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UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

THE GENERALIZED ASYMMETRIC RULE (GAR): THE OPTIMIZATION OF MIXTURE ASYMMETRY IN A NONCUBIC EQUATION OF STATE

A Dissertation

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

Doctor of Philosophy

By

STEVEN CHARLES HARMON

Norman, Oklahoma

1998

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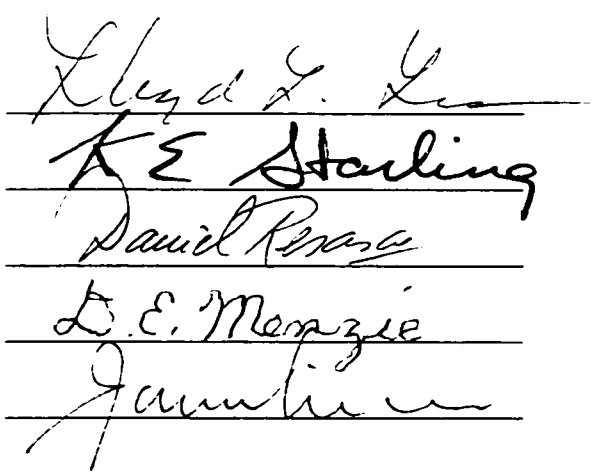
THE GENERALIZED ASYMMETRIC RULE (GAR): THE OPTIMIZATION OF MIXTURE ASYMMETRY IN A NONCUBIC EQUATION OF STATE

A DISSERTATION APPROVED FOR THE

SCHOOL OF CHEMICAL ENGINEERING AND MATERIALS SCIENCE

BY



ACKNOWLEDGMENTS

The author would like to thank the many people who played an influential role in the development of this work. First, I thank George Lynn Cross Professor Emeritus Kenneth Starling for his academic supervision and leadership in serving as my dissertation advisor. In all, he taught me much about the tremendous efforts involved in modeling equations of state as well as in producing a work of high quality. Next, I thank Professor Lloyd Lee for his insightful comments on abstract theory (most notably statistical-mechanical asymmetry and the Kronecker delta) as well as serving in the capacity of committee chair after Dr. Starling's retirement. Both of them have shown me some of the grandeur and enthusiasm involved in the quest to obtain more accurate thermodynamic models.

I would also like to thank the other members of this committee for their time, interest and enthusiasm in serving in this committee. I would like to thank Drs. Daniel Resasco and Don Menzie for serving all these years on my committee. Dr. Resasco has provided a wonderful example of professorial participation in his students' research activities, including extending help after hours and on weekends. Dr. Menzie, during his fifty years as a professor, taught both my father and uncle in petroleum engineering classes when they were undergraduates at this university. I thank him for being a mentor to me as well as showing how dedication to teaching and research can make academics a grand excursion through life.

Of course, I also thank Dr. Faruk Civan for serving as the outside-departmental committee member after Dr. Menzie's retirement. His interest and teaching in the natural-gas industry (along with his three degrees in chemical engineering) have proven quite complementary to this work. I thank him for his support of the work leading to this dissertation.

I thank Dr. Rex T. Ellington, Dr. Starling's graduate MS and PhD advisor, who at one point supplied me with one of his own hard-to-find conference papers from his garage . In addition, I also thank him for hearing about the replacement of binary interaction parameters that originated from this work. For me, the day I told my advisor's advisor of this replacement breakthrough truly comprised a historic moment. I also remember his comment on it taking so long for someone to accomplish this task; this truly shows that room for improvement in thermodynamic modeling will always exist.

Next, Dr. Wenzel's e-mail comes to mind concerning the publication of his and Kenneth Juris' generalized symmetric rule in that "those earlier papers were written with the hope that they would prove useful to some later practitioners in the field. That work, too, depended on the insights supplied by still earlier workers." So, too, does the author wish that the progress made toward the development of the generalized asymmetric rule herein will follow and continue this trend.

Of course, many other faculty and staff at the University of Oklahoma have greatly assisted in the development of this work. I would like to thank Larry Isley for his invaluable discussions on abstract theory, God and the nature of the universe.

Larry's discussions will always inspire me to think about approaching a complex topic through logic, hybrid reasoning, and simple common sense.

In addition, I thank the staff at University Computing Services that always remained on hand to offer their expertise on the mysteries of the mainframe computer. These include Glen Black, Mike Flournoy, Jim Winters, and so many others. Also, I thank the staff at the university's Writing Center for their editorial contributions and helpful suggestions in the preparation and correction of this work. Among the many, these include Writing Center Director Judith Drummond and secretary Ann Roberson, as well as the consultants who have discussed and supported the preparation of this dissertation. In particular, I thank Ashley Currier for the corrections and suggestions given regarding the text of this work.

Next, I thank the many people at the university and elsewhere who have provided me with the faith, hope, encouragement, and love that supported me through the process of earning a doctoral degree. Although I cannot remember everyone, I cannot forget the influence they have had on me.

In addition, I thank my family for their much-needed love, support, friendship, and encouragement that sustained me throughout the development of this work. I thank my parents, who helped me every step of the way with their constant example of hard work and guidance; my older brother, Bob, for his direct approach to problem-solving; and my younger brother, Brian, for his positive outlook on life and wide-ranging approaches for dealing with people.

Finally, I would especially like to thank my girlfriend, Karen Marrs, for her continual love, attention, assistance, advice, and so many other wonderful and unique qualities proffered. Karen's presence is truly heartfelt and a joy to behold.

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ABSTRACT

This work introduces the generalized asymmetric rule (GAR) for equation-of-state (EOS) models. The GAR constitutes a novel equation that models unlike-interaction parameters (UIPs) in the simulation of vapor-liquid equilibrium (VLE) mixture compositions.

The GAR can average numbers of positive, negative, and/or zero numerical values. Moreover, the GAR can invoke positive/negative sign changes for numbers of like and/or unlike signs. The GAR therefore holds potential for other fields whenever any given set of numbers must be averaged asymmetrically.

The GAR was developed by the author of this work and can replace binary interaction parameters (BIPs), a long-recognized UIP modeling standard. Overall, GARs present three basic advantages: First, GARs can provide up to a three-dimensional representation, or "mapping," of binary systems in lieu of one-dimensional BIP representations. Second, GARs indicate how much one component "outweighs" another for a given UIP. Third, GARs offer a nondivergent mechanism that guarantees a reliable asymmetry model for UIPs.

This work uses a preexisting, noncubic EOS to predict polar/nonpolar pure components. This EOS uses the mixing rules of a preexisting local composition model (LCM) that can simultaneously (1) simulate both liquid and vapor compositions and (2) employ one (or more) pure-component equation(s) of state. The practical application entailed composition predictions of natural-gas dehydrators,

including pure-component vapor-pressure and liquid-density simulations for ethylene glycol, diethylene glycol, triethylene glycol, five aromatic compounds, and two freons.

Overall, GARs surpassed BIPs in over half of all results. Furthermore, this work briefly reviews literature methods that can overcome limitations of insufficient binary VLE data. These methods include the use of (1) solubility data, (2) ternary data, (3) other thermodynamic property data, (4) infinite-dilution activity coefficients, (5) the substitution of alternate isomeric-component data, and (6) interpolation with the GAR. Two appendices suggest future methods of binary/multicomponent VLE modeling and overcoming parameter-correlation problems.

A third appendix details limiting cases of both the GSR and GAR; a fourth appendix lists literature sources of mixture data, including VLE and other thermodynamic properties. Finally, the dissertation also lists pure-component property sources including vapor pressure, liquid density, enthalpy, and other thermodynamic properties.

CHAPTER I

INTRODUCTION AND OVERVIEW

1.1 Summary

The work presented in this dissertation consists of several developments that must be carefully examined to improve future modeling efforts in the field of thermodynamics. First, the application of such modeling efforts must be clearly delineated to ensure a meaningful research objective. Section 1.2 accomplishes this with respect to practical applications for this work that pertain to the chemical-processing industry.

Second, this work concerns itself with the modeling of both pure components and mixtures of these components. As a result, Section 1.3 entails a preview of the efforts made for this work to predict pure components with a high degree of accuracy.

Third, Section 1.4 presents a brief discussion of the primary innovation of this work, namely, the generalized asymmetric rule (or GAR), an unlike-interaction equation intended for use in asymmetric EOS models as an alternative to the current usage of symmetric binary interaction parameters (BIPs). This alternative focuses on the simulation and prediction of binary and multicomponent properties of chemical mixtures, specifically that of vapor-liquid equilibrium (VLE) compositions.

Fourth, this work applies the GAR to the prediction of binary mixtures in an attempt to achieve more accurate simulations than those currently attained by BIPs. As briefly reviewed in Section 1.5, the GAR was developed to optimize mixture

asymmetry in a noncubic EOS. This section therefore describes the mixture models that led to the one modified in this work in an effort to achieve greater predictive accuracy. A brief summary then follows the description of the results obtained for this work, which prove the general case for asymmetry achieved through GARs as opposed to symmetry achieved through BIPs.

Fifth, Section 1.6 briefly previews several methods suggested to overcome the limitations of insufficient binary data sets in the simulation of multicomponent VLE systems. These methods may aid future investigators in their search for missing data in the thermodynamic literature.

Sixth, Section 1.7 discusses two separate conclusion-and-recommendation sections presented in this work that may be drawn from the results presented herein. As seen below, these recommendations may be applied to the LCM model utilized in this work as well as to other LCMs reviewed by it.

Seventh, Section 1.8 reviews the multitude of derivations, recommendations, and literature sources presented in Appendices A through D of this work. The recommendations in Appendices B and D are intended to supplement the recommendations provided in Section 1.7.

1.2 Practical/Industrial Applications

Generally speaking, the practical application of this work involves the prediction of binary and multicomponent vapor-liquid equilibrium (VLE) compositions. Specifically though, the primary application of this work involves the

prediction of binary and multicomponent VLE compositions found in natural-gas dehydration units. Typically, natural gas contains water vapor that can later condense in gas pipelines to the point of impeding flow. At low-temperature conditions, however, the water vapor can condense and freeze within the pipeline itself to form natural-gas solids, or hydrates. Such conditions can then cause further impedance to pipe flow, thereby leading to losses in production and revenue.

To avoid these unfavorable circumstances, several process exist to remove water vapor from natural-gas mixtures. These include triethylene-glycol contacting, glycol injection (with either mono- or diethylene glycol), and solid-bed desiccants (Smith and Dorsi, 1993). Among these processes, the widespread use of glycol contacting (giving rise to the term glycol dehydration) comprises the industrial application of this work since it involves direct distillation applications.

Finally, the choice of a particular glycol involves various factors, including location, price, availability, and operating conditions. For example, ethylene glycol often proves less expensive, but thermally decomposes at lower temperatures than the other two glycols, thereby making it less desirable for some applications. Triethylene glycol, on the other hand, may accommodate a wider temperature range, but remains more expensive. Nevertheless, Fitz and Hubbard (1987) note triethylene glycol as the most-highly used glycol for this process. With the varying importance of all three glycols in mind, this work focused on predicting all three glycols (as pure components) as well as the binary VLE mixtures of triethylene glycol that typically occur in glycol-dehydration systems.

In addition, this work also includes VLE simulations for a binary freon system, namely that of tetrafluoromethane (freon R14) and trifluoromethane (freon R23). In general, much effort has been made to replace chlorofluorocarbons, which have a tendency to accelerate decomposition of the ozone layer. Consequently, the ongoing trend for the past thirty years has consisted of replacing a given environmentally-unfriendly freon with a mixture of environmentally-friendly freons, thereby sustaining interest in the simulation of freon VLE mixtures (Juris, 1970). As seen in Chapter 7, the generalized asymmetric rule (GAR) for which this work is named provided the greatest improvement in mixture VLE predictions over all other simulations, including that of most glycol-dehydration systems.

1.3 Pure-Component Modeling Overview

To begin with, proper simulation of mixtures entails a thorough understanding of the equations used to model both mixture and pure-component properties. These equations are referred to in thermodynamics as compressibility equations or, more commonly, equations of state (EOS). Consequently, Chapter 2 provides a comprehensive review of four noncubic EOS in chronological order that exerted a significant impact in EOS development. These include (1) the Benedict-Webb-Rubin (BWR) EOS (Benedict et al., 1940), (2) the Benedict-Webb-Rubin-Starling (BWRS) EOS (Starling, 1971), (3) the three-parameter, corresponding-states, modified-Benedict-Webb-Rubin (3PCS-MBWR) EOS (Lee et al., 1977a, 1979) and (4) the Martin-Hou EOS. The first three of these four equations exist as precursors to the

Khan-Chung-Lee-Starling (KCLS) EOS used in this work as formulated by Khan (1983) and Chung et al. (1984). This review is then followed by a compilation of sixteen papers published by Nishiumi et al.[1] that extend both the BWRS (Starling, 1971) and Peng-Robinson (1976) equations of state (EOS) in terms of BWRS predictions of polar substances as well as various useful correlations for binary interaction parameters (BIPs) of both EOS.

Next, Chapter 3 presents the pure-component simulation results obtained for this work with the KCLS EOS. These results are preceded by a detailed review of multiproperty analysis (MPA), a concept conceived and applied by Starling et al.[2] at the University of Oklahoma to improve the simultaneous prediction of various thermodynamic properties. In short, MPA played a highly-influential role in the development of the BWRS, 3PCS-MBWR, and KCLS equations of state. This review of MPA therefore proved necessary to this work in its application to the simultaneous modeling of the vapor pressures and liquid densities of ten pure components that had not previously been predicted with the KCLS EOS.

In general, vapor pressure represents the most important thermodynamic property that must be accurately predicted by an EOS for purposes of VLE modeling.

[1]Throughout this work, Nishiumi et al. refers to both single-authored papers as well as collaborative/multiauthored papers that include Nishiumi as an author. The bibliography at the end of this work lists all of these papers in simultaneous alphabetical and chronological order.

[2]Throughout this work, Starling et al. refers to both single-authored papers as well as collaborative/multiauthored papers that include Starling as an author. The bibliography at the end of this work lists all of these papers in simultaneous alphabetical and chronological order.

This situation logically follows from the fact that the vapor pressure property itself represents the VLE condition of a pure component, and when predicted with accuracy, improves the mixture precision of the EOS of choice. As shown herein, the MPA of vapor pressure and liquid density proved superior to the single-property analysis (SPA) of vapor pressure alone, thereby justifying its application to the ten new components for the KCLS EOS.

1.4 Primary Innovation of this Work

The primary innovation of this work consists of the innovation and original presentation of the generalized asymmetric rule (or GAR), a novel equation used to model unlike-interaction parameters (UIPs) in the simulation of binary VLE systems. This equation is intended to replace binary interaction parameters (BIPs), a long-recognized standard used in UIP modeling. Specifically, the GAR is presented herein as an extension of the generalized symmetric rule (or GSR) originally presented in the late 1960s by Leonard Wenzel et al.[3] (Juris, 1970; Juris and Wenzel, 1974).

Chapter 4 reviews both the development and presentation of the GAR. This review entails (a) GAR applications to cases not covered by the GSR, (b) the conversion of both symmetric as well as asymmetric BIPs to asymmetric GARs

[3]Throughout this work, Wenzel et al. refers to both collaborative papers that include Leonard Wenzel as an author as well as Master's theses and PhD dissertations authored at Lehigh University that involved Wenzel in freon and/or Joule-Thomson coefficient research. The reader is referred to these two references listed in the bibliography at the end of this work for more information on research performed with the GSR.

through a comparative description of their applications to both combining and mixing rules, as well as (c) the advantages that GARs offer over BIPs. Specifically, GARs present three advantages over BIPs. The first advantage consists of the two- (and possibly even three-) dimensional representation of binary interactions provided by GARs between any two components for a clearer "mapping out" of binary systems in lieu of the typical one-dimensional representation between two components typically provided by symmetric BIPs. The second advantage consists of the relative indication that GARs provide in terms of exactly how much one component may outweigh that of the other (in terms of mixture effects) for a given unlike-interaction parameter. Third, each GAR offers a **nondivergent, asymmetric, unlike-interaction mechanism** that guarantees a reliable asymmetry model between any two (or more) components for the mixture parameters of any given EOS.

Next, Chapter 5 presents special cases for the GAR in terms of averaging pure-component parameters (PCPs) with either positive, negative, or even zero numerical values. This chapter therefore discusses special GAR cases that reflect the need to hold certain GAR parameters constant for various situations while regressing others, including the ability of the GAR to invoke sign changes (i.e., in terms of positive or negative values) for the unlike interaction regardless of whether the PCPs carry like and/or unlike signs. The GAR thus offers much potential for other fields outside of thermodynamics whenever any given set of numbers must be averaged asymmetrically.

1.5 Mixture Modeling Overview

The efforts on mixture modeling presented herein focus exclusively on the prediction of binary VLE compositions. Since the GAR was developed to optimize mixture asymmetry in a noncubic EOS, the aforementioned KCLS EOS was inserted into the mixing rules of the local composition model (LCM) proposed by Li et al. (1986). The use of these mixing rules, however, entails certain modifications to this LCM to accommodate the asymmetric properties of the GAR. As with the above review of pure-component modeling in Section 1.3, the modifications to this particular LCM require a certain understanding of previous work in this area. Specifically, the LCM of Li et al. (1986) extended certain activity-coefficient models that significantly influenced its own development.

Chapter 6 discusses some of these early, influential LCMs, beginning with the original Wilson concept of a LCM (1964) and follows through with the nonrandom, two-liquid (NRTL) LCM by Renon and Prausnitz (1968). As a mixture model, the LCM of Li et al. (1986) presented two advantages in that it (1) applied to the prediction of both the liquid and vapor phases without a separate EOS for the vapor phase and (2) allowed for the insertion of one (or more) pure-component equations of state. This chapter also describes the innovations of this LCM with its conception as a special case of two generalized LCM equations as also presented by Renon and Prausnitz (1968).

The aforementioned modifications to the LCM of Li et al. (1986) appear in terms of the five UIPs that comprise its mixture properties. Although only one of

these five UIPs was designed to work asymmetrically, Chapter 6 illustrates the theoretical approach taken to convert the other four UIPs from their symmetric forms into acceptable asymmetric forms.

Next, Chapter 7 presents the results of the LCM utilized and modified for this work. Specifically, this work applies the GAR to the prediction of binary mixtures in an attempt to achieve more accurate simulations than those currently attained by BIPs. This chapter therefore presents the predictive results for eighteen binary VLE systems in the form of (a) average absolute relative deviations (AARDs) over (b) forty-one isotherms, nine isobars, and twelve mixed temperature/pressure ranges. Overall, GARs surpassed BIPs in slightly over half of all AARD results presented in terms of the liquid-composition, vapor-composition, and K-value AARD sums of both components added together for each isotherm, isobar, and combined temperature/pressure range.

Interestingly enough, the binary freon system predicted in this work was improved the most by GARs over BIPs more than any other system herein. In fact, with only one exception for this system, GARs yielded equivalent and/or lesser predictive errors than BIPs for all phase-composition and K-value AARDs. Moreover, this result also occurred for each individual isotherm, and all isotherms simultaneously. Although the predictive results for other binary systems did not prove as successful, the results of this chapter do support the asymmetric approach taken by the other LCMs referred to in this work, while also proving a general case for asymmetry (i.e., with GARs) as opposed to symmetry (i.e., with BIPs).

1.6 Data Limitations

With the exception of the freon mixtures, the binary VLE systems predicted in this work were chosen to represent component mixtures typically encountered in triethylene-glycol dehydration units. Moreover, since a seven-component, triethylene-glycol system had already been published in the GPA Research Report RR-131 by Ng et al. (1991), it was hoped that sufficient binary data could be acquired for this purpose.

As shown in Chapter 8, a complete simulation of this particular system would require twenty-one binary sets of data. Unfortunately, a thorough review of the literature revealed a lack of several important binary mixtures for the simulations desired. In fact, although some data also exist for binary mixtures with ethylene glycol and diethylene glycol as well, not enough exist to model the six binary systems paired with each glycol and the other non-glycol components.

Nevertheless, certain procedures have been developed to account for missing binary VLE data in the thermodynamic literature. To be sure, not all procedures or methods may prove feasible for all investigations of choice, but they do offer several alternatives when binary data cannot be found. These methods include the use of (1) solubility data, (2) ternary data, (3) other thermodynamic property data for a given binary system, (4) infinite-dilution activity coefficients, and (5) the substitution of alternate isomeric-component data. In addition, interpolation with the generalized asymmetric rule (GAR) parameters presented in this work also affords a sixth method to account for missing binary data in future investigations. Although this work solely

employed the isomeric-substitution approach, GARs did substantiate the approach for two binary aromatic systems.

1.7 Conclusions and Recommendations

To begin with, Chapter 9 provides both conclusions and recommendations regarding future extensions of the GAR conceived herein as well as for other models reviewed by this work. These recommendations comprise two separate sections of suggestions designed to improve the accuracy of the LCM presented by Li et al. (1986). The first section describes a more concise means of approaching this LCM that closely coincides with other LCMs: This includes use of GARs to calculate UIP values directly from the Helmholtz configurational free energies calculated in this LCM, which would involve the regression of far fewer GAR parameters (or UIPs) than the eight used for polar mixtures in this work.

The second section includes other improvements than can be made to existing LCMs. In particular, the improvements suggest using both portions of the two generalized LCM equations presented by Renon and Prausnitz (1968), an approach later taken by Abrams and Prausnitz (1975) in their development of the universal quasi-chemical (UNIQUAC) LCM. Altogether, the GAR of this work definitely merits consideration in the future asymmetric modeling and simulation of binary (and, of course, multicomponent) VLE systems through various LCMs.

1.8 Appendices

Appendices A through D of this work include numerous derivations, recommendations, and literature sources. First, limiting cases of both the GSR and the GAR present entail derivations for both the geometric combining rule and the Halsey-Fender (Fender, 1962) combining rule. Appendix A provides the derivations of the geometric combining rule through L'Hospital's rule, while the Halsey-Fender derivations involve simple algebraic manipulations.

Second, Beattie (p. 266, 1955) briefly mentions both the second-virial Lorentz mixing rule as well as a rearranged version of it that separates its first-virial contribution from its second-virial contribution. This rearrangement of the Lorentz mixing rule inspired both the asymmetric-geometric modification to the GSR as well the development of the mixing-rule conjunction (MRC) by the author of this work. Simply put, the MRC represented the sum of any proportions of combining rules for all virial forms of mixing. Appendix B details the derivations necessary for rearrangement of the Lorentz mixing rule along with related suggestions for the modeling of binary and multicomponent vapor-liquid equilibrium (VLE) systems.

Third, several literature sources were consulted for the binary VLE data simulated in this work. These sources were found to contain VLE data as well as several other forms of chemical mixture data. Many of the literature sources exist in the form of monograph bibliographies that review most of the VLE data taken in the twentieth century. Moreover, some of the sources actually list the experimental data, most of which comprise several volumes of the DECHEMA data collection.

Appendix C summarizes both the bibliographic sources used herein as well as the actual data sources used for the binary VLE simulations presented in this work. In addition, Appendix C also provides several helpful remarks on the data, including (a) the type of data reviewed, (b) the publisher of each source, (c) whether or not each source contains modeling and/or lists the experimental data, and (d) the types of data listed within each source.

Fourth, correlation between PCPs became apparent while regressing over the pure-component properties of vapor pressure and liquid density (as noted in Chapter 3). The phenomenon of PCP correlation, however, led to the origination of several theoretical ideas in this work. Appendix D discusses correlation between PCP in detail and also includes a procedure to overcome correlation. In addition, Appendix D provides several recommendations on related aspects of thermodynamic modeling. Finally, it should be noted that the recommendations of Appendices B and D are intended to supplement the recommendations of Chapter 9 previously mentioned in Section 1.7.

CHAPTER II

ON THE DEVELOPMENT OF PAST AND PRESENT EQUATIONS OF STATE

2.1 Introduction and Overview

This work employs the Khan-Chung-Lee-Starling (KCLS) equation of state (EOS) of Khan (1983) and Chung et al. (1984) to predict the two pure-component properties of vapor pressure and liquid density. Although the KCLS EOS represents one of the most accurate equations of state to this day (i.e., in the prediction of both polar- and nonpolar-component properties), it arises from concepts employed in several precursor equations of state. Section 2.2 therefore describes four of these equations in detail along with their relations to each other, while Section 2.3 highlights the KCLS equation itself.

Finally, Section 2.4 mentions work presented in sixteen papers published by Nishiumi (e.g., 1980a, 1980b). Altogether, the different EOS presented in most of these papers extend the BWRS EOS and compare with the development of the five other equations presented in Sections 2.2 and 2.3. It is, however, the many EOS variations and extensions of the BWRS equation that Nishiumi et al. published that merits a separate review of their work in Section 2.4.

In short, Nishiumi et al. outlined several EOS that extended the BWRS EOS in comparative fashion to both the 3PCS-MBWR EOS and the KCLS EOS. In addition,

Nishiumi et al. also offered related work performed on the Peng-Robinson (1976) EOS.

2.2 On the Significance of Four Previous Equations of State

Although a multitude of noncubic equations of state (EOS) abounds within the thermodynamic literature, only four will be described in this section. These include (1) the Benedict-Webb-Rubin EOS (Benedict et al., 1940), (2) the Benedict-Webb-Rubin-Starling EOS (Starling, 1971), (3) the three-parameter, corresponding-states, modified-Benedict-Webb-Rubin (3PCS-MBWR) EOS (Lee et al., 1977a, 1979) and (4) the Martin-Hou EOS. The first three of these four equations exist as precursors to the KCLS equation described in Section 2.3.

Next, a modified form of the Martin-Hou EOS (Piacentini, 1966; Piacentini and Stein, 1967) bears mention since Wenzel et al. (Juris, 1970; Juris and Wenzel, 1974) inserted their generalized symmetric rule (or GSR) into this EOS to predict the Joule-Thomson coefficients of freon mixtures. As described in Section 4.2 of Chapter 4, the GSR precedes the generalized asymmetric rule (or GAR) described in Section 4.3.

Following the above equations, Table 1.15 of Walas (p.61, 1985) illustrates how noncubic equations of state typically adhere to the form of the virial equation of state,

$$P = RT\rho(1 + B\rho + C\rho^2 + D\rho^3 + \cdots) \quad . \quad (2.1)$$

With the density property multiplied through the parentheses, Equation (2.1) becomes

$$P = RT(\rho + B\rho^2 + C\rho^3 + D\rho^4 + \cdots) \quad . \quad (2.2)$$

Here, the so-called second-virial term $B\rho^2$ (with density raised to the second power) represents two-body, or *ij*, interactions, while the so-called third-virial term $C\rho^3$ (with density raised to the third power) represents three-body, or *ijk*, interactions, and so on.

Moreover, the above four EOS represent noncubic EOS. In other words, they include both exponential terms raised to the power of a density, as well as terms with density (or volume) raised to absolute powers greater than three. In contrast, a cubic EOS will contain terms with density (or volume) raised solely to absolute powers of three or less. Examples of cubic EOS include (a) the van der Waals EOS (van der Waals, 1873), (b) the Redlich-Kwong EOS (Redlich and Kwong, 1949), (c) the Soave-Redlich-Kwong EOS (Soave, 1972) and (d) Peng-Robinson EOS (Peng and Robinson, 1976). In general, however, noncubic EOS have been proven more accurate than cubic EOS for all thermodynamic property predictions as well as for cryogenic systems (Walas, p. 66, 1985). In fact, Soave (1990) later presented a quartic EOS (i.e., with density raised to the fourth power) while acknowledging that although cubic EOS can accurately predict vapor-liquid equilibrium compositions, they possess a weak point in terms of predicting PVT behavior.

Aside from their individual features, all four of the above EOS exist as single-fluid equations, as does the KCLS equation through the conformal solution model (CSM) by Lee et al. (1977b). For information on other EOS, Kwok (1970) provides a review and discussion on some of the earlier EOS that predate these four equations, as

does Walas (1985). Finally, Walas (1985) also provides an exhaustive review while also detailing the application of many EOS to most problems encountered within the thermodynamic literature.

2.2.1 The Benedict-Webb-Rubin (BWR) Equation of State

As noted by Walas (p.,60-68, 1985), the Benedict-Webb-Rubin (BWR) equation of state (Benedict et al., 1940) was designed as an improvement over the Beattie-Bridgeman (1927) equation,

$$P = RT\rho + \left(B_0 RT - A_0 - \frac{Rc}{T^2} \right)\rho^2 + \left(-B_0 bRT + A_0 a - \frac{RB_0 c}{T^2} \right)\rho^3 + \frac{RB_0 bc}{T^2}\rho^4 \quad , \qquad (2.3)$$

to overcome its inability to represent both liquids and gases above their critical density.

These improvements resulted in the BWR EOS formulation of

$$P = RT\rho + \left(B_0 RT - A_0 - \frac{C_0}{T^2} \right)\rho^2 + (bRT - a)\rho^3 + a\alpha\rho^6 + \frac{c}{T^2}\rho^3(1 + \gamma\rho^2)\exp(-\gamma\rho^2) \quad . \qquad (2.4)$$

As seen in Equation (2.2), the various terms in Equation (2.4) represent first-, second- and sixth-virial interactions, while the exponential (and therefore noncubic) terms of the BWR equation provide a way of accounting for all of the higher-virial terms.

Altogether, the BWR EOS contains eight pure-component parameters that must be fitted for each component of interest. For mixtures, Walas (p.62, 1985) points out that Bishnoi and Robinson (1972a, 1972b) incorporated binary interaction parameters (BIPs) into the BWR EOS.

2.2.2 The Benedict-Webb-Rubin-Starling (BWRS) Equation of State

As with the BWR improvement over the Beattie-Bridgeman EOS (1927), Starling (1971) designed the Benedict-Webb-Rubin-Starling (BWRS) EOS as an extension of its predecessor, the BWR EOS (Benedict et al., 1940) of Equation (2.4). Here, the BWRS EOS,

$$P = RT\rho + \left(B_0 RT - A_0 - \frac{C_0}{T^2} + \frac{D_0}{T^3} - \frac{E_0}{T^4} \right)\rho^2 + \left(bRT - a - \frac{d}{T} \right)\rho^3$$

$$+ \alpha\left(a + \frac{d}{T} \right)\rho^6 + \frac{c}{T^2}\rho^3(1+\gamma\rho^2)\exp(-\gamma\rho^2) \quad , \qquad (2.5)$$

contains the eight BWR pure-component parameters that must be fitted for each component of interest, along with the three new pure-component parameters D_0, E_0, and d.

Moreover, Han and Starling (1972a) generalized all eleven of these parameters as functions of each pure component's (a) acentric factor, (b) critical temperature, and (c) critical density. This generalization , known as the Han-Starling generalized correlation (or HSGC), thus allowed for extension of the BWRS EOS to other compounds of interest as a function of the critical density (ρ_{ci}), critical temperature

(T_{ci}), and acentric factor (ω_i) of each component. As an example, the BWRS parameter, C_0 (or C_{0i}), for an unknown component *i* would be calculated according to the relation

$$C_{0i} = \frac{RT_{ci}^3}{\rho_{ci}}\left(A_3 + B_3\omega_i\right) \quad . \qquad (2.6)$$

In terms of critical volume instead of density, Equation (2.6) may be expressed as

$$C_{0i} = RT_{ci}^3 V_{ci}\left(A_3 + B_3\omega_i\right) \quad . \qquad (2.7)$$

Furthermore, as with Bishnoi and Robinson (1972a, 1972b), Starling and Han (1972a, 1972b) incorporated binary interaction parameters (BIPs) into the BWRS EOS.

2.2.3 The Martin-Hou Equation of State

As first presented by Martin and Hou (1955), the Martin-Hou EOS consisted of the relation

$$P = \frac{RT}{V-b} + \frac{A_2 + B_2T + C_2\exp(-5.475T_r)}{(V-b)^2} + \frac{A_3 + B_3T + C_3\exp(-5.475T_r)}{(V-b)^3} + \frac{A_4}{(V-b)^4} + \frac{B_5}{(V-b)^5} \quad . \qquad (2.8)$$

Equation (2.8) was later modified by E. I. du Pont de Nemours and Co., Inc. and used by Piacentini (1966) and Piacentini and Stein (1967) to predict both pure-component

vapor pressures and vapor-liquid equilibrium compositions of two freons, tetrafluoromethane (refrigerant R14) and trifluoromethane (refrigerant R23). These modifications altered Equation (2.8) and, as seen in Equation (2.9), consisted of (a) generalizing the constant within the exponential terms (-5.475) into a parameter, k, that is regressed for each component, (b) adding a temperature-dependent term $B_4 T$ to the fourth-virial volume term A_4, (c) revamping the numerator of the fifth-virial volume term from B_5 to the temperature-dependent terms $A_5 + B_5 T + C_5 \exp(-kT_r)$ in analogy with the third-virial term, and (d) adding a temperature-dependent, inverse-exponential virial term. This resulted in the EOS relation

$$P = \frac{RT}{V-b} + \frac{A_2 + B_2 T + C_2 \exp(-kT_r)}{(V-b)^2} + \frac{A_3 + B_3 T + C_3 \exp(-kT_r)}{(V-b)^3} + \frac{A_4 + B_4 T}{(V-b)^4} + \frac{A_5 + B_5 T + C_5 \exp(-kT_r)}{(V-b)^5} + \frac{A_6 + B_6 T}{\exp(aV)} \quad . \qquad (2.9)$$

Later, Wenzel et al. (Juris, 1970; Juris and Wenzel, 1974) used Equation (2.9) to predict the Joule-Thomson coefficients of mixtures of tetrafluoromethane and trifluoromethane. Here, they inserted the generalized symmetric rule (or GSR),

$$B_{ij} = \frac{\left[B_i^N + B_j^N\right]^{1/N}}{2^{1/N}} \quad , \qquad (2.10)$$

into each mixture parameter of Equation (2.9) to describe the unlike interactions, B_{ij}, of this particular system. (The GSR is described in Section 4.2 of Chapter 4). In doing so, they suggested applying an identical value of N into all GSRs, thereby correlating each mixture in terms of a single parameter. This simpler approach drastically reduced the previous complexity encountered when using a different value of N for **each** GSR of **each** mixture parameter -- a practice reported by several researchers at Lehigh University and elsewhere, as summarized by both Juris (1970) and Juris and Wenzel (1974).

