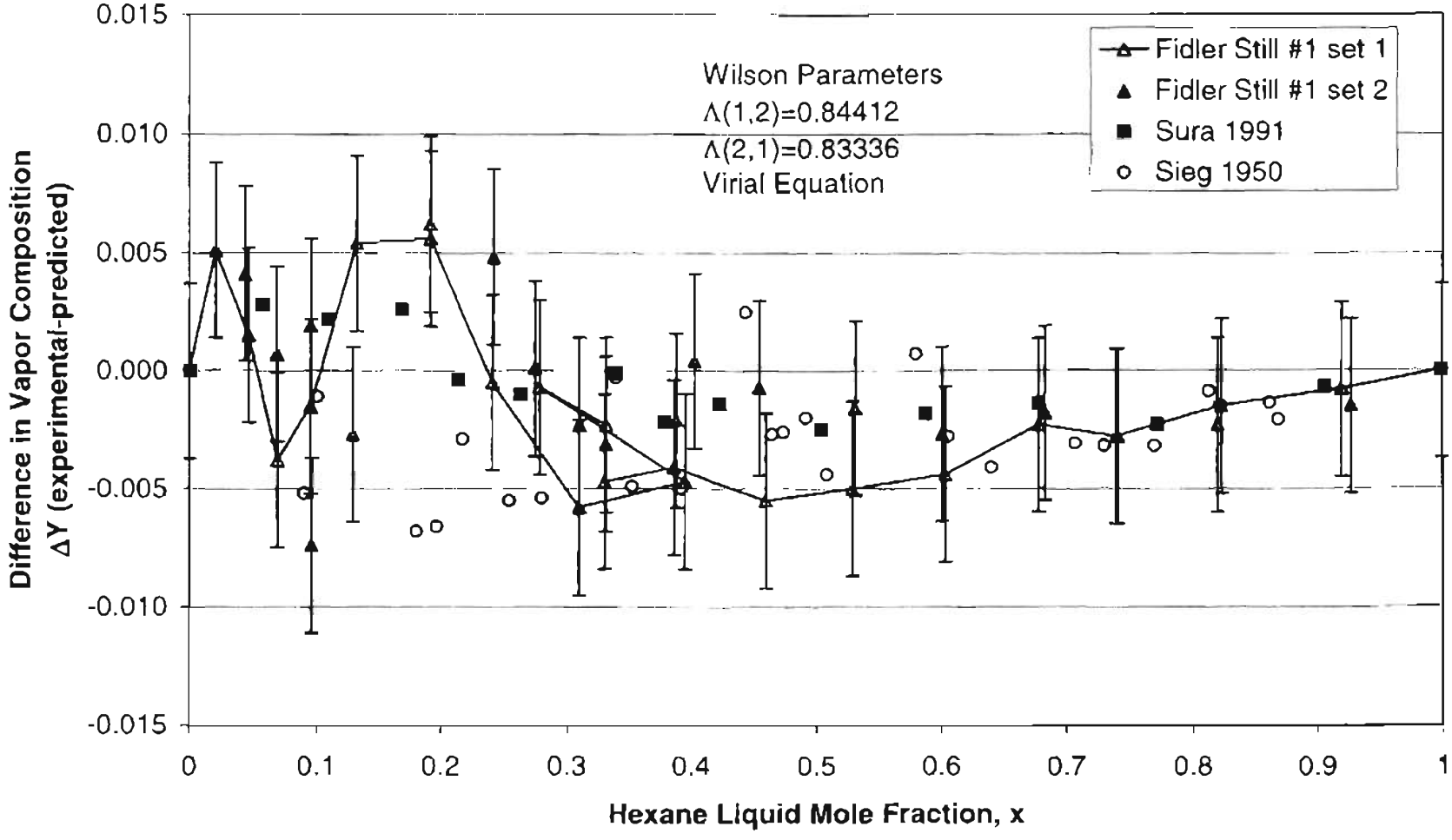

Figure 39. Detailed Comparison of Experimental Vapor Compositions for Hexane + Toluene at 760 mmHg

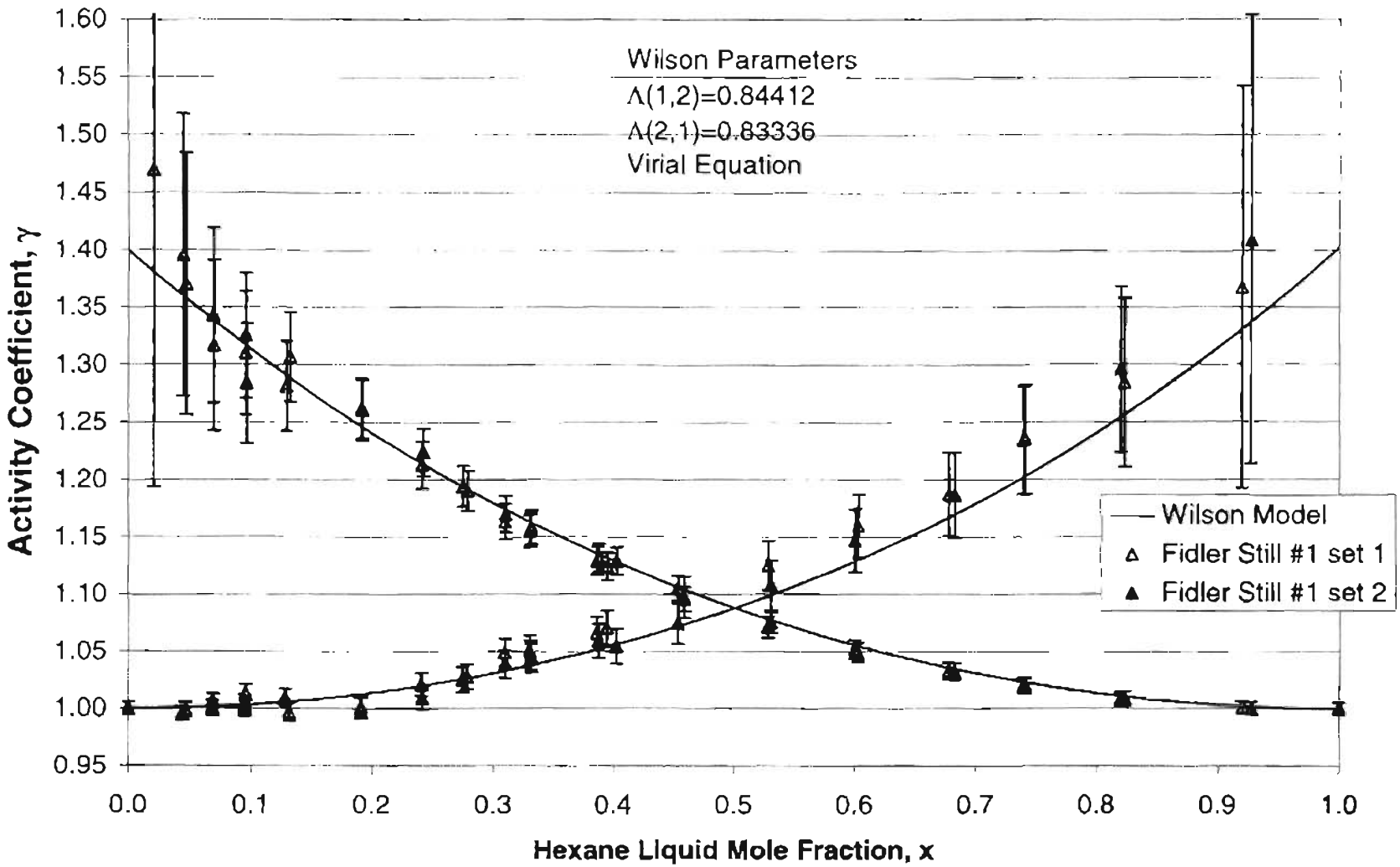

Figure 40. Activity Coefficients for Hexane+Toluene at 760 mmHg

Methylcyclohexane + Toluene at 90°C

The VLE data for the isothermal system of methylcyclohexane + toluene at 90 °C are listed in Table 12.

Table 12. Methylcyclohexane (1) + Toluene (2) at 90°C

Run	Liquid Mole Fraction x_1	Vapor Mole Fraction y_1	Pressure (mmHg)
1	1.0000	1.0000	552.39
1	0.9422	0.9473	550.37
1	0.8881	0.8994	547.72
1	0.8184	0.8381	543.40
1	0.7541	0.7850	538.61
1	0.6840	0.7273	532.45
1	0.6156	0.6703	525.36
1	0.5536	0.6184	518.25
2	0.5007	0.5735	511.79
1	0.4918	0.5660	510.33
1	0.4364	0.5168	502.47
2	0.4187	0.5012	499.96
2	0.3526	0.4402	489.31
2	0.2899	0.3784	477.93
2	0.2258	0.3111	465.10
2	0.1802	0.2593	455.00
2	0.1371	0.2051	444.80
2	0.0965	0.1510	434.46
2	0.0591	0.0982	424.29
2	0.0215	0.0386	413.63
2	0.0000	0.0000	406.29

Two literature sources (Schneider 1961; Sura 1991) were available for this system. Figure 41 shows the pressure versus composition relationships. There is good agreement with the three data sets except in the methylcyclohexane-rich region, where Sura (Sura 1991) shows a higher pressure for a given mole fraction. Figure 42 shows vapor mole