Finally, the above two alternatives of using different values of N versus identical values of N in Equation (2.10) present certain implications for an equation of state in general. First, this older practice of using different values of N implies a reformulation of the mixing rules designated for each mixture parameter. Although different values of N may simply reflect the a simple "reshuffling" of mixture-parameter combining rules to achieve near-identical accuracy in mixture predictions, it might also indicate that some degree of correlation exists between the pure-component parameters of a given EOS.

Second, the successful approach of Juris (1970) and Juris and Wenzel (1974) of using identical mixture values of N in Equation (2.10) also suggests a simpler approach towards pure-component values of equations of state as well. Generally speaking, the use of fewer pure-component parameters for an EOS significantly reduces the possibility of correlation **between** said pure-component parameters. Although the usage of four parameters has been proven in such cubic equations as the

Soave-Redlich-Kwong EOS (Soave, 1972) and the Peng-Robinson EOS (1976), this usage of four parameters in noncubic equations merits consideration as well. Logically, then, the choice of as few parameters as possible is desired in a noncubic EOS when modeling pure-component properties.

Summarily, the simpler approach of using fewer parameters in a noncubic EOS was foreshadowed by Juris (1970) and Juris and Wenzel (1974). Simply put, these researchers' suggestion on employing fewer mixture parameters with the Martin-Hou equation bears a striking resemblance to later work realized through two successive noncubic EOS with fewer pure-component parameters. These two equations consist of (1) the three-parameter, corresponding-states, modified-Benedict-Webb-Rubin (3PCS-MBWR) EOS (Lee et al., 1977a, 1979) of the following section and (2) the Khan-Chung-Lee-Starling (KCLS) EOS (Khan, 1983; Chung et al., 1984) in Section 2.3.

2.2.4 The Three-Parameter, Corresponding-States, Modified-Benedict-Webb Rubin (3PCS-MBWR) Equation of State

Lee et al. (1977a, 1979) introduced the three-parameter, corresponding-states, modified-Benedict-Webb-Rubin (3PCS-MBWR) EOS,

$$z = 1 + \left[B_1 - \frac{B_2}{T^*} - \frac{B_3}{\left(T^*\right)^3} + \frac{B_9}{\left(T^*\right)^4} - \frac{B_{11}}{\left(T^*\right)^5} \right] \rho^* + \left[B_5 - \frac{B_6}{T^*} - \frac{B_{10}}{\left(T^*\right)^2} \right] \left(\rho^*\right)^2$$

$$+\left[\frac{B_7}{T^*}-\frac{B_{12}}{\left(T^*\right)^2}\right]\left(\rho^*\right)^5+\frac{B_8\left(\rho^*\right)^2}{\left(T^*\right)^3}\left[1+B_4\left(\rho^*\right)^2\right]\exp\left[-B_4\left(\rho^*\right)^2\right] \quad , \tag{2.11}$$

as a modification of the BWRS EOS (Starling, 1971). Overall, the twelve pure-component parameters B_i seen in the 3PCS-MBWR EOS of Equation (2.11) represented an improvement over the BWRS EOS for the following variety of reasons.

First, the 3PCS-MBWR EOS of Equation (2.11) used only one dimensionless parameter to determine values for all of the above twelve parameters B_i . As Lee et al. noted (1977a), this EOS linearly split the BWRS parameters into both an isotropic part and an anisotropic part in the form of

$$B_i = a_i + \gamma b_i \quad , \tag{2.12}$$

where a_i represents the isotropic part and b_i signifies the anisotropic part. Here, the first parameter, γ , accounts for the orientation (Lee et al., 1977a) or shape (Lee et al., 1977b) of the non-spherical molecules comprising a pure component. Lee et al. (1979) report numerical values for the generalized parameters a_i and b_i.

Second, the 3PCS-MBWR EOS requires only two other dimensionless parameters to predict pure-component properties. Here, the second parameter, σ^3, indicates the characteristic distance between like molecules of a pure component.

When multiplied by the pure-component density, σ^3 yields (Lee et al., 1977a) a dimensionless density, ρ^*, according to the relation

$$\rho^* = \rho\sigma^3 \quad . \qquad (2.13)$$

In addition to the dimensionless-density relation, the final parameter, $\frac{\varepsilon}{k}$, represents a characteristic molecular-energy parameter used to calculate a dimensionless temperature, T^*, according to the relation

$$T^* = \frac{kT}{\varepsilon} \quad . \qquad (2.14)$$

These choices for dimensionless parameters follow some of the dimensionless groups suggested by Reid (1968).

As noted in Sections 2.2.3 and 3.4, the above use of as few as three parameters in the 3PCS-MBWR EOS (hence the name *three-parameter*) allows for a far lesser degree of correlation between these parameters when fitting them to a given pure component. Certainly, three parameters obviously contrasts with the excessive amount of fifteen pure-component parameters presented in a parallel extension of the BWRS EOS by Nishiumi and Saito (1975, 1977).

Third, the use of these three dimensionless parameters also allowed for much greater leeway in the description of their corresponding mixture parameters. In general, this leeway consisted of describing an anisotropic mixture (Lee et al., 1979) through such mixing rules as

$$\gamma_x^k \varepsilon_x^l \sigma_x^m = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \gamma_{ij}^k \varepsilon_{ij}^l \sigma_{ij}^m \quad , \qquad (2.15)$$

$$\gamma_x^p \varepsilon_x^q \sigma_x^r = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \gamma_{ij}^p \varepsilon_{ij}^q \sigma_{ij}^r \quad , \qquad (2.16)$$

and

$$\gamma_x^u \varepsilon_x^v \sigma_x^w = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \gamma_{ij}^u \varepsilon_{ij}^v \sigma_{ij}^w \quad . \qquad (2.17)$$

Lee et al. (1979) also specified values for the various powers k, l m p, q, r, u, v, and w so that Equations (2.15) through (2.17) respectively become

$$\sigma_x^{4.5} = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \sigma_{ij}^{4.5} \quad , \qquad (2.18)$$

$$\varepsilon_x \sigma_x^{4.5} = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \varepsilon_x \sigma_{ij}^{4.5} \quad , \qquad (2.19)$$

and

$$\gamma_x^2 \sigma_x^{3.5} = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \gamma_{ij}^2 \sigma_{ij}^{3.5} \quad . \qquad (2.20)$$

Here, it should be noted that the mixture relations in Equations (2.15) through (2.20) can only be accomplished through **dimensionless** parameters, since the use of **dimensional** parameters in these relations would create unit inconsistencies in such equations as the BWRS EOS.

Finally, this EOS was developed for nonpolar components. Consequently, both Khan (1983) and Chung et al. (1984) developed the Khan-Chung-Lee-Starling (KCLS) EOS as a dimensionless extension of the 3PCS-MBWR EOS in an

application to both polar- and nonpolar-component properties. Section 2.3 below therefore describes the KCLS equation used in this work.

2.3 The Khan-Chung-Lee-Starling (KCLS) Equation of State

Both Khan (1983) and Chung et al. (1984) developed the Khan-Chung-Lee-Starling (KCLS) equation of state (EOS) as an extension of the 3PCS-MBWR EOS to polar and nonpolar components alike. As a dimensionless variant of Equation (2.11), this equation takes the form

$$z-1=\left[A_1+\frac{A_2}{T^*}+\frac{A_3}{\left(T^*\right)^2}+\frac{A_4}{\left(T^*\right)^3}+\frac{A_5}{\left(T^*\right)^5}\right]\rho^*+\left[A_6+\frac{A_7}{T^*}\right]\left(\rho^*\right)^2+A_8\left(\rho^*\right)^3$$
$$+\left[\frac{A_9}{\left(T^*\right)^3}+\frac{A_{10}}{\left(T^*\right)^4}+\frac{A_{11}}{\left(T^*\right)^5}\right]\left(\rho^*\right)^2\exp\left[-A_{16}\left(\rho^*\right)^2\right]$$
$$+\left[\frac{A_{12}}{\left(T^*\right)^3}+\frac{A_{13}}{\left(T^*\right)^4}+\frac{A_{14}}{\left(T^*\right)^5}\right]\left(\rho^*\right)^4\exp\left[-A_{16}\left(\rho^*\right)^2\right]$$
$$+\frac{A_{15}}{T^*}\left(\rho^*\right)^5 \qquad . \qquad (2.21)$$

In comparison to the 3PCS-MBWR EOS of Equation (2.11), Khan (1983) and Chung et al. (1984) implemented certain changes in the pure-component parameters of the KCLS EOS. First, they replaced the replaced orientation/shape parameter, γ,

with a perturbation/structure parameter, λ, which modifies the relation expressed in Equation (2.12) into

$$A_i = \lambda B_i^{(0)} + (\lambda - 1) B_i^{(p)} \quad , \qquad (2.22)$$

where the parameters A_i of Equation (2.21) become functions of the universal constants, $B_i^{(0)}$ and $B_i^{(p)}$; a complete table of these constants may be found in both Khan (1983) and Chung et al. (1984).

Here, the constants $B_i^{(0)}$ represent isentropic argon constants determined by Khan (1983) and Chung et al. (1984) through the argon correlation presented by Twu et al. (1980). Next, the constants $B_i^{(p)}$ represent anisotropic perturbation constants determined by both Khan (1983) and Chung et al. (1984) through (a) the multiproperty regression analysis of vapor pressure, density, and enthalpy data for (b) the normal paraffins ethane through n-pentane. Moreover, it should be noted that the anisotropic perturbation is introduced in Equation (2.22) on a percentage basis, as opposed to the simple proportional basis seen in Equation (2.12).

Second, although the third parameter, $\frac{\varepsilon}{k}$, remains unchanged in Equation (2.14), the dimensionless temperature calculation in the 3PCS-MBWR EOS accounted for nonpolar pure components only. To extend the KCLS EOS to nonpolar

components, Khan (1983) and Chung et al. (1984) replaced $\frac{\varepsilon}{k}$ in Equation (2.14) with a temperature-dependent energy parameter $\frac{\varepsilon'}{k}$ according to the relation

$$\frac{\varepsilon'}{k} = \frac{\varepsilon}{k} + \frac{\kappa}{T\left(V^*\right)^2} \quad . \qquad (2.23)$$

Here, it should be noted that Cartaya et al. (1996) showed that Li et al. (1986) replaced the polar parameter, κ, with a conceptually-analogous polar parameter, D, according to the relation

$$D = \frac{\kappa}{\left(V^*\right)^2} \quad , \qquad (2.24)$$

thereby transforming Equation (2.23) into

$$\frac{\varepsilon'}{k} = \frac{\varepsilon}{k} + \frac{D}{T} \quad . \qquad (2.25)$$

In addition, the above temperature dependency of either Equations (2.23) or (2.25) then alters Equation (2.14) into the relation

$$T^* = \frac{kT}{\varepsilon'} \quad . \qquad (2.26)$$

Third and finally, Khan (1983) and Chung et al. (1984) replaced the relation of Equation (2.13) with

$$\rho^* = \rho V^* \quad , \qquad (2.27)$$

which involves substituting the molecular hard-core volume, V^*, for the characteristic molecular distance parameter, σ^3. Section 6.3.1 describes the extension of Equations (2.21) through (2.27) to mixtures by Li et al. (1986). Again, the four pure-component parameters allow for a far lesser degree of parameter correlation when fitted to a given pure component.

2.4 Extensions of the BWRS and Peng-Robinson Equations of State by Nishiumi et al.

The work of Nishiumi et al. in extending both the BWRS (Starling, 1971) and Peng-Robinson (1976) equations of state (EOS) bears mention for many reasons. First, the extensions of the BWRS EOS include the large number of parameters fitted to each component. Second, the extensions also entail the parallel developments between (a) the different EOS that Nishiumi et al. present and (b) both the 3PCS-MBWR EOS of Section 2.2.4 and the KCLS EOS of Section 2.3. In addition, Nishiumi et al. suggested several correlations for binary interaction parameters (BIPs) in both the BWRS and Peng-Robinson equations.

The following discussion primarily focuses on the BWRS extensions by Nishiumi et al. in Section 2.4.1. Afterward, Section 2.4.2 reviews the correlations that Nishiumi et al. modeled for binary interaction parameters in the BWRS EOS. Finally, Section 2.4.3 presents a brief review of similar work performed by Nishiumi et al. on the Peng-Robinson (1976) EOS that parallels the work of Sections 2.4.1 and 2.4.2 on the BWRS EOS.

Altogether, the work of Nishiumi et al. bore a direct impact on the preliminary research carried out by the author of this work that later led to the pure-component results presented in Chapter 3 that were based on the KCLS EOS. Moreover, the BWRS work and BIP correlations presented below might also prove of interest to future investigators.

2.4.1 Extensions of the BWRS Equation of State

First of all, Nishiumi et al.'s extensions of the BWRS equation of state (EOS) involved the addition of up to nine pure-component parameters -- to the previous eleven already suggested -- in the BWRS EOS. Although this addition may seem an excessive number of parameters to calculate, the polar (and nonpolar) extensions of the BWRS EOS did allow for the estimation of a wide variety of pure components with an acceptable degree of accuracy. To begin with, two early publications by Nishiumi and Saito (1975, 1977) introduced the EOS

$$P = RT\rho + \left(B_0 RT - A_0 - \frac{C_0}{T^2} + \frac{D_0}{T^3} - \frac{E_0}{T^4} \right)\rho^2$$

$$+ \left(bRT - a - \frac{d}{T} - \frac{e}{T^4} - \frac{f}{T^{23}} \right)\rho^3 + \alpha\left(a + \frac{d}{T} + \frac{e}{T^4} + \frac{f}{T^{23}} \right)\rho^6$$

$$+ \left(\frac{c}{T^2} + \frac{g}{T^8} + \frac{h}{T^{17}} \right)\rho^3 (1 + \gamma\rho^2) \exp(-\gamma\rho^2) . \qquad (2.28)$$

Here, the parameters e, f, g, and h extend the overall temperature dependence and accuracy of the BWRS EOS, thereby increasing number of parameters to fifteen. This EOS also appears in Nishiumi (1980a) and Arai and Nishiumi (1986).

Later, Nishiumi (1980b, 1983, 1984), Nishiumi and Robinson (1981), and Nishiumi et al. (1995) proposed the EOS

$$P = RT\rho + \left(B_0 RT - \left(A_0 + \Psi_A \right) - \frac{C_0}{T^2} + \frac{D_0}{T^3} - \frac{E_0 + \Psi_E}{T^4} \right) \rho^2$$

$$+ \left(bRT - a - \frac{d}{T} - \frac{e}{T^4} - \frac{f}{T^{23}} \right) \rho^3 + \alpha \left(a + \frac{d}{T} + \frac{e}{T^4} + \frac{f}{T^{23}} \right) \rho^6$$

$$+ \left(\frac{c}{T^2} + \frac{g}{T^8} + \frac{h}{T^{17}} + T\Psi_s \right) \rho^3 (1 + \gamma\rho^2) \exp(-\gamma\rho^2) \qquad (2.29)$$

with the two polar parameters Ψ_A and Ψ_E defined according to the relations

$$\Psi_A = \Psi_A^* RT_c V_c \qquad (2.30)$$

and

$$\Psi_E = \Psi_E^* RT_c^5 V_c \qquad (2.31)$$

Here, the dimensionless polar parameters, Ψ_A^* and Ψ_E^*, were determined from second-virial coefficient data functions of pure-component critical properties. Equations (2.30) and (2.31) correspond to similar functions of critical properties presented for the original eleven BWRS EOS parameters in the Han-Starling (1972a) generalized correlation (HSGC). The third polar parameter, Ψ_s, follows the temperature-dependent relation

$$\Psi_s = s_3 + \frac{s_1}{T_r^{s_2}} \quad . \qquad (2.32)$$

When taken as a whole, Equations (2.29) through (2.32) constitute a total of twenty pure-component parameters.

In their latest-known development, Nishiumi et al. (1991) reformulated Equation (2.29) in terms of reduced temperature and density as

$$\frac{P_r z_c}{\rho_r T_r} = 1 + \left(B_0^* - \frac{A_0^* + \Psi_A^*}{T_r} - \frac{C_0^*}{T_r^3} + \frac{D_0^*}{T_r^4} - \frac{E_0^* + \Psi_E^*}{T_r^5} \right) \rho_r$$

$$+ \left(b^* - \frac{a^*}{T_r} - \frac{d^*}{T_r^2} - \frac{e^*}{T_r^5} - \frac{f^*}{T_r^{24}} \right) \rho_r^2 + \alpha^* \left(\frac{a^*}{T_r} + \frac{d^*}{T_r^2} + \frac{e^*}{T_r^5} + \frac{f^*}{T_r^{24}} \right) \rho_r^5$$

$$+ \left(\frac{c^*}{T_r^3} + \frac{g^*}{T_r^9} + \frac{h^*}{T_r^{18}} + \Psi_s^* \right) \rho_r^2 \left(1 + \gamma^* \rho_r^2 \right) \exp\left(-\gamma^* \rho_r^2 \right) \qquad (2.33)$$

with Equation (2.32) also expressed in reduced form as

$$\Psi_s^* = s_3^* + \frac{s_1^*}{T_r^{s_2}} \quad , \qquad (2.34)$$

and Ψ_A^* and Ψ_E^* of Equations (2.30) and (2.31) inserted directly into Equation (2.33).

Generally speaking, the above work by Nishiumi et al. represents developments similar to those of the 3PCS-MBWR EOS described in Section 2.2.4 and the KCLS EOS outlined in Section 2.3. In regarding the EOS of Equation (2.28)

-- and also those of Equations (2.29) and (2.33) with the three polar parameters Ψ_A^*, Ψ_E^*, and Ψ_S (or Ψ_S^*) set equal to zero -- an extension of the BWRS EOS may be perceived that parallels the development of the nonpolar 3PCS-MBWR EOS of Lee et al. (1977a, 1979). As more easily seen in Equation (2.33), the fifteen reduced, nonpolar parameters correspond to the three dimensionless 3PCS-MBWR terms described in Section 2.2.4. Moreover, the extension of **(a)** the above nonpolar EOS of Equation (2.28) into the polar EOS of Equations (2.29) through (2.34) represents a parallel extension of **(b)** the nonpolar 3PCS-MBWR EOS into the polar KCLS EOS of Khan (1983) and Chung et al. (1984). In this case, the twenty terms in the reduced form of Equation (2.33) correspond to the four dimensionless KCLS terms described in Section 2.3.

In addition, the above work by Nishiumi et al. also bears mention due to its focus on a multitude of polar components and their mixtures. As with the KCLS EOS, this focus included such polar substances as alcohols and ammonia (Nishiumi, 1980b, 1984), water (Nishiumi, 1984; Nishiumi and Robinson, 1981), and freons (Nishiumi and Robinson, 1981; Nishiumi et al., 1991, 1993, 1995), as well as hydrogen mixtures with various components (Nishiumi, 1983).

2.4.2 Correlations for Binary Interaction Parameters (BIPs)

As a whole, Nishiumi et al. published nine papers on the correlation of binary interaction parameters (BIPs) on the prediction of binary vapor-liquid equilibrium

(VLE) systems. Six of these papers include the Nishiumi et al. extensions of the BWRS (Starling, 1971) equation of state (EOS) and three on the Peng-Robinson (1976) EOS, which are reviewed and discussed as follows.

The landmark paper of the above nine papers consists of that by Nishiumi and Saito (1977), which formally introduced the theoretical means of correlating BIPs. In this paper, Nishiumi and Saito (1977) correlated the "cross-second" virial coefficients (i.e., the unlike-interaction terms A_{0ij}, B_{0ij}, C_{0ij}, D_{0ij} and E_{0ij}) of the extended-BWRS EOS of Equation (2.28). In other words, these correlations altered the Han-Starling (1972a) generalized correlation (HSGC) for pure-component parameters (namely, A_{0i}, B_{0i}, C_{0i}, D_{0i} and E_{0i}) into more accurate generalizations of unlike-interaction parameters (namely, A_{0ij}, B_{0ij}, C_{0ij}, D_{0ij} and E_{0ij}) for mixtures.

As an example of their work on the BWRS EOS, Nishiumi and Saito (1977) formulated the pure-component relation for the pure-component parameter C_{0i} in Equation (2.7) into the unlike-interaction parameter C_{0ij} as

$$C_{0ij} = RT_{cij}^3 V_{cij}\left(A_{3ij} + B_{3ij}\omega_{ij}\right) \quad . \qquad (2.35)$$

For Equation (2.35), Nishiumi and Saito (1977) empirically determined A_{3ij} and B_{3ij} as

$$A_{3ij} = 0.356306 \qquad (2.36)$$

and

$$B_{3ij} = 1.70871 \quad , \qquad (2.37)$$

along the same lines as their pure-component counterparts presented in the HSGC. For the other three unlike-interaction parameters of Equation (2.35), Nishiumi and Saito (1977) also included a geometric combining rule for critical temperature,

$$T_{cij} = m_{ij}\sqrt{T_{ci}T_{cj}} \quad , \qquad (2.38)$$

a Lorentz combining rule for critical volume,

$$V_{cij} = \frac{\left(V_{ci}^{1/3} + V_{cj}^{1/3}\right)^3}{8} \quad , \qquad (2.39)$$

and a simple linear combining rule for the acentric factor,

$$\omega_{ij} = \frac{\left(\omega_i + \omega_j\right)}{2} \quad . \qquad (2.40)$$

Here, m_{ij} represents Nishiumi and Saito's (1977) unique concept of a BIP, a concept furthered in the other papers by Nishiumi et al. and related (Nishiumi, 1983) to the BIP k_{ij} by Han and Starling (1972a).

The BIP k_{ij} presented by Han and Starling (1972a) exists in Equation (4.14) of Chapter 4 in the form of

$$B_x = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j \left(1 - k_{ij}\right) B_{ij} \quad . \qquad (2.41)$$

Nishiumi and Saito (1977), however, chose to employ the relation

$$m_{ij} = 1 - k_{ij} \quad , \qquad (2.42)$$

thereby altering Equation (2.41) into

$$B_x = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j m_{ij} B_{ij} \quad . \qquad (2.43)$$

This alteration resulted in values of unity for pure substances, i.e.,

$$m_{ii} = 1 \quad , \qquad (2.44)$$

and values near unity to describe unlike-interactions instead of the small, numeric values provided through k_{ij}. Both Lee et al. (1977a, 1979) with the 3PCS-MBWR EOS and Li et al. (1986) with the KCLS EOS have independently supported this practice.

Nishiumi and Saito (1977) derived their above concept of a BIP for m_{ij} in terms of a Lennard-Jones energy potential. This concept consisted of the initial expression

$$m_{ij} = 64\left\{\left[k_1\left(\frac{V_{ci}}{V_{cj}}\right)\right]^{1/6} + \left[k_1\left(\frac{V_{ci}}{V_{cj}}\right)\right]^{-1/6}\right\}^{-6} + k_2 \quad , \qquad (2.45)$$

which was found difficult to correlate. Nishiumi and Saito (1977) modified Equation (2.45) into the simpler polynomial expression

$$m_{ij} = k_3 + k_4\left(\frac{V_{ci}}{V_{cj}}\right) + k_5\left(\frac{V_{ci}}{V_{cj}}\right)^2 \quad , \qquad \left(\frac{V_{ci}}{V_{cj}}\right) \geq 1 \quad . \qquad (2.46)$$

Nishiumi (1980a) followed up on this work with a generalization similar to Equation (2.46) for paraffins C10 to C20 and binary VLE systems paired with hydrogen (1983). Nishiumi and Fukushima (1989) later modified Equation (2.46) into the expression

$$m_{ij} = aT_c^2(1-T_r)^2 + b \quad , \quad (2.47)$$

where

$$a = \frac{-1.250x10^{-5}}{(V_c - 0.065)^{0.4}} + 0.118x10^{-5} \quad (2.48)$$

and either

$$b = 0.940 + 3.13V_c \quad , \quad V_c \leq 0.15 \quad (2.49)$$

or

$$b = 1.492 - 0.55V_c \quad , \quad V_c > 0.15 \quad (2.50)$$

with V_c defined as the critical volume of the non-hydrogen component. Subsequent to these developments, Nishiumi et al. (1993, 1995) introduced an expression similar to Equation (2.46) for freon mixtures.

Of all these correlations for m_{ij}, however, that of Equation (2.46) probably holds the most potential in generalizing correlations for binary VLE mixtures. Such an approach might be applied in the future to the generalized asymmetric rule (GAR) of Chapter 4.

Most importantly, although the work covered by Equations (2.45) through (2.50) applied to the modified BWRS EOS of Equations (2.38-2.44) of Section 2.4.1,

it could easily be applied to any mixture EOS of choice. In fact, as discussed in Section 2.4.3, Nishiumi et al. themselves provided proof of applications to other EOS through similar developments they made with the Peng-Robinson EOS (1976), as noted in Section 2.4.3.

Finally, the above BWRS work also included a separate paper by Nishiumi (1988) that described methods of pressure determination of VLE mixtures with the BWRS extensions of Section 2.4.1.

2.4.3 Comparative Work Performed on the Peng-Robinson Equation of State

This section briefly reviews work performed by Nishiumi et al. on the Peng-Robinson (1976) equation of state (EOS) in comparison to their similar work reviewed above on the BWRS EOS. Such work began with that of Arai and Nishiumi (1986) in comparing the relative accuracy of this EOS with three other EOS in the predictions of nonpolar, pure-component vapor pressures. These equations included the Peng-Robinson EOS as well as the Redlich-Kwong, Soave-Redlich-Kwong, and BWRS EOS.

Nishiumi et al. published three (but essentially two) additional papers on the Peng-Robinson (PR) EOS with the intent of correlating binary interaction parameters (BIPs). These works, however, largely correspond to the previous work mentioned above on the BWRS EOS. In this case, Nishiumi and Arai (1988) began correlating BIPs in the form of Equation (2.46) on the PR EOS in the composition predictions of several vapor-liquid equilibrium (VLE) mixtures.

In addition to their PR-EOS modeling of binary VLE mixtures of alkanes, the predictions of Nishiumi and Arai (1988) also included binary VLE systems composed of alkanes with other types of components. The other components included (a) alkenes, (b) aromatic components, (c) heavier alkanes, (d) carbon dioxide, (e) nitrogen, (f) hydrogen sulfide, and (g) acetylene. This work remains virtually identical to an earlier, in-house publication of Hosei University (with Japanese text) by Arai and Nishiumi (1987). Moreover, this work closely follows predictions made over the same sets of VLE mixtures as Nishiumi and Saito (1977). Afterward, Nishiumi and Gotoh (1990) focused on correlating BIPs for the PR EOS against binary VLE systems containing hydrogen as one of the two components. This paper also complemented earlier work by Nishiumi (1983) on the BWRS EOS.

CHAPTER III

PREDICTION OF PURE-COMPONENT DATA

3.1 Introduction and Overview

As noted in Section 2.1, the results presented in this work for pure-component property predictions were obtained through the Khan-Chung-Lee-Starling (KCLS) equation of state (EOS) presented by Khan (1983) and Chung et al. (1984). Aside from the development of this particular EOS from those that preceded it in Section 2.2 of Chapter 2, however, one other theoretical concept must receive attention in the prediction of pure-component properties, namely that of multiproperty analysis (or MPA).

Section 2.3 of Chapter 2 mentions the determination of the KCLS universal constants $B_i^{(p)}$ were determined by both Khan (1983) and Chung et al. (1984) through the MPA regression of three pure-component properties: vapor pressure, density, and enthalpy. This application of MPA, however, also included the determination of all four KCLS pure-component parameters (PCPs) for a wide variety of components through MPA as well. With this in mind, one must then contemplate the use of MPA in this work when regressing KCLS PCPs for components not originally included by Khan (1983) and Chung et al. (1984).

This chapter therefore presents the prediction of pure-component data for this work through the KCLS EOS as viewed from a MPA perspective. First, Section 3.2 defines some of the basic relations of MPA with a brief review of some of its

applications. Second, Section 3.3 both presents and discusses the results obtained through the KCLS EOS when using vapor-pressure data alone (Section 3.3.3) and also in conjunction with density data (Section 3.3.4).

3.2 Multiproperty Analysis (MPA)

3.2.1 Formal Definitions

First of all, the regression of any number of parameters against a given set of data involves (a) the iterative updating and evaluation of those parameters in the pursuit of (b) improving the predictions of that set of data. Here, the actual improvement of these predictions may be evaluated through some type of predetermined function -- typically referred to as an objective function (Himmelblau, p. 9, 1972) or a fitting function -- that in some way averages the errors involved in predicting each data point. Sometimes, the fitting function may involve the sums of the squared errors obtained in predicting the data point -- hence the term least-squares regression.

For example, one may wish to minimize the squared error in predicting the vapor pressure of a component according to the relation adapted from Starling (1970),

$$Q = \sum_{id=1}^{ND} \left[\frac{P_v^{EXP} - P_v^{CALC}}{P_v^{EXP}} \right]_{id}^2 = \sum_{id=1}^{ND} \left[1 - \frac{P_v^{CALC}}{P_v^{EXP}} \right]_{id}^2 , \qquad (3.1)$$

where Q represents the objective function, id the *idth* data point, ND the total number of data points, P_v^{EXP} the experimental value of vapor-pressure data point

id, and P_v^{CALC} the calculated value of vapor-pressure data point id. Here, the addition of other thermodynamic properties such as density and enthalpy into the fitting function then expands Equation (3.1) into the relation (Starling, 1970)

$$Q = W_{(P_v)} \sum_{id=1}^{ND} \left[1 - \frac{P_v^{CALC}}{P_v^{EXP}} \right]_{id}^2 + W_{(\rho)} \sum_{id=1}^{ND} \left[1 - \frac{\rho^{CALC}}{\rho^{EXP}} \right]_{id}^2$$

$$+ W_{(H)} \sum_{id=1}^{ND} \left[1 - \frac{H^{CALC}}{H^{EXP}} \right]_{id}^2 \quad , \qquad (3.2)$$

where ρ represents density, H represents enthalpy, and the three terms $W_{(P_v)}$, $W_{(\rho)}$, and $W_{(H)}$ represent weighting factors for vapor pressure, density, and enthalpy, respectively. These weighting factors may represent either simple percentages (that would then sum to unity), or relative weights that could be converted into percentages.

Next, Equation (3.2) may be adapted and generalized from Starling (1970) for any number of thermodynamic properties and phases as

$$Q = \sum_{j=1}^{NPr} \sum_{k=1}^{NPh} W_{(jk)} \sum_{id=1}^{ND} \left[1 - \frac{\eta_{jk}}{R_{jk}} \right]_{id}^2 \quad , \qquad (3.3)$$

where j represents the jth property, NPr the total number of properties, k the kth phase, NPh the total number of phases, η_{jk} the calculated value of thermodynamic

property jk, and R_{jk} the experimental value of thermodynamic property jk. The following section discusses the implications of Equations (3.1) through (3.3).

3.2.2 Implications of MPA

To begin with, Starling and Wolfe (1966, 1971) formally introduced the concept of MPA as a means of predicting thermodynamic properties more accurately through a given EOS. Simply put, an EOS can predict all thermodynamic properties. For pure components and/or mixtures, these include enthalpy, Gibbs free energy, liquid/vapor density, liquid/vapor volume, viscosity, excess enthalpy, critical properties, etc.

Altogether, the simultaneous regression of either pure-component or mixture parameters with more than one thermodynamic property can improve the accuracy of the EOS -- not only in predicting the property data regressed over, but perhaps also in predicting other properties not included within the original regression strategy. Accordingly, Kwok et al. (1972) note that MPA "becomes especially valuable when data for one property are of lower accuracy or less complete than data for another property (p. 89)." MPA thus takes on more significance in the sense that it can allow for some extrapolation of EOS parameters in predicting thermodynamic properties for which little, if any data exist.

Moreover, Lin et al. (1972) comment that "an accurate description of one property does not guarantee an accurate description of other related properties (p. 645)." Consequently, MPA provides an alternative to the limitations of an EOS based

on single-property data as observed by Starling (1970) in reviewing the majority of the development of the BWR EOS on density data (Benedict et al., 1940). The next section reviews several publications on MPA regression strategies.

3.2.3 Literature Review

In addition to the above work by Starling and Wolfe (1966, 1971) on the Benedict-Webb-Rubin (BWR) EOS (Benedict et al., 1940), Starling (1970) considerably extended the work already performed on MPA. This work continued to develop in conjunction with the temperature dependence of certain BWR EOS parameters as seen in Cox (1968). In the same year, Roberts (1968) demonstrated the superiority of the Gauss-Newton method over the Newton-Rhapson method when simultaneously regressing BWR parameters over density and enthalpy data.

Later, Bono (1969) and Bono and Starling (1970) proved the superiority of using density as the response variate instead of compressibility (or pressure) in regressing BWR parameters over experimental density data. In other words, the regression of EOS parameters over density data -- also interpreted as pressure-volume-temperature (PVT) data -- should yield more accurate results by making density a direct function of temperature and pressure through the EOS of interest. This new response variate contrasts with the popular approach (both then and now) of iteratively fitting the density as a function of temperature and pressure. All of the above work, including that of Starling and Powers (1970) on mixture enthalpies of methane and propane, eventually culminated in the formulation of the Benedict-Webb-Rubin-Starling (BWRS) EOS (Starling, 1971). Kwok (1970) provides both an

expanded discussion of MPA as well as general algorithms for the computational procedures involved in this process.

Further examples of the above work on MPA supervised by Starling exist within the thermodynamic literature. These include the simultaneous regression of PVT and enthalpy data by Cox et al. (1971), with the later inclusion of vapor pressure data as seen in the work presented by Lin et al. (1972) and Kwok et al. (1972). This MPA work later included a study by Wang et al. (1976) on the simultaneous regression of sonic velocity and heat capacity data along with density and enthalpy data. In addition, Clements et al. (1972) also reported a more efficient method of employing nonlinear regression techniques through MPA than those of Bono (1969), while also extending the temperature dependence of two BWR EOS parameters in the early development of the BWRS EOS.

The above work bears mention because of its impact on the KCLS EOS developed by Chung et al. (1984) and used in this work. Generally speaking, the KCLS EOS of Section 2.3 represents an extension of the BWRS EOS not only in terms of its applicability to polar and nonpolar components, but also in terms of the its design through MPA. As with the BWRS EOS, the development of the KCLS EOS -- as seen in Chung et al. (1984) and Khan (1983) -- involved the simultaneous regression of density, enthalpy and vapor-pressure data. Moreover, it also entailed the use of MPA on a much wider range of components than before -- possibly a feat unsurpassed to this day.

3.3 Results Obtained for This Work with the Khan-Chung-Lee-Starling (KCLS) Equation of State

3.3.1 Choice of Pure Components for Simulation

This section describes the rationale for choosing ten pure components to simulate in this work with the KCLS EOS presented by Khan (1983) and Chung et al. (1984). As discussed below (and later shown in Tables 3.2-3.7 and 3.9), these ten components include three glycols, six aromatic compounds, and two freons. Aside from these choices, other KCLS PCPs necessary for mixture-simulation purposes in this work have already been determined by both Khan (1983) and Chung et al. (1984). These other components included benzene and toluene, with the following discussion explaining the reasoning behind choosing these twelve components as a whole for this work.

Generally speaking, the choice of pure components for simulation herein focuses on the prediction of components that occur in the processing of natural-gas dehydration units. First of all, these units normally use any of three common glycol compounds: ethylene (also known as monoethylene) glycol , diethylene glycol and triethylene glycol (Ng et al. 1991, 1993; Ng and Chen, 1994). Process schematics on these systems may be seen in Fitz and Hubbard (1987) and Smith and Dorsi (1993). With these three glycols varying in importance, the author decided to choose all three of them for pure-component simulation purposes in this work.

Next, the pure components extracted from the natural gas with the glycols must also be chosen for simulation. First, since glycols function as desiccants for wet

natural gas, water must obviously be included. Second, after contacting the wet natural gas, the glycol of choice will also entrain other components; this is referred to as a "rich" glycol (Hlavinka et al., 1993). This rich glycol must then be regenerated, or "stripped", of both water and these other components (Hlavinka et al., 1993), which typically consist of such aromatic components commonly known as BTEX (benzene-toluene-ethylbenzene-xylene). Subsequently, mixture simulations of the glycols and entrained components require KCLS PCPs for all five compounds.

Moreover, xylene consists of three isomers forms: *ortho*-, *meta* and *para*-xylene. Since Section 8.6 of Chapter 8 discusses the alternative use of binary vapor-liquid equilibrium (VLE) systems containing isomers other than the one desired, the author regressed KCLS PCPs over all three xylene isomers. Furthermore, although Khan (1983) and Chung et al. (1984) did present KCLS parameters for *ortho*-xylene, they did not present these parameters for *meta* and *para*-xylene. Consequently, all six aromatic components were chosen for pure-component simulations, with the KCLS parameters for benzene, toluene, and water determined by Khan (1983) and Chung et al. (1984), thereby leaving the regression of KCLS parameters in this work to ethylbenzene and the three xylene isomers.

Third, as mentioned in Section 8.7 of Chapter 8, the unlike-interaction parameters (UIPs) of some binary systems may be obtained through interpolation between other binary systems. In such cases, the UIPs of all binary systems would logically contain a common component. For example (as noted in Section 8.7), data could not be found in the thermodynamic literature for the system methane-

ethylbenzene, thereby leading to a possible interpolative scheme between binary systems of methane with benzene, toluene, and n-propylbenzene. Moreover, since n-propylbenzene parameters were not previously determined, this component was chosen as an eighth component for KCLS PCP regression in this work.

Finally, although the mixture simulations presented in Chapter 7 focus on glycol-dehydration mixtures, the generalized asymmetric rule (GAR) of Chapter 4 should also be applied to predict other types of systems as well for comparative purposes. For example, it should be noted that the influential work on freon mixtures by Wenzel et al. (Juris, 1970; Juris and Wenzel, 1974) on the generalized symmetric rule (GSR) led to the formulation of the GAR in this work. As a tribute to Wenzel et al.'s work on trifluoromethane and tetrafluoromethane, the PCPs of these two freons are also simulated herein, along with the binary VLE mixture that they form in Chapter 7.

3.3.2 Literature Data Sources Consulted

The author consulted several literature sources for experimental vapor-pressure and liquid-density data on the ten components introduced into the KCLS EOS of Section 3.3.1. In addition, when modeling pure-component properties, some equations of state require other property data such as molecular weight, critical properties (e.g., temperature, pressure, density/volume, etc.), and acentric factor. In such cases, Reid et al. (1977) provide a very comprehensive list of values for other

properties over a wide variety of compounds in their appendix, which was complemented a decade later by Stephenson et al. (1987).

Next, a thorough literature search initiated with these bibliographic sources by the author then resulted in the actual list of experimental vapor-pressure and liquid-density data used in regressing the KCLS EOS parameters. Table 3.1 lists these sources (for each of the above ten components) for both data properties along with the number of data points and temperature and pressure ranges from each source.

3.3.3 Results Obtained Using Vapor-Pressure Data Alone

As a thermodynamic property, vapor pressure constitutes the VLE property of a pure component. Consequently, since this work focuses on predicting VLE mixture compositions, the accurate prediction of this single property alone retains far greater importance in the prediction of these compositions. For this reason, KCLS-EOS PCPs were regressed against vapor-pressure data of the ten components noted in Section 3.3.1, with an objective function consisting of Equation (3.1) multiplied by 100% and divided by the total number of data points.

To begin with, an indication of the accuracy of all pure-component and mixture predictions reported in this work is presented in terms of average absolute relative deviations (AARDs). These AARDs are calculated according to

Table 3.1

General Sources of Pure-Component Vapor-Pressure and Liquid Density Data

Author(s)	Publisher	Source Type	Lists Actual Data?	Modeling Provided	Properties	Remarks
Rossini et al. (1953)	Carnegie Press	Data tables	Yes	Antoine relation	P^V, ρ^L, H, etc.	Excellent source of many properties
Jordan (1954)	Interscience Publishers	Data tables, plates	Yes	Antoine relation	P^V	Semilog-plot component comparisons
Boublik et al. (1973)	Elsevier	Data tables	Yes	Antoine relation	P^V	Excellent source
Vargaftik (1975)	Hemisphere	Data tables	Yes	None	P^V, ρ^L, viscosity, heat capacity	Includes saturated properties
Yaws (1977)	McGraw-Hill	Plotted-curve compilation	No	Rackett relation for liquid density	P^V, ρ^L, H, etc.	Comparisons between similar components
Stephan and Hildwein (1987)	DECHEMA	Monograph. data tables	Yes	Antoine relation, many other properties	P^V, ρ^L, H, etc.	Very comprehensive compilation

$$AARD = \frac{\sum_{id=1}^{ND} \left| \frac{P_v^{EXP} - P_v^{CALC}}{P_v^{EXP}} \right|_{id} x100\%}{ND} = \frac{\sum_{id=1}^{ND} \left| 1 - \frac{P_v^{CALC}}{P_v^{EXP}} \right|_{id} x100\%}{ND} \quad . \quad (3.4)$$

Simply put, Equation (3.4) consists of (1) summing the absolute relative error (i.e., the deviation between an experimental and calculated value divided by the experimental value), (2) dividing the sum by the total number of data points to obtain an average, and (3) multiplying this average by 100 to obtain a percentage value.

3.3.3.1 AARD Results for Vapor-Pressure Predictions

As seen in Table 3.2 below, the results of the pure-component vapor-pressure predictions prove quite favorable. First, the AARD vapor pressures of all three glycols have been predicted to within 2.5 %. Here, the AARD for triethylene glycol holds a lesser value (1.7%), probably due to the lesser number of (roughly half as many) data points employed.

Although the AARDs of the glycols comprised the largest values of all ten components, these values remain somewhat less than those obtained by both Khan (1984) and Chung et al. (1984). As seen below in Table 3.8, these authors report vapor-pressure AARDs for such alcohols as methanol and ethanol of 7.0% and 5.16%, respectively. In addition, Khan (1983) reports a lesser AARD value for propanol of 3.86%.

Second, the AARDs of the five aromatic components (i.e., ethylbenzene, three

Table 3.2

Vapor-Pressure AARDs for Pure Components

Component	Number of Data Points	Thermo. Property	AARD %	Temp. Range (°R)	Pressure Range (psia)	Reference
Ethylene glycol	52	P^v	2.3	635.67-918.00	0.0967-45.9380	Boublik (1973); Stephan and Hildwein (1987)
Diethylene glycol	46	P^v	2.5	779.67-1020.82	0.8315-51.4799	Rinkenbach (1927); Daubert et al. (1987)
Triethylene glycol	20	P^v	1.7	822.29-971.51	0.6135-8.7995	Daubert et al. (1987)
Ortho-Xylene	45	P^v	0.36	514.17-753.39	0.0580-15.0841	Pitzer and Scott (1943); Willingham et al. (1945); Forziati et al. (1949)
Meta-Xylene	43	P^v	0.20	536.67-743.81	0.1615-15.0841	Pitzer and Scott (1943); Willingham et al. (1945); Forziati et al. (1949)
Para-Xylene	49	P^v	0.66	527.67-742.46	0.1255-15.0839	Pitzer and Scott (1943); Willingham et al. (1945); Forziati et al. (1949); Smith (1990)

Table 3.2

(Continued)

Ethylbenzene	56	P^V	0.30	491.69-738.56	0.0371-15.0839	Scott and Brickwedde (1945); Willingham et al. (1945); Forziati et al. (1949)
N-Propylbenzene	39	P^V	0.17	627.83-780.10	0.9214-15.0845	Willingham et al. (1945); Forziati et al. (1949);
Trifluoromethane (Freon refrigerant R23)	12	P^V	0.64	284.54-344.12	1.3729-14.8681	Valentine et al. (1975)
Tetrafluoromethane (Freon refrigerant R14)	18	P^V	0.51	166.50-262.55	0.0290-15.4482	Menzel and Mohry (1933)

xylene isomers and n-propylbenzene) have been predicted to within 0.66% as seen in Table 3.2. These results appear more accurate than those seen in Table 3.8 as reported by Khan (1983) and Chung et al. (1984), with 1.23% for benzene and 1.73% for toluene. Also, as mentioned above in Section 3.3.1, these two authors reported a result for *ortho*-xylene only (with an AARD of 0.56%) that was only slightly surpassed by the result obtained for this work with an AARD of 0.36%. Following this difference in error, the AARD vapor pressures of the two freons (R14 and R23) have been predicted to within 0.64%, which also compared favorably to the AARD values reported by Khan (1983) for the three freons (R12, R21, and R22) at 0.69%.

Third, Table 3.3 below presents the PCPs obtained for the KCLS EOS on the basis of vapor pressure data alone. Here, the trends examined might again best be compared to those reported by Khan (1983) and Chung et al. (1984) for methanol, ethanol, and propanol; Table 3.4, in turn, shows PCPs determined by these authors for these and other selected components on the basis of vapor pressure, liquid density, and enthalpy data.

For the three glycols in Table 3.2, the polar parameter, κ, increases with carbon number, thus constituting a trend similar to the respective values of the alcohols. In addition, the glycol trend for the molecular hard-core volume, V^*, also followed a steadily-increasing trend similar to the alcohols, while the structure parameter, λ, only slightly decreased for the glycols as contrasted with a slight increase for the alcohols. Finally, the energy parameter, $\frac{\varepsilon}{k}$, showed a definite

increase for the glycols, as compared with a disparate, highest value for methanol, a lowest value for ethanol, and a median value for propanol.

Table 3.3

KCLS Pure-Component Parameters Based on Vapor Pressure Alone

(This Work)

Component	$\frac{\varepsilon}{k}$ (°R)	V^* (ft^3/lbmol)	λ (-)	κ $(°R)^2$ /$(ft^3$/lb-mole$)^2$
Ethylene glycol	799.986	0.293615	1.98213	9114.08
Diethylene glycol	825.379	0.313275	1.92360	9168.14
Triethylene glycol	954.870	0.485752	1.80964	9762.61
Ortho-Xylene	690.616	0.706397	2.31582	0.0
Meta-Xylene	690.604	0.691596	2.26100	0.0
Para-Xylene	690.611	0.680421	2.25547	0.0
Ethylbenzene	658.973	0.783266	2.39078	0.0
N-Propylbenzene	659.131	0.900463	2.63781	0.0
Trifluoromethane (Freon refrigerant R23)	272.309	0.537124	2.86715	19.400
Tetrafluoromethane (Freon refrigerant R14)	270.498	0.296717	1.75224	0.0

Fourth, the KCLS PCPs for xylene isomers determined for Table 3.3 proved comparable in value to those reported in Table 3.4. Of course, this is not particularly surprising, since the PCP values presented in Table 3.4 for *ortho*-xylene were used as starting values for all three xylene isomers, whose final values changed very little. In addition, binary VLE data containing an alternative isomer might need to be used for multicomponent simulations (as discussed in more detail in Section 8.6 of Chapter 8).

Table 3.4

KCLS Pure-Component Parameters Based on

Vapor Pressure, Liquid Density and Enthalpy

as Reported by Khan (1983) and Chung et al. (1984)

Component	$\frac{\varepsilon}{k}$ (°R)	V^* (ft^3/lbmol)	λ (-)	κ $(°R)^2$ /(ft^3/lb-mole)^2
Methanol	525.791	0.267275	2.11110	4235.92
Ethanol	476.325	0.333049	2.15632	10992.0
Propanol	506.038	0.404247	2.47944	12032.8
Ortho-Xylene	690.612	0.698227	2.31868	0.0
Benzene	669.312	0.506596	1.82792	0.0
Toluene	658.809	0.610572	2.16520	0.0
Dichlorodifluoromethane (Freon refrigerant R12)	459.703	0.441159	1.75124	0.0
Fluorodichloromethane (Freon refrigerant R21)	529.761	0.392497	1.85043	168.985
Chlorodifluoromethane (Freon refrigerant R22)	451.387	0.376581	1.27521	4534.43
Fluoromethane (Methyl Fluoride; also Freon refrigerant R41)	351.61	0.292249	1.66562	720.803
Methane	270.804	0.25905	1.03331	0.0

Consequently, it should be noted (as seen in Tables 3.2 and 3.6) that both the vapor-pressure and liquid-density data used for all three xylene isomers were taken from identical sources with the exception of more recent data published by Smith (1990) for *para*-xylene. The use of the Smith (1990) data for the *para*-xylene isomer alone

may well account for its vapor-pressure prediction containing a larger AARD than the other two isomers.

Fifth, the PCP values for both ethylbenzene and n-propylbenzene in Table 3.3 continue the trend shown in Table 3.4 for benzene and toluene. Here, the numerical values for all three nonpolar PCPs show a slight, consistent increase with the addition of each methyl group (or carbon number) to the benzene ring. Likewise, the value of the fourth (and only polar) PCP, κ, was intentionally held constant at zero for all aromatic components for two reasons: First, the zero value deliberately coincides with the approach previously taken by Khan (1983) and Chung et al. (1984); second, the zero value may be justified since these aromatic components typically possess low dipole moments of roughly 0.4 Debyes (McClellan, 1963, 1974)

Sixth, the PCP values for the two freons in this work (Table 3.3) are similar in value to each other, but vary significantly from those presented for the three freons (Table 3.4) by Khan (1983) and Chung et al. (1984). The most striking difference in the numerical values obtained for this work appears in a variation of two orders of magnitude for the polar parameters (κ), which change noticeably between (a) freon R23 (Table 3.3) and (b) freons R21 and R22. Computationally, this difference may be explained in terms of the high degree of correlation observed by the author in regressing this parameter, where the first estimate of κ typically does not change throughout the course of the regression procedure applied. (In such cases, the author used various estimates for κ, and then chose the estimate that gave the least initial error in the fitting function).

A similar degree of correlation also occurred to a far lesser (but noticeable) extent in the energy parameter $\frac{\varepsilon}{k}$ with $\kappa = 0$. Accordingly, Appendix D (a) discusses correlation between parameters in detail, (b) includes a procedure to overcome correlation problems, and (c) also provides several recommendations on related aspects of thermodynamic modeling. Chemically, however, the variations in these two parameters can be attributed to the absence of chlorine in these two freons. In either case, the greatest similarity in PCP values occurred in the molecular hard-core volume (V^*) -- more for freon R14 than R23 (Table 3.3); this similarity makes sense when considering that all five freons consist of halogenated methane molecules.

3.3.3.2. AARD Results for Liquid-Density Predictions

Next, a concern arises with respect to the accuracy obtained with the new KCLS PCPs in terms of predicting other thermodynamic properties. As noted in Section 3.2, the regression of PCPs tends to improve in accuracy when regressing against more than one thermodynamic property. Since Khan (1983) and Chung et al. (1984) simultaneously regressed KCLS PCPs against vapor pressure, density, and enthalpy data, due consideration should be given to the predictions obtained after (1) regressing PCPs against only one property -- such as vapor pressure -- and then (2) evaluating the EOS predictive accuracy of other thermodynamic properties when holding the PCPs constant. For this work, liquid density was chosen as the other thermodynamic property, since a density search must be carried out prior to the EOS

fugacity calculations in simulating both pure-component vapor pressures as well as VLE mixture compositions.

Moreover, the evaluation of the KCLS-EOS PCPs of Table 3.3 for vapor pressure was in fact carried out for each of the ten components listed in terms of their prediction of liquid density. Table 3.5 below presents the results of this evaluation, using the identical data points, temperature/pressure conditions, and references as those listed in Table 3.6.

As evidenced in Tables 3.5, the predictions for liquid density appear an order of magnitude greater than those for the vapor pressures for all ten components. Interestingly enough, this result supports a finding paid specific attention to later in various publications by Starling et al. (e.g., Starling, 1966; Starling and Wolfe, 1972; Lin et al., 1972), who noticed that the BWRS EOS had previously been based on PVT (i.e., single-property) data. This finding, as published earlier by Ellington and Eakin (1963), reported an uncertainty (or error) one order of magnitude greater than the prediction of PVT data for other thermodynamic properties that required either differentiation or integration of the EOS. Although the results presented in Table 3.5 seem to occur in reverse order of the Ellington-Eakin (1963) finding, they do support them in the sense of an interpretation of density errors directly based on the EOS as a differentiation of the Gibbs-fugacity EOS integral used to predict vapor pressures.

The variations in error observed in density AARDs for the ten components may be explained as follows: First, the glycol density errors make sense in light of the above discussion. Second, the density AARDs for ethylbenzene and n-propylbenzene

Table 3.5

Comparison between KCLS Vapor-Pressure and Liquid-Density AARDs for Pure Components Based on Vapor-Pressure PCPs Only (This Work)

Component	AARD % for Vapor Pressure P^v	AARD % for Liquid Density ρ^L
Ethylene glycol	2.3	22.5
Diethylene glycol	2.5	25.3
Triethylene glycol	1.7	25.1
Ortho-Xylene	0.36	1.5
Meta-Xylene	0.20	3.1
Para-Xylene	0.66	5.1
Ethylbenzene	0.30	9.2
N-Propylbenzene	0.17	10.4
Trifluoromethane (Freon refrigerant R23)	0.64	53.6
Tetrafluoromethane (Freon refrigerant R14)	0.51	3.3

show the same order-of-magnitude larger error since they were regressed from initial PCP values for toluene supplied by Khan (1983) and Chung et al. (1984). Third, the density errors for freon R23 also reflect this trend as well because the initial PCP values for this component were taken from those reported by the above authors for methyl fluoride (fluoromethane), which has a greater dipole moment (roughly 1.8-1.85 Debyes) than R23 (roughly 1.6-1.65 Debyes).

Fourth, the much lesser liquid-density AARDs for the three xylenes may be accounted for by the fact that their initial PCP values (a) consisted of those reported by (and, as mentioned above, varied little from) those provided by Khan (1983) and Chung et al. (1984) for *ortho*-xylene and (b) already determined by MPA over vapor pressure, liquid density, and enthalpy data. This liquid-density predictive result thus lends support to the use of MPA, as further supported by the lesser density-AARD error for freon R14, which also reflects a similarity in regressed values for the initial PCPs reported by these authors for methane.

Obviously, one should then employ MPA to obtain reliable PCPs for new pure components of interest in lieu of the single-property analysis (SPA) of vapor-pressure data alone. Since the results in Table 3.5 suggest the need to include liquid-density data in the MPA regression scheme, data for this property were included for all ten of these components. Section 3.3.4. therefore both reports and discusses the results obtained for these components through MPA of both vapor-pressure and liquid-density data.

3.3.4 Results Obtained Using Both Vapor-Pressure and Liquid-Density Data

Following the above results reported in Section 3.3.3, KCLS PCPs were regressed against both vapor pressure and liquid density for components listed in Tables 3.3 and 3.5. The objective function for these regression simulations consisted of Equation (3.2) multiplied by 100% and divided by the total number of data points with (a) weights of unity for both vapor pressure and liquid density and (b) a weight

Table 3.6

Simultaneous Vapor-Pressure and Liquid-Density AARDs for Pure Components

(This Work)

Component	Number of Data Points	Thermo. Property	AARD %	Temp. Range (^{o}R)	Pressure Range (psia)	Reference
Ethylene glycol	52	P^{V}	2.6	635.67-918.00	0.0967-45.9380	Boublik (1973); Stephan and Hildwein (1987)
	8	ρ^{L}	1.8	545.67-761.04	14.696	Tawfik and Teja (1989)
Diethylene glycol	52	P^{V}	2.8	779.67-1020.82	0.8315-51.4799	Rinkenbach (1927); Daubert et al. (1987)
	8	ρ^{L}	2.1	545.76-762.12	14.696	Tawfik and Teja (1989)
Triethylene glycol	20	P^{V}	1.3	822.29-971.51	0.6135-8.7995	Daubert et al. (1987)
	7	ρ^{L}	1.9	538.38-761.04	14.696	Tawfik and Teja (1989)

Table 3.6

(Continued)

Ortho-Xylene	45	P^v	0.66	514.17-753.39	0.0580-15.0841	Pitzer and Scott (1943); Willingham et al. (1945); Forziati et al. (1949)
	39	ρ^L	1.2	536.67-986.67	14.50-5801.53	Vargaftik (1975)
Meta-Xylene	43	P^v	0.39	536.67-743.81	0.1615-15.0841	Pitzer and Scott (1943); Willingham et al. (1945); Forziati et al. (1949)
	60	ρ^L	1.1	527.67-986.67	14.50-5801.53	Vargaftik (1975)
Para-Xylene	49	P^v	0.88	527.67-742.46	0.1255-15.0839	Pitzer and Scott (1943); Willingham et al. (1945); Forziati et al. (1949); Smith (1990)
	54	ρ^L	0.91	509.67-986.67	14.50-5801.53	Vargaftik (1975)

Table 3.6

(Continued)

Ethylbenzene	56	P^V	0.66	491.69-738.56	0.0371-15.0839	Scott and Brickwedde (1945); Willingham et al. (1945); Forziati et al. (1949)
	24	ρ^L	2.3	329.67-743.67	14.696	Vargaftik (1975)
N-Propylbenzene	39	P^V	1.9	627.83-780.10	0.9214-15.0845	Willingham et al. (1945); Forziati et al. (1949);
	48	ρ^L	2.5	309.67-779.67	14.696	Rossini, et al. (1953)
Trifluoromethane (Freon refrigerant R23)	12	P^V	1.2	284.54-344.12	1.3729-14.8681	Valentine et al. (1975)
	133	ρ^L	1.2	275.67-537.67	0.87-695.11	Rossini et al. (1953); Stewart et al. (1986)
Tetrafluoromethane (Freon refrigerant R14)	18	P^V	0.61	166.50-262.55	0.0290-15.4482	Menzel and Mohry (1933)
	86	ρ^L	0.40	239.67-407.67	5.72-526.70	Stewart et al. (1986)

of zero for enthalpy. Table 3.6 presents the results obtained from this regression, with the AARD results from both SPA (Table 3.2) and MPA (Table 3.6) repeated together in Table 3.7 to facilitate more direct comparisons between these two methods. These results are discussed in detail in Sections 3.3.4.1 and 3.3.4.2.

3.3.4.1 AARD Results for Liquid-Density Predictions

First, Table 3.7 shows that MPA significantly improved the liquid-density AARD predictions for all components. In addition, it should be noted that the only difference in data used consisted of adding six vapor-pressure points to diethylene glycol in the MPA regression, which had previously been discarded on the basis of poor predictions in the range of 13.4 to 47.0%. Otherwise, the same data points found application in both the SPA results (reported in Tables 3.2 and 3.5) and the MPA results (reported in Table 3.6).

Second, Table 3.7 directly compares the AARD results obtained from both SPA and MPA. As can be seen, the use of MPA significantly improved the KCLS liquid-density predictions for all ten components. In fact, the AARDs for density actually decreased more than an order of magnitude for both the three glycols and the two freons. (This improvement may also be seen in this table to a lesser extent for ethylbenzene and n-propylbenzene). Obviously, the AARD predictions for the three xylene isomers lie very close to one another (0.91-1.2%), which, as noted in Section 3.3.3.2 above, stems from the liquid-density data for these three components that originate from the same source.

Table 3.7

AARD Comparison between SPA (Vapor Pressure Only)

and MPA (Vapor Pressure and Liquid Density)

for Pure Components

(This Work)

Component	SPA AARD % for Liquid Density ρ^L	MPA AARD % for Liquid Density ρ^L	SPA AARD % for Vapor Pressure P^v	MPA AARD % for Vapor Pressure P^v
Ethylene glycol	22.5	1.8	2.3	2.6
Diethylene glycol	25.3	2.1	2.5	2.8
Triethylene glycol	25.1	1.9	1.7	1.3
Ortho-Xylene	1.5	1.2	0.36	0.66
Meta-Xylene	3.1	1.1	0.20	0.39
Para-Xylene	5.1	0.91	0.66	0.88
Ethylbenzene	9.2	2.3	0.30	0.66
N-Propylbenzene	10.4	2.5	0.17	1.9
Trifluoromethane (Freon refrigerant R23)	53.6	1.2	0.64	1.2
Tetrafluoromethane (Freon refrigerant R14)	3.3	0.40	0.51	0.61

3.3.4.2 AARD Results for Vapor-Pressure Predictions

In contrast to the changes in AARD for liquid density, the vapor-pressure errors did not change significantly from those reported in Section 3.3.3.1. In this case, the AARD increased only slightly for the three glycols, three xylene isomers,

ethylbenzene, and freon R14. In addition, the only significant increases in vapor-pressure error occurred for n-propylbenzene and freon R-23, most likely due to (a) the wider temperature ranges (Table 3.6) covered by the density data for these two components, as well as (b) the predictions for R23 containing the largest number of density data points for all components regressed. In any case, the final AARD errors for these two components lie within 1.9%. This situation also holds true for the three xylenes, which may be interpreted as the KCLS PCPs that slightly deviate from the vapor-pressure data to accommodate the liquid-density data simultaneously. At any rate, these results also compare favorably with those reported by Khan (1984) and Chung et al. (1984) in Table 3.8.

Third, as with the PCPs of Section 3.3.3.1, the numerical values of the KCLS PCPs should be examined when employing MPA in lieu of SPA. In comparing the results of Table 3.3 (from SPA) with those of Table 3.9 (from MPA), certain trends emerge. As before, the polar parameter, κ, increases with carbon number, only with greater differences in numerical value that more closely reflects the results previously observed for the three alcohols of Table 3.4. Also, the molecular hard-core volume, V^*, increases for the glycols with greater numerical differences as well. Next, the structure parameters, λ, increase somewhat more, while the trend for the energy parameter, $\frac{\varepsilon}{k}$, now shows the same disparate trend for these components as mentioned above in Section 3.3.3.1 for the three alcohols of Table 3.4.

Next, the MPA-determined PCP values of Table 3.9 for the three xylene

Table 3.8

Simultaneous Vapor-Pressure, Liquid-Density and Enthalpy AARDs for Pure Components

as Reported by Khan (1983) and Chung et al. (1984)

Component	Number of Data Points	Thermo. Property	AARD %	Temp. Range (^{o}R)	Pressure Range (psia)	Reference
Methanol	33	P^{V}	7.0	473.7-922.8	0.299-1143.7	Young (1910)
	232	ρ^{L}	4.5	491.7-923.7	0.572-1135.9	Ramsey and Young (1887); Young (1910)
Ethanol	42	P^{V}	5.2	527.0-925.1	0.831-891.7	Young (1910)
	289	ρ^{L}	3.8	491.7-1122.	0.237-10000.	Ramsey and Young (1887); Young (1910)
Propanol	54	P^{V}	3.9	526.4-966.1	0.284-749.8	Kemme and Kreps (1969); Ambrose and Townsend (1963);
	38	ρ^{L}	2.5	635.7-959.7	7.27-698.12	Ambrose and Sparke (1970) International Critical Tables (1926)

Table 3.8

(Continued)

Ortho-Xylene	41	P^V	0.56	473.7-1137.	0.011-552.3	Vargaftik (1975)
	59	ρ^L	1.1	536.7-986.7	14.50-5800.	Vargaftik (1975)
Benzene	36	P^V	1.2	504.7-996.	0.760-636.9	Vargaftik (1975)
	60	ρ^L	1.6	923.7-1104.	375.3-867.4	Chao (1978)
Toluene	33	P^V	1.7	491.7-1060.	0.130-547.4	Vargaftik (1975)
	13	ρ^L	0.91	491.7-689.7	0.130-547.4	Vargaftik (1975)

Table 3.8

(Continued)

Dichlorodifluoromethane (Freon refrigerant R12)	40	P^V	0.58	307.7-689.7	0.140-577.0	ASHRAE (1969)
	189	ρ^L	1.0	307.7-919.7	0.140-440.0	ASHRAE (1969)
	40	$H-H^o$	0.31	307.7-689.7	0.140-577.0	ASHRAE (1969)
Fluorodichloromethane (Freon refrigerant R21)	51	P^V	0.51	383.7-812.5	0.367-812.5	ASHRAE (1969)
	300	ρ^L	0.57	491.7-851.7	14.50-2901.	ASHRAE (1969)
Chlorodifluoromethane (Freon refrigerant R22)	16	P^V	0.69	455.7-664.7	35.62-723.2	ASHRAE (1969)
	17	ρ^L	3.8	319.7-859.7	0.450-497.3	ASHRAE (1969)
Fluoromethane (Methyl Fluoride; also Freon refrigerant R41)	28	P^V	1.74	269.7-538.3	0.620-701.4	ASHRAE (1969)
	107	ρ^L	0.58	269.7-899.7	0.620-400.0	ASHRAE (1969)
Methane	128	P^V	0.41	163.5-342.0	1.774-655.7	Matthews and Hurd (1946); Prydz and Goodwin (1972)
	40	ρ^L	0.54	206.2-1122.0	129.7-606.5	Van Itterbeek et al. (1963); Douslin et al. (1964); Vennix (1967); Jones (1962); Yesavage 1968)
	38	$H-H^o$	0.51	209.7-509.7	450.0-2000.0	

Table 3.9

KCLS Pure-Component Parameters Based on

Vapor Pressure and Liquid Density

(This Work)

Component	$\frac{\varepsilon}{k}$ (°R)	V^* (ft³/lbmol)	λ (-)	κ (°R)²/(ft³/lb-mole)²
Ethylene glycol	736.776	0.344594	2.40324	9059.02
Diethylene glycol	657.495	0.541865	3.88095	13671.2
Triethylene glycol	723.280	0.781100	3.88136	16566.1
Ortho-Xylene	687.135	0.696648	2.34328	0.0
Meta-Xylene	679.961	0.705833	2.32255	0.0
Para-Xylene	677.714	0.705297	2.32409	0.0
Ethylbenzene	692.856	0.728859	2.19135	0.0
N-Propylbenzene	716.653	0.839093	2.25533	0.0
Trifluoromethane (Freon refrigerant R23)	341.243	0.254751	2.04165	52.465
Tetrafluoromethane (Freon refrigerant R14)	272.097	0.288868	1.73999	0.0

isomers once more agree with those for *ortho*-xylene in Table 3.4. Here, the only noticeable change occurs in the energy parameter, as the three isomeric values now spread apart from each other in Table 3.9; nevertheless, this change only amounts to a numerical difference of 1.4%. Moreover, the values for the energy parameters of ethylbenzene and n-propylbenzene now lie closer together, with little change in the other two nonpolar parameters.

Finally, the PCP values for freon R14 remain very nearly the same, while those for R23 now deviate from their previous values with the greatest change again noted in the energy parameter. In fact, the new freon-R23 (trifluoromethane) value for the energy parameter now lies closer to the value of freon R41 (fluoromethane). Again, this result might once more be attributed to the use of more density-data points (55%) for R23 than for freon R14 (tetrafluoromethane), but more importantly to the fact that freon R41 differs from R23 by **two** fluorine atoms as opposed the difference of **three** fluorine atoms between freons R41 and R14. In any case, all of the MPA results taken as a whole prove the consistency of the KCLS EOS in predicting thermodynamic properties in terms of accuracy as well as in PCP values.

3.3.4.3 Weighting Factors for MPA of Different Thermodynamic Properties

Fourth, the interpretation of PCPs that accommodate different types of data for the xylene isomers through the KCLS EOS bears further discussion. In general, some change in both EOS PCPs and accuracy is to be expected when applying MPA in lieu of SPA. At this point, the question arises: What relative amounts of data points should be used for each thermodynamic property (e.g., vapor pressure, liquid density, etc.) when determining PCPs for any given EOS? This question in turn leads to a more far-reaching question: What weighting factors -- such as those presented in Equations 3.2-3.3 in Section 3.2.1 -- should be used for these different properties during the course of the regression procedure?

The answer to both questions was briefly addressed by Jacobsen et al. (1988). In this case, these authors reported simultaneous regressions of density, heat capacity, and sonic-velocity data for ethylene. In their report, these authors applied different weighting schemes to the above three thermodynamic properties, including **(a)** weights of unity, **(b)** lumped-parameter weighting (i.e., a consistent weight based on an uncertainty for each property), **(c)** weights consisting of the reciprocal of pressure (a good choice for a relatively-low pressure/density EOS such as those reviewed in Chapter 2), **(d)** error propagation (i.e., the error in predicting each data point/property, regardless of inaccuracies in the experimental data itself), and **(e)** complete-error propagation (i.e., the error for each point/property along with experimental data inaccuracies).

The results reported by Jacobsen et al. (1988) revealed numerous insights into these MPA weighting strategies. First, the absence of sonic-velocity data seemed to exert the least influence on the accuracy of the other two properties. This finding supports the publication by Wang et al. (1976) for the MPA of ethane, which employed fixed weights of (a) unity for four properties (liquid density, enthalpy, vapor pressure, and heat capacity) and (b) a value of 0.002 for sonic velocity.