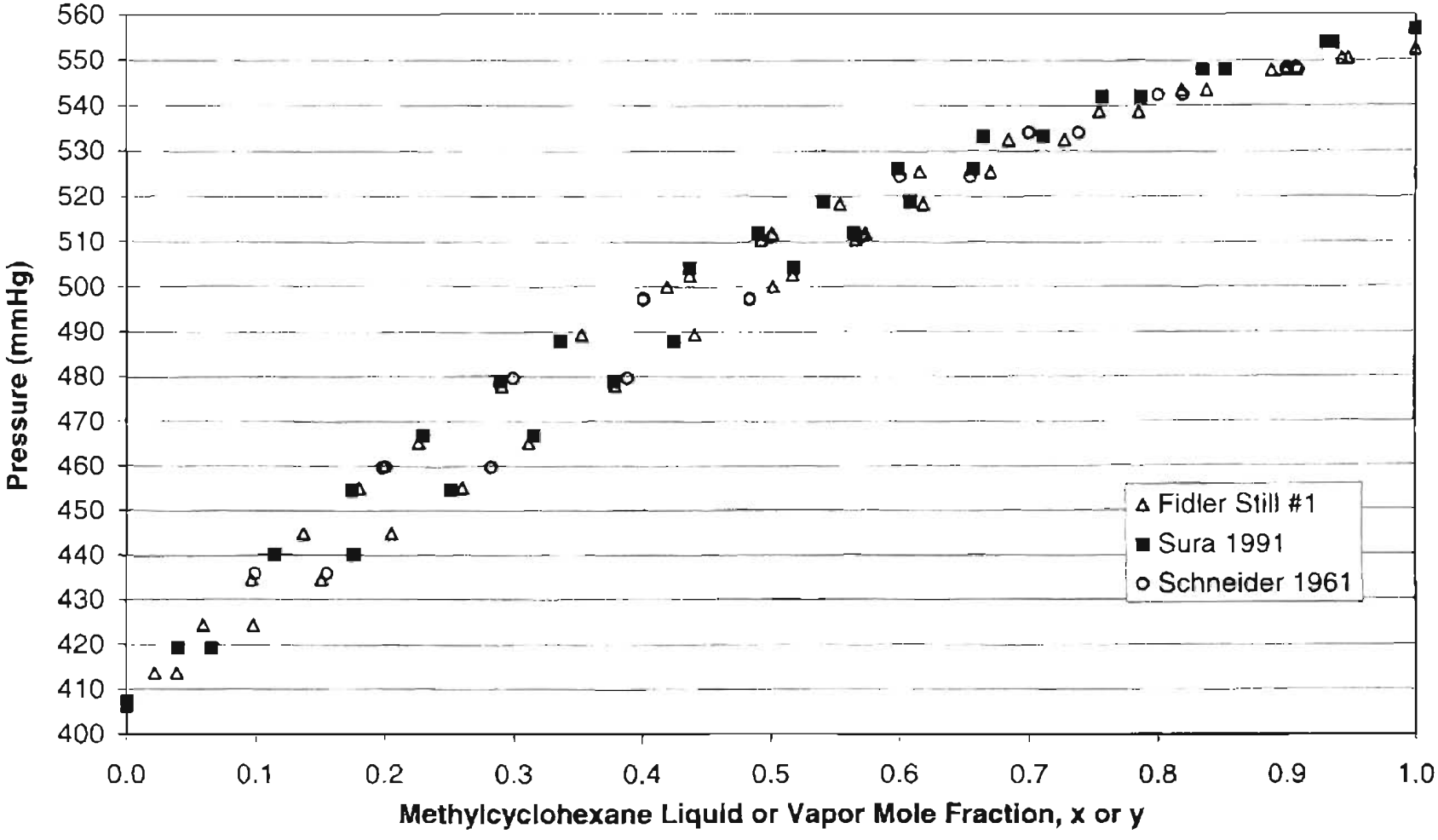

Figure 41. Methylcyclohexane + Toluene at 90°C, Temperature versus Composition

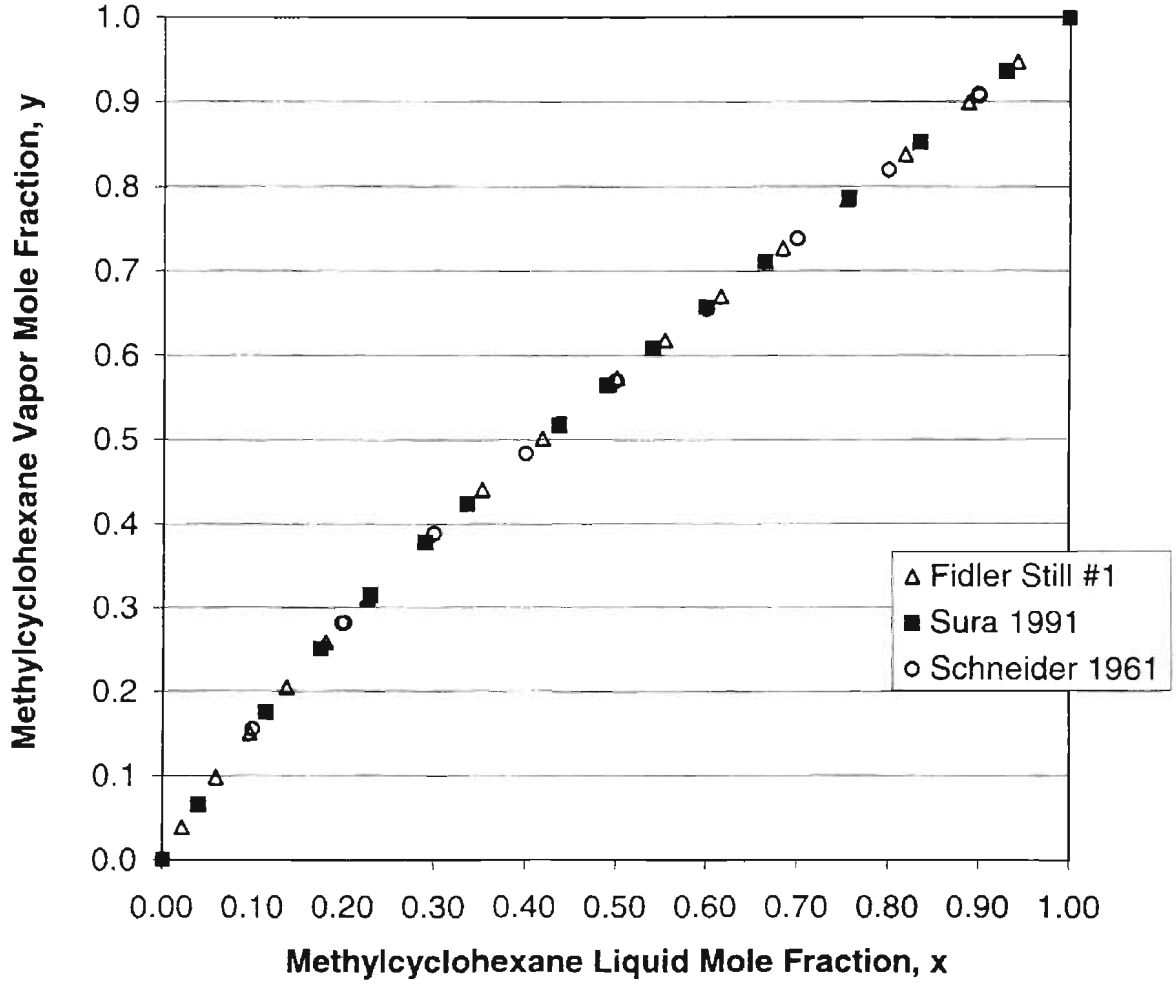

Figure 42. Methylcyclohexane + Toluene at 90°C, Vapor Mole Fraction versus Liquid Mole Fraction

fraction versus liquid mole fraction for the three researchers. There appears to be no gross errors on this plot. Once again the data from this work were used to obtain optimized parameters for further data analysis. The results of the model regression are shown in Table 13.

Table 13. Results of Model Regression for Methylcyclohexane + Toluene at 90°C

Activity Coefficient Model	Equation of State	Root Mean Square Deviation (RMSD) P (mmHg)	y, Vapor Composition	Model Parameters Λ(1,2)	Λ(2,1)
Wilson	Ideal	0.0801	0.0019	0.80294	0.94674
Wilson	Virial	0.0806	0.0008	0.78474	0.97142
Van Laar	Ideal	0.0815	0.0019	0.27233	0.25146
Van Laar	Virial	0.0819	0.0008	0.27059	0.24395

The Wilson model and virial equation truncated after the second term were chosen for further data analysis. Figure 43 shows the deviation of calculated pressures from experimental pressures for this work. There is significant scatter and several of the data points are not within the RMSD calculated by GEOS. Figure 44 shows the comparison of experimental pressures with calculated pressures for this work and the literature sources. The work of Schneider (Schneider 1961) is not within uncertainty of this work but does scatter uniformly about this work. The experimental uncertainty of Schneider is unknown, so it cannot be determined if the two works agree within their experimental uncertainties. The work of Sura (Sura 1991) shows serious deviation from this work and the work of Schneider above 0.3 methylcyclohexane liquid mole fraction. Figure 45

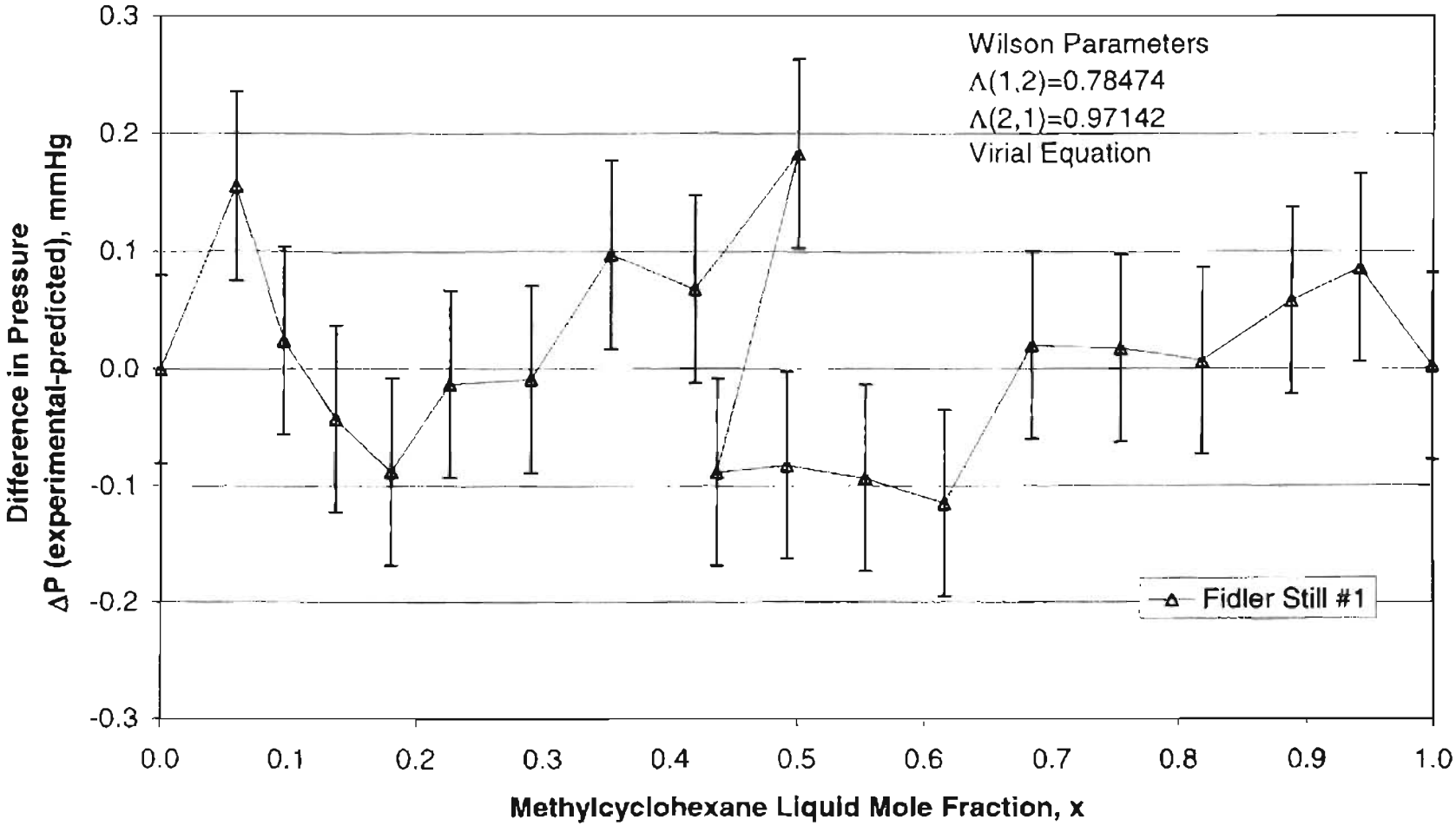

Figure 43. Deviation of Calculated Pressures for Methylcyclohexane + Toluene at 90°C

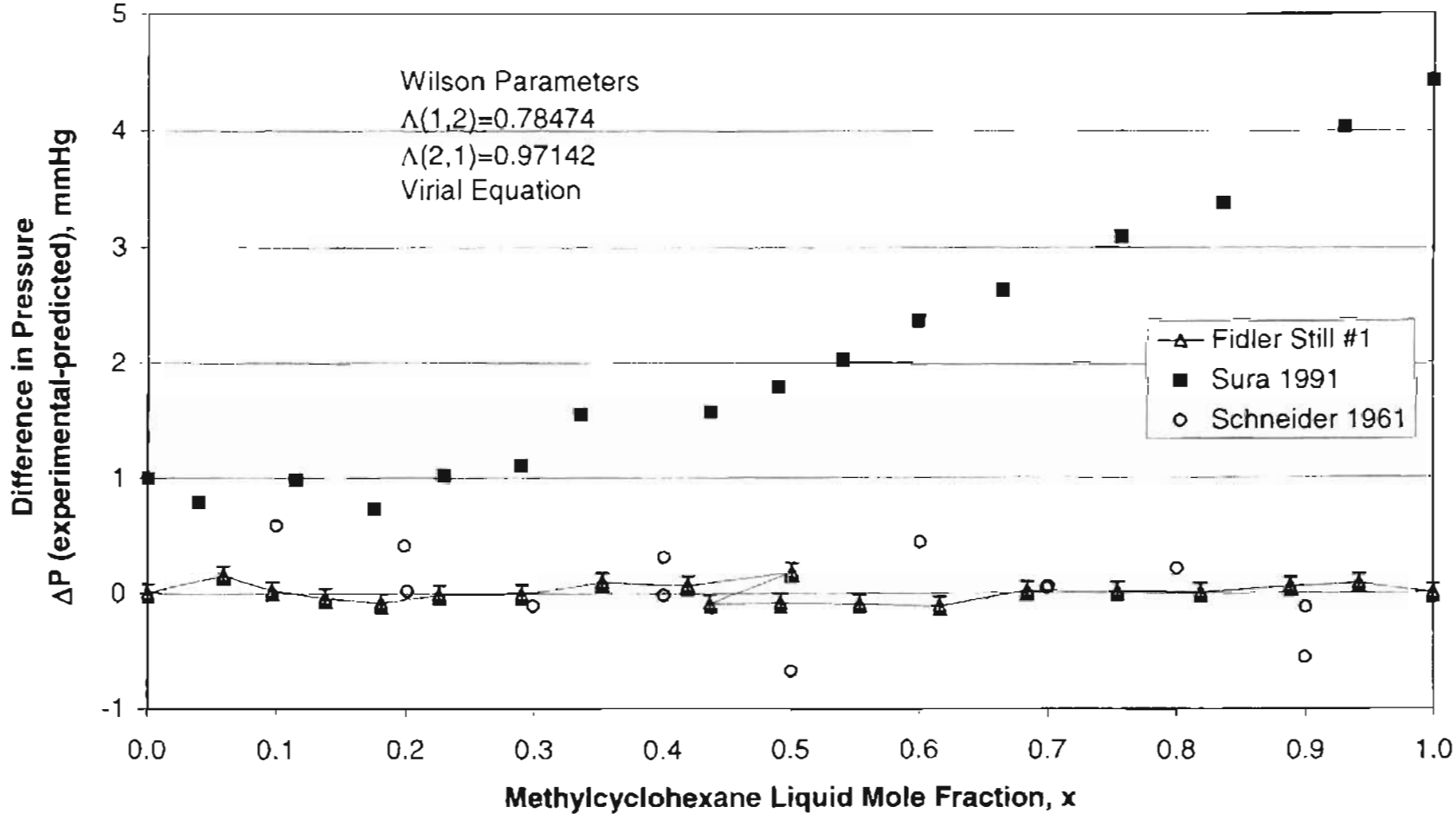

Figure 44. Comparison of Experimental Pressures for Methylcyclohexane + Toluene at 90°C

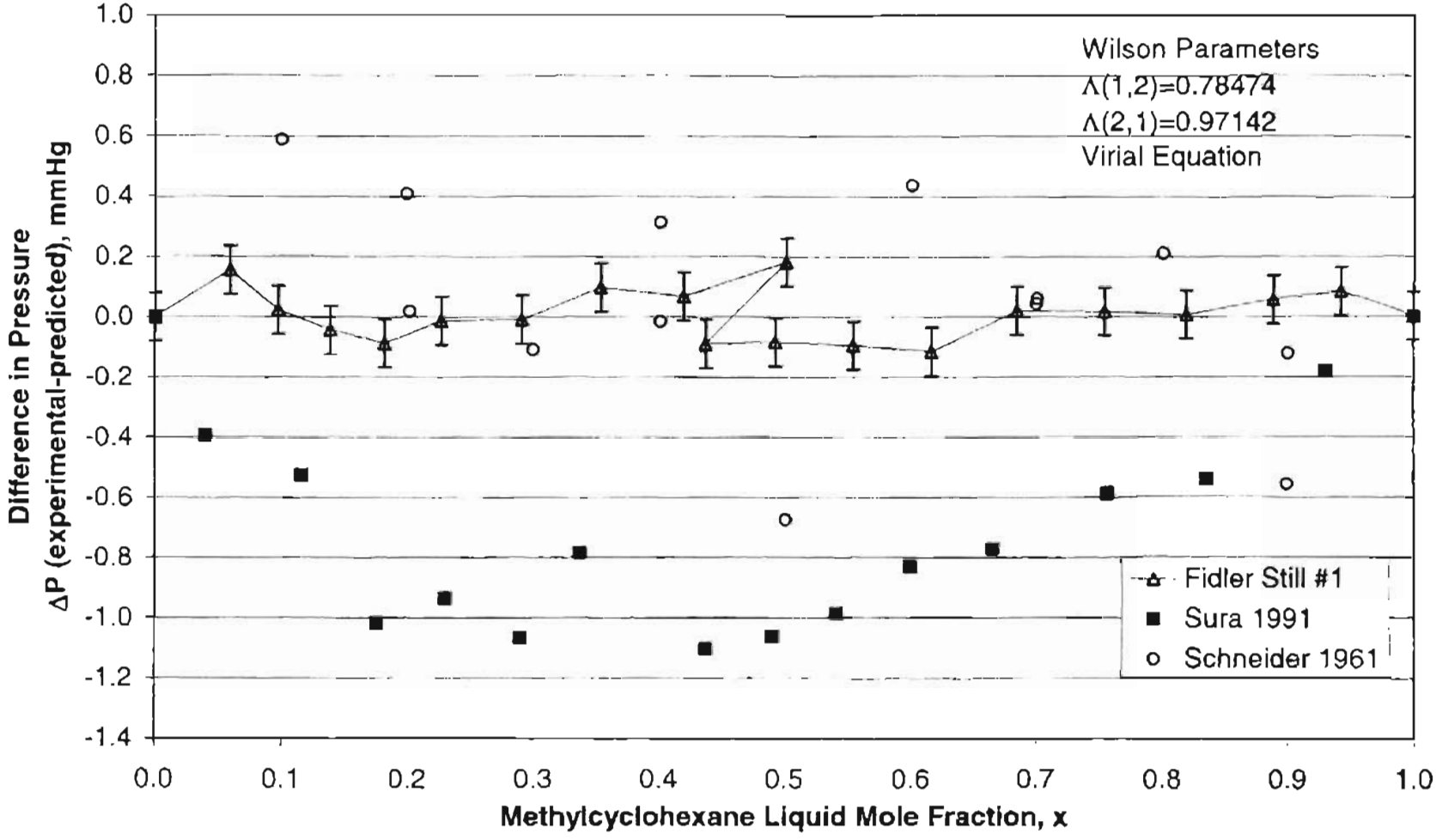

Figure 45. Detailed Comparison of Experimental Pressures for Methylcyclohexane + Toluene at 90°C

shows a more detailed comparison of the three works with the Antoine constants adjusted to give zero error for the pure components. The work of Sura agrees better when the end points are adjusted, but still shows more deviation from this work than Schneider. Figure 46 shows the deviation of calculated vapor compositions from experimental vapor compositions. The error bars are based on the calibration curve for this system. Nearly all of the data points are within the experimental uncertainty; therefore, this plot supports the probability of thermodynamic consistency. The two literature sources are shown on Figure 47. For vapor composition, Sura (Sura 1991) agrees with this work better than Schneider (Schneider 1961). However, if the experimental uncertainty of Schneider were considered, the data would likely be in agreement. The activity coefficients for this system are shown on Figure 48. The error bars are based on the propagation of experimental error, see Appendix E for more detail. All of the data points are within the experimental uncertainty which supports the probability of thermodynamic consistency.