In addition to these insights, Jacobsen (1988) also reported that the liquid-density property appears more sensitive to the number of data points used, which supports the MPA result reported in Section 3.3.4.2 of this work for freon R23 (trifluoromethane). The author of this work confirms this finding through a result not reported herein, in which the vapor-pressure weight was fixed at two and the liquid-

density weight held at unity, effectively supplying a weight of two-thirds to the vapor pressure and one-third to the liquid density. Of course, the intention of this approach lay in obtaining greater accuracy for the vapor-pressure predictions while also retaining comparative accuracy for the liquid-density predictions. Unfortunately, the results of this approach presented conflicting trends, in which the AARDs for both properties either slightly rose, decreased, and/or remained the same. Nevertheless, this outcome for the weights lends support to Jacobsen et al.'s (1988) results.

In addition, this report also stressed a need for the data of each thermodynamic property to cover a wide range of temperatures and pressures. Obviously, the determination of the weights of various thermodynamic properties can be facilitated when the data for each property exist within similar ranges of temperature and pressure. Although not reported above, the pure-component, vapor-pressure data of Linder (1931) was not used in the regression of KCLS PCPs for the opposite reason, namely that of a limited temperature/pressure range. Here, the data reported within this publication (for ethylbenzene, all three xylenes and n-propylbenzene) were taken for the sole purpose of ascertaining vapor-pressure data at around 0°C. Although Linder's (1931) work was intended to correct for previous defects in experimental vapor-pressure readings at these conditions, it did not report vapor-pressure data taken at higher-temperature conditions. Moreover, it did not compare the data actually taken to those of other authors. Although much more data have been taken since Linder's work in 1931, this example does stress the need for data of different thermodynamic properties to coincide at similar temperature/pressure ranges.

Finally, Jacobsen et al. (1988) also noted that EOS predictions become most accurate with the assignment of unity to all MPA, thermodynamic-property weights. Here, it should be noted that these authors employed three least-squares methods: (1) fixed-function (SFIT), in which each EOS term is previously specified and unaltered; (2) stepwise regression (PFIT), in which single EOS terms are added on the basis of their statistical significance; and (3) a selection algorithm (WFIT), that both adds and removes EOS terms on the basis of statistical significance/insignificance. Although these methods can indicate that an EOS might more accurately predict each property with the addition of other properties, they do not completely address the effects of error propagation in terms of a **final** regressed weight for each property. Recommendations for these final weights are discussed below.

At this point, the author of this work recommends a thermodynamic approach that applies a previously-reported statistical approach. For instance, the application of other statistical methods might extend the work by Jacobsen et al. (1988). As noted in a statistical paper by Marx (1996), these methods include iteratively-reweighted partial-least squares (IRPLS), in which the weights are iteratively regressed to arrive at optimal weights for each property. IRPLS extends the concept of partial-least squares (PLS), in which some weights are regressed while others are held constant. Consequently, if IRPLS were applied to the MPA regression scheme, the resultant weights of these properties might be ascertained more readily.

Moreover, the attempt reported above by the author of this work on different fixed weights for vapor pressure and density also suggests the following

thermodynamic approach in addition to the statistical one. Specifically, since different components reflect slightly different trends in the AARD accuracy of either property, an investigator could choose whether or not to employ **different** property weights for **each** pure component. This approach would coincide with the thermodynamic principle of corresponding states, namely, that different pure components with the same reduced properties exhibit similar behavior (Walas, p. 16, 1985), an idea that has been extended by various researchers including, for example, Stiel (1968). Furthermore, the different property weights for each pure component could in turn be asymmetrically averaged through the GAR. The additional GAR parameters regressed in averaging the pure-component property weights would thus allow for a greater number of modeling options in the prediction of mixture thermodynamic properties.

Of course, it is commonly known that the corresponding-states principle does not apply to certain substances (e.g., water and hydrogen), yet it does lend credit to the fact that different components do exhibit different behavior, a fact that certainly supports this idea. Indeed, the idea of regressing pure-component and/or mixture property weights has not previously been suggested in any publication of which the author is aware and is put forth herein as an original idea suggested by the author of this work.

CHAPTER IV

THE GENERALIZED ASYMMETRIC RULE (GAR)

4.1 Introduction and Overview

The generalized asymmetric rule (herein referred to as the GAR) represents a more universal method by which pure-component chemical parameters may be averaged. Such averages then yield unlike-interaction parameters for the prediction of either binary and/or multicomponent mixtures. More specifically, the GAR provides a representation of the asymmetric effects that occur in mixtures of dissimilar chemical components. These mixtures may consist of, for example, polar-nonpolar, polar-associating, and nonpolar-associating components.

The GAR originates from its predecessor, herein referred to as the generalized symmetric rule (referred to as the GSR in this work) by Wenzel et al. (Juris, 1970; Juris and Wenzel, 1974) . Section 4.2 therefore describes the innovation of the GSR and its subsequent applications. Finally, Section 4.3 then discusses the derivation of the GAR from Wenzel et al.'s GSR (Juris, 1970; Juris and Wenzel, 1974) , along with the GAR's subsequent applications as presented in this work.

4.2 The Generalized Symmetric Rule (GSR)

Roughly thirty years ago, Leonard Wenzel et al. (Juris, 1970; Juris and Wenzel, 1974) introduced the concept of a generalized symmetric combining rule for

combining pure-component parameters. This combining rule, herein referred to as the GSR, took the form of

$$\text{GSR:} \qquad B_{ij} = \frac{\left[B_i^N + B_j^N\right]^{1/N}}{2^{1/N}} \quad . \qquad (4.1)$$

As outlined in Juris (1970, p. 19-22), the GSR surmounted the complexity of various combining rules assigned to the unlike-interaction parameters of a given mixture equation of state (EOS).

Next, Juris (1970, p. 19-22) reviewed the following four combining rules in Equations (4.2-4.5) and described how each of them constituted limiting cases of the GSR of Equation (4.1):

$$\text{Linear} \quad (N = 1): \qquad B_{ij} = \frac{\left(B_i + B_j\right)}{2} \quad . \qquad (4.2)$$

$$\text{Geometric} \quad \left(\lim_{N \downarrow 0}\right): \qquad B_{ij} = \sqrt{B_i B_j} \quad . \qquad (4.3)$$

$$\text{Lorentz} \quad (N = 1/3): \qquad B_{ij} = \frac{\left(B_i^{1/3} + B_j^{1/3}\right)^3}{8} \quad . \qquad (4.4)$$

$$\text{Halsey-Fender} \ (N = -1): \qquad B_{ij} = \frac{2B_i B_j}{\left(B_i + B_j\right)} \quad . \qquad (4.5)$$

As seen above, the GSR of Equation (4.1) becomes (a) the linear combining rule of Equation (4.2) with a value of N equal to unity $(N = 1)$, (b) the geometric combining rule of Equation (4.3) when the value of N asymptotically approaches zero as a limit

(i. e., $\lim_{N \downarrow 0}$), (c) the Lorentz combining rule of Equation (4.4) with a value of N equal to one-third ($N=1/3$), and (d) the Halsey-Fender (Fender, 1962), or harmonic, combining rule of Equation (4.5) with a value of N equal to unity ($N = -1$). Obviously, the special cases of both the linear and Lorentz combining rules may be obtained from Equation (4.1) by direct substitution of the appropriate values of N; the more complex derivations for both the geometric and Halsey-Fender (Fender, 1962) combining rules are provided in Sections A.3.1 and A.3.2 of Appendix A.

4.3 The Generalized Asymmetric Rule (GAR)

The concept for the GAR arose from the GSR as first introduced by Wenzel et al. (Juris, 1970; Juris and Wenzel, 1974). To begin with, the author first encountered the rearranged form of the Lorentz mixing rule of Equation (4.4),

$$B_X = \frac{1}{4}\sum_{j=1}^{n} x_i B_i + \frac{3}{4}\sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j B_i^{2/3} B_j^{1/3} \quad , \qquad (4.6)$$

in Bloomer et al. (1953). In their work, Bloomer et al. (1953) applied Equation (4.6) to the mixture parameter, B_0, of the Benedict-Webb-Rubin (BWR) equation of state (Benedict et al., 1940) to predict methane-ethane pressure-volume-temperature (PVT) mixtures of methane and ethane. The application of Equation (4.6) stemmed from similar work performed by Benedict et al. (1942) in the prediction of PVT mixture data that consisted of the pairing of methane with ethane, propane, and n-butane. This use of Equation (4.6) by Benedict et al. (1942) was in turn adapted from its prior use by Beattie and Ikehara (1930) on the Beattie-Bridgeman (1927) equation of state

(EOS) parameter, B_0, as well. Beattie (p. 266, 1955) provides a detailed discussion on the application of Equation (4.6), while a complete derivation of Equation (4.6) from the second-virial mixture form of Equation (4.4) presented by the author of this dissertation may be seen in Appendix B.

The second-virial combining rule of Equation (4.6) could, however, be applied independently as

$$B_{ij} = B_i^{2/3} B_j^{1/3} \quad . \qquad (4.7)$$

Here, the author noticed that, although the GSR of Equation (4.5) constitutes a generalized case of Equations (4.1-4.4), it did not constitute a generalized case for Equation (4.7). Accordingly, the closest approximation to Equation (4.7) may be achieved by multiplying the geometric combining rule of Equation (4.2) by the term $B_i^{\alpha} B_j^{-\alpha}$ to yield

$$B_{ij} = B_i^{1/2+\alpha} B_j^{1/2-\alpha} \quad . \qquad (4.8)$$

Consequently, Equation (4.8) becomes equivalent to Equation (4.7) when $\alpha = 1/6$. Initially, then, the author modified Wenzel et al.'s (Juris, 1970; Juris and Wenzel, 1974) GSR by multiplying Equation (4.1) by the term $B_i^{\alpha} B_j^{-\alpha}$ to obtain

$$B_{ij} = \frac{B_i^{\alpha} B_j^{-\alpha} \left[B_i^N + B_j^N \right]^{1/N}}{2^{1/N}} \quad , \qquad (4.9)$$

a generalized combining rule with <u>geometric asymmetry</u>.

Later, the author realized that, if Equation (4.1) can be modified to yield geometric asymmetry, it could also be modified to yield linear asymmetry. Consequently, the author modified the linear portion of Equation (4.9) -- through multiplication of the term B_i^N by γ and the term B_j^N by $(2-\gamma)$ -- to yield the GAR as

$$\boxed{B_{ij} = \frac{B_i^{\alpha} B_j^{-\alpha}\left[\gamma B_i^N + (2-\gamma) B_j^N\right]^{1/N}}{2^{1/N}}} \quad . \qquad (4.10)$$

The GAR of Equation (4.10) thus presents a more generalized combining rule than the GSR, with the GSR constituting a special case of the GAR when $\alpha = 0$ and $\gamma = 1$.

As seen above, Equation (4.10) represents the GAR as a second-virial combining rule and in third-virial form becomes

$$C_{ijk} = \frac{C_i^{\alpha} C_j^{\beta} C_k^{-\alpha-\beta}\left[\gamma C_i^N + \delta C_j^N + (3-\gamma-\delta) C_k^N\right]^{1/N}}{3^{1/N}} \quad , \qquad (4.11)$$

while in any higher-virial (e.g., *Wth*) form, Equation (4.10) becomes

$$D_{ij\cdots(n-1)n} = \left\{ D_i^{\alpha(1)} D_j^{\alpha(2)} \cdots D_{n-1}^{\alpha(W-1)} D_n^{\left[-\alpha(1)-\alpha(2)-\cdots-\alpha(W-1)\right]} \right\}$$

$$\times\left\{\frac{\left[\gamma_{(1)}D_i^N+\gamma_{(2)}D_j^N+\cdots+\gamma_{(W-1)}D_{n-1}^N+\left(W-\gamma_{(1)}-\gamma_{(2)}-\cdots-\gamma_{(W-1)}\right)D_n^N\right]^{1/N}}{W^{1/N}}\right\} \qquad (4.12)$$

This work solely employs the GAR as a second-virial combining rule, since it employs the local composition model (LCM) as presented by Li et al. (1986), which itself exists as a second-virial mixture model. Since the LCM as well as many other mixture equations of state presently employ binary interaction parameters (BIPs), Section 4.4 outlines the underlying concepts for the conversion of BIPs to GARs. Moreover, since the LCM constitutes a multifluid equation of state, use of the GAR in the LCM presents the potential for improving the accuracy of single-fluid equations of state. Section 4.6 discusses this potential in detail.

4.4 Conversion of Binary Interaction Parameters (BIPs) to Generalized Asymmetric Rules (GARs)

4.4.1 Introduction

Much data have been presented in the thermodynamic literature on binary interaction parameters (BIPs) for various equations of state (EOS). Consequently, the conversion of results reported in the form of BIPs to that of GARs will prove useful, especially to researchers desiring to extend the predictions of a given EOS to other chemical systems.

4.4.2 Brief Description of Combining and Mixing Rules

For single-fluid equations of state (EOS), a typical, second-virial mixture parameter, B_x, may be related to its pure-component compositions by the relation

$$B_x = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j B_{ij} \quad . \qquad (4.13)$$

Here, n represents the number of components, x_i and x_j represent the compositions of pure components i and j, respectively, and B_{ij} represents the unlike interaction occurring between components i and j. Of course, the numerical value for B_{ij} typically represents some sort of numerical average of the pure-component parameter values B_i and B_j (again for components i and j, respectively). This average, known as a combining rule, exists in a variety of forms throughout the literature (e.g., linear, geometric, etc.).

At this point, it should be noted that a combining rule (as represented by the average B_{ij}) constitutes a portion of a mixing rule. As seen on the right-hand side of Equation (4.13), a mixing rule represents the overall expression for a mixture parameter (in this case, for B_x) that includes both the pure-component compositions x_i and x_j as well as the unlike interactions occurring between the pure components (in this case, B_{ij}).

This work observes the convention of combining and mixing rules. Moreover, it should be noted that the GAR simply represents a combining rule only. Nevertheless, since the GAR may be applied to other fields outside of

thermodynamics (e.g., genetics) to yield asymmetric averages of other types of parameters, the author chose to eliminate the word "combining" from the GAR acronym.

4.4.3 Brief Description of Binary Interaction Parameters (BIPs)

In general, binary interaction parameters (BIPs) serve as **nonideal** correction factors to combining-rule averages. Such corrections then enable a given mixture equation of state (EOS) to predict binary mixtures with greater accuracy. For example, Equation (4.13) may be "corrected" according to the relation

$$B_x = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \left(1 - k_{ij}\right) B_{ij} \quad , \qquad (4.14)$$

where k_{ij} represents the BIP correcting for the unlike interaction occurring between components i and j, typically represented by symmetric relations for B_{ij}. In other words, this BIP corrects for the "nonideal," or asymmetric, aspect of binary chemical mixtures as opposed to the "ideal," or symmetric, aspect of binary chemical mixtures. This ideal aspect may be seen in Equations (4.1-4.5), where the numerical value of the combining-rule average lies exactly halfway between that of the pure components for the combining rule of choice. In fact, if a binary mixture were ideal (i. e., the pure-component parameter values averaged evenly), the numerical value of the BIP would be zero, thereby making Equation (4.14) equivalent to Equation (4.13). Otherwise, BIPs are usually regressed with a small starting value, thereby resulting in a final

value of $(1-k_{ij})$ differing from unity depending on the relative degree of nonideality between two components.

Typically, most binary interaction parameters in the thermodynamic literature have been presented as symmetric unlike interactions. (In fact, at this time the author is not aware of any usage of asymmetric unlike interactions involving BIPs). Nevertheless, the following sections explain how asymmetrical BIPs may be employed for a given unlike-interaction parameter with respect to GARs.

4.4.4 Separation of Like and Unlike Interactions

Equation (4.1) contains both like and unlike interactions between molecules. On further examination of Equation (4.1), however, the like interactions between **similar** pure-component molecules (i. e., B_{ii} and B_{jj}) may be separated from the unlike interactions between **dissimilar** pure-component molecules (i. e., B_{ij} and B_{ji}). Equation (4.13) then becomes

$$B_x = \sum_{i=1}^{n} x_i x_i B_{ii} + \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j B_{ij} \quad , \qquad j \neq i . \tag{4.15}$$

After simplification, Equation (4.15) becomes

$$B_x = \sum_{i=1}^{n} x_i^2 B_{ii} + \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j B_{ij} \quad , \qquad j \neq i . \tag{4.16}$$

Furthermore, since the term B_{ii} in Equation (4.16) solely represents interactions between molecules of component *i*, it may be represented by the pure-component parameter, B_i, such that

$$B_i = B_{ii} \quad . \tag{4.17}$$

Substituting Equation (4.17) into Equation (4.16) yields

$$B_x = \sum_{i=1}^{n} x_i^2 B_i + \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j B_{ij} \quad , \quad j \neq i \, . \tag{4.18}$$

Equation (4.18) effectively separates the like-interaction terms in the first-virial (or single) summation from the unlike-interaction terms in the second-virial (or double) summation. More importantly, Equation (4.10) provides the starting relation for the conversion of binary interaction parameters (BIPs) into GARs. First, Section 4.4.5. discusses the comparative equations for like and unlike interactions, while Section 4.4.6 presents comparative equations for asymmetrical BIPs and asymmetrical GARs. Finally, Section 4.4.7 illustrates the comparative equations for symmetrical BIPs and asymmetrical GARs.

4.4.5 Comparative Equations for Like and Unlike Interactions

For symmetrical unlike interactions,

$$B_{ij} = B_{ji} \quad . \tag{4.19}$$

Substituting Equation (4.19) into Equation (4.18) yields

$$B_x = \sum_{i=1}^{n} x_i^2 B_i + 2 \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} x_i x_j B_{ij} \quad . \tag{4.20}$$

For asymmetrical unlike interactions, however,

$$B_{ij} \neq B_{ji} \quad , \tag{4.21}$$

and Equation (4.18) still holds. If BIPs were employed with Wenzel et al.'s (Juris, 1970; Juris and Wenzel, 1974) GSR, Equation (4.1) could be inserted into Equation (4.21) to yield

$$\left(1-k_{ij}\right)\frac{\left[B_i^N + B_j^N\right]^{1/N}}{2^{1/N}} \neq \left(1-k_{ji}\right)\frac{\left[B_j^N + B_i^N\right]^{1/N}}{2^{1/N}} \quad . \tag{4.22}$$

Since the GSR is symmetric, it may be factored out of Equation (4.22), leaving

$$\left(1-k_{ij}\right) \neq \left(1-k_{ji}\right) \tag{4.23}$$

and finally,

$$k_{ij} \neq k_{ji} \quad . \tag{4.24}$$

In the typical literature case of symmetric BIPs,

$$k_{ij} = k_{ji} \quad . \tag{4.25}$$

Next, since GARs remain asymmetric in nature as long as $\alpha \neq 0$ and $\gamma \neq 1$, they will always follow Equation (4.21) with

$$B_{ij} = \frac{B_i^{\alpha} B_j^{-\alpha}\left[\gamma B_i^N + (2-\gamma)B_j^N\right]^{1/N}}{2^{1/N}} \tag{4.26}$$

and

$$B_{ji} = \frac{B_j^{\alpha} B_i^{-\alpha}\left[\gamma B_j^N + (2-\gamma)B_i^N\right]^{1/N}}{2^{1/N}} \quad . \tag{4.27}$$

Here, it should be noted that this work applies only symmetric unlike-interaction parameters within the GAR. In other words,

$$\alpha_{ij} = \alpha_{ji} \quad , \tag{4.28}$$

$$N_{ij} = N_{ji} \quad , \tag{4.29}$$

and

$$\gamma_{ij} = \gamma_{ji} \quad . \tag{4.30}$$

In following the above convention of Equations (4.28-4.30) throughout this work, the *ij* subscripts become unnecessary for the parameters of the GAR and are therefore omitted from the GAR equations presented in this work, e. g., as in Equation (4.10).

4.4.6 Comparative Equations for Asymmetrical BIPs and Asymmetrical GARs

For the atypical case of **asymmetrical** BIPs and asymmetrical GARs, $B_{ij}^{(BIP)}$ and $B_{ji}^{(BIP)}$ represent the respective *i-j* and *j-i* unlike interactions obtained from any given combining rule through BIPs. Accordingly, the same unlike interactions may be represented by GARs through similar unlike-interaction parameters, $B_{ij}^{(GAR)}$ and $B_{ji}^{(GAR)}$. This convention then applies to both single- and multi-fluid equations of state, respectively.

For a single-fluid mixture, Equation (4.18) may be presented through BIPs as

$$B_x^{(BIPs)} = \sum_{i=1}^{n} x_i^2 B_i + \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j B_{ij}^{(BIP)} \quad , \qquad j \neq i \, . \tag{4.31}$$

Likewise, Equation (4.18) may be presented in terms of GARs as

$$B_x^{(GARs)} = \sum_{i=1}^{n} x_i^2 B_i + \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j B_{ij}^{(GAR)} \quad , \qquad j \neq i . \tag{4.32}$$

Next, since both BIPs and GARs may be used to calculate the mixture-fluid parameter B_x of Equation (4.18), their two separate mixture expressions may be set equivalent to one another in the form

$$B_x^{(BIPs)} = B_x^{(GARs)} \quad . \tag{4.33}$$

The substitution of Equations (4.31) and (4.32) into Equation (4.33) then yields

$$\sum_{i=1}^{n} x_i^2 B_i + \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j B_{ij}^{(BIP)} = \sum_{i=1}^{n} x_i^2 B_i + \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j B_{ij}^{(GAR)} \quad ,$$

$$j \neq i \quad . \tag{4.34}$$

Since the first-virial summations for B_i on both sides of Equation (4.34) solely represent pure-component parameters, they are equivalent to one another and may be subtracted to obtain

$$\sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j B_{ij}^{(BIP)} = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j B_{ij}^{(GAR)} \quad , \qquad j \neq i . \tag{4.35}$$

Since the same summation limits hold for both sides of Equation (4.35), they may then be eliminated, resulting in

$$x_i x_j B_{ij}^{(BIP)} + x_j x_i B_{ji}^{(BIP)} = x_i x_j B_{ij}^{(GAR)} + x_j x_i B_{ji}^{(GAR)} \quad , \; j \neq i \; .$$

(4.36)

Next, the term $x_i x_j$ may be factored out of both sides of Equation (4.36) to yield

$$B_{ij}^{(BIP)} + B_{ji}^{(BIP)} = B_{ij}^{(GAR)} + B_{ji}^{(GAR)} \quad , \qquad j \neq i . \tag{4.37}$$

Obviously, it could be inferred from Equation (4.35) that

$$B_{ij}^{(BIP)} = B_{ij}^{(GAR)} \quad , \quad j \neq i \tag{4.38}$$

and

$$B_{ji}^{(BIP)} = B_{ji}^{(GAR)} \quad , \quad j \neq i \, . \tag{4.39}$$

Equations (4.38) and (4.39) also hold for a multi-fluid equation of state.

4.4.7 Comparative Equations for Symmetrical BIPs and Asymmetrical GARs

For the typical case of **symmetrical** BIPs and asymmetrical GARs, $B_{ij}^{(BIP)}$ and $B_{ji}^{(BIP)}$ represent the respective *i-j* and *j-i* unlike interactions obtained from any given combining rule through BIPs. Since the BIPs in this case are symmetric, however, Equation (4.19) holds and becomes

$$B_{ij}^{(BIP)} = B_{ji}^{(BIP)} \quad . \tag{4.40}$$

Next, the same unlike interactions may be represented by GARs through the asymmetric unlike-interaction parameters, $B_{ij}^{(GAR)}$ and $B_{ji}^{(GAR)}$. Once more, this convention also applies to both single- and multi-fluid equations of state, respectively.

For a single-fluid mixture, Equation (4.20) may be presented in terms of symmetric unlike interactions (see Section 4.4.5) through BIPs as

$$B_x^{(BIPs)} = \sum_{i=1}^{n} x_i^2 B_i + 2 \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} x_i x_j B_{ij}^{(BIP)} \, , \quad j \neq i \quad . \tag{4.41}$$

Likewise, Equation (4.18) may again be presented in terms of GARs as

$$B_x^{(GARs)} = \sum_{i=1}^{n} x_i^2 B_i + \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j B_{ij}^{(GAR)} \quad , \qquad j \neq i \quad . \tag{4.42}$$

Next, since both BIPs and GARs may be used to calculate the mixture-fluid parameter, B_x, of Equation (4.18), their two separate mixture expressions may once more be set equivalent to one another in the form

$$B_x^{(BIPs)} = B_x^{(GARs)} \quad . \tag{4.43}$$

The substitution of Equations (4.41) and (4.42) into Equation (4.43) then yields

$$\sum_{i=1}^{n} x_i^2 B_i + 2 \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} x_i x_j B_{ij}^{(BIP)} = \sum_{i=1}^{n} x_i^2 B_i + \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j B_{ij}^{(GAR)} \, ,$$

$$j \neq i \quad . \tag{4.44}$$

Since the first-virial summations for B_i on both sides of Equation (4.44) solely represent pure-component parameters, they are equivalent to one another and may be subtracted to obtain

$$2 \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} x_i x_j B_{ij}^{(BIP)} = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j B_{ij}^{(GAR)} \, , \qquad j \neq i \, . \tag{4.45}$$

Since the same summation limits hold for both sides of Equation (4.45), they may then be eliminated, resulting in

$$2 x_i x_j B_{ij}^{(BIP)} = x_i x_j B_{ij}^{(GAR)} + x_j x_i B_{ji}^{(GAR)} \quad , \qquad j \neq i \, . \tag{4.46}$$

The term $x_i x_j$ may then be factored out of both sides of Equation (4.46) to yield a single-fluid expression of

$$\boxed{2B_{ij}^{(BIP)} = B_{ij}^{(GAR)} + B_{ji}^{(GAR)}} \quad , \quad j \neq i \quad . \qquad (4.47)$$

For a multi-fluid equation of state, it could be inferred from Equation (4.47) that

$$B_{ij}^{(BIP)} = B_{ij}^{(GAR)} \quad , \quad j \neq i \qquad (4.48)$$

and

$$B_{ij}^{(BIP)} = B_{ji}^{(GAR)} \quad , \quad j \neq i \, . \quad . \qquad (4.49)$$

Alternatively, Equation (4.47) could have been obtained by substituting Equation (4.40) into Equation (4.37).

4.5 Advantages of GARs over BIPs

When compared to BIPs, GARs provide three basic advantages over BIPs. First of all, the three GAR parameters provide (a) at least a two- (and possibly even three-) dimensional representation of binary interactions between any two components as opposed to (b) the typical one-dimensional representation between two components provided by symmetric BIP values. This feature of the GAR thus allows for a clearer "mapping" of binary interactions between said components that can even be used to estimate unlike interactions for missing binary data.

Second, the GAR parameters also provide a relative indication of exactly how much one component may outweigh the other (in terms of mixture effects) for a given unlike-interaction parameter. The GAR therefore offers much potential in fields outside of thermodynamics whenever any given set of numbers must be averaged asymmetrically. As mentioned in Section 4.3, the GAR parameter α provides an

indication of relative geometric asymmetry, while the GAR parameter γ provides an indication of relative linear asymmetry. When used together, these two parameters can further provide a sort of "fine-tuning" effect that can optimize any required asymmetric average.

Third, GARs prevent the possibility of divergence that can occur when regressing either asymmetric BIPs or directly regressing the values of the unlike-interaction parameters themselves. For example, when regressing the actual unlike-interaction values, these values can either (a) diverge from one another in the course of the regression or (b) remain too highly correlated such that one of the two values remains too close to its initial estimate while the other adjusts to accommodate it. The GARs of Equations (4.10-4.12) therefore offer a **nondivergent, asymmetric, unlike-interaction mechanism** that guarantees a reliable asymmetry model between any two (or more) components for the mixture parameters of any given EOS.

4.6 Accuracy versus Single- and Multi-Fluid Equations of State

Most importantly with regard to Section 4.3, the potential of achieving greater predictive accuracy through the GAR with single-fluid equations of state (EOS) should be considered. First of all, whether BIPs or GARs are used for a given mixture parameter such as B_x of Equation (4.13), it should be noted that all BIP or GAR terms will always sum to that mixture parameter. In other words, **single-fluid models do not discriminate between symmetry and asymmetry** *per se* as seen in BIPs and

GARs. Instead, they simply "lump" all unlike-interaction terms together regardless of their model formulation.

As a consequence of this situation, whether one replaces either (a) asymmetric BIPs with GARs through Equations (4.38) and (4.39) **or** (b) symmetric BIPs with GARs through Equation (4.47), this replacement will in all likelihood not accomplish more than simply replace one numerical value with another. As a result, GARs will probably not achieve greater accuracy for a single-fluid EOS. Nevertheless, this minor limitation of single-fluid models can be surmounted when the EOS of interest is couched in the form of a multi-fluid EOS.

To this end, the local composition model (LCM) of Li et al. (1986) as described in Chapter 6 provides an excellent multi-fluid framework into which any mixture EOS may be placed and therefore constitute a second-virial, multi-fluid EOS. Here, the combined natural logarithmic and exponential terms (as found in the LCM mixture pressure and fugacity expressions) will yield asymmetric additive expressions that do accommodate and therefore reflect the asymmetrical properties of GARs. In other words, **multi-fluid models do discriminate between symmetry and asymmetry** *per se*.

CHAPTER V

SPECIAL CASES FOR THE

GENERALIZED ASYMMETRIC RULE (GAR)

5.1 Introduction

Although the second-virial version of the generalized asymmetric rule (GAR) of Equation (4.10),

$$\text{GAR:} \qquad B_{ij} = \frac{B_i^{\alpha} B_j^{-\alpha} \left[\gamma B_i^N + (2-\gamma) B_j^N \right]^{1/N}}{2^{1/N}} \quad , \qquad (5.1)$$

contains three parameters, not all of them need be regressed simultaneously against a given set of binary data. Indeed, special cases arise that make it advantageous to keep one (or even two) GAR parameters constant while regressing the other parameter(s). This chapter therefore discusses these special cases in detail to reflect this need to hold certain GAR parameters constant in different situations while regressing others.

5.2 Holding the Symmetric GAR parameter *N* Constant

As seen in Wenzel et al.'s (Juris, 1970; Juris and Wenzel, 1974) generalized symmetric rule (GSR) of Equation (4.1), the symmetric parameter N plays a very significant role in determining the actual form of a given combining rule. As this parameter yields the four common combining rules of Equations (4.2) through (4.5), it then becomes obvious that N will play an even more significant role in determining

the values of both α and γ. This section thus discusses the reasoning behind holding N constant for the applications presented in this work.

To begin with, taking the limit as N approaches zero for the GAR follows a mathematical derivation similar to that of the GSR. First, Appendix Section A.3 demonstrates this limiting-case derivation for the GSR, while Appendix Section A.4 shows this limiting-case derivation for the GAR. Second, in repeating the result of the GAR derivation of Equation (A.36) of Appendix Section A.4.1,

$$\therefore \lim_{N \downarrow 0} \frac{B_i^{\alpha} B_j^{-\alpha} \left[\gamma B_i^N + (2-\gamma) B_j^N \right]^{1/N}}{2^{1/N}} = B_i^{\left(\alpha + \frac{\gamma}{2}\right)} B_j^{\left(1-\alpha-\frac{\gamma}{2}\right)} \quad , \qquad (5.2)$$

it becomes obvious that, as N approaches zero, the other two parameters α and γ gradually coalesce to the point of functioning as a single parameter. This single parameter may be viewed as the term $\left(\alpha + \frac{\gamma}{2}\right)$ -- in this case, an asymmetric-geometric parameter that incorporates the two basic mathematical operations of multiplication and/or division.

To be sure, a good model should employ the four basic mathematical operations: (1) addition, (2) subtraction, (3) multiplication and (4) division. Here, the linear GAR parameter γ employs the first two operations (i.e., addition/subtraction), while the geometric parameter α employs the last two operations (i.e., multiplication/division). Consequently, it seems only logical that the greatest fine-tuning of a given unlike-interaction parameter (UIP) value can be effected **only when**

both the first two and last two operations can occur independently of one another. Moreover, since these two sets of operations will occur independently of each other when α and γ do not coalesce in the limit as N approaches zero, N should therefore be held constant to allow α and γ to perform both sets of operations.

At this point, the question arises: To which value should N be held constant? The simulations performed in this work to predict binary vapor-liquid equilibrium (VLE) systems indicate that more accurate predictions are obtained when $N = 1$. In fact, this simple choice of unity for N also allows for a simpler interpretation of the parameter γ when raised to the power of $\frac{1}{N}$ (now only the power of unity) in Equation (5.1) of the GAR. Here, with $N = 1$, Equation (5.1) becomes

$$B_{ij} = \frac{B_i^{\alpha} B_j^{-\alpha} \left[\gamma B_i + (2-\gamma) B_j \right]}{2} \quad . \tag{5.3}$$

This choice of $N = 1$ thus appears at the time of this writing as the best choice for the GAR.

Finally, the desired representation obtained becomes important when holding the symmetric parameter N constant in general, not just as $N = 1$. As noted in Section 4.5 of Chapter 4, GARs offer a distinct advantage over binary interaction parameters (BIPs) in that their two parameters α and γ in Equation (5.1) can yield a two-dimensional representation for a given UIP, as opposed to the more limited one-dimensional representation afforded by BIPs. Furthermore, this two-dimensional representation could later be made three-dimensional if (1) α and γ were, for

example, first regressed with $N = 1$, and then (2) α and γ were held constant while regressing N. If, then, N were regressed at this point, an even greater distinction could be made between the values of each UIP for different binary systems, especially for those systems that might yield similar values of α and γ (e.g., for binary systems containing one component as paired with different isomers).

Altogether, the above features afforded by holding the symmetric parameter N constant -- at least for the first regression stage in step (a) above -- most definitely do not restrict the widespread applicability of the GAR. Rather, these features enhance the GAR in terms of its other asymmetric parameters, α and γ. As a result, all simulation results presented in this work hold N constant at a value of $N = 1$.

5.3 Holding the Asymmetric-Geometric GAR Parameter Constant

As seen in Equation (5.1), the asymmetric-geometric GAR parameter α allows for a variable degree of asymmetry within the form of a **geometric combining rule**. Nevertheless, certain cases can arise -- i.e., in terms of the numerical values of pure-component parameters -- that favor holding α constant and regressing either γ and/or N instead. This section presents a discussion on two such cases as follows: (1) pure-component parameters with negative numerical values and (2) pure-component parameters with numerical values of zero.