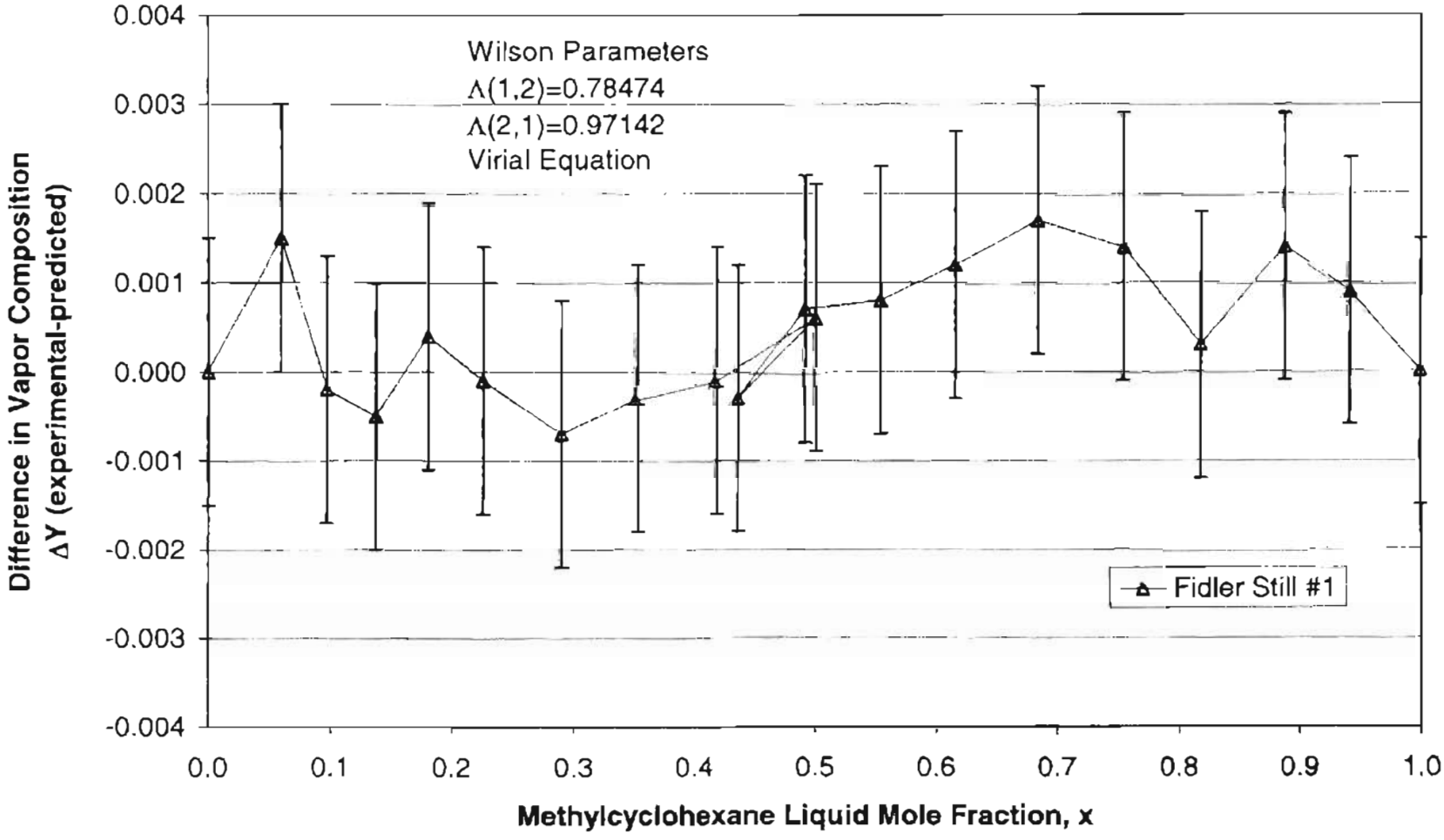

Figure 46. Deviation of Calculated Vapor Compositions for Methylcyclohexane + Toluene at 90°C

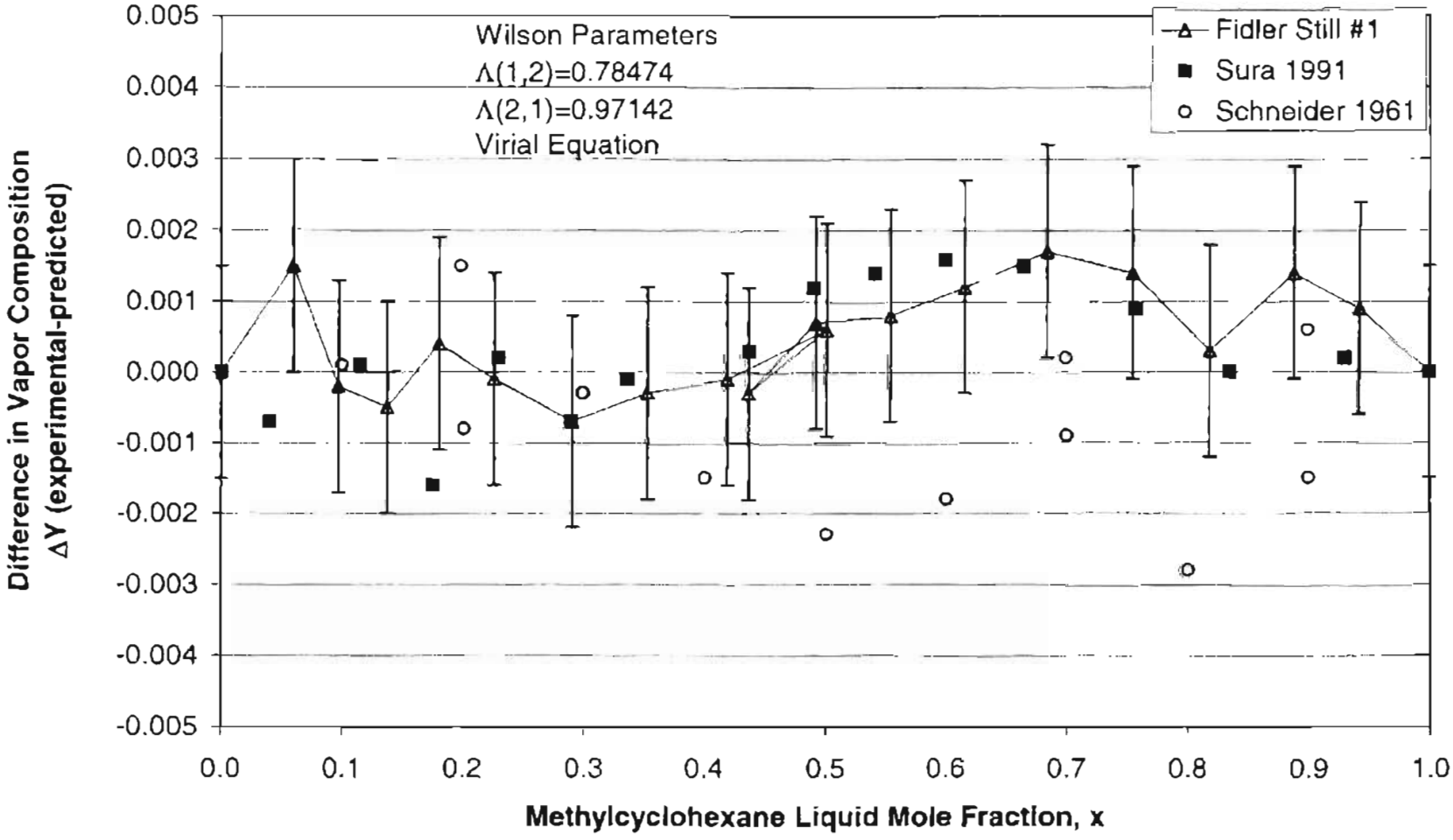

Figure 47. Comparison of Experimental Vapor Compositions for Methylcyclohexane + Toluene at 90°C

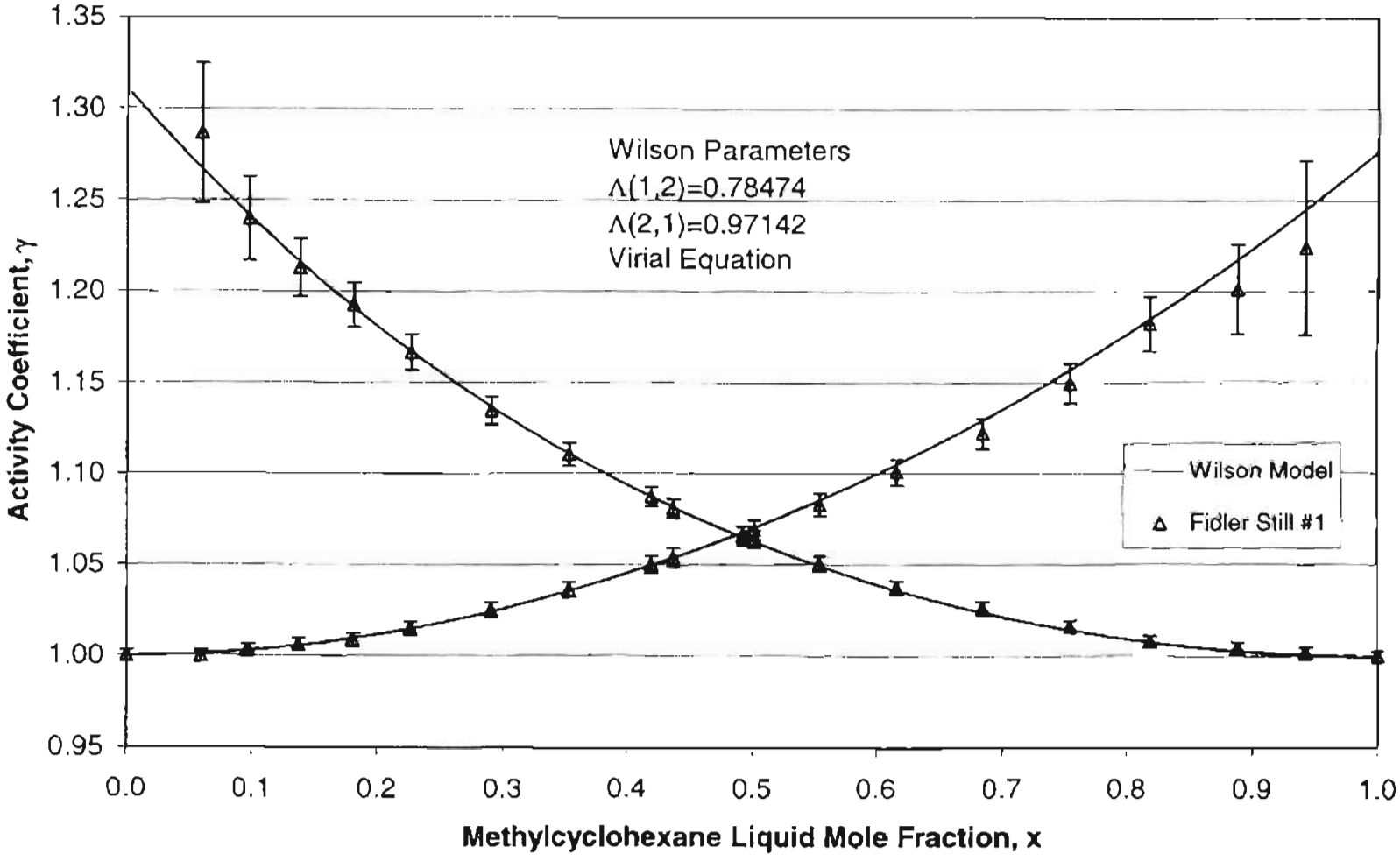

Figure 48. Activity Coefficients for Methylcyclohexane + Toluene at 90°C

Chapter 6

Conclusions and Recommendations

The purpose of this study is to evaluate two existing equilibrium stills and determine the reliability and ease of use of each and, most importantly, the accuracy of the data they produce. The objective is to establish a reliable facility for obtaining thermodynamically consistent low-pressure vapor liquid equilibrium data. The evaluation of the equilibrium stills consisted of data collection and analysis. Data collected included vapor pressures, isobaric VLE data, and isothermal VLE data. The vapor-pressure measurements were taken in the range of 350 mmHg to 760 mmHg for deionized water, methylcyclohexane, hexane, and toluene. The binary data consisted of the following systems: methylcyclohexane + toluene at 760 mmHg, hexane + toluene at 760 mmHg, and methylcyclohexane + toluene at 90°C. The data analysis methods included thermodynamic consistency tests and external consistency tests.

The conclusions of this work are as follows:

- Precise vapor-pressure data can be obtained in Still #1 and Still #2.
- Accurate vapor-pressure data can be obtained in Still #1 and Still #2 near atmospheric pressure, however at low pressures this work disagrees with literature sources by more than experimental uncertainty.
- Still #2 should not be used to collect VLE data due to its instability and 2 to 3°C error in temperature measurement.
- No conclusive evidence was found to explain the poor behavior of Still #2.

- For the methylcyclohexane + toluene at 760 mmHg system, thermodynamically consistent data were obtained and the data were externally consistent.
- For the hexane + toluene at 760 mmHg system, temperature fluctuations of 0.1°C were observed during operation and this observed uncertainty was used for data analysis. Predictive tests for temperature and activity coefficients supported the probability of thermodynamic consistency. Most of the vapor composition errors were within the RMSD from GEOS. There is significant scatter in literature data so it is difficult to assess external consistency, but this work appears to be in agreement with the bulk of the literature data.
- For the methylcyclohexane + toluene at 90°C system, predictive tests for vapor composition and activity coefficient support thermodynamic consistency. The error in the pressure exceeds the experimental uncertainty of the equipment as was seen with the vapor-pressure data. The work of Schneider scatters about this work but since the uncertainty is unknown, agreement can only be surmised. The other available literature source does not agree with this work or Schneider's work.

Recommendations from this study are as follows:

- Recalibrate the temperature and pressure equipment before any further measurements are taken.
- After recalibration, repeat some of the vapor-pressure and VLE measurements. If errors still exceed the experimental uncertainty of the equipment, investigate the cause, e.g. use a different thermometer in the still, compare the two thermometers in an oil bath at high system temperatures, compare the two thermometers at the

ice point and triple point, find a reliable pressure gauge to measure still pressure, and compare the two pressure gauges at several operating pressures.

- Purchase autosampling equipment for the refractometer and computer software that will simultaneously log temperature, pressure, and composition data. This will allow data to be taken even without the presence of the researcher resulting in more data points, and eliminate the possibility of transcription errors when manually entering data.
- Consider increasing the size of the holding chamber to reduce concentration fluctuations in the boiling chamber thereby reducing temperature fluctuations. This is only necessary when using pure components with drastically different normal boiling points such as hexane and toluene.
- Construct a Plexiglas box with temperature control capability to maintain constant ambient temperature around the still, condenser, and manifold. This box would also serve as a safety device if the still was damaged and its contents released.
- Equilibrium Still #1 should be used for pure-component vapor pressures and VLE data at near-atmospheric pressures, provided the VLE components do not have drastically different normal boiling points.

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Appendix A

Calibration Curves

Table 14 contains calibration measurements for the methylcyclohexane + toluene system. The refractive index versus methylcyclohexane mole fraction is plotted in Figure 49. A third-order polynomial trendline, shown on the figure, was used to obtain an equation for calculating mole fraction. The deviation of the calculated mole fraction from the experimental mole fraction is shown in Figure 50.

Table 14. Calibration Measurements for Methylcyclohexane + Toluene

η_D, Refractive Index	Experimental Methylcyclohexane Mole Fraction	Calculated Methylcyclohexane Mole Fraction	Difference (exp – calc)
1.49689	0.0	-0.00067	0.00067
1.49203	0.05094	0.05105	-0.00011
1.48746	0.10008	0.10058	-0.00050
1.48313	0.14793	0.14849	-0.00055
1.47860	0.19917	0.19981	-0.00064
1.47428	0.25003	0.25006	-0.00004
1.47032	0.29774	0.29739	0.00035
1.46593	0.35181	0.35143	0.00038
1.46235	0.39754	0.39684	0.00070
1.45816	0.45181	0.45164	0.00017
1.45491	0.49491	0.49546	-0.00056
1.45112	0.54829	0.54813	0.00017
1.44744	0.60149	0.60096	0.00053
1.44117	0.69563	0.69514	0.00049
1.43791	0.74622	0.74630	-0.00008
1.43468	0.79763	0.79858	-0.00094
1.43137	0.85286	0.85384	-0.00099
1.42862	0.89970	0.90112	-0.00142
1.42601	0.94879	0.94717	0.00162
1.42312	1.0	0.99955	0.00045