5.3.1 Pure-Component Parameters with Negative Numerical Values

When pure-component parameters have negative numerical values, caution must be applied concerning which values should be used for the asymmetric-geometric parameter, α. Obviously, if either $\alpha \leq -1$ or $\alpha \geq 1$, any UIP of interest may calculated from negative pure-component parameter values. Computationally, this may be achieved in FORTRAN by taking the opposite sign(s) of each negative pure-component value(s), calculating the now-positive pure-component value to the power of $\pm\alpha$, and again taking the opposite sign(s) of each value(s) obtained.

If, however, $-1 < \alpha < 1$, partial roots of the pure-component parameters will be obtained. For negative pure-component values, the partial roots will result in imaginary values for the UIPs regardless of the computational procedure adopted. This situation typically constitutes an undesirable result in thermodynamic, combining-rule applications. Moreover, the same situation could occur in terms of the symmetric GAR parameter, N, when $-1 < N < 1$ as well. In such cases, if $\alpha = 0$, then both pure-component parameters B_i and B_j become equal to unity, thereby eliminating the GAR's asymmetric-geometric effect altogether. In addition, this undesirable result may also be avoided for N through the assignment of $N = 1$.

Unfortunately, an unconstrained regression algorithm may inadvertently adjust either the asymmetric-geometric parameter, α, and/or the symmetric parameter, N, so that it/they reside(s) within the undesirable ranges of $-1 < \alpha < 1$ and/or $-1 < N < 1$, respectively. In addition, this situation becomes further compounded by the fact that the above two ranges typically include values for α and

N that tend to yield UIP values from positive pure-component parameters. Such values may be seen, for example, in the values of N approaching zero ($\lim_{N \downarrow 0}$) for the geometric combining rule and $N = 1/3$ for the Lorentz combining rule of Equations (4.3) and (4.4), respectively, in Chapter 4. As a similar range of values are likely to result for α and N in terms of negative pure-component parameters for an unconstrained regression algorithm, a constrained regression algorithm might prove more desirable.

Furthermore, although a constrained regression algorithm might avoid the range values for α and N, this situation cannot necessarily be guaranteed. In fact, when applying a given penalty function to the objective function of a regression algorithm, as in the flexible-tolerance method (Himmelblau, p. 341), it may happen that the **near-feasible region** -- in this case, the region for the parameter values of α and N lying slightly within their undesirable ranges -- may contain optimal parameter values for α and N in the first place. In other words, neither a constrained regression algorithm nor an unconstrained regression algorithm may keep values of α and N outside of $-1 < \alpha < 1$ and $-1 < N < 1$.

To safeguard against and avoid completely the undesired result of imaginary UIP values, the author of this work recommends the following choices for α and N: First, α should be held equal to zero, thereby making both pure-component parameters B_i and B_j equal to unity, thus eliminating the GAR's asymmetric-geometric effect altogether. Second, to retain the asymmetric effect of the GAR, γ

should be regressed instead of α to utilize the GAR's linear asymmetry. Finally, N should be held equal to unity, a choice recommended for other reasons discussed in Section 5.2. These same recommendations are suggested for both α and N in the following section on pure-component parameters with numerical values of zero.

5.3.2 Pure-Component Parameters with Numerical Values of Zero

Of course, when pure-component parameters have numerical values of zero, they will yield numerical values of zero when raised to any power(s) of α and/or N in the GAR. This particular situation then eliminates the need for using any given value(s) of α and/or N in the first place. Such a situation may be viewed in light of the following illustration: For example, suppose that for the GAR of Equation (5.1), B_i represents a positive pure-component parameter, and $B_j = 0$. Consequently, B_j will then make the entire value of B_{ij} in Equation (5.1) equal to zero. To forestall this possibility, α should be held equal to zero while regressing γ instead, as recommended in Section 5.3.1. When $\alpha = 0$, Equation (5.1) becomes

$$B_{ij} = \frac{\left[\gamma B_i^N + (2-\gamma) B_j^N\right]^{1/N}}{2^{1/N}} \quad . \qquad (5.4)$$

The insertion of $B_j = 0$ into Equation (5.4) then yields

$$B_{ij} = \frac{\left[\gamma B_i^N + (2-\gamma)(0)\right]^{1/N}}{2^{1/N}} = \frac{\left[\gamma B_i^N + 0\right]^{1/N}}{2^{1/N}} = \frac{\left[\gamma B_i^N\right]^{1/N}}{2^{1/N}} = \frac{\gamma^{1/N} B_i}{2^{1/N}} \quad . \qquad (5.5)$$

$$\therefore B_{ij} = \left(\frac{\gamma}{2}\right)^{1/N} B_i \qquad . \qquad (5.6)$$

In Equation (5.6), both γ and N now represent simple scaling factors for B_i. Since only one scaling factor proves necessary, N should be held equal to unity (as in Sections 5.2 and 5.3.1). This choice reduces Equation (5.6) to

$$B_{ij} = \left(\frac{\gamma}{2}\right) B_i \qquad . \qquad (5.7)$$

To sum up, α should be held equal to zero and N should be held equal to unity when encountering pure-component parameters with numerical values of zero.

5.4 Holding the Asymmetric-Linear GAR Parameter Constant

As seen in Equation (5.1), the asymmetric-linear GAR parameter, γ, allows for a variable degree of asymmetry within the form of a **linear combining rule**. As with the asymmetric-geometric GAR parameter, α, certain cases can arise that favor holding γ constant and regressing either α and/or N instead. Unlike the cases described in Section 5.3, however, only one special case generally occurs with γ : invoking a sign change in the pure-component parameters when generating the UIP of interest.

To be sure, different values of α, γ, and/or N will incorporate different proportions of pure-component parameters B_i and B_j in Equation (5.1). Consequently, when B_i and B_j contain opposite signs, these differing proportions can yield unlike-interaction values of either sign. Nevertheless, when B_i and B_j

contain the same sign, γ (unlike α and N) can still invoke a sign change either when $\gamma < 0$ or when $\gamma > 2$. Here, a "normal" range of values for γ might include $0 \leq \gamma \leq 2$, with a value of $\gamma = 0$ completely favoring B_i, and a value of $\gamma = 2$ completely favoring B_j.

Finally, in any of the above cases, the symmetric parameter N can compound the problem of sign change. Here, this may occur when $-1 < N < 1$ and γ yields a negative term inside the expression $\left[\gamma B_i^N + (2-\gamma) B_j^N\right]^{1/N}$ of Equation (5.1). As in the case of negative pure-component parameter values in Section 5.3.1, this situation can also result in imaginary values for the UIPs. As a result, the author once again recommends (as in Sections 5.2 and 5.3) holding $N = 1$.

In addition to obtaining imaginary values for UIPs with $N \neq 1$, other unfavorable conditions may arise from invoking sign changes through the asymmetric-linear parameter, γ. For instance, the need may occur to obtain UIP values B_{ij} and B_{ji} of only one sign -- i.e., only positive or only negative -- so as to render a given thermodynamic model computationally feasible. These potential circumstances may be illustrated by the local composition model (LCM) of Li et al. (1986) discussed in Chapter 6 of this work.

First, the local composition model (LCM) of Li et al. (1986) contains the UIPs F_{ij} and F_{ji}. These parameters, referred to as coordination volume characterization ratios for a mixture, occur inside the natural-logarithmic terms of the

LCM Helmholtz expression of Equation (6.1) as well as the LCM fugacity expression of Equation (6.4). Obviously, the numerical values of both F_{ij} and F_{ji} must be positive since both the molar fractions and exponential terms are positive by definition. Second, Li et al. (1986) define F_{ij} and F_{ji} in Equations (6.9) and (6.10) as

$$F_{ij} = \frac{V_{ij}^*}{V_{jj}^*} = \frac{V_{ij}^*}{V_j^*} \tag{5.8}$$

and

$$F_{ji} = \frac{V_{ji}^*}{V_{ii}^*} = \frac{V_{ji}^*}{V_i^*} \quad , \tag{5.9}$$

where both V_i^* and V_j^* represent positive quantities. As a result of these definitions, a sign change through γ cannot be tolerated. For this situation, the author instead recommends holding γ in Equation (5.1) constant at $\gamma = 1$ (and also $N = 1$ as above and in Sections 5.2 and 5.3) while regressing α by itself. These two choices then simplify Equation (5.1) to

$$B_{ij} = \frac{B_i^{\alpha} B_j^{-\alpha} \left[B_i + B_j \right]}{2} \quad . \tag{5.10}$$

To sum up, both γ and N should be held equal to unity when applying the GAR to models that cannot tolerate a sign change while averaging pure-component parameter values in the form of UIP expressions.

CHAPTER VI

ON THE DEVELOPMENT OF PAST AND PRESENT LOCAL COMPOSITION MODELS

6.1 Introduction and Overview

6.1.1 Introduction

This chapter describes the development of local composition models (LCMs) designed to predict both binary and multicomponent vapor-liquid equilibrium (VLE) compositions. More importantly, however, the development of these LCMs later influenced the formulation of the LCM by Li et al. (1986) for this work. As both used and modified herein, the LCM proposed by Li et al. (1986) presented new mixing rules to the Khan-Chung-Lee-Starling (KCLS) equation of state (EOS) developed by Chung et al. (1984).

Overall, as Li et al. (1986) note, previous LCMs had been developed for highly-nonideal liquid mixtures. These LCMs include the Wilson equation (1964), the nonrandom, two-liquid (NRTL) model by Renon and Prausnitz (1968), and the universal quasi-chemical (UNIQUAC) equation by Abrams and Prausnitz (1975). Generally speaking, these models were designed to predict multicomponent VLE compositions with due consideration to local versus bulk compositions in such mixtures.

Furthermore, as seen in Section 6.2, LCM models vary in their choices of symmetrical versus asymmetrical unlike-interaction parameters (UIPs). Specifically,

Li et al. (1986) presented their LCM with only one asymmetric UIP and four symmetric UIPs, all of which were obtained through averages of pure-component parameters (PCPs). This work, however, presents a **first-time modification** of Li et al.'s (1986) LCM through the use of five asymmetric UIPs, each of which is calculated from PCPs through the GAR of Chapter 4. These modifications reflect the intention of obtaining more accurate VLE composition predictions. Consequently, if **any** improvement can be made through asymmetric UIPs (through GARs) as opposed to symmetric UIPs (through BIPs), then the generalized asymmetric rule (GAR) of Chapter 4 would logically find use in other LCMs, with the potential for improving their predictive accuracy as well..

6.1.2 Overview

The following overview describes the arrangement in this chapter of various LCMs. First, Section 6.2 entails the development of previous LCMs that both predate and lead to Li et al.'s (1986) LCM. Second, Section 6.3 discusses the basic equations for the LCM of Li et al. (1986) as well as the modifications made to it this work through the insertion of the GAR described in Chapter 4.

6.2 Development of Previous Local Composition Models (LCMs)

6.2.1 Origin: The Wilson Equation

To begin with, both the LCM and other activity-coefficient models originate from the well-known Wilson (1964) equation. As noted by Walas (p. 192, 1985),

Wilson (1964) defined interactions between two molecules (e.g., molecules *j* and *k*) as a function of local compositions of these two molecules as opposed to their bulk compositions in a fluid mixture. Renon and Prausnitz (1968) show these local compositions in the form of

$$x_{kj} + x_{jj} = 1 \tag{6.1}$$

and

$$x_{jk} + x_{kk} = 1 \tag{6.2}$$

or alternatively,

$$x_{jj} = 1 - x_{kj} \tag{6.3}$$

and

$$x_{kk} = 1 - x_{jk} \tag{6.4}$$

Here, x_{kj} represents the proportion of *k* molecules surrounding a single *j* molecule, while x_{jj} represents the proportion of *j* molecules surrounding a single *j* molecule (i.e., an interaction between identical *j* molecules). Likewise, x_{jk} signifies the proportion of *j* molecules surrounding a single *k* molecule, while x_{kk} signifies the proportion of *k* molecules surrounding a single *k* molecule (in this case, an interaction between identical *k* molecules). Consequently, Equations (6.1) and (6.3) describe the total proportion (summing to unity) of molecules surrounding a single molecule *j*, while Equations (6.2) and (6.4) describe the total proportion of molecules surrounding a single molecule *k*.

Next, Renon and Prausnitz (1968) note that Wilson (1964) then introduced the relation between the local compositions for Equations (6.1) and (6.3) as

$$\frac{x_{kj}}{x_{jj}} = \frac{x_k \exp(-g_{kj} / RT)}{x_j \exp(-g_{jj} / RT)} \quad , \qquad (6.5)$$

where g_{kj} represents the energy of interaction between molecules k and j, g_{jj} represents the energy of interaction between two identical molecules j, and x_j and x_k represent the bulk compositions of components j and k, respectively. The exponential terms in Equation (6.5) may be combined in the form of

$$\frac{x_{kj}}{x_{jj}} = \frac{x_k}{x_j} \exp\left[-\left(g_{kj} - g_{jj}\right) / RT\right] \quad . \qquad (6.6)$$

The insertion of Equation (6.3) into Equation (6.6) yields

$$\frac{x_{kj}}{1 - x_{kj}} = \frac{x_k}{x_j} \exp\left[-\left(g_{kj} - g_{jj}\right) / RT\right] \quad , \qquad (6.7)$$

while the rearrangement of Equation (6.7) leads to

$$x_{kj} = \left(1 - x_{kj}\right) \frac{x_k}{x_j} \exp\left[-\left(g_{kj} - g_{jj}\right) / RT\right] \quad . \qquad (6.8)$$

Consequently,

$$x_{kj}\left\{1 + \frac{x_k}{x_j} \exp\left[-\left(g_{kj} - g_{jj}\right) / RT\right]\right\} = \frac{x_k}{x_j} \exp\left[-\left(g_{kj} - g_{jj}\right) / RT\right], \qquad (6.9)$$

and

$$x_{kj} = \frac{x_k \exp\left[-\left(g_{kj} - g_{jj}\right)/RT\right]}{x_j\left\{1 + \frac{x_k}{x_j}\exp\left[-\left(g_{kj} - g_{jj}\right)/RT\right]\right\}} = \frac{x_k \exp\left[-\left(g_{kj} - g_{jj}\right)/RT\right]}{x_j + x_k \exp\left[-\left(g_{kj} - g_{jj}\right)/RT\right]} \quad . \qquad (6.10)$$

Wilson's (1964) consideration of local-volume compositions V_k and V_j to accompany Equation (6.10) then led to the multicomponent, excess-Gibbs expression

$$\frac{g^E}{RT} = -\left[\sum_{j=1}^{n} x_j \ln\left\{\sum_{k=1}^{n} x_k \frac{V_k}{V_j}\exp\left[-\left(g_{kj} - g_{jj}\right)/RT\right]\right\}\right] \qquad (6.11)$$

and the activity-coefficient expression

$$\ln(\gamma_i) = \left[1 - \ln\left\{\sum_{k=1}^{n} x_k \frac{V_k}{V_j}\exp\left[-\left(g_{kj} - g_{jj}\right)/RT\right]\right\}\right]$$

$$- \sum_{j=1}^{n} x_j \frac{\frac{V_i}{V_j}\exp\left[-\left(g_{ij} - g_{jj}\right)/RT\right]}{\sum_{k=1}^{n} x_k \frac{V_k}{V_j}\exp\left[-\left(g_{kj} - g_{jj}\right)/RT\right]} \quad . \qquad (6.12)$$

Here, it should be noted that asymmetric derivations could be made in similar fashion (i.e., for *j-k* molecular interactions instead of *k-j* interactions) for Equations (6.5) through (6.12) with the insertion of Equation (6.4) into the relation

$$\frac{x_{jk}}{x_{kk}} = \frac{x_j \exp(-g_{jk}/RT)}{x_k \exp(-g_{kk}/RT)} \quad . \qquad (6.13)$$

6.2.2 Generalization of Several LCMs

In following Wilson's (1964) conception of an LCM of Section 6.2.1, Renon and Prausnitz (1968) showed that many LCMs represent special cases of a more generalized LCM formulation. This formulation consisted of the generalization of Equation (6.5) as

$$\frac{x_{kj}}{x_{lj}} = \frac{x_k \exp(-\alpha_{jk} g_{kj} / RT)}{x_l \exp(-\alpha_{jl} g_{lj} / RT)} \quad , \tag{6.14}$$

where x_{kj} describes the local composition of molecules k surrounding molecule j and x_{lj} describes the local composition of molecules l surrounding molecule j.

Next, Renon and Prausnitz (1968) generalized the excess-Gibbs expression of Equation (6.11) as

$$\frac{g^E}{RT} = -q\left[\sum_{j=1}^{n} x_j \ln\left(\sum_{k=1}^{n} x_k G_{kj}\right)\right] + p\left[\sum_{j=1}^{n} \frac{\sum_{k=1}^{n} x_k \tau_{kj} G_{kj}}{\sum_{k=1}^{n} x_k G_{kj}}\right] \quad , \tag{6.15}$$

where

$$G_{kj} = \rho_{kj} \exp\left(-\alpha_{kj} \tau_{kj}\right) \tag{6.16}$$

and

$$\tau_{kj} = \frac{\left(g_{kj} - g_{jj}\right)}{RT} \quad . \tag{6.17}$$

In addition,

$$G_{jk} = \rho_{jk} \exp\left(-\alpha_{jk} \tau_{jk}\right) \tag{6.18}$$

and

$$\tau_{jk} = \frac{\left(g_{jk} - g_{kk}\right)}{RT} \quad , \tag{6.19}$$

thereby leading to the asymmetric relations

$$\rho_{kj} \neq \rho_{jk} \tag{6.20}$$

and

$$\tau_{kj} \neq \tau_{jk} \quad . \tag{6.21}$$

In contrast, it should be noted that Renon and Prausnitz (1968) assumed symmetric values for the nonrandomness parameter, α_{kj}, for binary *k-j* interactions in the form of

$$\alpha_{kj} = \alpha_{jk} \quad . \tag{6.22}$$

Finally, Renon and Prausnitz (1968) generalized the activity-coefficient expression of Equation (6.12) as

$$\ln(\gamma_i) = q\left[1 - \ln\left(\sum_{k=1}^{n} x_k G_{ki}\right) - \sum_{j=1}^{n} x_j \frac{G_{ij}}{\sum_{k=1}^{n} x_k G_{kj}}\right]$$

$$+ p\left[\sum_{k=1}^{n} x_k \frac{\tau_{ki} G_{ki}}{\sum_{k=1}^{n} x_k G_{ki}} + \sum_{j=1}^{n} x_j \frac{G_{ij}}{\sum_{k=1}^{n} x_k G_{kj}}\left(\tau_{ij} - \frac{\sum_{k=1}^{n} x_k \tau_{kj} G_{kj}}{\sum_{k=1}^{n} x_k G_{kj}}\right)\right]$$

. (6.23)

As Renon and Prausnitz (1968) note, the Wilson expressions for both the excess-Gibbs property of Equation (6.11) and activity-coefficient model of Equation (6.12) constitute special cases of the generalized Equations (6.15) and (6.23), respectively. Although Table 6.1 illustrates these conditions, these two generalized equations also include a multitude of other LCM special cases as well. In fact, Renon and Prausnitz (1968) also noted other such special cases as the Heil (1966) LCM and as introduced in their paper for the first time, their own NRTL LCM, too. Moreover, it should be noted at this point that Abrams and Prausnitz (1975) later reformulated the generalized portions, p and q, of Equations (6.15) and (6.23) into combinatorial and residual portions in their original presentation of the universal quasi-chemical (UNIQUAC) LCM. Nevertheless, Equations (6.15) and (6.23) provide a simpler representation of the NRTL and other LCMs described herein. Furthermore, Table 6.1 also extends the generalization of these three equations to include the LCM formulated by Li et al. (1986) of Section 6.3.1 and, more importantly, the modifications made to this particular LCM for this work as described in Section 6.3.2.

6.3 The Local Composition Model (LCM) of Li et al. (1986)

6.3.1 Previous Model

Typically, the above models of Equations (6.1-6.3) were presented as activity-coefficient models to predict liquid-phase compositions alone, with an EOS used to predict the vapor phase. As Li et al. (1985, 1986) note, however, Lee et al. (1983)

Table 6.1 Special Cases for Parameters Contained in

Generalized Equations (6.15) and (6.23)

Local Composition Model	p	q	ρ_{kj}	α_{kj}	τ_{kj}	Conditions/ Implications
Wilson (1964)	0	1	$\frac{V_k}{V_j}$	1	$\frac{\left(g_{jk}-g_{kk}\right)}{RT}$	$\rho_{kj}\neq\rho_{jk}$ $\tau_{kj}\neq\tau_{jk}$
Heil (1966)	1	1	$\frac{V_k}{V_j}$	1	$\frac{\left(g_{jk}-g_{kk}\right)}{RT}$	$\rho_{kj}\neq\rho_{jk}$ $\tau_{kj}\neq\tau_{jk}$
NRTL (Renon and Prausnitz, 1968)	1	0	1	α_{kj} =0.5 or 0.25	$\frac{\left(g_{jk}-g_{kk}\right)}{RT}$	$\alpha_{kj}=\alpha_{jk}$ $\tau_{kj}\neq\tau_{jk}$
LCM (Li et al., 1986)	0	1	F_{kj}	α' =0.5	$\frac{\left(A'_{kj}\right)}{RT}$	$F_{kj}\neq F_{jk}$ $\tau_{kj}=\tau_{jk}$
LCM (this work)	0	1	F_{kj}	α' =0.5	$\frac{\left(A'_{kj}-A'_{jj}\right)}{RT}$	$F_{kj}\neq F_{jk}$ $\tau_{kj}\neq\tau_{jk}$

later laid the theoretical groundwork for their LCM "using the statistical-mechanical relations utilized for equations of state (Li et al., p. 222, 1985)." Simply put, this approach of Lee et al. (1983) theoretically allowed for an EOS to be inserted into an LCM framework, thereby enabling the EOS to accurately predict both liquid- and vapor-phase compositions.

Here, Li et al. (1986) presented an LCM and applied it to the KCLS EOS developed by Chung et al. (1984). As Li et al. (1986) noted, the LCM provided a more accurate set of mixing rules for the KCLS EOS than the mixing rules previously provided for it by Lee et al. (1977b) through a conformal solution model (CSM).

As noted by Li (1984), the LCM of Li et al. (1986) employed a configurational Helmholtz free energy expression in the form of

$$\frac{-\alpha' A'}{RT} = \sum_j x_j \ln\left[\sum_k x_k F_{kj} \exp\left(-\frac{\alpha' A'_{kj}}{RT}\right)\right] \quad . \qquad (6.24)$$

Li (1984) then noted that Equation (6.24) can de differentiated with respect to volume to yield the pressure form of the LCM equation of state as

$$P = \sum_j x_j \frac{\sum_k x_k F_{kj} P_{kj} \exp\left(-\frac{\alpha' A'_{kj}}{RT}\right)}{\sum_k x_k F_{kj} \exp\left(-\frac{\alpha' A'_{kj}}{RT}\right)} \quad , \qquad (6.25)$$

with an unlike-interaction expression for the configurational compressibility of

$$z_{kj} - 1 = \left[A_1 + A_2\left(T^*_{kj}\right)^{-1} + A_3\left(T^*_{kj}\right)^{-2} + A_4\left(T^*_{kj}\right)^{-3} + A_5\left(T^*_{kj}\right)^{-5}\right]\rho^*$$

$$+\left[A_6 + A_7\left(T_{kj}^*\right)^{-1}\right]\left(\rho^*\right)^2 + A_8\left(\rho^*\right)^3$$

$$+\left[A_9\left(T_{kj}^*\right)^{-3} + A_{10}\left(T_{kj}^*\right)^{-4} + A_{11}\left(T_{kj}^*\right)^{-5}\right]\left(\rho^*\right)^2 \exp\left[-A_{16}\left(\rho^*\right)^2\right]$$

$$+\left[A_{12}\left(T_{kj}^*\right)^{-3} + A_{13}\left(T_{kj}^*\right)^{-4} + A_{14}\left(T_{kj}^*\right)^{-5}\right]\left(\rho^*\right)^4 \exp\left[-A_{16}\left(\rho^*\right)^2\right]$$

$$+A_{15}\left(T_{kj}^*\right)^{-1}\left(\rho^*\right)^5 \quad , \qquad (6.26)$$

with

$$A_i = \lambda_{kj} B_i^{(0)} + (\lambda_{kj} - 1) B_i^{(p)} \quad . \qquad (6.27)$$

and a fugacity expression of

$$\ln\left(\frac{\hat{f}_i}{x_i}\right) = -\frac{1}{\alpha'}\left\{\ln\left[\sum_k x_k F_{ki} \exp\left(-\frac{\alpha' A'_{ki}}{RT}\right)\right] - 1 + \sum_j x_j \frac{F_{ij} \exp\left(-\frac{\alpha' A'_{ij}}{RT}\right)}{\sum_k x_k F_{kj} \exp\left(-\frac{\alpha' A'_{kj}}{RT}\right)}\right\}$$

$$+\frac{1}{\alpha'}\left\{\ln\left[\sum_k x_k F_{ki}\right] - 1 + \sum_j x_j \frac{F_{ij}}{\sum_k x_k F_{kj}}\right\}$$

$$+(z-1)\left[1 + \bar{R}_i\right] \quad . \qquad (6.28)$$

Li (1984) defined the derivative for $\bar{R}_i$ as

$$\bar{R}_i = \frac{1}{V_x^*}\frac{\partial V_x^*}{\partial n_i}\bigg|_{T,V,n_{j\neq i}} = 2\left[\frac{\sum_j x_j V_{ij}^*}{V_x^*} - 1\right] \quad . \qquad (6.29)$$

Here, it should be noted that for mixtures, Equations (6.24-6.26) and (6.28) employ a multifluid temperature model in the form of

$$T_{kj}^{*} = \frac{kT}{\varepsilon_{kj} + D_{kj} / T} \tag{6.30}$$

and a single-fluid density model in the form of

$$\rho_{kj}^{*} = \rho V_{x}^{*} \quad , \tag{6.31}$$

where

$$V_{x}^{*} = \sum_{k=1}^{n} \sum_{j=1}^{n} x_k x_j V_{kj}^{*} \quad . \tag{6.32}$$

As a result, λ, ε, D, and V^{*} of Equations (6.27) and (6.30-6.32) constitute the four symmetric UIPs (out of a total of five) for a given mixture. This symmetrical condition arises from the concept of combinatorial symmetry (Lee, p. 277, 1988), whereby intermolecular distances L_{kj} and L_{jk} between two molecules k and j -- as well as the other parameters implied by this distance (e.g., characteristic energy of separation) -- must by definition be equal, i.e.,

$$L_{kj} = L_{jk} \tag{6.33}$$

Next, Li et al. (1986) also define the coordination volume characterization ratios F_{ij} and F_{ji} as

$$F_{kj} = \frac{V_{kj}^{*}}{V_{jj}^{*}} = \frac{V_{kj}^{*}}{V_{j}^{*}} \tag{6.34}$$

and

$$F_{jk} = \frac{V^*_{jk}}{V^*_{kk}} = \frac{V^*_{jk}}{V^*_{k}} \tag{6.35}$$

Consequently, F of Equations (6.34) and (6.35) constitutes the only asymmetric UIP (of all five UIPs) for a given mixture. Moreover, these two equations do not violate combinatorial symmetry due to their representation as **divisive-residual** relations involving the division of V^*_{kj} by V^*_{jj} and V^*_{jk} by V^*_{kk} In contrast, Section 6.3.2 introduces **subtractive-residual** relations for the other four UIPs, which makes them asymmetric as well. This accounts for the differences in Table 6.1 for the generalized parameter τ_{kj} in the LCM of Li et al. (1986), which is expressed solely as a function of the configurational Helmholtz free energies A'_{kj}, but modified in this work to comprise a function of both A'_{kj} and A'_{jj}.

In addition, it should be noted that as a mixture model, the LCM of Li et al. (1986) presented two advantages. First, it applied to the prediction of both the liquid and vapor phases. This two-phase predictive ability presented an advantage over previous liquid-phase, activity-coefficient LCMs in that it did not require an outside EOS to simulate the vapor phase. Second, this LCM also allowed for the insertion of one (or more) pure-component equation(s) of state into both the generic, configurational Helmholtz free energy expression of Equation (6.24) and the generic total-pressure expression of Equation (6.25). The two-phase advantage was

formulated with the intention of using the most accurate EOS for each pure component of interest so as to optimize the resultant mixture simulations.

6.3.2 Modifications Made to the LCM in This Work

This work introduces certain modifications to the LCM of Lee et al. (1986) of Section 6.3.1 that allow for the insertion of the GAR of Chapter 4. As seen in Table 6.1, these modifications result in differences between the previous LCM and its modified version that vary in their functional dependence of the generalized parameter, τ_{kj}, on the configurational Helmholtz free energy. For the previous LCM, Li et al. (1986) employed

$$\tau_{kj} = \frac{\left(A'_{kj}\right)}{RT} \quad , \tag{6.36}$$

which implies the relation

$$A'_{kj} = A'_{jk} \tag{6.37}$$

that results in

$$\tau_{kj} = \tau_{jk} \quad . \tag{6.38}$$

This work, on the other hand, employs the subtractive-residual relations

$$\tau_{kj} = \frac{\left(A'_{kj} - A'_{jj}\right)}{RT} \tag{6.39}$$

and

$$\tau_{jk} = \frac{\left(A'_{jk} - A'_{kk}\right)}{RT} \tag{6.40}$$

which due to combinatorial asymmetry also obey Equation (6.37) but instead imply that

$$\tau_{kj} \neq \tau_{jk} \quad . \tag{6.41}$$

Here, it should be noted that Equations (6.39-6.41) apply only indirectly in this work. In contrast, the direct application of subtractive-residual expressions for the modified LCM exists in the form of the relations employed for the UIPs λ, ε, D, and V^* as seen in Table 6.2. Moreover, Table 6.2 also shows that the modified LCM maintains the same relations of Equations (6.34-6.35) for F. This model then represents a **first-time modification** of Li et al.'s (1986) LCM through the use of five asymmetric UIPs, each of which is calculated from PCPs through the GAR of Chapter 4 as follows.

To begin with, all five UIPs for this LCM exist as averages of PCPs according to the GAR of Equation (4.10):

$$\text{GAR:} \qquad B_{ij} = \frac{B_i^{\alpha} B_j^{-\alpha} \left[\gamma B_i^N + (2-\gamma) B_j^N\right]^{1/N}}{2^{1/N}} \quad . \tag{6.42}$$

Like the arguments presented in Section 5.2 of Chapter 5, N is held at unity, thereby resulting in Equation 5.3:

$$B_{ij} = \frac{B_i^{\alpha} B_j^{-\alpha} \left[\gamma B_i + (2-\gamma) B_j\right]}{2} \quad . \tag{6.43}$$

Table 6.2 Unlike-Interaction Expressions for the Local Composition Models of Section 6.3

Local Composition Model	Mixture Expression for λ	Mixture Expression for ε	Mixture Expression for D	Mixture Expression for V^*	Mixture Expression for F	Result for τ_{kj}	Conditions/ Implications
LCM (Li et al., 1986)	λ_{kj}	ε_{kj}	D_{kj}	V^*_{kj}	$\frac{V^*_{kj}}{V^*_{jj}}$	$\frac{\left(A'_{kj}\right)}{RT}$	$\tau_{kj} = \tau_{jk}$
LCM (this work)	$\lambda_{kj} - \lambda_{jj}$	$\varepsilon_{kj} - \varepsilon_{jj}$	$D_{kj} - D_{jj}$	$V^*_{kj} - V^*_{jj}$	$\frac{V^*_{kj}}{V^*_{jj}}$	$\frac{\left(A'_{kj} - A'_{jj}\right)}{RT}$	$\tau_{kj} \neq \tau_{jk}$

Next, since the numerical values of the PCPs λ, ε, and V^* are all positive, their asymmetric mixture expressions consist of

$$\lambda_{ij} = \frac{\lambda_i^{\alpha}\lambda_j^{-\alpha}\left[\gamma\lambda_i + (2-\gamma)\lambda_j\right]}{2} \quad , \tag{6.44}$$

$$\varepsilon_{ij} = \frac{\varepsilon_i^{\alpha}\varepsilon_j^{-\alpha}\left[\gamma\varepsilon_i + (2-\gamma)\varepsilon_j\right]}{2} \quad , \tag{6.45}$$

and

$$V_{ij}^* = \frac{\left(V_i^*\right)^{\alpha}\left(V_j^*\right)^{-\alpha}\left[\gamma V_i^* + (2-\gamma)V_j^*\right]}{2} \quad . \tag{6.46}$$

In addition, the UIP D can consist of zero and nonzero PCP values. As a result, Equation (6.43) for D in this work follows the arguments outlined in Section 5.3.2 where $\alpha = 0$, resulting in

$$D_{ij} = \frac{\left[\gamma D_i + (2-\gamma)D_j\right]}{2} \quad . \tag{6.47}$$

In addition, the UIP F cannot tolerate sign changes with positive-only PCP values for V^*. In conjunction with the arguments outlined in Section 5.4, $\gamma = 1$, with Equation (6.43) becoming

$$\left(V_{ij}^*\right)_F = \frac{\left(V_i^*\right)^{\alpha}\left(V_j^*\right)^{-\alpha}\left[V_i^* + V_j^*\right]}{2} \quad . \tag{6.48}$$

Obviously, Equations (6.44-6.48) reflect the intention of obtaining more accurate VLE composition predictions. As a result, even if minor improvements in accuracy can be obtained through this approach, the GAR of Chapter 4 should then logically find use in other LCMs (such as those mentioned in Table 6.1) to improve their predictive accuracy as well.. Lastly, it should be noted that this work also employs Equations (6.24-6.32) and (6.35) to simulate both the binary and multicomponent systems examined in this work.

CHAPTER VII

PREDICTION OF BINARY VAPOR-LIQUID EQUILIBRIUM (VLE) SYSTEMS FOR THIS WORK

7.1 Overview

This chapter presents final results in the prediction of binary vapor-liquid equilibrium (VLE) systems for this work. These results were obtained through the regression of both binary interaction parameters (BIPs) and generalized asymmetric rules (GARs) over a variety of temperatures, pressures, and binary VLE systems. Appendix C lists the general literature sources consulted for all VLE data reviewed in this work along with the data sources used for the binary VLE simulations presented herein.

The following sections present the results of several simulations in the following order. First, Section 7.2 describes the approach taken in the regression of unlike-interaction parameters (UIPs) over the data sets of interest. Second, Section 7.3 presents the predictive results for eighteen binary VLE systems in the form of average absolute relative deviations (AARDs) over forty-one isotherms, nine isobars, and twelve mixed temperature/pressure ranges. Altogether, GARs surpassed BIPs in slightly over half of all AARD results presented in terms of the liquid composition, vapor-composition, and K-value AARD sums of both components added together -- that is, $AARD(x_1) + AARD(x_2)$, $AARD(y_1) + AARD(y_2)$, and $AARD(K_1) + AARD(K_2)$ for each isotherm, isobar, and combined

temperature/pressure range. The fugacity equivalence of each component in each phase was used as the objective function for all mixture simulations.

Third, Section 7.4 presents the numerical values of GAR parameters regressed against these binary systems. In all, these values show a few rough trends between separate isotherms and binary systems containing similar components, which in turn suggests their use in future simulations. In addition, the consideration of these rough values suggests further refinement before attempting their correlation and/or improvement for the systems simulated in this work. Nevertheless, their presentation does constitute a first-time showing of such values in this or any other work in the thermodynamic literature, in conjunction with the original development of the GAR in this work.

7.2 Regression of Unlike-Interaction Parameters (UIPs) Over Data Sets

The results obtained herein suggest a certain approach to the regression of UIPs over data sets through the local composition model (LCM) with the Khan-Chung-Lee-Starling (KCLS) equation of state (EOS) developed by Chung et al. (1984). Specifically, the results indicate the feasibility of **(1)** regressing the UIPs of interest (i.e., BIPs or GARs) for the LCM-KCLS EOS over separate data sets (e.g.,, isotherms, isobars) first, followed by **(2)** subsequently regressing UIPs over all such data sets simultaneously.

First of all, the above approach offers the advantage of detecting any outliers along a given isotherm/isobar. Outlier detection can prove significant, since the

alternative of UIP regression over all data sets simultaneously tends to "mask" any outliers for the separate data sets, thereby "leading" the regressed UIPs to non-optimal values for all data as a whole, while attempting to fit a few rogue data points. In contrast, when regressing separate data sets per isotherm or isobar, however, these outliers become much more obvious, thereby facilitating their elimination from a particular data set. The single-isotherm/isobar approach thus provides a definite advantage (in terms of predictive accuracy) when later regressing UIPs over all data sets of interest for a given binary system.

Second, the regression of UIPs over separate data sets also allows for the evaluation of trends in the final values of the UIPs as functions of temperature and/or pressure. For example, it has long been known (e.g., Cartaya et al., 1996) that BIPs may be correlated as functions of temperature. Such trends may then arise (and be more readily detected) when presenting the regressed results over each data set, as accomplished in this work.

7.3 Predictive Average Absolute Relative Deviation (AARD) Results for Binary VLE Systems

This section both presents and discusses the predictive results of all binary VLE simulations conducted for this work. Tables 7.1-7.11 present the results in the form of AARDs, the formulas of which are discussed in Section 3.3.3 of Chapter 3. Here, AARDs are presented for both liquid and vapor compositions (i.e., x_i and y_i), as well as vaporization-equilibrium ratios -- commonly known as K-values (K_i),

Table 7.1

Liquid-Composition, Vapor-Composition, and K-Value AARDs for the Benzene-*Meta*-Xylene and Benzene-*Para*-Xylene VLE Systems

System	Number of Data Points	Temp. Range (°R)	Pressure Range (psia)	Method Chosen	Liquid-Composition % AARDs:		Vapor-Composition % AARDs:		K-Value % AARDs:	
					x_1	x_2	y_1	y_2	K_1	K_2
Benzene-*meta*-Xylene	9	536.67	0.57-1.72	BIPs	0.9	2.8	0.21	4.0	1.0	2.0
				GARs	0.8	3.1	0.2	4.1	0.7	1.2
Benzene-*meta*-Xylene	13	558.27	0.43-2.91	BIPs	2.8	2.9	0.6	2.9	2.3	1.4
				GARs	1.7	2.3	0.5	2.0	1.7	1.6
Benzene-*meta*-Xylene	13	581.67	0.82-4.92	BIPs	3.5	6.0	0.5	5.2	3.2	3.2
				GARs	3.5	5.9	0.5	4.8	3.2	3.4
Benzene-*meta*-Xylene	9	655.27-716.31	14.696	BIPs	8.8	5.4	5.2	16.1	8.5	12.1
				GARs	7.5	6.8	5.8	13.9	7.5	9.4
Benzene-*meta*-Xylene (All data sets)	44	536.67-716.31	0.43-14.696	BIPs	2.3	1.9	1.7	6.4	2.8	6.4
				GARs	3.0	2.0	1.5	5.9	3.5	6.0
Benzene-*para*-Xylene (Single isobar only)	13	642.15-723.87	14.696	BIPs	1.7	1.7	1.1	2.7	0.9	1.7
				GARs	1.8	1.9	1.1	2.9	1.0	1.6

Table 7.2

Liquid-Composition, Vapor-Composition, and K-Value AARDs for the Toluene-*Meta*-Xylene and Toluene-*Para*-Xylene VLE Systems

System	Number of Data Points	Temp. Range (°R)	Pressure Range (psia)	Method Chosen	Liquid-Composition % AARDs:		Vapor-Composition % AARDs:		K-Value % AARDs:	
					x_1	x_2	y_1	y_2	K_1	K_2
Toluene-*meta*-Xylene	15	672.48	5.12-10.33	BIPs	2.1	2.4	1.4	4.5	2.3	2.9
				GARs	2.2	3.1	1.4	5.2	2.1	2.6
Toluene-*meta*-Xylene	9	690.48	6.92-14.29	BIPs	9.6	4.7	9.0	5.8	3.5	2.9
				GARs	6.2	4.3	5.0	5.3	5.5	1.7
Toluene-*meta*-Xylene	9	708.66	9.42-18.60	BIPs	7.4	5.0	5.4	4.7	2.8	3.3
				GARs	7.2	7.0	4.3	6.5	4.5	3.1
Toluene-*meta*-Xylene	9	699.21-725.44	14.696	BIPs	7.0	12.6	5.5	14.5	6.2	3.1
				GARs	6.2	5.8	5.3	9.2	1.7	5.2
Toluene-*meta*-Xylene (All data sets)	42	672.48-725.44	5.12-18.60	BIPs	5.4	4.8	4.0	5.8	3.6	3.4
				GARs	4.3	3.8	2.7	5.4	4.0	3.6
Toluene-*para*-Xylene (Single isotherm only)	12	653.67	4.04-6.28	BIPs	1.8	1.9	1.5	3.1	1.5	1.6
				GARs	1.5	1.6	1.4	2.7	1.4	1.6

Table 7.3

Liquid-Composition, Vapor-Composition, and K-Value AARDs for the Benzene-Toluene and Ethylbenzene-*Ortho*-Xylene VLE Systems

System	Number of Data Points	Temp. Range (°R)	Pressure Range (psia)	Method Chosen	Liquid-Composition % AARDs: x_1		Vapor-Composition % AARDs: y_1		K-Value % AARDs: K_1	K_2
Benzene-Toluene	88	637.69-691.02	14.696	BIPs	5.1	4.5	4.9	5.4	1.9	3.0
				GARs	5.5	4.5	5.1	5.6	1.7	2.6
Benzene-Toluene	4	617.67	7.96-8.20	BIPs	0.9	1.4	0.8	3.6	0.9	3.3
				GARs	4.7	7.5	1.6	6.7	3.0	3.2
Benzene-Toluene (All data sets)	92	617.67-691.02	7.96-14.696	BIPs	4.9	4.2	4.8	5.2	1.8	3.2
				GARs	4.3	3.7	4.3	4.5	1.7	2.6
Ethylbenzene-*ortho*-Xylene	15	671.67	3.90-4.91	BIPs	3.0	1.2	3.1	1.5	0.1	0.4
				GARs	2.9	1.3	3.0	1.5	0.2	0.3
Ethylbenzene-*ortho*-Xylene	13	594.99-606.87	0.97	BIPs	7.5	6.7	7.8	7.6	0.9	1.5
				GARs	7.7	6.9	8.0	7.9	1.0	1.5
Ethylbenzene-*ortho*-Xylene	13	658.71-671.13	3.87	BIPs	1.6	3.7	1.3	3.3	0.8	0.5
				GARs	1.6	3.5	1.4	3.2	0.6	0.5
Ethylbenzene-*ortho*-Xylene (All data sets)	41	594.99-671.67	0.97-4.91	BIPs	4.8	4.4	4.6	4.9	0.7	0.9
				GARs	5.3	5.1	4.7	5.9	1.2	1.3

Table 7.4

Liquid-Composition, Vapor-Composition, and K-Value AARDs for the Benzene-Ethylbenzene and Toluene-Ethylbenzene VLE Systems

System	Number of Data Points	Temp. Range (°R)	Pressure Range (psia)	Method Chosen	Liquid-Composition % AARDs:		Vapor-Composition % AARDs:		K-Value % AARDs:	
					x_1	x_2	y_1	y_2	K_1	K_2
Benzene-Ethylbenzene (Single isobar only)	11	637.63-735.23	14.696	BIPs	8.0	6.9	8.2	8.0	1.4	2.9
				GARs	8.6	7.6	8.1	8.1	1.1	1.2
Toluene-Ethylbenzene	4	536.67	0.27-0.52	BIPs	11.4	14.6	11.3	19.8	3.9	6.5
				GARs	11.2	14.2	11.2	19.4	3.7	6.9
Toluene-Ethylbenzene	15	671.67	5.25-10.46	BIPs	2.0	8.2	0.8	7.7	1.3	0.4
				GARs	1.8	8.1	0.7	7.5	1.2	0.5
Toluene-Ethylbenzene (Both isotherms)	19	536.67-671.67	0.27-10.46	BIPs	3.8	8.8	3.0	9.6	1.7	1.6
				GARs	6.1	10.7	3.9	12.4	2.3	3.2

Table 7.5

Liquid-Composition, Vapor-Composition, and K-Value AARDs for the Methane-Benzene VLE System

System	Number of Data Points	Temp. Range (°R)	Pressure Range (psia)	Method Chosen	Liquid-Composition % AARDs:		Vapor-Composition % AARDs:		K-Value % AARDs:	
					x_1	x_2	y_1	y_2	K_1	K_2
Methane-Benzene	13	609.67	100.00-4000.00	BIPs	8.5	4.8	0.7	17.3	7.7	18.3
				GARs	3.7	3.1	0.8	18.3	5.0	17.9
Methane-Benzene	6	757.89	288.19-2949.19	BIPs	12.3	4.6	2.4	8.4	13.3	4.3
				GARs	4.6	0.7	2.7	9.6	4.1	9.3
Methane-Benzene	5	831.33	438.23-2364.15	BIPs	2.1	0.6	1.3	2.1	2.5	2.5
				GARs	2.1	0.5	2.1	4.6	2.1	4.2
Methane-Benzene	5	902.07	743.18-1982.34	BIPs	2.3	0.6	1.8	2.0	1.3	1.5
				GARs	2.4	0.6	2.3	2.5	1.2	1.9
Methane-Benzene (All data sets)	29	609.67-902.07	100.00-4000.00	BIPs	11.4	6.5	6.1	29.9	20.2	26.5
				GARs	8.5	4.2	4.9	28.5	15.3	24.0

Table 7.6

Liquid-Composition, Vapor-Composition, and K-Value AARDs for the Methane-Toluene VLE System

System	Number of Data Points	Temp. Range (°R)	Pressure Range (psia)	Method Chosen	Liquid-Composition % AARDs:		Vapor-Composition % AARDs:		K-Value % AARDs:	
					x_1	x_2	y_1	y_2	K_1	K_2
Methane-Toluene	12	459.67	50.00-2500.00	BIPs	25.4	10.3	0.03	16.6	18.6	15.1
				GARs	9.2	3.0	0.03	16.0	8.4	14.2
Methane-Toluene	11	499.67	50.00-2500.00	BIPs	25.3	8.4	0.03	11.2	19.2	11.6
				GARs	3.5	0.7	0.01	4.1	3.4	4.0
Methane-Toluene	11	609.67	100.00-4000.00	BIPs	8.7	6.1	0.3	14.7	7.6	14.8
				GARs	1.4	0.9	0.2	11.1	1.5	12.0
Methane-Toluene	6	760.41	293.19-2939.20	BIPs	5.2	2.2	0.4	4.2	4.3	3.2
				GARs	1.0	0.2	0.4	2.9	0.9	3.0
Methane-Toluene	7	831.69	294.36-3341.43	BIPs	2.0	0.7	1.3	4.1	2.3	4.2
				GARs	3.9	2.4	2.1	7.1	4.8	8.6
Methane-Toluene	6	901.35	292.45-2446.44	BIPs	2.5	0.6	1.7	1.9	2.1	2.2
				GARs	5.7	1.6	4.0	5.3	4.0	5.6
Methane-Toluene	3	977.67	446.32-1022.40	BIPs	14.8	0.7	15.0	6.7	2.8	6.0
				GARs	13.8	0.9	12.1	5.1	8.9	4.2
Methane-Toluene (All data sets)	56	459.67-977.67	50.00-4000.00	BIPs	47.7	19.7	2.4	12.3	77.0	28.5
				GARs	16.6	6.4	2.7	16.7	20.8	20.1

Table 7.7

Liquid-Composition, Vapor-Composition, and K-Value AARDs for the Methane-*Ortho*-Xylene and Methane-n-Propylbenzene VLE Systems

System	Number of Data Points	Temp. Range (°R)	Pressure Range (psia)	Method Chosen	Liquid-Composition % AARDs:		Vapor-Composition % AARDs:		K-Value % AARDs:	
					x_1	x_2	y_1	y_2	K_1	K_2
Methane-*ortho*-Xylene (Single isotherm only)	10	599.67	142.23-4267.00	BIPs	4.2	3.1	0.1	19.2	4.1	17.4
				GARs	5.1	4.2	0.1	19.6	5.4	17.3
Methane-n-Propylbenzene	7	564.48	739.70-5076.34	BIPs	12.1	8.0	0.4	64.1	11.9	52.9
				GARs	19.6	15.2	0.19	30.3	22.6	37.8
Methane-n-Propylbenzene	4	706.86	1522.90-4394.66	BIPs	1.1	1.0	0.3	14.4	0.9	13.3
				GARs	8.1	7.1	0.4	28.6	9.1	30.6
Methane-n-Propylbenzene (Both isotherms)	11	564.48-706.86	739.70-5076.34	BIPs	16.4	11.1	2.4	168.	18.2	142.
				GARs	20.6	13.7	0.3	29.8	19.8	37.0

Table 7.8

Liquid-Composition, Vapor-Composition, and K-Value AARDs for the Methane-Water VLE System

System	Number of Data Points	Temp. Range (°R)	Pressure Range (psia)	Method Chosen	Liquid-Composition % AARDs:		Vapor-Composition % AARDs:		K-Value % AARDs:	
					x_1	x_2	y_1	y_2	K_1	K_2
Methane-Water	6	600.66-932.94	192.47-935.64	BIPs	656.3	0.7	10.5	7.6	17.6	7.2
				GARs	3.8	.002	0.5	0.9	4.3	0.9
Methane-Water	17	559.67	200.00-10000.00	BIPs	1096.10.8	2.1	0.02	20.8	15.3	19.2
				GARs		0.03	0.02	22.1	10.3	22.1
Methane-Water	16	619.67	200.00-8000.00	BIPs	8.1	0.02	0.03	7.9	7.8	7.8
				GARs	8.6	0.02	0.03	7.8	8.7	7.8
Methane-Water	17	679.67	200.00-9000.00	BIPs	7.9	0.02	0.09	8.2	7.5	8.2
				GARs	7.9	0.02	0.09	8.6	7.6	8.6
Methane-Water	11	739.67	200.00-3500.00	BIPs	1.6	0.003	0.2	1.5	1.7	1.5
				GARs	1.6	0.002	0.2	2.3	1.7	2.3
Methane-Water	12	799.67	200.00-4000.00	BIPs	1.9	0.003	0.7	2.0	1.5	2.0
				GARs	2.8	0.006	0.6	1.8	2.4	1.8
Methane-Water (All Data sets)	79	559.67-932.94	192.47-10000.00	BIPs	19.2	0.04	0.3	9.3	18.0	9.3
				GARs	15.7	0.04	0.3	11.6	14.9	11.6

Table 7.9

Liquid-Composition, Vapor-Composition, and K-Value AARDs for the Methane-Triethylene Glycol VLE System

System	Number of Data Points	Temp. Range (°R)	Pressure Range (psia)	Method Chosen	Liquid-Composition % AARDs: x_1		Vapor-Composition % AARDs: y_1		K-Value % AARDs: K_1	K_2
Methane-Triethylene Glycol	9	536.67	16.46-2823.89	BIPs	1.8	0.06	0.1	100.	1.8	100.
				GARs	1.9	0.05	0.08	83.0	1.9	83.0
Methane-Triethylene Glycol	9	581.67	16.06-2440.99	BIPs	3.2	0.1	0.09	87.9	3.3	87.8
				GARs	2.0	0.05	0.09	86.5	2.0	86.5
Methane-Triethylene Glycol	11	626.67	15.84-2855.80	BIPs	19.1	1.0	0.09	85.3	15.5	85.7
				GARs	2.6	0.1	0.08	82.3	2.6	82.3
Methane-Triethylene Glycol	10	671.67	16.37-2790.54	BIPs	12.7	0.5	0.07	74.3	13.2	74.0
				GARs	2.6	0.1	0.07	71.8	2.5	71.8
Methane-Triethylene Glycol	10	716.67	18.46-2744.12	BIPs	2.4	0.09	0.06	61.1	2.4	61.2
				GARs	2.5	0.11	0.06	58.7	2.4	58.7
Methane-Triethylene Glycol (All data sets)	49	536.67-716.67	15.84-2855.80	BIPs	3.0	0.1	1.0	95.7	3.0	95.7
				GARs	13.4	0.5	0.08	77.3	12.6	77.4

Table 7.10

Liquid-Composition, Vapor-Composition, and K-Value AARDs for the Triethylene Glycol - Water, Benzene - Triethylene Glycol, and Toluene - Triethylene Glycol VLE Systems

System	Number of Data Points	Temp. Range (^{o}R)	Pressure Range (psia)	Method Chosen	Liquid-Composition % AARDs: x_1	Liquid-Composition % AARDs: x_2	Vapor-Composition % AARDs: y_1	Vapor-Composition % AARDs: y_2	K-Value % AARDs: K_1	K-Value % AARDs: K_2
Triethylene Glycol - Water (Single isotherm only)	15	859.67	18.53-76.04	BIPs	1.5	5.7	9.5	0.2	8.8	5.7
				GARs	0.8	2.8	5.9	0.2	5.5	2.9
Benzene - Triethylene Glycol (Single isobar only)	11	638.37-771.75	14.696	BIPs	15.6	19.6	0.03	22.3	15.4	26.5
				GARs	19.2	26.9	0.03	22.8	18.5	26.1
Toluene - Triethylene Glycol (Single isobar only)	10	693.45-796.59	14.696	BIPs	16.9	26.8	0.1	17.2	15.4	33.3
				GARs	21.6	29.3	0.1	17.0	17.3	35.8

Table 7.11

Liquid-Composition, Vapor-Composition, and K-Value AARDs for the Tetrafluoromethane-Trifluoromethane VLE System

System	Number of Data Points	Temp. Range (^{o}R)	Pressure Range (psia)	Method Chosen	Liquid-Composition % AARDs: x_1		Vapor-Composition % AARDs: y_1		K-Value % AARDs: K_1	K_2
Tetrafluoromethane-Trifluoromethane	14	309.67	10.68-68.20	BIPs	4.7	10.3	0.6	6.5	4.1	9.2
				GARs	3.6	8.5	0.6	6.2	3.1	7.7
Tetrafluoromethane-Trifluoromethane	18	359.67	26.78-218.82	BIPs	5.5	7.2	2.1	5.4	6.0	3.9
				GARs	4.2	4.5	2.1	4.1	4.7	2.4
Tetrafluoromethane-Trifluoromethane	14	404.67	89.86-489.70	BIPs	2.8	4.4	1.1	2.9	2.4	2.1
				GARs	2.1	3.9	1.0	2.5	1.7	2.1
Tetrafluoromethane-Trifluoromethane	9	459.67	283.28-703.71	BIPs	3.3	1.1	2.9	2.4	4.2	2.3
				GARs	3.2	0.9	2.6	2.0	4.3	2.4
Tetrafluoromethane-Trifluoromethane	12	509.67	519.56-753.46	BIPs	13.6	1.7	9.9	1.8	6.6	1.5
				GARs	8.6	0.9	6.1	1.0	2.8	0.6
Tetrafluoromethane-Trifluoromethane (All data sets)	67	309.67-509.67	10.68-753.46	BIPs	5.7	6.6	2.8	4.4	6.0	5.6
				GARs	5.2	5.1	2.4	3.3	5.0	4.5

which follow the relation

$$K_i = \frac{y_i}{x_i} \qquad . \qquad (7.1)$$

As can be seen, these tables present results for both BIPs and GARs in an effort to compare their accuracy. Here, BIPs were employed in symmetrical form only, thereby representing the concept of symmetry in the LCM-KCLS EOS. The GARs, on the other hand, were employed in asymmetrical form, thus representing the alternative concept of asymmetry seen in such models as the nonrandom, two-liquid (NRTL) LCM model by Renon and Prausnitz (1968). Although the LCMs described in this work comprise multifluid models, the comparison between BIPs and GARs for single-fluid models in Section 4.4.7 of Chapter 4 (in terms of conversion between BIP and GAR forms) still provides an excellent distinction between symmetrical BIPs and asymmetrical GARs.

Moreover, since the following results encompass a wide array of compounds, their presentation has been arranged into four groups: (1) binary aromatic mixtures; (2) binary mixtures of methane with aromatic compounds and water; (3) binary mixtures of triethylene glycol with methane, aromatic compounds, and water; and (4) binary mixtures of two freons.

Finally, it should be noted that a review of all results revealed that GARs surpassed BIPs in slightly over half of all AARD results presented in terms of the liquid-composition, vapor-composition, and K-value AARD sums of both components added together -- that is, $AARD(x_1) + AARD(x_2)$,

$AARD(y_1) + AARD(y_2)$, and $AARD(K_1) + AARD(K_2)$ for each isotherm, isobar, and combined temperature/pressure range. This review suggests that asymmetric GARs yield results similar to symmetric BIPs while also offering potential predictive improvements, thereby supporting the asymmetrical approach taken by other LCMs referred to in this work.

7.3.1 AARD Results for Binary Aromatic Mixtures

Tables 7.1-7.4 present AARD results for binary aromatic mixtures. First, Table 7.1 shows AARD results for mixtures of benzene with *meta*- and *para*-xylene isomers. Accordingly, the system benzene-*meta*-xylene can be predicted accurately, with GARs showing improvement over BIPs for both isotherms and isobars, with a maximum improvement for the K-value of *meta*-xylene at the 14.696-psia isobar. Obviously, this isobar showed the least accurate predictions, which are expected since BIPs (and, most likely, GARs as well) remain quite temperature-dependent. Also, these predictions compare closely in AARD value for all data sets simultaneously as well. In addition, both BIPs and GARs predicted the benzene-*para*-xylene with similar accuracy and a maximum AARD difference between them of 0.2%.

Second, Table 7.2 shows similar trends with binary systems formed by toluene and the same xylene isomers. Here, the maximum improvement of GARs over BIPs consisted of a difference of 6.8% in the liquid composition of the toluene-*meta*-xylene isobar, with improvements in the other three phase compositions as well as the K-value of toluene. In addition, GARs also proved slightly more accurate than BIPs for

the toluene-*para*-xylene system in both phase-composition AARDs and the K-value for toluene as well.

Third, Table 7.3 presents results for both the benzene-toluene and ethylbenzene-*ortho*-xylene systems. The first system shows a maximum difference in the 14.696-psia isobar of 0.4%, with BIPs proving more accurate than GARs for the isotherm for a maximum of 6.1%. With the isobar and isotherm taken together, however, GARs prove more accurate with a maximum AARD improvement of 0.7%. For the ethylbenzene-*ortho*-xylene systems, however, these results fluctuate, with BIPs appearing more accurate for the isotherm and two isobars reported. In addition, a maximum difference occurs in all AARD values for this system between GARs and BIPs of only 0.2% for each separate data set and 1.0% for all data sets. Altogether, the results of this table merely reveal the outcome of near-equivalent results between BIPs and GARs in terms of symmetrical and asymmetrical modeling. Table 7.4 for the benzene-ethylbenzene and toluene-ethylbenzene systems exhibits similar trends as well.

7.3.2 AARD Results for Binary Mixtures of Methane with Aromatic Compounds and Water

Tables 7.5-7 present AARD results for binary mixtures of methane with aromatic compounds and water. First, the methane-benzene results for GARs in Table 7.5 prove quite comparable to those of BIPs overall. For single isotherms, a maximum improvement occurred in GARs over BIPs of 9.2% (for the methane K-

value at 757.89 °R), as compared to a maximum of 5.% for the K-value of benzene. For all

data sets, however, GARs attained more accurate predictions (over 1.0%) for all data sets predicted simultaneously for compositions and K-values alike.

Here, large errors in the prediction of both methane-liquid and benzene-vapor compositions (and the K-values of each) at lower temperatures occur due to the great difference in molecular weight and boiling points of the two components. This condition is referred to as a wide degree of phase separation, whereby a lighter component, methane, occupies most of the vapor phase and the heavier component, benzene, occupies most of the liquid phase.

The phase-separation situation compounds the problem of modeling binary interactions, for which experimentalists usually take such data at high pressures. At high pressures, a portion of the lighter component condenses when the system pressure exceeds its vapor pressure. (Such a case may be observed in the binary methane - triethylene glycol system). Either choice is intended to reach a "true" VLE condition in which a significant portion of each component resides in each phase. Accordingly, the methane-benzene and methane-toluene systems of Tables 7.6-7.7 represent such high-pressure systems. In contrast, low-pressure data (either atmospheric and/or subatmospheric) may be taken for binary components with similar molecular weights and boiling points. When these low pressures are reached, a portion of the heavier component boils off the liquid into the vapor when its vapor

pressure exceeds that of the system. (This accounts for several of the isobars and low pressures reported for the aromatic binary systems of Tables 7.1-7.4).

Next, Table 7.6 presents results of the methane-toluene system similar to those shown of the methane-benzene system. At the two lowest temperatures (459.67 and 499.67 °R), GARs predict the methane compositions more accurately than BIPs for the vapor compositions and K-values of both components for all data sets simultaneously. Although Table 7.7 shows more accurate BIP results for methane-*ortho*-xylene and methane-n-propylbenzene, the simultaneous GAR predictions for both methane-n-propylbenzene isotherms reveals significant improvement in AARD predictions for n-propylbenzene vapor compositions and K-values. The results of these two tables then suggest both the comparative accuracy of GARs to BIPs, as well as the potential improvements that GARs can occasionally provide.

The results of Table 7.8 also reflect these potential improvements made by GARs in the methane-water system. Here, GARs are surpassed by BIPs with a maximum of 1.9% (for the K-value of water at 559.67 °R) in separate isotherms, while GARs show a maximum improvement of 5.0% (for the K-value of methane also at 559.67 °R).

7.3.3 AARD Results for Binary Mixtures of Triethylene Glycol with Methane, Aromatic Compounds, and Water

Tables 7.9-7.10 present AARD results for binary mixtures of triethylene glycol (TEG) with methane, aromatic compounds, and water. Here, Table 7.9 reflects

the aforementioned wide degree of phase separation occurring between TEG and methane, along with the high pressures at which this system was measured. Overall, all single-isotherm results GARs prove superior to BIPs for all liquid-methane and TEG-vapor-compositions as well as the K-value AARDS of both components. The sole exception to this trend occurs when BIPs surpass GARs by a mere 0.1% for methane vapor at both 536.67 °R and 716.67 °R. The only substantial AARDs in these trends appear in the regression over all data sets for the liquid composition and K-values of methane, due to the low methane composition in the liquid phase (with less than one molar percentage).

Table 7.10 reveals that GARs surpassed all BIP AARDs for the TEG-water system, with a minimum improvement of 0.7% for liquid-TEG composition and a maximum improvement of 3.6% for liquid-water composition. The TEG-aromatic results compare in accuracy for BIPs and GARs, with BIPs surpassing GARs only in liquid compositions.

7.3.4 AARD Results for Binary Mixtures of Freons

Lastly, the binary VLE results of this work conclude with AARD results for the binary freon mixture consisting of tetrafluoromethane (freon R14) and trifluoromethane (freon R23). Table 7.11 presents these results and with the sole exception of the BIP AARD being 0.1% less than that the GAR AARD for the K-value of R23 at 459.67 °R, GARs yielded equivalent and/or lesser AARDs than BIPs for all other quantities in this table. Moreover, this result occurred for each individual

isotherm as well as all data sets simultaneously.

Simply put, the results of Table 7.11 represent an improvement in only one VLE system. Nevertheless, they do prove that GARs present a potential advantage over BIPs in terms of their predictive accuracy for other VLE systems outside of those in glycol-dehydration applications. Obviously, such a result could prove true for other systems as well, but they must be left to future investigations beyond this work. Finally, the freon results also prove that the asymmetrical properties of GARs bear future investigation in terms of "mapping out," or discriminating between, other binary systems. This "mapping out" of binary systems is discussed in the following section.

7.4 Numerical Values of GAR Parameters for Binary VLE Systems

Tables 7.12-7.33 present the numerical values of GAR parameters regressed for all five LCM UIPs described in Chapters 3 and 6 of this work. These tables are, however, split into two separate sections, namely that of GAR values for the first two LCM UIPs (Tables 7.12-7.22) and the last three LCM UIPs (Tables 7.23-7.33).