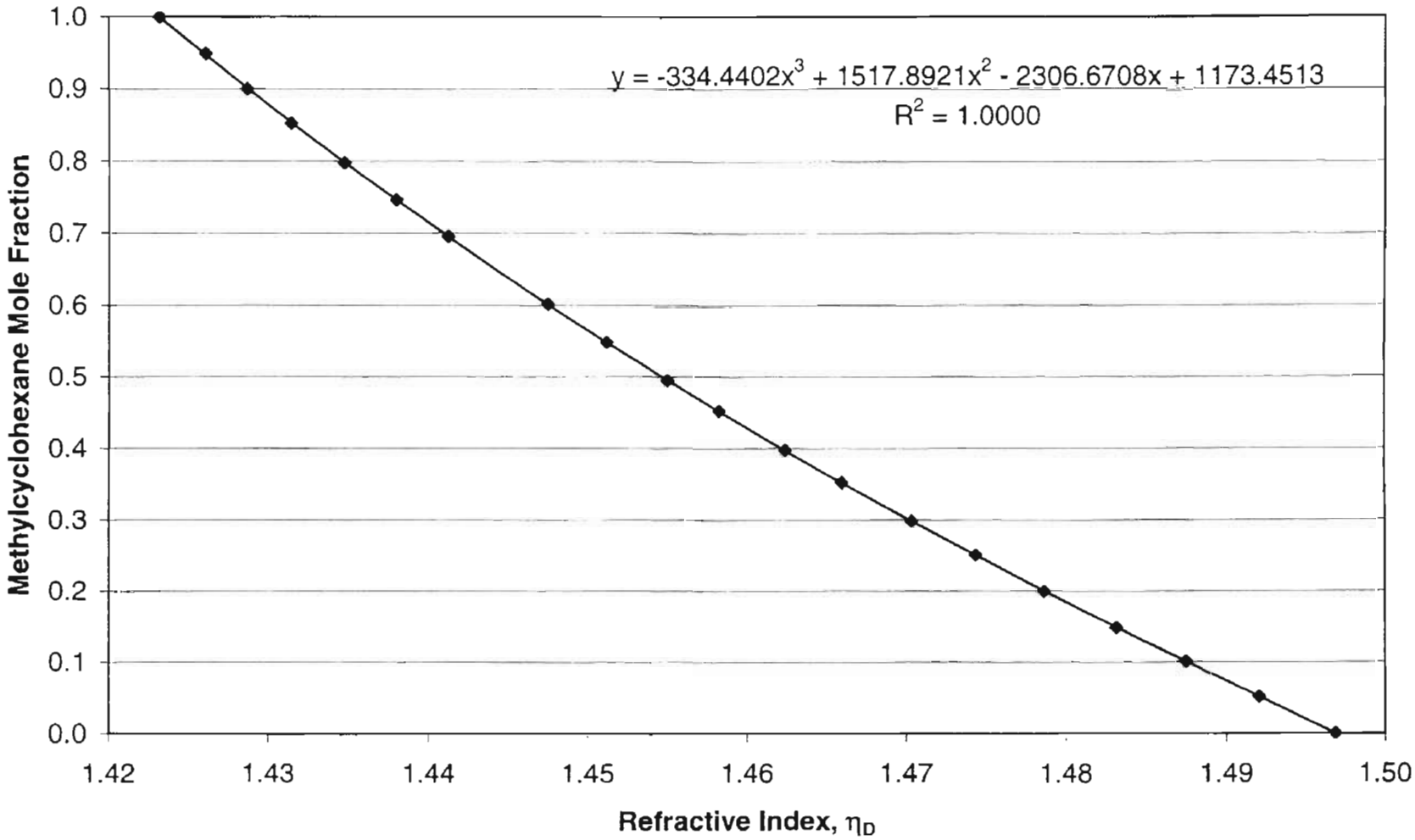

Figure 49. Calibration Curve for Methylcyclohexane + Toluene

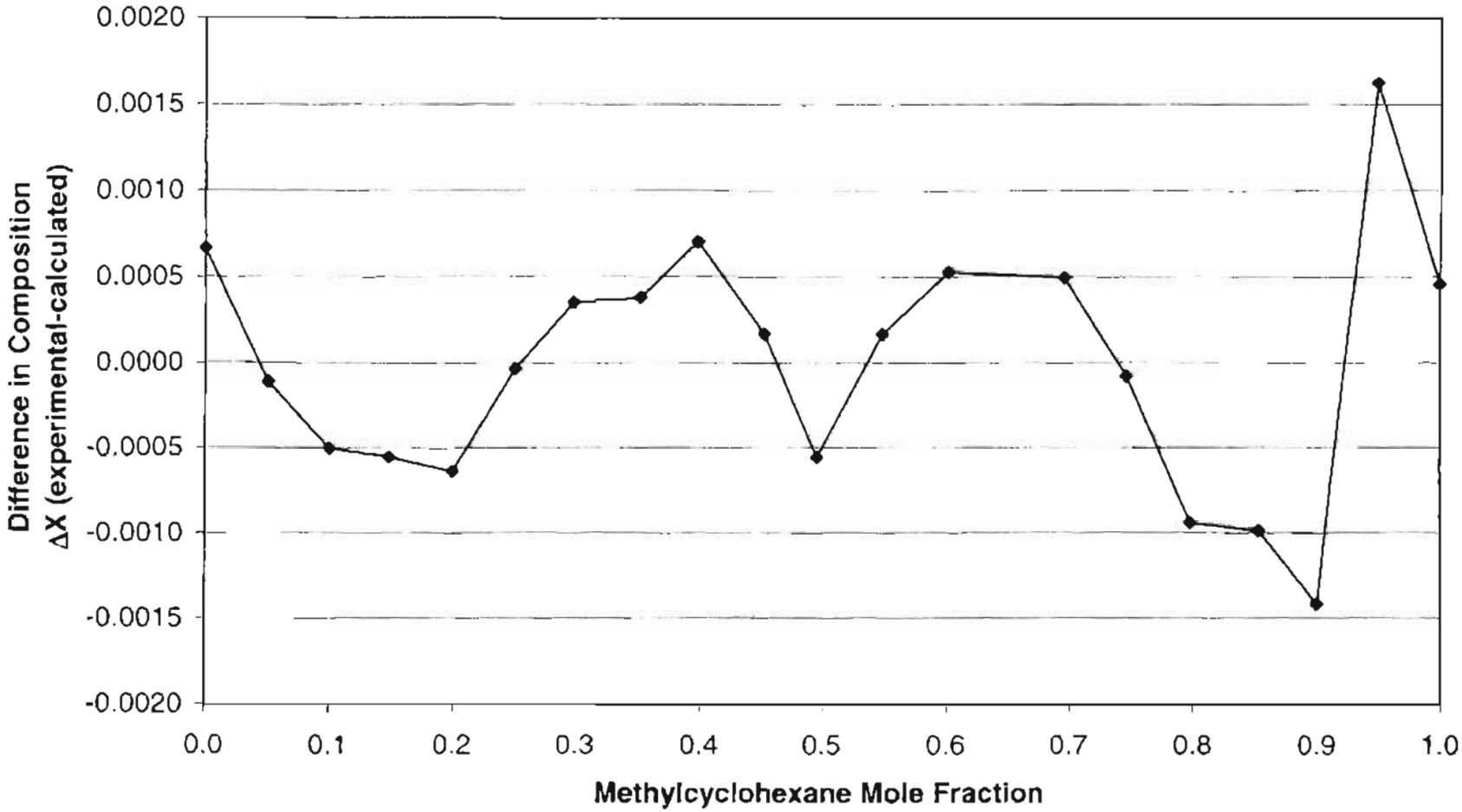

Figure 50. Deviation of Calculated Compositions for Methylcyclohexane + Toluene

The calibration measurements for hexane + toluene are shown in Table 15. Figure 51 shows the calibration curve and equation of the third-order polynomial trendline. The deviations of the calculated mole fraction from the experimental mole fraction are shown in Figure 52.

Table 15. Calibration Measurements for Hexane + Toluene

η_D, Refractive Index	Experimental Hexane Mole Fraction	Calculated Hexane Mole Fraction	Difference (exp – calc)
1.49691	0.0	-0.00048	0.00048
1.49059	0.04283	0.04375	-0.00092
1.48221	0.10279	0.10296	-0.00017
1.47558	0.15006	0.15037	-0.00031
1.46875	0.19947	0.19986	-0.00039
1.46256	0.24453	0.24536	-0.00082
1.45609	0.29408	0.29366	0.00042
1.44909	0.34896	0.34689	0.00207
1.44351	0.38848	0.39011	-0.00163
1.43562	0.45332	0.45255	0.00077
1.43048	0.49318	0.49413	-0.00094
1.41733	0.60275	0.60409	-0.00134
1.41186	0.65292	0.65149	0.00144
1.40726	0.69054	0.69216	-0.00162
1.40141	0.74484	0.74501	-0.00017
1.39605	0.79478	0.79459	0.00018
1.38985	0.85409	0.85340	0.00068
1.38543	0.89612	0.89632	-0.00021
1.37911	0.95895	0.95920	-0.00025
1.37507	1.0	1.00035	-0.00035