In all, most of the GAR parameters regressed appear fairly consistent in value, with the most notable difference occurring in sign rather than in numerical value. Here, the methane-water GAR values of Tables 7.19 and 7.30 support this trend, as do those for the methane-TEG system in Tables 7.20 and 7.31. This positive/negative value outcome is expected, since GAR parameters may be either positive or negative to indicate the dominance of a given component in a mixture for each parameter), a

Table 7.12

GAR Parameter Values for the for the Benzene-*Meta*-Xylene and Benzene-*Para*-Xylene VLE Systems

(First Two LCM Parameters)

System	Number of Data Points	Temp. Range (°R)	Pressure Range (psia)	GAR Parameter $\alpha_{ij}(\lambda_i,\lambda_j)$	GAR Parameter $\gamma_{ij}(\lambda_i,\lambda_j)$	GAR Parameter $\alpha_{ij}(V_i^*,V_j^*)$	GAR Parameter $\gamma_{ij}(V_i^*,V_j^*)$
Benzene-*meta*-Xylene	9	536.67	0.57-1.72	0.68646	-3.9530	0.50052	-2.8612
Benzene-*meta*-Xylene	13	558.27	0.43-2.91	0.47404	-4.0800	0.49959	-3.5280
Benzene-*meta*-Xylene	13	581.67	0.82-4.92	0.62586	-2.6043	-0.22816	-23.508
Benzene-*meta*-Xylene	9	655.27-716.31	14.696	0.64439	-7.3750	0.50021	-15.223
Benzene-*meta*-Xylene (All data sets)	44	536.67-716.31	0.43-14.696	0.64437	-0.35817	-0.10183	1.3758
Benzene-*para*-Xylene (Single isobar only)	13	642.15-723.87	14.696	0.81392	-0.75127	0.30727	-0.76543

Table 7.13

GAR Parameter Values for the Toluene-*Meta*-Xylene and Toluene-*Para*-Xylene VLE Systems

(First Two LCM Parameters)

System	Number of Data Points	Temp. Range (^{o}R)	Pressure Range (psia)	GAR Parameter $\alpha_{ij}(\lambda_i,\lambda_j)$	GAR Parameter $\gamma_{ij}(\lambda_i,\lambda_j)$	GAR Parameter $\alpha_{ij}(V_i^*,V_j^*)$	GAR Parameter $\gamma_{ij}(V_i^*,V_j^*)$
Toluene-*meta*-Xylene	15	672.48	5.12-10.33	-16.417	16.873	-0.50002	23.540
Toluene-*meta*-Xylene	9	690.48	6.92-14.29	0.28804	1.0406	0.21095	1.1203
Toluene-*meta*-Xylene	9	708.66	9.42-18.60	-0.096384	1.0361	0.22063	1.0775
Toluene-*meta*-Xylene	9	699.21-725.44	14.696	-4.9853	33.982	-0.30511	177.82
Toluene-*meta*-Xylene (All data sets)	42	672.48-725.44	5.12-18.60	-2.3219	12.470	-0.50082	19.682
Toluene-*para*-Xylene (Single isotherm only)	12	653.67	4.04-6.28	-2.1680	19.320	-0.37610	78.470

Table 7.14

GAR Parameter Values for the Benzene-Toluene and Ethylbenzene-*Ortho*-Xylene VLE Systems

(First Two LCM Parameters)

System	Number of Data Points	Temp. Range (°R)	Pressure Range (psia)	GAR Parameter $\alpha_{ij}(\lambda_i,\lambda_j)$	GAR Parameter $\gamma_{ij}(\lambda_i,\lambda_j)$	GAR Parameter $\alpha_{ij}(V_i^*,V_j^*)$	GAR Parameter $\gamma_{ij}(V_i^*,V_j^*)$
Benzene-Toluene	88	637.69-691.02	14.696	0.045928	-3.4192	0.50113	-2.9628
Benzene-Toluene	4	617.67	7.96-8.20	-0.096189	0.93332	0.10736	1.0763
Benzene-Toluene (All data sets)	92	617.67-691.02	7.96-14.696	3.0974	-3.2269	0.46698	0.66137
Ethylbenzene-*ortho*-Xylene	15	671.67	3.90-4.91	0.099337	0.027729	0.47648	0.56235
Ethylbenzene-*ortho*-Xylene	13	594.99-606.87	0.97	-1.4181	3.1508	0.50083	4.3952
Ethylbenzene-*ortho*-Xylene	13	658.71-671.13	3.87	4.4945	-4.7305	0.45111	-2.6255
Ethylbenzene-*ortho*-Xylene (All data sets)	41	594.99-671.67	0.97-4.91	0.23431	0.89899	0.013276	0.98444

Table 7.15

GAR Parameter Values for the Benzene-Ethylbenzene and Toluene-Ethylbenzene VLE Systems

(First Two LCM Parameters)

System	Number of Data Points	Temp. Range (°R)	Pressure Range (psia)	GAR Parameter $\alpha_{ij}(\lambda_i,\lambda_j)$	GAR Parameter $\gamma_{ij}(\lambda_i,\lambda_j)$	GAR Parameter $\alpha_{ij}(V_i^*,V_j^*)$	GAR Parameter $\gamma_{ij}(V_i^*,V_j^*)$
Benzene-Ethylbenzene (Single isobar only)	11	637.63-735.23	14.696	1.8624	-3.3158	-0.45066	-9.4760
Toluene-Ethylbenzene	4	536.67	0.27-0.52	37.451	-39.863	0.018376	-13.123
Toluene-Ethylbenzene	15	671.67	5.25-10.46	0.13800	0.92151	0.13127	1.1256
Toluene-Ethylbenzene (Both isotherms)	19	536.67-671.67	0.27-10.46	0.49148	0.96751	-0.0094692	1.1245

Table 7.16

GAR Parameter Values for the Methane-Benzene VLE System (First Two LCM Parameters)

System	Number of Data Points	Temp. Range (^{o}R)	Pressure Range (psia)	GAR Parameter $\alpha_{ij}(\lambda_i,\lambda_j)$	GAR Parameter $\gamma_{ij}(\lambda_i,\lambda_j)$	GAR Parameter $\alpha_{ij}(V_i^*,V_j^*)$	GAR Parameter $\gamma_{ij}(V_i^*,V_j^*)$
Methane-Benzene	13	609.67	100.00-4000.00	0.41070	1.1361	-0.37735	1.3414
Methane-Benzene	6	757.89	288.19-2949.19	0.47052	1.2786	0.23308	1.3350
Methane-Benzene	5	831.33	438.23-2364.15	0.47608	0.78191	-0.50101	1.3993
Methane-Benzene	5	902.07	743.18-1982.34	0.52315	1.2439	0.17429	1.0958
Methane-Benzene (All data sets)	29	609.67-902.07	100.00-4000.00	0.35131	1.1180	-0.30827	1.3420

Table 7.17

GAR Parameter Values for the Methane-Toluene VLE System

(First Two LCM Parameters)

System	Number of Data Points	Temp. Range (°R)	Pressure Range (psia)	GAR Parameter $\alpha_{ij}(\lambda_i,\lambda_j)$	GAR Parameter $\gamma_{ij}(\lambda_i,\lambda_j)$	GAR Parameter $\alpha_{ij}(V_i^*,V_j^*)$	GAR Parameter $\gamma_{ij}(V_i^*,V_j^*)$
Methane-Toluene	12	459.67	50.00-2500.00	0.47631	1.4498	-0.020551	1.3031
Methane-Toluene	11	499.67	50.00-2500.00	0.48639	1.4122	0.45191	1.7594
Methane-Toluene	11	609.67	100.00-4000.00	0.66328	1.0622	0.40978	1.1883
Methane-Toluene	6	760.41	293.19-2939.20	0.15083	1.0186	-0.13220	1.0015
Methane-Toluene	7	831.69	294.36-3341.43	0.21083	0.91938	0.077279	0.98637
Methane-Toluene	6	901.35	292.45-2446.44	0.34249	0.88435	-0.010452	0.77072
Methane-Toluene	3	977.67	446.32-1022.40	1.5964	-0.64450	0.22346	2.4690
Methane-Toluene (All data sets)	56	459.67-977.67	50.00-4000.00	0.35983	1.4320	0.50095	1.5153

Table 7.18

GAR Parameter Values for the Methane-*Ortho*-Xylene and Methane-n-Propylbenzene VLE Systems

(First Two LCM Parameters)

System	Number of Data Points	Temp. Range (^{o}R)	Pressure Range (psia)	GAR Parameter $\alpha_{ij}(\lambda_i,\lambda_j)$	GAR Parameter $\gamma_{ij}(\lambda_i,\lambda_j)$	GAR Parameter $\alpha_{ij}(V_i^*,V_j^*)$	GAR Parameter $\gamma_{ij}(V_i^*,V_j^*)$
Methane-*ortho*-Xylene (Single isotherm only)	10	599.67	142.23-4267.00	0.74401	1.1699	0.28668	2.2029
Methane-n-Propylbenzene	7	564.48	739.70-5076.34	1.5949	-0.58761	-0.12798	1.30253
Methane-n-Propylbenzene	4	706.86	1522.90-4394.66	0.22226	0.94178	0.47392	0.27069
Methane-n-Propylbenzene (Both isotherms)	11	564.48-706.86	739.70-5076.34	1.6326	-0.73473	-0.065561	0.26931

Table 7.19

GAR Parameter Values for the Methane-Water VLE System

(First Two LCM Parameters)

System	Number of Data Points	Temp. Range (^{o}R)	Pressure Range (psia)	GAR Parameter $\alpha_{ij}(\lambda_i,\lambda_j)$	GAR Parameter $\gamma_{ij}(\lambda_i,\lambda_j)$	GAR Parameter $\alpha_{ij}(V_i^*,V_j^*)$	GAR Parameter $\gamma_{ij}(V_i^*,V_j^*)$
Methane-Water	6	600.66-932.94	192.47-935.64	0.23824	3.5846	0.51816	0.90630
Methane-Water	17	559.67	200.00-10000.00	3.6011	-1.7954	1.3915	-1.6317
Methane-Water	16	619.67	200.00-8000.00	5.1758	-1.9345	1.9835	-1.0722
Methane-Water	17	679.67	200.00-9000.00	3.3622	-1.0710	1.5931	-1.1492
Methane-Water	11	739.67	200.00-3500.00	1.4491	-3.4059	0.094459	-2.2854
Methane-Water	12	799.67	200.00-4000.00	1.1503	-3.5769	0.066065	-0.97604
Methane-Water (All Data sets)	79	559.67-932.94	192.47-10000.00	3.1681	-2.1942	1.1542	-1.3650

Table 7.20

GAR Parameter Values for the Methane-Triethylene Glycol VLE System

(First Two LCM Parameters)

System	Number of Data Points	Temp. Range (^{o}R)	Pressure Range (psia)	GAR Parameter $\alpha_{ij}(\lambda_i,\lambda_j)$	GAR Parameter $\gamma_{ij}(\lambda_i,\lambda_j)$	GAR Parameter $\alpha_{ij}(V_i^*,V_j^*)$	GAR Parameter $\gamma_{ij}(V_i^*,V_j^*)$
Methane-Triethylene Glycol	9	536.67	16.46-2823.89	0.077941	1.0710	0.42435	0.71121
Methane-Triethylene Glycol	9	581.67	16.06-2440.99	0.18850	0.77087	0.67919	0.58660
Methane-Triethylene Glycol	11	626.67	15.84-2855.80	0.029675	1.3857	0.34463	0.57199
Methane-Triethylene Glycol	10	671.67	16.37-2790.54	-0.19680	1.6785	0.51180	0.65040
Methane-Triethylene Glycol	10	716.67	18.46-2744.12	-0.17752	1.5979	0.37420	0.76906
Methane-Triethylene Glycol (All data sets)	49	536.67-716.67	15.84-2855.80	-0.19935	1.6122	0.46694	0.72657

Table 7.21

GAR Parameter Values for the Triethylene Glycol - Water,

Benzene - Triethylene Glycol, and Toluene - Triethylene Glycol VLE Systems

(First Two LCM Parameters)

System	Number of Data Points	Temp. Range (°R)	Pressure Range (psia)	GAR Parameter $\alpha_{ij}(\lambda_i,\lambda_j)$	GAR Parameter $\gamma_{ij}(\lambda_i,\lambda_j)$	GAR Parameter $\alpha_{ij}(V_i^*,V_j^*)$	GAR Parameter $\gamma_{ij}(V_i^*,V_j^*)$
Triethylene Glycol - Water (Single isotherm only)	15	859.67	18.53-76.04	-0.88204	3.4579	-0.30562	3.3504
Benzene - Triethylene Glycol (Single isobar only)	11	638.37-771.75	14.696	-2.0362	3.2548	2.0918	4.2255
Toluene - Triethylene Glycol (Single isobar only)	10	693.45-796.59	14.696	-3.7465	4.2377	4.2030	8.5207

Table 7.22

GAR Parameter Values for the Tetrafluoromethane-Trifluoromethane VLE System

(First Two LCM Parameters)

System	Number of Data Points	Temp. Range (^{o}R)	Pressure Range (psia)	GAR Parameter $\alpha_{ij}(\lambda_i,\lambda_j)$	GAR Parameter $\gamma_{ij}(\lambda_i,\lambda_j)$	GAR Parameter $\alpha_{ij}(V_i^*,V_j^*)$	GAR Parameter $\gamma_{ij}(V_i^*,V_j^*)$
Tetrafluoromethane-Trifluoromethane	14	309.67	10.68-68.20	0.19836	5.6617	-2.7516	9.2610
Tetrafluoromethane-Trifluoromethane	18	359.67	26.78-218.82	1.8143	5.8802	-7.0589	9.0645
Tetrafluoromethane-Trifluoromethane	14	404.67	89.86-489.70	0.22863	7.1183	-5.8454	6.6442
Tetrafluoromethane-Trifluoromethane	9	459.67	283.28-703.71	9.0419	-7.2095	-5.5467	2.9786
Tetrafluoromethane-Trifluoromethane	12	509.67	519.56-753.46	3.8211	5.1460	3.2044	-0.34760
Tetrafluoromethane-Trifluoromethane (All data sets)	67	309.67-509.67	10.68-753.46	5.9436	-4.9255	5.2742	-2.5578

Table 7.23

GAR Parameter Values for the Benzene-*Meta*-Xylene and Benzene-*Para*-Xylene VLE Systems

(Last Three LCM Parameters)

System	Number of Data Points	Temp. Range (°R)	Pressure Range (psia)	GAR Parameter $\alpha_{ij}(\varepsilon_i,\varepsilon_j)$	GAR Parameter $\gamma_{ij}(\varepsilon_i,\varepsilon_j)$	LCM: GAR Parameter $F{:}\alpha_{ij}(V_i^*,V_j^*)$	GAR Parameter $\gamma_{ij}(D_i,D_j)$
Benzene-*meta*-Xylene	9	536.67	0.57-1.72	0.12429	-0.043334	-0.31752	---
Benzene-*meta*-Xylene	13	558.27	0.43-2.91	0.26967	-0.33031	0.50122	---
Benzene-*meta*-Xylene	13	581.67	0.82-4.92	-0.38651	-0.08403	0.34230	---
Benzene-*meta*-Xylene	9	655.27-716.31	14.696	-0.47093	0.50094	0.50060	---
Benzene-*meta*-Xylene (All data sets)	44	536.67-716.31	0.43-14.696	-0.044926	-0.50093	-0.50047	---
Benzene-*para*-Xylene (Single isobar only)	13	642.15-723.87	14.696	0.097592	0.47266	0.35434	---

Table 7.24

GAR Parameter Values for the Toluene-*Meta*-Xylene and Toluene-*Para*-Xylene VLE Systems

(Last Three LCM Parameters)

System	Number of Data Points	Temp. Range (°R)	Pressure Range (psia)	GAR Parameter $\alpha_{ij}(\varepsilon_i,\varepsilon_j)$	GAR Parameter $\gamma_{ij}(\varepsilon_i,\varepsilon_j)$	LCM: GAR Parameter $F{:}\alpha_{ij}(V_i^*,V_j^*)$	GAR Parameter $\gamma_{ij}(D_i,D_j)$
Toluene-*meta*-Xylene	15	672.48	5.12-10.33	0.23074	0.44536	0.50097	---
Toluene-*meta*-Xylene	9	690.48	6.92-14.29	0.21255	0.50003	0.28173	---
Toluene-*meta*-Xylene	9	708.66	9.42-18.60	-0.04351	0.19173	0.17223	---
Toluene-*meta*-Xylene	9	699.21-725.44	14.696	0.50002	-0.49847	-0.50106	---
Toluene-*meta*-Xylene (All data sets)	42	672.48-725.44	5.12-18.60	0.50117	0.49340	-0.48226	---
Toluene-*para*-Xylene (Single isotherm only)	12	653.67	4.04-6.28	-0.49869	0.091475	-0.50145	---

Table 7.25

GAR Parameter Values for the Benzene-Toluene and Ethylbenzene-*Ortho*-Xylene VLE Systems

(Last Three LCM Parameters)

System	Number of Data Points	Temp. Range (°R)	Pressure Range (psia)	GAR Parameter $\alpha_{ij}(\varepsilon_i,\varepsilon_j)$	GAR Parameter $\gamma_{ij}(\varepsilon_i,\varepsilon_j)$	LCM: GAR Parameter $F{:}\alpha_{ij}(V_i^*,V_j^*)$	GAR Parameter $\gamma_{ij}(D_i,D_j)$
Benzene-Toluene	88	637.69-691.02	14.696	-0.28924	-0.49924	0.49080	---
Benzene-Toluene	4	617.67	7.96-8.20	0.14866	0.43920	0.24060	---
Benzene-Toluene (All data sets)	92	617.67-691.02	7.96-14.696	-0.37713	-0.48215	-0.085247	---
Ethylbenzene-*ortho*-Xylene	15	671.67	3.90-4.91	-0.33565	0.49483	0.49777	---
Ethylbenzene-*ortho*-Xylene	13	594.99-606.87	0.97	-0.49639	-0.15793	0.50059	---
Ethylbenzene-*ortho*-Xylene	13	658.71-671.13	3.87	0.17403	0.35173	0.32329	---
Ethylbenzene-*ortho*-Xylene (All data sets)	41	594.99-671.67	0.97-4.91	0.18289	0.50000	0.50185	---

Table 7.26

GAR Parameter Values for the Benzene-Ethylbenzene and Toluene-Ethylbenzene VLE Systems

(Last Three LCM Parameters)

System	Number of Data Points	Temp. Range (°R)	Pressure Range (psia)	GAR Parameter $\alpha_{ij}(\varepsilon_i,\varepsilon_j)$	GAR Parameter $\gamma_{ij}(\varepsilon_i,\varepsilon_j)$	LCM: GAR Parameter $F{:}\alpha_{ij}(V_i^*,V_j^*)$	GAR Parameter $\gamma_{ij}(D_i,D_j)$
Benzene-Ethylbenzene (Single isobar only)	11	637.63-735.23	14.696	0.37496	-0.49105	-0.0005559	---
Toluene-Ethylbenzene	4	536.67	0.27-0.52	-0.50096	-0.50033	-0.19498	---
Toluene-Ethylbenzene	15	671.67	5.25-10.46	-0.17033	0.45118	0.24358	---
Toluene-Ethylbenzene (Both isotherms)	19	536.67-671.67	0.27-10.46	-0.50054	0.49723	-0.53189	---

Table 7.27

GAR Parameter Values for the Methane-Benzene VLE System (Last Three LCM Parameters)

System	Number of Data Points	Temp. Range (°R)	Pressure Range (psia)	GAR Parameter $\alpha_{ij}(\varepsilon_i,\varepsilon_j)$	GAR Parameter $\gamma_{ij}(\varepsilon_i,\varepsilon_j)$	LCM: GAR Parameter $F{:}\alpha_{ij}(V_i^*,V_j^*)$	GAR Parameter $\gamma_{ij}(D_i,D_j)$
Methane-Benzene	13	609.67	100.00-4000.00	0.12195	0.094002	-0.19179	---
Methane-Benzene	6	757.89	288.19-2949.19	-0.43374	0.29165	-0.082164	---
Methane-Benzene	5	831.33	438.23-2364.15	-0.16192	-0.47752	-0.49222	---
Methane-Benzene	5	902.07	743.18-1982.34	-0.49238	0.31340	-0.15596	---
Methane-Benzene (All data sets)	29	609.67-902.07	100.00-4000.00	-0.021860	0.25407	-0.16802	---

Table 7.28

GAR Parameter Values for the Methane-Toluene VLE System

(Last Three LCM Parameters)

System	Number of Data Points	Temp. Range (°R)	Pressure Range (psia)	GAR Parameter $\alpha_{ij}(\varepsilon_i,\varepsilon_j)$	GAR Parameter $\gamma_{ij}(\varepsilon_i,\varepsilon_j)$	LCM: GAR Parameter $F{:}\alpha_{ij}(V_i^*,V_j^*)$	GAR Parameter $\gamma_{ij}(D_i,D_j)$
Methane-Toluene	12	459.67	50.00-2500.00	0.13192	-0.13322	-0.065184	---
Methane-Toluene	11	499.67	50.00-2500.00	0.042271	-0.19437	0.49657	---
Methane-Toluene	11	609.67	100.00-4000.00	0.13792	-0.15038	0.50101	---
Methane-Toluene	6	760.41	293.19-2939.20	-0.065102	0.13197	-0.10551	---
Methane-Toluene	7	831.69	294.36-3341.43	-0.084827	0.13086	-0.13124	---
Methane-Toluene	6	901.35	292.45-2446.44	-0.34832	0.50105	-0.46026	---
Methane-Toluene	3	977.67	446.32-1022.40	-0.50088	-0.49867	-0.494725	---
Methane-Toluene (All data sets)	56	459.67-977.67	50.00-4000.00	0.07073	-0.18271	0.33045	---

Table 7.29

GAR Parameter Values for the Methane-*Ortho*-Xylene and Methane-n-Propylbenzene VLE Systems

(Last Three LCM Parameters)

System	Number of Data Points	Temp. Range (°R)	Pressure Range (psia)	GAR Parameter $\alpha_{ij}(\varepsilon_i,\varepsilon_j)$	GAR Parameter $\gamma_{ij}(\varepsilon_i,\varepsilon_j)$	LCM: GAR Parameter $F{:}\alpha_{ij}(V_i^*,V_j^*)$	GAR Parameter $\gamma_{ij}(D_i,D_j)$
Methane-*ortho*-Xylene (Single isotherm only)	10	599.67	142.23-4267.00	0.50105	-0.47209	0.33671	---
Methane-n-Propylbenzene	7	564.48	739.70-5076.34	0.49942	-0.46078	0.49388	---
Methane-n-Propylbenzene	4	706.86	1522.90-4394.66	0.50101	-0.44168	0.50060	---
Methane-n-Propylbenzene (Both isotherms)	11	564.48-706.86	739.70-5076.34	0.37773	-0.34556	0.49856	---

Table 7.30

GAR Parameter Values for the Methane-Water VLE System (Last Three LCM Parameters)

System	Number of Data Points	Temp. Range (°R)	Pressure Range (psia)	GAR Parameter $\alpha_{ij}(\varepsilon_i, \varepsilon_j)$	GAR Parameter $\gamma_{ij}(\varepsilon_i, \varepsilon_j)$	LCM: GAR Parameter $F{:}\alpha_{ij}(V_i^*, V_j^*)$	GAR Parameter $\gamma_{ij}(D_i, D_j)$
Methane-Water	6	600.66-932.94	192.47-935.64	0.49377	-0.50017	0.50100	0.48301
Methane-Water	17	559.67	200.00-10000.00	0.50104	-0.49983	-0.49182	0.33222
Methane-Water	16	619.67	200.00-8000.00	0.46887	-0.48638	-0.50078	0.49553
Methane-Water	17	679.67	200.00-9000.00	0.49690	-0.50067	-0.49367	-0.50076
Methane-Water	11	739.67	200.00-3500.00	0.38472	0.47565	0.50067	0.47230
Methane-Water	12	799.67	200.00-4000.00	0.46075	0.45030	0.50006	-0.011377
Methane-Water (All Data sets)	79	559.67-932.94	192.47-10000.00	0.50159	-0.49658	0.18363	0.50005

Table 7.31

GAR Parameter Values for the Methane-Triethylene Glycol VLE System

(Last Three LCM Parameters)

System	Number of Data Points	Temp. Range (^{o}R)	Pressure Range (psia)	GAR Parameter $\alpha_{ij}(\varepsilon_i,\varepsilon_j)$	GAR Parameter $\gamma_{ij}(\varepsilon_i,\varepsilon_j)$	LCM: GAR Parameter $F{:}\alpha_{ij}(V_i^*,V_j^*)$	GAR Parameter $\gamma_{ij}(D_i,D_j)$
Methane-Triethylene Glycol	9	536.67	16.46-2823.89	-0.29485	0.026614	0.12119	-0.47002
Methane-Triethylene Glycol	9	581.67	16.06-2440.99	-0.25189	-0.34378	0.072118	0.49977
Methane-Triethylene Glycol	11	626.67	15.84-2855.80	-0.47006	0.30442	0.17982	-0.41886
Methane-Triethylene Glycol	10	671.67	16.37-2790.54	-0.33418	-0.036168	-0.055648	-0.48089
Methane-Triethylene Glycol	10	716.67	18.46-2744.12	-0.24218	-0.11664	-0.015216	-0.49336
Methane-Triethylene Glycol (All data sets)	49	536.67-716.67	15.84-2855.80	-0.24719	-0.25531	0.073330	0.16567

Table 7.32

GAR Parameter Values for the Triethylene Glycol - Water,

Benzene - Triethylene Glycol, and Toluene - Triethylene Glycol VLE Systems

(Last Three LCM Parameters)

System	Number of Data Points	Temp. Range (°R)	Pressure Range (psia)	GAR Parameter $\alpha_{ij}(\varepsilon_i,\varepsilon_j)$	GAR Parameter $\gamma_{ij}(\varepsilon_i,\varepsilon_j)$	LCM: GAR Parameter $F{:}\alpha_{ij}(V_i^*,V_j^*)$	GAR Parameter $\gamma_{ij}(D_i,D_j)$
Triethylene Glycol - Water (Single isotherm only)	15	859.67	18.53-76.04	-0.47555	-0.39131	-0.45357	-0.11925
Benzene - Triethylene Glycol (Single isobar only)	11	638.37-771.75	14.696	-0.41768	-0.33062	-0.12810	-0.50069
Toluene - Triethylene Glycol (Single isobar only)	10	693.45-796.59	14.696	-0.42218	-0.042425	-0.49929	-0.48711

Table 7.33

GAR Parameter Values for the Tetrafluoromethane-Trifluoromethane VLE System

(Last Three LCM Parameters)

System	Number of Data Points	Temp. Range (°R)	Pressure Range (psia)	GAR Parameter $\alpha_{ij}(\varepsilon_i,\varepsilon_j)$	GAR Parameter $\gamma_{ij}(\varepsilon_i,\varepsilon_j)$	LCM: GAR Parameter $F{:}\alpha_{ij}(V_i^*,V_j^*)$	GAR Parameter $\gamma_{ij}(D_i,D_j)$
Tetrafluoromethane-Trifluoromethane	14	309.67	10.68-68.20	-0.50114	-0.46842	-0.49226	0.29688
Tetrafluoromethane-Trifluoromethane	18	359.67	26.78-218.82	-0.50091	-0.50064	0.49996	-0.50009
Tetrafluoromethane-Trifluoromethane	14	404.67	89.86-489.70	-0.39796	-0.50167	-0.45812	-0.33754
Tetrafluoromethane-Trifluoromethane	9	459.67	283.28-703.71	-0.49304	-0.27339	-0.49883	0.41206
Tetrafluoromethane-Trifluoromethane	12	509.67	519.56-753.46	-0.50009	-0.49985	0.49537	0.49043
Tetrafluoromethane-Trifluoromethane (All data sets)	67	309.67-509.67	10.68-753.46	-0.50083	-0.49991	0.33470	0.18321

feature that does not usually occur in BIPs. Such a result might indicate that each parameter may be forced by the regression algorithm to proceed along a given search vector to arrive at an optimal result independent of sign; at the very least, the GAR values indicate that the GAR remains well-behaved as a function in terms of its estimation properties. In fact, the GAR rarely caused computer failure over any of the systems regressed. Since little, however, is known at this time of the properties of GAR parameters, only general trends are discussed herein for numerical GAR values.

Overall, sixty-two regressions were carried out for this work in terms of isotherms, isobars, and various temperature/pressure ranges. To begin with, one of the most striking patterns that occurs in Tables 7.23-7.33 consists of the LCM-GAR Parameter $F{:}\alpha_{ij}(V_i^*, V_j^*)$. in terms of its absolute value occurring close to 0.5 (actually in the range 0.45357-0.53189) thirty-three times. In fact, the extreme absolute values for this parameter occur with a near-zero value (-0.0005559) for the benzene-ethylbenzene isobar (which constitutes the only data available for this system), and 0.35434 for the lone benzene-para-xylene isobar (again the only data available for a system). The most striking exception to this trend appears in the results for the methane-TEG system of Table 7.31; since this GAR parameter reflects the original asymmetric UIP in the LCM, this exception indicates that the other asymmetrical GARs parameters do account for asymmetry.

Next, a comparison may be made between binary systems involving different isomeric components. In Tables 7.12 and 7.23, the GAR parameters for benzene-*meta*-xylene and benzene-*para*-xylene appear opposite only in sign, with the sole

exceptions occurring for occasionally-low values of the parameter $\gamma_{ij}(\varepsilon_i, \varepsilon_j)$. A similar trend appears between the toluene-*meta*-xylene and toluene-*para*-xylene systems. In all, however, significant deviations do not arise for most GAR parameters between these two systems, thereby lending some support to the idea of using a given binary set of data with an alternate isomeric component when binary data for the preferred component is unavailable.

Finally, GAR values do appear fairly consistent in absolute value (but again not in sign) for the two freons in Tables 7.22 and 7.33. Since this system comprised the most accurate system predicted by GARs over BIPs, the GAR values support the use of GARs as an asymmetric, two-dimensional standard over the symmetric, one-dimensional standard of BIPs, but require future investigation to discern a more visible trend.

Altogether, the results of Tables 7.12-7.33 definitely show tendencies for the GAR parameters to yield similar trends in absolute values for all eight parameters in terms of different isotherms of the same binary system. These trends, however, might have been more discernible if fewer GAR parameters were regressed, or if only one GAR parameter had been regressed for each UIP. In addition, the flexible-tolerance method of Himmelblau (1972) was used to constrain the GARs according to

$$0.5 \leq \alpha_{ij} \leq 0.5 \qquad (7.1)$$

and

$$3.0 \leq \gamma_{ij} \leq 3.0 \qquad (7.2)$$

Obviously, the flexible-tolerance method did not constrain as desired for Equations (7.1-7.2) in the TEG systems of Tables 7.20-7.21 and the freons of Table 7.22. These results then suggest other constrained algorithms for future research. At the same time, however, the absence of any values several orders of magnitude larger than the constraints in Equations (7.1-7.2) shows a certain degree of robustness for the two GAR parameters regressed for all five LCM UIPs.

At any rate, the competitive accuracy of GARs with respect to BIPs illustrates their potential for use in other LCMs, especially when some of these LCMs (e.g., the NRTL LCM) employ asymmetrical parameters. The similar trends displayed and discussed in this section show that, far from yielding meaningless parameter values, GARs provide rough parameter estimates that can aid in the simulation of other binary VLE systems.

7.5 Numerical Values of BIP Parameters for Binary VLE Systems

Tables 7.34-7.44 present the final values for BIPs regressed over all binary VLE systems simulated in this work. Here, it should be noted that all five UIPs for the LCM employed symmetric BIPs -- i.e.,

$$m_{ij} = m_{ji} \quad , \qquad (7.3)$$

through the symmetric-linear combining rule of Equation (4.2) of Chapter 4:

$$\text{Linear } (N = 1, \alpha = 0, \lambda = 1): \qquad B_{ij} = m_{ij} \frac{\left(B_i + B_j\right)}{2} \quad . \qquad (7.4)$$

As seen in Equation (7.4) and explained in detail in Sections 4.2-4.3, the linear

Table 7.34

BIP Values for the Benzene-*Meta*-Xylene and Benzene-*Para*-Xylene VLE Systems

(All Five LCM Parameters)

System	Number of Data Points	Temp. Range (°R)	Pressure Range (psia)	BIP Param. m_{ij} for (λ_i, λ_j)	BIP Param. m_{ij} for (V_i^*, V_j^*)	BIP Param. m_{ij} for $(\varepsilon_i, \varepsilon_j)$	BIP Param. m_{ij} for F: (V_i^*, V_j^*)	BIP Param. m_{ij} for (D_i, D_j)
Benzene-*meta*-Xylene	9	536.67	0.57-1.72	0.99565	0.98908	0.98733	1.0203	---
Benzene-*meta*-Xylene	13	558.27	0.43-2.91	0.99874	0.99307	1.0033	0.98291	---
Benzene-*meta*-Xylene	13	581.67	0.82-4.92	0.98694	0.99204	0.99613	1.0618	---
Benzene-*meta*-Xylene	9	655.27-716.31	14.696	2.3549	0.88534	1.2467	0.049180	---
Benzene-*meta*-Xylene (All data sets)	44	536.67-716.31	0.43-14.696	1.0001	0.99180	0.98531	1.0224	---
Benzene-*para*-Xylene (Single isobar only)	13	642.15-723.87	14.696	1.0001	1.0037	0.98593	0.99752	---

Table 7.35

BIP Values for the Toluene-*Meta*-Xylene and Toluene-*Para*-Xylene VLE Systems

(All Five LCM Parameters)

System	Number of Data Points	Temp. Range (°R)	Pressure Range (psia)	BIP Param. m_{ij} for (λ_i, λ_j)	BIP Param. m_{ij} for (V_i^*, V_j^*)	BIP Param. m_{ij} for $(\varepsilon_i, \varepsilon_j)$	BIP Param. m_{ij} for F: (V_i^*, V_j^*)	BIP Param. m_{ij} for (D_i, D_j)
Toluene-*meta*-Xylene	15	672.48	5.12-10.33	0.99923	1.0110	0.99532	1.0037	---
Toluene-*meta*-Xylene	9	690.48	6.92-14.29	0.98656	1.2905	0.87802	0.89195	---
Toluene-*meta*-Xylene	9	708.66	9.42-18.60	1.1366	0.88527	0.97269	0.88842	---
Toluene-*meta*-Xylene	9	699.21-725.44	14.696	0.79465	0.72709	1.2054	0.85182	---
Toluene-*meta*-Xylene (All data sets)	42	672.48-725.44	5.12-18.60	1.1330	0.78728	0.99250	0.90657	---
Toluene-*para*-Xylene (Single isotherm only)	12	653.67	4.04-6.28	1.0273	0.93349	1.0036	1.0318	---

Table 7.36

BIP Values for the Benzene-Toluene and Ethylbenzene-*Ortho*-Xylene VLE Systems

(All Five LCM Parameters)

System	Number of Data Points	Temp. Range (°R)	Pressure Range (psia)	BIP Param. m_{ij} for (λ_i, λ_j)	BIP Param. m_{ij} for (V_i^*, V_j^*)	BIP Param. m_{ij} for $(\varepsilon_i, \varepsilon_j)$	BIP Param. m_{ij} for F: (V_i^*, V_j^*)	BIP Param. m_{ij} for (D_i, D_j)
Benzene-Toluene	88	637.69-691.02	14.696	1.0058	0.98650	0.99624	1.0062	---
Benzene-Toluene	4	617.67	7.96-8.20	0.98649	1.0477	0.98929	0.89641	---
Benzene-Toluene (All data sets)	92	617.67-691.02	7.96-14.696	1.0017	1.0047	0.99264	1.0104	---
Ethylbenzene-*ortho*-Xylene	15	671.67	3.90-4.91	1.0005	1.0136	0.99574	1.0023	---
Ethylbenzene-*ortho*-Xylene	13	594.99-606.87	0.97	0.99873	1.0141	0.99603	1.0009	---
Ethylbenzene-*ortho*-Xylene	13	658.71-671.13	3.87	0.99620	1.0158	0.99665	1.0001	---
Ethylbenzene-*ortho*-Xylene (All data sets)	41	594.99-671.67	0.97-4.91	0.99800	1.0128	0.99677	1.0038	---

Table 7.37

BIP Values for the Benzene-Ethylbenzene and Toluene-Ethylbenzene VLE Systems

(All Five LCM Parameters)

System	Number of Data Points	Temp. Range (°R)	Pressure Range (psia)	BIP Param. m_{ij} for (λ_i, λ_j)	BIP Param. m_{ij} for (V_i^*, V_j^*)	BIP Param. m_{ij} for $(\varepsilon_i, \varepsilon_j)$	BIP Param. m_{ij} for F: (V_i^*, V_j^*)	BIP Param. m_{ij} for (D_i, D_j)
Benzene-Ethylbenzene (Single isobar only)	11	637.63-735.23	14.696	0.99944	1.0239	0.97837	0.96891	
Toluene-Ethylbenzene	4	536.67	0.27-0.52	0.98200	1.0149	0.99763	0.97875	---
Toluene-Ethylbenzene	15	671.67	5.25-10.46	1.0008	1.0130	0.99428	1.0035	---
Toluene-Ethylbenzene (Both isotherms)	19	536.67-671.67	0.27-10.46	0.97426	1.0734	0.99058	1.0262	---

Table 7.38

BIP Values for the Methane-Benzene VLE System

(All Five LCM Parameters)

System	Number of Data Points	Temp. Range (°R)	Pressure Range (psia)	BIP Param. m_{ij} for (λ_i, λ_j)	BIP Param. m_{ij} for (V_i^*, V_j^*)	BIP Param. m_{ij} for $(\varepsilon_i, \varepsilon_j)$	BIP Param. m_{ij} for F: (V_i^*, V_j^*)	BIP Param. m_{ij} for (D_i, D_j)
Methane-Benzene	13	609.67	100.00-4000.00	0.98126	0.89689	0.86141	1.0807	---
Methane-Benzene	6	757.89	288.19-2949.19	1.0790	1.2232	0.80878	1.3043	---
Methane-Benzene	5	831.33	438.23-2364.15	2.3125	1.0415	0.68555	0.92673	---
Methane-Benzene	5	902.07	743.18-1982.34	1.2372	1.0551	0.88514	1.1665	---
Methane-Benzene (All data sets)	29	609.67-902.07	100.00-4000.00	0.54997	1.2574	0.91833	1.3391	---

Table 7.39

BIP Values for the Methane-Toluene VLE System

(All Five LCM Parameters)