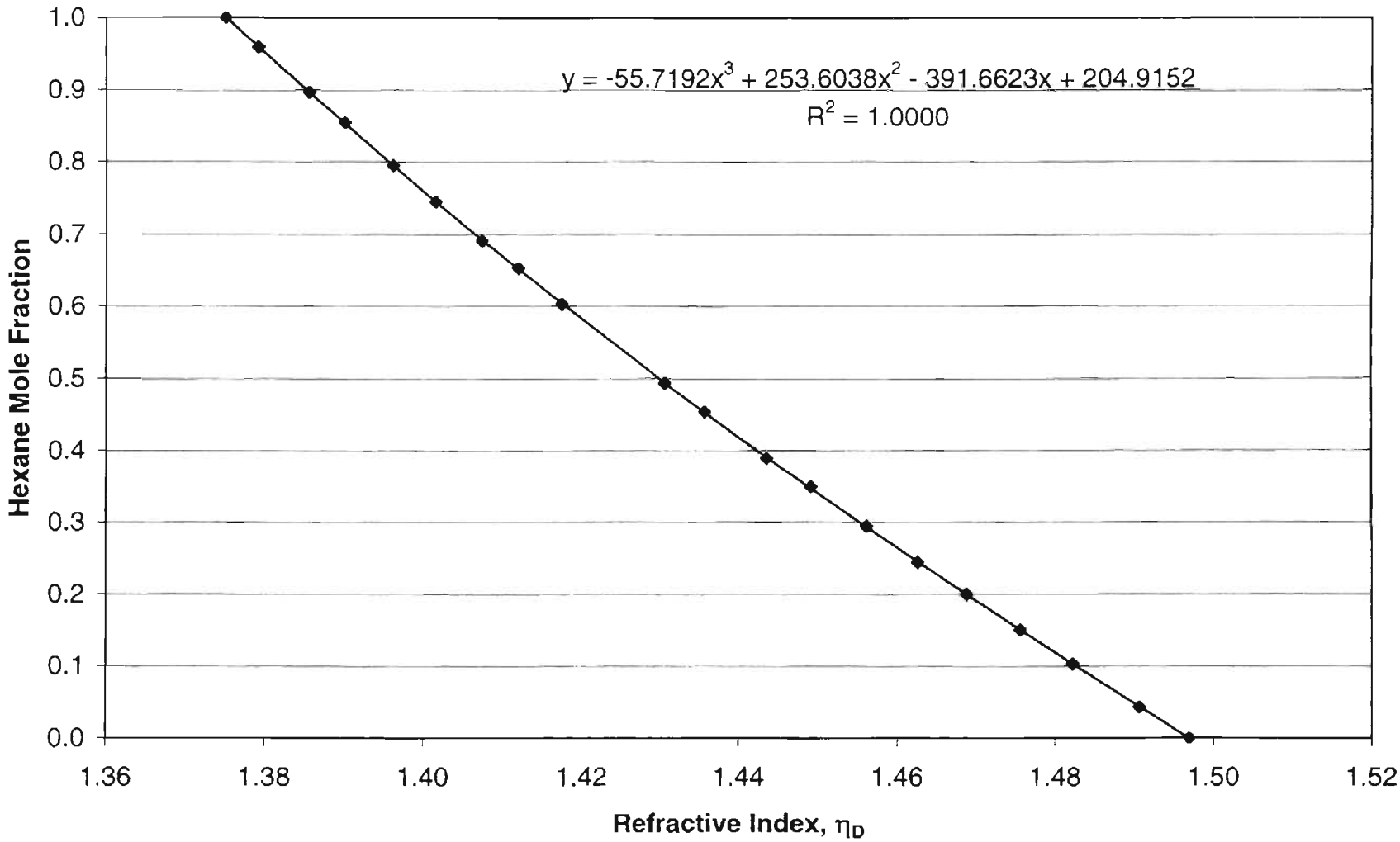

Figure 51. Calibration Curve for Hexane + Toluene

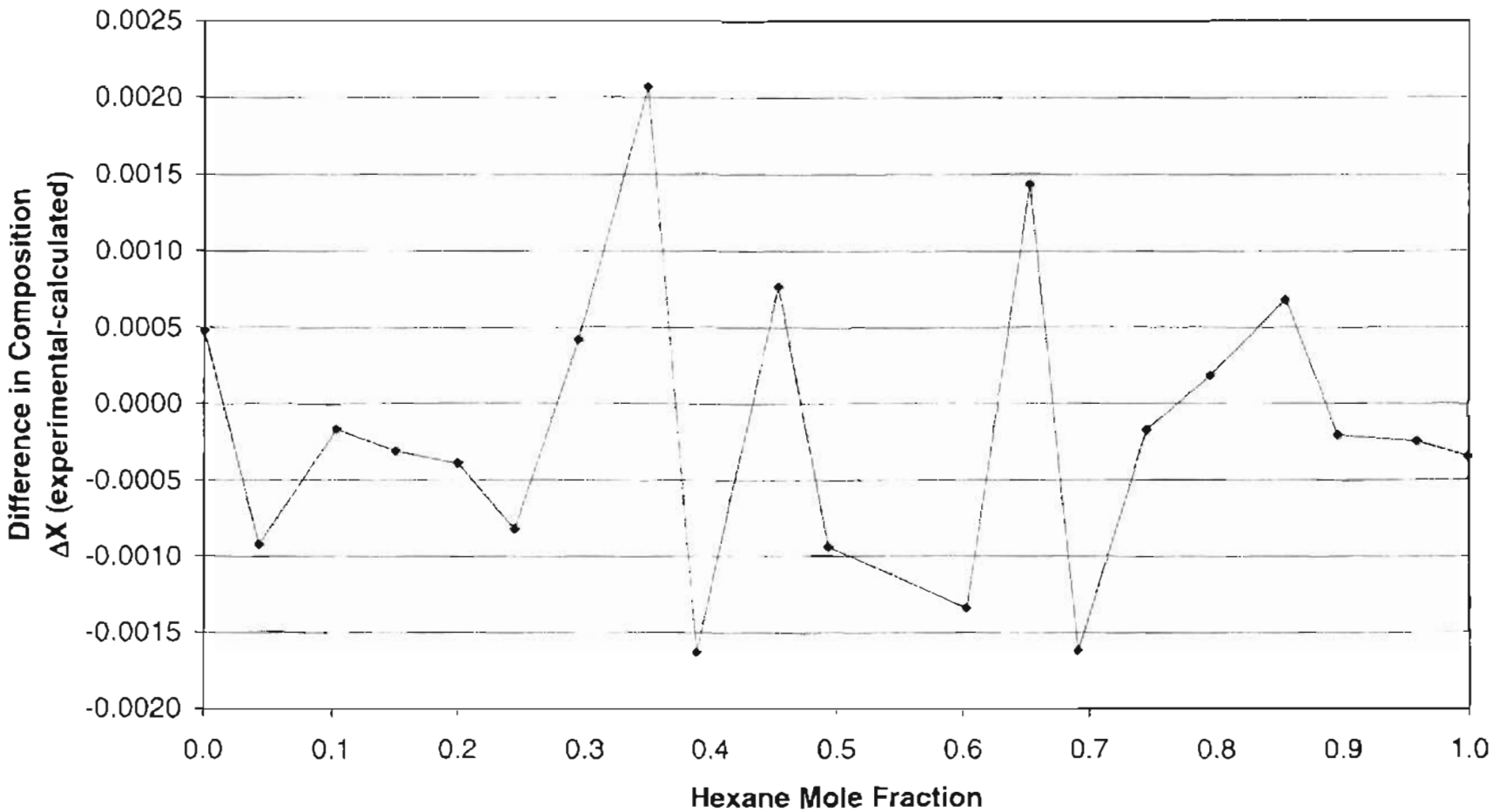

Figure 52. Deviation of Calculated Composition for Hexane + Toluene

Appendix B

Critical Properties and Antoine Constants

The Antoine constants used in this work were obtained by optimizing experimental vapor-pressure data in the PFP program (Gasem 1999) previously described. Table 16 contains the Antoine constants for the following equation:

$$\ln P = A - \frac{B}{T + C} \qquad \text{(B-1)}$$

where P = pressure (mmHg)

A, B, C = Antoine constants

T = temperature (K)

Table 16. Antoine Constants

Compound	A	B (K)	C (K)
Methylcyclohexane	15.667	2891.902	-54.013
Hexane	15.785	2661.500	-51.027
Toluene	16.155	3177.953	-50.004

The critical properties used in the GEOS program (Gasem 1997) were obtained from the literature (Reid, Prausnitz et al. 1987) and are listed in Table 17.

Table 17. Critical Properties

Compound	T_c (K)	P_c (bar)	Z_c	ω
Methylcyclohexane	572.2	34.7	0.268	0.236
Hexane	507.5	30.1	0.264	0.299
Toluene	591.8	41.06	0.263	0.263

Appendix C

Sample Printout from Pure-Fluid Properties (Gasem 1999) Program

The following page provides a sample of the output from the Pure-Fluid Properties program previously described. The data are listed as follows:

X(I)	=	Experimental temperature (K)
Y(I)	=	Experimental pressure (mmHg)
FIT(I)	=	Pressure calculated with Antoine Equation (mmHg)
DEV	=	Difference in pressure (calculated – experimental)
%DEV	=	Percent difference in pressure (calculated – experimental)
WDEV	=	Weighted difference in pressure
W(I)	=	Weighting factor
RMSE	=	Root mean squared deviation
AAPD	=	Absolute average percent deviation
WRMS	=	Weighted root mean squared deviation
NO PT	=	Number of data points
X	=	Antoine constants obtained from data regression

Methylcyclohexane vapor pressure Fidler Still #1 Ruska only 4/28/00

0

DATA	X(I)	Y(I)	FIT(I)	DEV	%DEV	WDEV	W(I)
1	348.8280	350.000	350.01380	0.01380	0.00394	0.01380	1.00000
2	350.9150	375.000	374.99931	-0.00069	-0.00018	-0.00069	1.00000
3	352.8940	400.000	399.98144	-0.01856	-0.00464	-0.01856	1.00000
4	356.5800	450.000	450.02032	0.02032	0.00452	0.02032	1.00000
5	359.9510	500.000	499.99960	-0.00040	-0.00008	-0.00040	1.00000
6	363.0650	550.000	549.96324	-0.03676	-0.00668	-0.03676	1.00000
7	363.0650	550.000	549.96324	-0.03676	-0.00668	-0.03676	1.00000
8	365.9710	600.000	600.05333	0.05333	0.00889	0.05333	1.00000
9	368.6850	650.000	650.00012	0.00012	0.00002	0.00012	1.00000
10	369.9840	675.000	675.02846	0.02846	0.00422	0.02846	1.00000
11	371.2430	700.000	699.99869	-0.00131	-0.00019	-0.00131	1.00000
12	372.2260	720.000	719.99144	-0.00856	-0.00119	-0.00856	1.00000
13	373.1890	740.000	740.00654	0.00654	0.00088	0.00654	1.00000
14	374.1300	760.000	759.98064	-0.01936	-0.00255	-0.01936	1.00000

0

RMSE = 0.0236003 WRMS = 0.02
AAPD = 0.0031899 NO PT = 14

X = 0.1566720E+02 0.2891902E+04 -0.5401337E+02

Appendix D

Sample Printout from GEOS (Gasem 1997) program

The following pages provide a sample of the output from the GEOS program previously described. The output contains four sections which list the calculated values for pressure, vapor composition, and the two activity coefficients. The heading of each section shows the two components and the temperature at which the data were taken, with the activity coefficient model and equation of state listed below the heading. The following list may be helpful in reading the GEOS output:

TEMP	=	Experimental temperature (C)
BP(EXP)	=	Experimental bubble point pressure (mmHg)
X(EXP)	=	Experimental liquid mole fraction
BP(CALC)	=	Bubble point pressure calculated with regressed model parameters
DEV	=	Deviation (calculated – experimental)
E(1,2)	=	Regressed model parameters 1 and 2
RMSE	=	Root mean squared deviation
AAD	=	Absolute average deviation
NPTS	=	Number of data points
YEXP(1)	=	Experimental vapor mole fraction of component 1
AEXP(2)	=	Activity coefficient of component 1 calculated with experimental values

Methylcyclohexane(1) + Toluene(2) at 90 C (Ant const fr exp
VAN LAAR MODEL /
VIRIAL-2G EQUATION OF STATE

DATA	TEMP (C)	BP(EXP) (MMHG)	XEXP(1)	BP(CAL)	DEV	%DEV	
1	90.00	406.29	0.0000	406.2908	0.0008	0.00	1.000
2	90.00	424.29	0.0591	424.1252	-0.1648	-0.04	0.000
3	90.00	434.46	0.0965	434.4260	-0.0340	-0.01	0.000
4	90.00	444.80	0.1371	444.8347	0.0347	0.01	0.000
5	90.00	455.00	0.1802	455.0832	0.0832	0.02	0.000
6	90.00	465.10	0.2258	465.1120	0.0120	0.00	0.000
7	90.00	477.93	0.2899	477.9426	0.0126	0.00	0.000
8	90.00	489.31	0.3526	489.2195	-0.0905	-0.02	0.000
9	90.00	499.96	0.4187	499.8995	-0.0605	-0.01	0.000
10	90.00	511.79	0.5007	511.6127	-0.1773	-0.03	0.000
11	90.00	502.47	0.4364	502.5657	0.0957	0.02	0.000
12	90.00	510.33	0.4918	510.4182	0.0882	0.02	0.000
13	90.00	518.25	0.5536	518.3467	0.0967	0.02	0.000
14	90.00	525.36	0.6156	525.4748	0.1148	0.02	0.000
15	90.00	532.45	0.6840	532.4256	-0.0244	0.00	0.000
16	90.00	538.61	0.7541	538.5849	-0.0251	0.00	0.000
17	90.00	543.40	0.8184	543.3832	-0.0168	0.00	0.000
18	90.00	547.72	0.8881	547.6521	-0.0679	-0.01	0.000
19	90.00	550.37	0.9422	550.2771	-0.0929	-0.02	1.000
20	90.00	552.39	1.0000	552.3883	-0.0017	0.00	1.000

C(1,2), D(1,2) = 0.00000E+00 0.00000E+00
E(1).....E(N) = 0.27059E+00 0.24395E+00 0.10000E+01 0.10000E+01
0.00000E+00 0.00000E+00 0.97471E+00 0.97488E+00
0.97471E+00 0.97488E+00 0.00000E+00 0.00000E+00

RMSE = 0.0819 AAD = 0.0647 %AAD = 0.01
BIAS = -0.0109 NPTS = 20

Methylcyclohexane(1) + Toluene(2) at 90 C (Ant const fr exp
VAN LAAR MODEL /
VIRIAL-2G EQUATION OF STATE

DATA	TEMP (C)	PRESS (MMHG)	YEXP(1)	YCAL(1)	DEV	%DEV
1	90.00	406.29	0.0000	0.0000	0.0000	0.00
2	90.00	424.13	0.0982	0.0967	-0.0015	-1.50
3	90.00	434.43	0.1510	0.1512	0.0002	0.14
4	90.00	444.83	0.2051	0.2056	0.0005	0.26
5	90.00	455.08	0.2593	0.2589	-0.0004	-0.14
6	90.00	465.11	0.3111	0.3112	0.0001	0.05
7	90.00	477.94	0.3784	0.3791	0.0007	0.18
8	90.00	489.22	0.4402	0.4405	0.0003	0.07
9	90.00	499.90	0.5012	0.5013	0.0001	0.03
10	90.00	511.61	0.5735	0.5729	-0.0006	-0.10
11	90.00	502.57	0.5168	0.5171	0.0003	0.06
12	90.00	510.42	0.5660	0.5653	-0.0007	-0.12
13	90.00	518.35	0.6184	0.6176	-0.0008	-0.13
14	90.00	525.47	0.6703	0.6691	-0.0012	-0.18
15	90.00	532.43	0.7273	0.7255	-0.0018	-0.24
16	90.00	538.58	0.7850	0.7836	-0.0014	-0.18
17	90.00	543.38	0.8381	0.8378	-0.0003	-0.04
18	90.00	547.65	0.8994	0.8980	-0.0014	-0.15

19	90.00	550.28	0.9473	0.9464	-0.0009	-0.10
20	90.00	552.39	1.0000	1.0000	0.0000	0.00

C(1,2), D(1,2) = 0.00000E+00 0.00000E+00
E(1).....E(N) = 0.27059E+00 0.24395E+00 0.10000E+01 0.10000E+01
0 00000E+00 0.00000E+00 0.97471E+00 0.97488E+00
0.97471E+00 0.97488E+00 0.00000E+00 0.00000E+00

RMSE = 0.0008 AAD = 0.0007 %AAD = 0.18
BIAS = -0.0004 NPTS = 20

Methylcyclohexane(1) + Toluene(2) at 90 C (Ant const fr exp
VAN LAAR MODEL /
VIRIAL-2G EQUATION OF STATE

DATA	TEMP (C)	PRESS (MMHG)	AEXP(1)	ACAL(1)	DEV	%DEV	
1	90.00	406.29	1.3107	1.3107	0.0000	0.00	1.000
2	90.00	424.13	1.2866	1.2668	-0.0198	-1.54	1.000
3	90.00	434.43	1.2399	1.2415	0.0016	0.13	1.000
4	90.00	444.83	1.2128	1.2160	0.0032	0.26	1.000
5	90.00	455.08	1.1926	1.1911	-0.0014	-0.12	1.000
6	90.00	465.11	1.1665	1.1670	0.0006	0.05	1.000
7	90.00	477.94	1.1347	1.1368	0.0021	0.19	1.000
8	90.00	489.22	1.1103	1.1109	0.0006	0.05	1.000
9	90.00	499.90	1.0870	1.0872	0.0002	0.02	1.000
10	90.00	511.61	1.0639	1.0625	-0.0014	-0.13	1.000
11	90.00	502.57	1.0806	1.0815	0.0008	0.08	1.000
12	90.00	510.42	1.0661	1.0650	-0.0011	-0.10	1.000
13	90.00	518.35	1.0503	1.0491	-0.0012	-0.11	1.000
14	90.00	525.47	1.0373	1.0357	-0.0016	-0.16	1.000
15	90.00	532.43	1.0262	1.0237	-0.0025	-0.25	1.000
16	90.00	538.58	1.0159	1.0141	-0.0018	-0.18	1.000
17	90.00	543.38	1.0080	1.0075	-0.0004	-0.04	1.000
18	90.00	547.65	1.0045	1.0028	-0.0016	-0.16	1.000
19	90.00	550.28	1.0019	1.0007	-0.0011	-0.11	1.000
20	90.00	552.39	1.0000	1.0000	0.0000	0.00	1.000

C(1,2), D(1,2) = 0.00000E+00 0.00000E+00
E(1).....E(N) = 0.27059E+00 0.24395E+00 0.10000E+01 0.10000E+01
0.00000E+00 0.00000E+00 0.97471E+00 0.97488E+00
0 97471E+00 0.97488E+00 0.00000E+00 0.00000E+00

RMSE = 0 0047 AAD = 0.0022 %AAD = 0.18
BIAS = -0.0013 NPTS = 20

Methylcyclohexane(1) + Toluene(2) at 90 C (Ant const fr exp
VAN LAAR MODEL /
VIRIAL-2G EQUATION OF STATE

DATA	TEMP (C)	PRESS (MMHG)	AEXP(2)	ACAL(2)	DEV	%DEV	
1	90.00	406.29	1.0000	1.0000	0.0000	0.00	1.000
2	90.00	424.13	0.9998	1.0010	0.0012	0.12	1.000
3	90.00	434.43	1.0031	1.0027	-0.0003	-0.03	1.000

4	90.00	444.83	1.0061	1.0055	-0.0006	-0.06	1.000
5	90.00	455.08	1.0087	1.0094	0.0007	0.07	1.000
6	90.00	465.11	1.0149	1.0147	-0.0002	-0.02	1.000
7	90.00	477.94	1.0251	1.0240	-0.0011	-0.11	1.000
8	90.00	489.22	1.0360	1.0352	-0.0008	-0.07	1.000
9	90.00	499.90	1.0497	1.0493	-0.0004	-0.04	1.000
10	90.00	511.61	1.0689	1.0700	0.0011	0.10	1.000
11	90.00	502.57	1.0539	1.0535	-0.0005	-0.04	1.000
12	90.00	510.42	1.0657	1.0676	0.0019	0.17	1.000
13	90.00	518.35	1.0828	1.0852	0.0025	0.23	1.000
14	90.00	525.47	1.1008	1.1050	0.0042	0.38	1.000
15	90.00	532.43	1.1220	1.1293	0.0072	0.64	1.000
16	90.00	538.58	1.1495	1.1568	0.0073	0.64	1.000
17	90.00	543.38	1.1822	1.1846	0.0024	0.20	1.000
18	90.00	547.65	1.2013	1.2174	0.0161	1.34	1.000
19	90.00	550.28	1.2240	1.2449	0.0209	1.71	1.000
20	90.00	552.39	1.2763	1.2763	0.0000	0.00	1.000

```
C(1,2), D(1,2) = 0.00000E+00 0.00000E+00
E(1).....E(N) = 0.27059E+00 0.24395E+00 0.10000E+01 0.10000E+01
                0.00000E+00 0.00000E+00 0.97471E+00 0.97488E+00
                0.97471E+00 0.97488E+00 0.00000E+00 0.00000E+00

RMSE =    0.0065        AAD =    0.0035        %AAD =    0.30
BIAS =    0.0031                              NPTS =    20
-----------------------------------------------------------------------
--
```

Appendix E

Error Propagation

Evaluation of experimental results has meaning only when the errors in the measurements are known. Since experimental results are generally recorded by numbers, the uncertainty in these numbers and the effect each uncertainty has on the final result is important to know. "All measurements in physics and science generally are inaccurate in some degree," (Topping 1960) and the goal of the researcher is to determine that degree and ensure that the inaccuracy is small enough "not to affect the conclusions he infers from his results. The difference between the observed value of any physical quantity and the "accurate" value is called the error of observation. Errors of observation are usually grouped as accidental and systematic," (Topping 1960) or random and systematic. Systematic errors may be due to the technique of the observer or the equipment. Equipment in need of calibration may produce precise but not accurate measurements. If equipment has a constant offset when compared to known standards, this may be accounted for by adjusting readings by that constant. However, equipment may produce systematic errors that vary in some way and these cannot be accounted for as easily. Random errors may be due to the observer, the accuracy and repeatability of the equipment, slight changes in ambient conditions, or some other unknown influence. Statistical methods exist to help the researcher deal with random errors. For this work, direct measurements such as pressure and temperature were assumed to have the uncertainty claimed by the equipment manufacturer. However, the experimental activity

coefficient was calculated using the experimental values of pressure, liquid mole fraction, vapor mole fraction, and saturation pressure. The activity coefficient is a function of products and sums and Topping (Topping 1960) provides a method for finding the standard error of such a compound quantity as follows:

$$\gamma = \gamma\left(P, x, y, P^s\right) \tag{E-1}$$

$$\left(\frac{\sigma_\gamma}{\gamma}\right)^2 = \left(\frac{\sigma_y}{y}\right)^2 + \left(\frac{\sigma_x}{x}\right)^2 + \left(\frac{\sigma_P}{P}\right)^2 + \left(\frac{\sigma_{P^s}}{P^s}\right)^2 \tag{E-2}$$

where σ_i = standard error of quantity i

Saturation pressure can be related to temperature as follows:

$$\left(\frac{\sigma_{P^s}}{P^s}\right)^2 = \left(\frac{\sigma_T}{P^s \dfrac{dT}{dP}}\right)^2 \tag{E-3}$$

Using the above equations, the experimental uncertainty for activity coefficient measurements may be calculated. The following values were obtained from the Engineering Sciences Data Unit (1982; 1984; 1986):

$$\left(\frac{dT}{dP}\right)_{methylcyclohexane} = 0.0467 \frac{^\circ C}{mmHg}$$

$$\left(\frac{dT}{dP}\right)_{hexane} = 0.0419 \frac{^\circ C}{mmHg}$$

$$\left(\frac{dT}{dP}\right)_{toluene} = 0.0463 \frac{^\circ C}{mmHg}$$

An average value of 0.045°C/mmHg was used for the mixtures. An example calculation is shown on the following page.

The standard error of the activity coefficient for the methylcyclohexane(1) + toluene(2) at 760 mmHg system for the following values:

$$x_1 = 0.0628$$
$$y_1 = 0.0978$$
$$\gamma_1 = 1.252$$
$$\frac{dT}{dP} = 0.045 \frac{^{o}C}{mmHg}$$

in Equations E-2 and E-3 would be calculated as:

$$\sigma_{\gamma_1} = 0.036$$

The standard deviations of pressure, temperature, and mole fraction are 0.038 mmHg, 0.04°C, and 0.0015, respectively, as previously discussed.

VITA

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Master of Science

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