System	Number of Data Points	Temp. Range (°R)	Pressure Range (psia)	BIP Param. m_{ij} for (λ_i, λ_j)	BIP Param. m_{ij} for (V_i^*, V_j^*)	BIP Param. m_{ij} for $(\varepsilon_i, \varepsilon_j)$	BIP Param. m_{ij} for F: (V_i^*, V_j^*)	BIP Param. m_{ij} for (D_i, D_j)
Methane-Toluene	12	459.67	50.00-2500.00	0.93780	0.80484	0.79455	1.1758	---
Methane-Toluene	11	499.67	50.00-2500.00	0.90665	0.88716	0.80493	1.1794	---
Methane-Toluene	11	609.67	100.00-4000.00	0.81104	0.92360	0.89937	1.1280	---
Methane-Toluene	6	760.41	293.19-2939.20	0.92302	1.0040	0.88674	1.1433	---
Methane-Toluene	7	831.69	294.36-3341.43	1.0205	1.0104	0.87479	1.1292	---
Methane-Toluene	6	901.35	292.45-2446.44	1.1040	0.94948	0.95031	1.1294	---
Methane-Toluene	3	977.67	446.32-1022.40	6.4549	0.59284	0.78974	0.64404	---
Methane-Toluene (All data sets)	56	459.67-977.67	50.00-4000.00	0.54055	1.3044	0.85097	1.3863	---

Table 7.40

BIP Values for the Methane-*Ortho*-Xylene and Methane-n-Propylbenzene VLE Systems

(All Five LCM Parameters)

System	Number of Data Points	Temp. Range (°R)	Pressure Range (psia)	BIP Param. m_{ij} for (λ_i, λ_j)	BIP Param. m_{ij} for (V_i^*, V_j^*)	BIP Param. m_{ij} for $(\varepsilon_i, \varepsilon_j)$	BIP Param. m_{ij} for F: (V_i^*, V_j^*)	BIP Param. m_{ij} for (D_i, D_j)
Methane-*ortho*-Xylene (Single isotherm only)	10	599.67	142.23-4267.00	1.6271	1.0119	0.64733	1.0168	---
Methane-n-Propylbenzene	7	564.48	739.70-5076.34	1.7260	0.46502	0.81703	0.30546	---
Methane-n-Propylbenzene	4	706.86	1522.90-4394.66	1.1366	0.70034	0.64971	0.43499	---
Methane-n-Propylbenzene (Both isotherms)	11	564.48-706.86	739.70-5076.34	4.2614	0.72977	0.53568	0.49706	---

Table 7.41

BIP Values for the Methane-Water VLE System (All Five LCM Parameters)

System	Number of Data Points	Temp. Range (°R)	Pressure Range (psia)	BIP Param. m_{ij} for (λ_i, λ_j)	BIP Param. m_{ij} for (V_i^*, V_j^*)	BIP Param. m_{ij} for $(\varepsilon_i, \varepsilon_j)$	BIP Param. m_{ij} for F: (V_i^*, V_j^*)	BIP Param. m_{ij} for (D_i, D_j)
Methane-Water	6	600.66-932.94	192.47-935.64	0.36820	1.1494	1.0684	1.4072	0.32301
Methane-Water	17	559.67	200.00-10000.00	1.0033	0.55805	0.47984	0.96975	1.4300
Methane-Water	16	619.67	200.00-8000.00	1.2686	0.79489	0.47807	1.0558	0.85080
Methane-Water	17	679.67	200.00-9000.00	1.2165	0.79679	0.47041	1.0507	0.72467
Methane-Water	11	739.67	200.00-3500.00	1.0853	0.90836	0.50190	1.1307	1.1702
Methane-Water	12	799.67	200.00-4000.00	1.2452	0.99042	0.50233	1.1638	1.4806
Methane-Water (All Data sets)	79	559.67-932.94	192.47-10000.00	0.86976	0.82013	0.48843	1.0814	1.2828

Table 7.42

BIP Values for the Methane-Triethylene Glycol VLE System

(All Five LCM Parameters)

System	Number of Data Points	Temp. Range (°R)	Pressure Range (psia)	BIP Param. m_{ij} for (λ_i, λ_j)	BIP Param. m_{ij} for (V_i^*, V_j^*)	BIP Param. m_{ij} for $(\varepsilon_i, \varepsilon_j)$	BIP Param. m_{ij} for F: (V_i^*, V_j^*)	BIP Param. m_{ij} for (D_i, D_j)
Methane-Triethylene Glycol	9	536.67	16.46-2823.89	1.0090	1.0344	0.31809	0.92810	0.86705
Methane-Triethylene Glycol	9	581.67	16.06-2440.99	1.1766	1.1028	0.63523	1.4291	1.1599
Methane-Triethylene Glycol	11	626.67	15.84-2855.80	1.0630	0.95364	0.69483	1.3699	0.96911
Methane-Triethylene Glycol	10	671.67	16.37-2790.54	0.94740	1.1734	0.70631	1.4231	0.97882
Methane-Triethylene Glycol	10	716.67	18.46-2744.12	1.3916	1.0250	0.65183	1.2733	1.1573
Methane-Triethylene Glycol (All data sets)	49	536.67-716.67	15.84-2855.80	1.0286	1.0838	0.23658	0.82261	0.86379

Table 7.43

BIP Values for the Triethylene Glycol - Water,

Benzene - Triethylene Glycol, and Toluene - Triethylene Glycol VLE Systems

(All Five LCM Parameters)

System	Number of Data Points	Temp. Range (^{o}R)	Pressure Range (psia)	BIP Param. m_{ij} for (λ_i, λ_j)	BIP Param. m_{ij} for (V_i^*, V_j^*)	BIP Param. m_{ij} for $(\varepsilon_i, \varepsilon_j)$	BIP Param. m_{ij} for F: (V_i^*, V_j^*)	BIP Param. m_{ij} for (D_i, D_j)
Triethylene Glycol - Water (Single isotherm only)	15	859.67	18.53-76.04	1.1529	0.77496	0.81834	0.83464	0.85159
Benzene - Triethylene Glycol (Single isobar only)	11	638.37-771.75	14.696	1.2777	1.4995	0.54167	1.0449	0.76293
Toluene - Triethylene Glycol (Single isobar only)	10	693.45-796.59	14.696	1.3062	1.4738	0.68826	1.3220	1.3511

Table 7.44

BIP Values AARDs for the Tetrafluoromethane-Trifluoromethane VLE System

(All Five LCM Parameters)

System	Number of Data Points	Temp. Range (^{o}R)	Pressure Range (psia)	BIP Param. m_{ij} for (λ_i, λ_j)	BIP Param. m_{ij} for (V_i^*, V_j^*)	BIP Param. m_{ij} for $(\varepsilon_i, \varepsilon_j)$	BIP Param. m_{ij} for F: (V_i^*, V_j^*)	BIP Param. m_{ij} for (D_i, D_j)
Tetrafluoromethane-Trifluoromethane	14	309.67	10.68-68.20	0.96466	0.98044	0.91958	1.0796	0.94357
Tetrafluoromethane-Trifluoromethane	18	359.67	26.78-218.82	0.95232	0.96935	0.93310	1.0691	0.93381
Tetrafluoromethane-Trifluoromethane	14	404.67	89.86-489.70	0.99431	0.98499	0.90594	1.0222	1.0063
Tetrafluoromethane-Trifluoromethane	9	459.67	283.28-703.71	0.99693	1.0386	0.87888	1.0165	1.0247
Tetrafluoromethane-Trifluoromethane	12	509.67	519.56-753.46	1.0884	1.0752	0.82317	1.0121	0.99362
Tetrafluoromethane-Trifluoromethane (All data sets)	67	309.67-509.67	10.68-753.46	0.77819	1.0607	0.99519	1.1413	0.72461

combining rule represents a limiting case for (a) the generalized symmetric rule (GSR) by Wenzel et al. (Juris, 1970; Juris and Wenzel, 1974) in Section 4.2 when $N = 1$ and (b) the GAR of Section 4.3 when $N = 1$, $\alpha = 0$, and $\lambda = 1$.

As expected, BIPs yield slight deviations from their initial values of unity for all five LCM UIPs. Of course, exceptions to this trend may be seen in the value of 2.3549 for the BIP parameter $m_{ij}(\lambda_i, \lambda_j)$ in the benzene-*meta*-xylene isobar (at 14.696 psia) of Table 7.34 and the low values (0.23658-0.70631) in the parameter $m_{ij}(\varepsilon_i, \varepsilon_j)$ for the methane-TEG system of Table 7.42. In addition, inconsistent trends also appear in BIP parameters in the polar BIP $m_{ij}(D_i, D_j)$ for the methane-water results of Table 7.41.

Next, it remains well-known that BIPs are temperature-dependent and can be correlated to some extent by isothermal VLE data. Moreover, the correlations for BIPs provided by Nishiumi et al. (as discussed in Section 2.4.2 of Chapter 2) through critical-volume ratios provide additional insight into the modeling of binary VLE systems. Unfortunately, little understanding seems to exist beyond these two generalizations for either equations of state or LCMs. Since this simple one-dimensional standard offers little understanding in the way of "mapping out" binary VLE systems, it is hoped that the two-dimensional standard of GARs might provide greater differentiation between these systems.

Finally, it should be noted that the simulation of nonpolar systems for this work required the regression of four BIPs (as opposed to five for systems containing a

polar component), as compared to seven GAR parameters (as opposed to eight for systems containing a polar component). Obviously, the regression of fewer parameters for each system might then decrease the number of multiple solutions (i.e., differences in numerical value) possible in UIP values. To this end, Section 9.2 discusses the regression of fewer UIPs in LCMs, with a preference toward asymmetry as seen in the NRTL LCM, along with suggestions on how to employ this approach with both the GAR and the LCM utilized for this work.

CHAPTER VIII

PROCEDURES TO ACCOUNT FOR MISSING BINARY DATA

8.1 Overview

Certain procedures have been developed to account for missing binary vapor-liquid equilibrium (VLE) data in the thermodynamic literature. To be sure, the prediction of multicomponent systems typically requires the prior development of unlike-interaction parameters (UIPs) based on binary data. In fact, Gleason (p. 125, 1981), Jackson (1991, p. 238), and Walas (p. 33, 1985) independently show that the presence of n components in a multicomponent system requires N_C sets of binary data according to the relation

$$N_C = \frac{1}{2} n(n-1) \qquad . \qquad (8.1)$$

In the less likely case of multicomponent predictions based on ternary VLE data, Jackson (1991, p.238) points out the requirement of N_C sets of ternary data according to the relation

$$N_C = \frac{1}{6} n(n-1)(n-2) \qquad . \qquad (8.2)$$

As derived by the author of this work, the relations of both Equations (8.1) and (8.2) may then be generalized (on the basis of c components within a given data set) to yield the requirement of N_C sets of c-component VLE data according to the relation

$$N_C = \frac{n}{c!}\prod_{k=1}^{c-1}(p-k) \qquad . \qquad (8.3)$$

Frequently, however, certain binary mixture data cannot be found in the thermodynamic literature, with far less ternary mixture data available as well. As seen in Equations (8.1) through (8.3), the number of required data sets rises with the number of components present in the multicomponent system of interest. As an example, Equation (8.1) shows that predicting the seven-component triethylene glycol system published in the GPA Research Report RR-131 (Ng et al., 1991) requires twenty-one binary sets of data. This requirement becomes even larger for multicomponent predictions based on ternary data, with Equation (8.2) calculating the need for thirty-five ternary sets of data to predict the same seven-component system. Obviously, data limitations in the thermodynamic literature will restrict most VLE models to be based on binary data alone.

Nevertheless, several investigators have presented a variety of indirect methods to overcome the obstacle of missing binary VLE data needed for UIP predictions. Basically, these methods approximate either the missing binary data or the required UIPs themselves. The following sections in this chapter review several of these indirect methods -- as well as their applications relative to this work in Section 8.6 -- that can overcome this obstacle. These methods include the use of (1) solubility data, (2) ternary data, (3) other thermodynamic property data for a given binary system, (4) infinite-dilution activity coefficients, and (5) the substitution of alternate isomeric-component data. In addition, interpolation with the generalized asymmetric

rule (GAR) parameters presented in this work affords a sixth method to account for missing binary data.

8.2 Solubility Data

To begin with, although much aqueous (i.e., water) binary data exist in both VLE and solubility forms, far less VLE data exist for aqueous aromatic-water binary systems. In fact, for aqueous binary systems containing BTEX (benzene-toluene-ethylbenzene-xylene) components, the only data found by the author consisted of aqueous VLE data for benzene as taken by Burd et al. (1968) and Rajendran et al. (1989). For toluene, ethylbenzene and xylene, however, the only data found approaching that of VLE measurements consisted of the solubility data reported by Sanemasa et al. (1982). This and other solubility data have been reviewed extensively in Shaw (1989a, 1989b).

8.3 Ternary Data

The use of ternary data provides a unique advantage for an investigator desiring to approximate the properties of a missing binary system. As seen in Equations (8.1) and (8.3), the prediction of a ternary system requires binary data for three different systems. When data on only two of these three systems prove available, the UIPs for the unknown third binary system of interest may be obtained by (1) regressing them directly against the ternary system itself, while (2) keeping the UIPs for the other two binary systems constant. This approach of regressing unknown

UIPs against a multicomponent system was, in fact, previously attempted by Cunningham et al. (1993) in simulating the seven-component, triethylene glycol VLE system presented in the GPA Research Report RR-131 by Ng et al. (1991). Cunningham et al. (1993) then validated their simulations by comparisons to aromatic plant-emission data.

Hopefully, the tertiary interactions involved will not greatly affect the unlike interactions (now held constant) obtained through available data from the other two binary systems. For example, the literature review performed by the author resulted in the discovery of a paper by Griswold and Wong (1952) that reported data on the ternary VLE system acetone-methanol-water; this paper also included VLE data on all three binary systems as well. Such data can be used to simulate "missing" UIPs by regressing them over two out of three binary systems, and in turn regressing UIPs for the "missing" binary against the ternary system itself. Moreover, in the course of these simulations, the UIPs determined from each binary can be used to simulate the ternary system, thus providing a test in accuracy when predicting multicomponent (in this case ternary) VLE compositions.

8.4 Other Binary Thermodynamic Property Data

To be sure, other types of binary data exist apart from the single property of vapor-liquid equilibrium (VLE) compositions. These include binary data for (1) enthalpy, (2) Gibbs free energy, (3) liquid/vapor density, (4) liquid/vapor volume, (5) sonic velocity, (6) viscosity, and (7) critical properties (temperature, pressure, etc.).

8.5 Infinite-Dilution Activity Coefficients

One experimental method of interest that has arisen in recent years in the thermodynamic literature consists of infinite-dilution activity coefficients. To be sure, an abundance of binary vapor-liquid equilibrium (VLE) data for glycol-water systems exists within the open literature, obviously a reflection of the excellent dehydrating properties of glycols themselves.

For glycol-aromatic systems, on the other hand, far less data exist within the public domain. For example, this work focuses on three basic glycols used in natural gas dehydration: ethylene glycol (EG), diethylene glycol (DEG) and triethylene glycol (TEG). Typically, the natural gas itself will contain all four BTEX components. Altogether, however, the three glycols and four aromatic components can combine to yield twelve possible glycol-aromatic binary systems. Of these twelve systems, however, the author could locate only three DEG binaries in the literature (i.e., with benzene, toluene and o-xylene), and only two TEG binaries (i.e., with benzene and toluene) This total of five binaries thus leaves over half of the desired binary systems unaccounted for.

The above situation may, however, be remedied through the use of infinite-dilution activity coefficients. In fact, the Chemistry Data Series volumes published in Germany by DECHEMA includes a two-volume compilation on infinite-dilution activity coefficients alone (Tiegs et al., 1986a,b). The first of these two volumes (1986a) includes infinite-dilution activity coefficients for all twelve aforementioned

glycol-aromatic binary systems, thus providing an excellent alternative to the more costly option of taking more VLE data through distillation experiments.

8.6 Substitution of Alternate Isomeric-Component Data

Occasionally, binary vapor-liquid equilibrium (VLE) data containing an isomeric component may not exist within the open thermodynamic literature. In such cases, alternate sets of binary data (containing an isomer of the desired component) may be substituted for the one of interest. For example, the GPA Research Report RR-131 (Ng et al., 1991) contains experimental, seven-component VLE data with the *ortho*-xylene isomer, while xylene as a compound includes the three isomers, *ortho*-xylene, *meta*-xylene, and *para*-xylene.

In searching for *ortho*-xylene binary systems containing the other six components, a review of the thermodynamic literature revealed a scarcity of binary VLE data for four systems: (1) triethylene glycol - *ortho*-xylene, (2) benzene - *ortho*-xylene, (3) toluene - *ortho*-xylene, and (4) water - *ortho*-xylene. Unfortunately, data for the first system could not be found within the thermodynamic literature. Next, although binary water data exist for all three xylene isomers in the form of solubility data as published by Sanemasa et al. (1982), they could not be found in the form of actual VLE compositions. Finally, data did exist, however, for binary systems of benzene and toluene with *meta*- and *para*-xylene. The results of simulations over these binary systems are presented in Chapter 7.

8.7 Interpolation with the GAR

Interpolation with the GAR affords yet another method to approximate missing binary VLE data. Simply put, the GAR parameters allow for the "mapping out," or differentiation of UIPs between existing sets of binary VLE data, a procedure which could be followed by interpolation to account for missing data.

The above approach could be used in future investigations where such data permit, as in the case for missing methane-ethylbenzene data. In this case, the author found binary VLE data for methane binary systems containing the aromatic components benzene, toluene, and n-propylbenzene. Since ethylbenzene lies between toluene and n-propylbenzene (i.e., in terms of a straight-chain hydrocarbon grouping on a benzene ring), the regression of GAR parameters over the three existing VLE binary systems might then allow for interpolation of the missing methane-ethylbenzene system. Although the results of this approach in Chapter 7 did not provide a sufficient trend for this purpose through either GARs or BIPs, a refinement of this method in the future might assist modeling efforts in this direction, especially when considering the two-dimensional advantages of GARs.

CHAPTER IX

CONCLUSIONS AND RECOMMENDATIONS

9.1 Overview

The generalized asymmetric rule (GAR) of Equations (4.10-4.12) in Chapter 4 offers a nondivergent, asymmetric, unlike-interaction mechanism. As opposed to binary interaction parameters (BIPs), the GAR guarantees a reliable asymmetry model between any two (or more) components for the mixture parameters of any given equation of state (EOS). Although the use of GARs in this work revealed results comparative to BIPs and slightly superior to them in over half the data sets regressed, they do show that asymmetry (in terms of GARs) works just as well as symmetry (in terms of BIPs), and in some cases, with significant improvement. Consequently, this outcome provides independent support of other LCMs that already incorporate asymmetry from the view that for the reasons described below in Section 9.2, the GAR can calculate and represent vapor-liquid equilibrium (VLE) mixture compositions. These LCMs include, for example, the nonrandom, two-liquid (NRTL) model by Renon and Prausnitz (1968).

In addition, both the LCMs of Chapter 6 and the results of Chapter 7 suggest numerous possibilities for future research. The following sections describe the these suggestions in detail and show that far from constituting a failure, the GAR of Chapter 4 opens up several options for various LCMs presented throughout the thermodynamic literature, including the LCM used in this work. Next, Appendix B

details several recommendations that stem from related implications concerning the rearrangement of the Lorentz mixing rule (Beattie, p. 266, 1955). Finally, Appendix D discusses several theoretical recommendations on correlation between pure-component parameters (PCPs) along with related aspects of thermodynamic modeling observed throughout the preparation of this dissertation.

9.2 Regression of Fewer UIPs

Obviously, the regression of fewer UIPs allows for a simpler representation of a given VLE mixture system. Since LCMs other than the one employed in this work predict these systems with greater general accuracy, the question arises: How can the LCM of Li et al. (1986) be altered to approximate other LCMs in form such as the nonrandom, two-liquid (NRTL) model by Renon and Prausnitz (1968) and the universal quasi-chemical (UNIQUAC) equation by Abrams and Prausnitz (1975)?

First, other LCMs **do** require the use of fewer unlike-interaction parameters (UIPs) to predict each binary system. Typically, these LCMs employ between one and three parameters, while the LCM of Li et al. (1986) requires the computation of three UIPs and the LCM employed in this work requires five UIPs. This requirement can in turn be compounded by the use of more than one GAR parameter for each UIP. (For this work, the author regressed a total of eight GAR parameters for each binary system). Consequently, the following approach concerns the use of fewer GAR parameters in a given LCM.

To be sure, the unlike-interaction expressions presented in Table 6.2 for the LCM of this work implies the relations (presented in terms of *i-j* interactions) of

$$\tau_{ij} = \frac{\left(A'_{ij} - A'_{jj}\right)}{RT} \tag{9.1}$$

and

$$\tau_{ji} = \frac{\left(A'_{ji} - A'_{ii}\right)}{RT} \quad . \tag{9.2}$$

These two relations consist of only one UIP, τ, which could be calculated directly by the GAR through the two relations

$$\tau_{ij} = \frac{\left(\tau_i\right)^{\alpha}\left(\tau_j\right)^{-\alpha}\left[\gamma\tau_i^N + (2-\gamma)\tau_j^N\right]^{1/N}}{2^{1/N}} \tag{9.3}$$

and

$$\tau_{ji} = \frac{\left(\tau_j\right)^{\alpha}\left(\tau_i\right)^{-\alpha}\left[\gamma\tau_j^N + (2-\gamma)\tau_i^N\right]^{1/N}}{2^{1/N}} \quad . \tag{9.4}$$

Equations (9.3-9.4) would, of course, entail that both τ_i and τ_j comprise nonzero quantities in direct contrast to their values of **(a)** zero in the NRTL LCM and **(b)** unity in the UNIQUAC model. In any case, the values obtained for both τ_{ij} and τ_{ji} could be compared to those obtained by other LCMs. Since Equations (9.3-9.4) can obtain positive and/or negative values in terms of the sign changes that may be invoked (as noted in Chapter 5) through the asymmetric-linear GAR parameter, γ.

Alternatively, the two relations for the Helmholtz configurational free energies A'_{ij} and A'_{ji} may be computed through the GAR according to

$$A'_{ij} = \frac{\left(A'_i\right)^{\alpha}\left(A'_j\right)^{-\alpha}\left[\gamma\left(A'_i\right)^{N} + (2-\gamma)\left(A'_j\right)^{N}\right]^{1/N}}{2^{1/N}} \tag{9.5}$$

and

$$A'_{ji} = \frac{\left(A'_j\right)^{\alpha}\left(A'_i\right)^{-\alpha}\left[\gamma\left(A'_j\right)^{N} + (2-\gamma)\left(A'_i\right)^{N}\right]^{1/N}}{2^{1/N}} \; . \tag{9.6}$$

Although the use of Equations (9.5-9.6) instead of (9.3-9.4) would result in values for A'_{ij} and A'_{ji} not directly comparable to those of other LCMs, they would provide the practical advantage of identifying trends in the actual unlike-interaction values needed to optimize this LCM. Moreover, Li et al.'s (1986) LCM was designed to allow for the insertion of any EOS designed to predict pure components. Since different equations of state predict pure-component properties with varying degrees of accuracy, this LCM design intentionally allows for the insertion of more than one EOS at any given time, thereby providing the values needed for A'_i and A'_j in any of the forms chosen from Equations (9.1-9.6). Of course, the UIPs, τ_{ij} and τ_{ji}, could always be calculated from Equations (9.5-9.6) through the respective application of Equations (9.1-9.2), while A'_{ij} and A'_{ji}

could conversely be calculated from Equations (9.3-9.4) through Equations (9.1-9.2) as well.

Regardless of the choice made to employ either Equations (9.3-9.4) or (9.5-9.6), the use of the LCM UIP, F would still require consideration. Here, two possibilities arise: First, F could be employed as in Chapter 6 according to Equation (6.48), where

$$\left(V_{ij}^{*}\right)_{F} = \frac{\left(V_{i}^{*}\right)^{\alpha}\left(V_{j}^{*}\right)^{-\alpha}\left[V_{i}^{*}+V_{j}^{*}\right]}{2} \quad , \qquad (9.7)$$

which utilizes the single GAR parameter, α, to avoid sign changes as outlined in Section 5.4 of Chapter 5. Second, simple values of unity could be assigned to both F_{ij} and F_{ji}, as already chosen by definition for F_{ii} and F_{jj}. The first possibility would entail the use of up to three GAR parameters, assuming that the symmetric GAR parameter, N, is held constant at unity; the second choice would use up to two GAR parameters, with the same assumption for N.

The above procedures entail other advantages as well. Here, as noted by Walas (1985), some LCMs (e.g., UNIQUAC) produce values for τ_{ij} and τ_{ji} that remain fairly independent of temperature, since the temperature dependence is usually built into the Gibbs (or Helmholtz) pure-component contributions for the LCM of interest (p. 232). This feature provides an apparent advantage over BIPs, which are known to be temperature-dependent.

Next, as noted by Walas (1985), values for the Wilson terms $RT\tau_{ij}$ and $RT\tau_{ji}$ can vary considerably in numerical values between -500 and 3,500, thereby constituting changes in magnitude and/or sign (p. 194). This outcome occurs as a result of the multiple solutions available when regressing more than one parameter simultaneously, and can then also occur in other LCMs that employ more than one UIP as well. Fortunately, as noted in Section 4.5 of Chapter 4, the GAR provides a **nondivergent, asymmetric, unlike-interaction mechanism** that guarantees a reliable asymmetry model between any two (or more) components.

Furthermore, since the GAR can provide numerical values for two asymmetric quantities such as τ_{ij} and τ_{ji} for a given UIP, τ, it can therefore reduce the numbers of asymmetric parameters to be regressed, possibly reducing the number of parameters to be regressed to one parameter. In fact, this possibility may comprise the greatest contribution of the GAR itself. In addition, this approach also holds one other merit in that τ_{ij} and τ_{ji} represent **dimensionless** quantities (and therefore a more universal representation of unlike interactions) as opposed to the **dimensional** quantities found in either configurational Helmholtz or Gibbs unlike interactions. Finally, the use of fewer parameters in the regression algorithm applied would also allow for quicker convergence of the solution(s) desired.

Aside from the above considerations, the GAR would most likely show improvement in VLE predictions when inserted into other asymmetric LCMs as well.

Applications of this nature would certainly result in a clearer "mapping out" of binary VLE systems, if not more accurate representations of such systems.

9.3 Other Improvements to Existing LCMs

Aside from potential improvements that can be attained through the GAR, other improvements can also be made to existing LCMs, too. When considering the generalized LCM expressions presented by Renon and Prausnitz (1968) in Section 6.2.2 of Chapter 6, it should be realized that the generalized relations of that section (as seen in Table 6.1) never employed values of unity to the two generalized, second-virial LCM model coefficients p and q. Instead they either employed a value of unity for one coefficient and zero for the other, or unity for the other and zero for the one. (Interestingly enough, the LCM chosen for this work also employs only one coefficient, as seen in Table 6.1). If, then, both coefficients were given values of unity, it could logically be expected that more accurate predictions might be obtained.

In fact, this greater accuracy was later accomplished by Abrams and Prausnitz (1975) in their presentation of the UNIQUAC LCM, who used nonzero values for both coefficients as a later extension to the NRTL LCM by Renon and Prausnitz (1968). Here, Abrams and Prausnitz (1975) reformulated the generalized expressions of Section 6.2.2 according to the UNIQUAC model, which, as with the NRTL LCM, also presents numerous other LCMs as special cases in a somewhat more complex fashion (hence the simpler choice of generalizations chosen for that section as well as Table 6.1).

If , however, the unused portion of the LCM of Li et al. (1986) were also used (thus entailing a value for the coefficient p of unity), then the GAR might allow for more accurate VLE predictions either with or without the recommendations of Section 9.2. Either way, the choice of nonzero-coefficient values for p and/or q presents a total of three potential models for the LCM employed in this work. Alternatively, p and q might be viewed as percentage weights -- in analogous fashion to the multiproperty analysis (MPA) weights discussed and recommended in Section .3.43 of Chapter 3. This approach would entail the use of only one additional regression parameter, i.e., either the coefficient p or the coefficient q according to the relation

$$q = p - 1 \quad , \qquad (9.8)$$

or the reverse of it, namely,

$$p = q - 1 \quad . \qquad (9.9)$$

As with the improvements suggested in Section 9.2, the numerical values chose for p and q offer an additional avenue for improving predictions of VLE mixture compositions.

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APPENDIX A

DERIVATIONS FOR LIMITING CASES OF THE GENERALIZED SYMMETRIC RULE (GSR) AND THE GENERALIZED ASYMMETRIC RULE (GAR)

A.1 Overview

This appendix provides derivations for limiting cases of both the generalized symmetric rule (GSR) and the generalized asymmetric rule (GAR) . These limiting cases include the geometric combining rule and the Halsey-Fender (Fender, 1962) combining rule.

First of all, Sections A.3.1 and A.4.1 respectively describe the derivation for the geometric combining rule as a limiting case of both the GSR formulated by Wenzel et al. (Juris, 1970; Juris and Wenzel, 1974) and the GAR invented by the author for this work. Both derivations originate from similar applications of L'Hospital's rule as seen in various editions (e.g., third, fourth, and fifth) of Salas and Hille's Calculus: One and Several Variables with Analytic Geometry (p. 498, 1978; p. 516-517, 1982; p. 621-622, 1986). For this work, Section A.2 presents this application in greater detail than Salas and Hille did. Furthermore, Section 5.2 discusses the implications of this limiting case for the GAR in terms of modeling aspects.

Next, Sections A.3.2 and A.4.2 respectively describe the derivation of the Halsey-Fender (Fender, 1962) combining rule as a limiting case of both the GSR

formulated by Wenzel et al. (Juris, 1970; Juris and Wenzel, 1974) and the GAR invented by the author for this work. These derivations prove simpler to derive than those presented in Sections A.3.1 and A.4.1.

A.2 A Detailed Application of L'Hospital's Rule

As presented by Salas and Hille (p. 498, 1978; p. 516-517, 1982; p. 621-622, 1986), the aforementioned application of L'Hospital's rule involved determining the limit of the expression

$$\lim_{x \downarrow 0} (1+x)^{1/x} \quad . \qquad \text{(A.1)}$$

Obviously, L'Hospital's rule applies only in the case of an indeterminate formula containing both a numerator and a denominator. Consequently, taking the natural logarithm of the expression inside the limit of Equation (A.1) makes this possible:

$$\lim_{x \downarrow 0} \left[\ln(1+x)^{1/x} \right] = \lim_{x \downarrow 0} \left[\frac{1}{x} \ln(1+x) \right] = \lim_{x \downarrow 0} \frac{\ln(1+x)}{x} \quad . \qquad \text{(A.2)}$$

L'Hospital's rule involves taking the partial derivative of both the numerator and denominator with respect to x as

$$\lim_{x \downarrow 0} \frac{\ln(1+x)}{x} \overset{*}{=} \lim_{x \downarrow 0} \frac{(0+1)/(1+x)}{1} = \lim_{x \downarrow 0} \frac{1/(1+x)}{1} = \lim_{x \downarrow 0} \frac{1}{(1+x)} \quad . \qquad \text{(A.3)}$$

Actually applying the limit of x tending to zero then yields

$$\lim_{x \downarrow 0} \frac{1}{(1+x)} = \frac{1}{(1+0)} = \frac{1}{1} = 1. \qquad \text{(A.4)}$$

$$\therefore \lim_{x \downarrow 0} \left[\ln(1+x)^{1/x} \right] = 1. \qquad \text{(A.5)}$$

Next, since the natural logarithm was taken of the expression inside the limit of Equation (A.1), taking the natural logarithm itself as the power of an exponential yields

$$\lim_{x \downarrow 0} \left\{ \exp\left[\ln(1+x)^{1/x} \right] \right\} = \lim_{x \downarrow 0} (1+x)^{1/x} \quad , \qquad \text{(A.6)}$$

an expression identical to Equation (A.1).

Here, since the presence of the exponential term prevents the direct application of L'Hospital's rule, the actual solution of Equation (A.1) must be obtained by analogy as follows: as the limit in Equation (A.5) approaches unity, the exponential of the limit in Equation (A.5) then logically approaches the value of an exponential raised to the power of unity. In equation form, this approach implies raising an exponential to the power of the left-hand side of Equation (A.5):

$$\exp\left\{ \lim_{x \downarrow 0} \left[\ln(1+x)^{1/x} \right] \right\} \quad . \qquad \text{(A.7)}$$

At this point, the application of Equation (A.5) itself to Equation (A.7) results in

$$\exp\left\{ \lim_{x \downarrow 0} \left[\ln(1+x)^{1/x} \right] \right\} = \exp\{1\} = e^1 = e \quad , \qquad \text{(A.8)}$$

i.e., the value of an exponential itself. If, then, the exponential on the left hand-side of Equation (A.8) were taken <u>inside the limit of</u> Equation (A.8),

$$\exp\left\{ \lim_{x \downarrow 0} \left[\ln(1+x)^{1/x} \right] \right\} = \lim_{x \downarrow 0} \left\{ \exp\left[\ln(1+x)^{1/x} \right] \right\} \quad . \qquad \text{(A9)}$$

Finally, substituting Equation (A.8) into the left-hand side of Equation (A.9) and Equation (A.6) into the right-hand side of Equation (A.9) yields

$$e = \lim_{x \downarrow 0} (1+x)^{1/x} \quad . \quad \text{(A.10)}$$

$$\therefore \lim_{x \downarrow 0} (1+x)^{1/x} = e \quad . \quad \text{(A.11)}$$

A.3 Limiting Cases of the Generalized Symmetric Rule (GSR)

A.3.1 Derivation of the Geometric Combining Rule

This section describes the derivation for the geometric combining rule as a limiting case of the GSR of Wenzel et al. (Juris, 1970; Juris and Wenzel, 1974) . This derivation originates from a similar application of L'Hospital's rule as seen in the detailed derivation of Section A.2.

First, in repeating the second-virial expression of the GSR from Equation (4.1) of Chapter 4,

GSR:
$$B_{ij} = \frac{\left[B_i^N + B_j^N\right]^{1/N}}{2^{1/N}} \quad . \quad \text{(A.12)}$$

Taking the limit of Equation (A.12) as N approaches zero yields

$$\lim_{N \downarrow 0} B_{ij} = \lim_{N \downarrow 0} \frac{\left[B_i^N + B_j^N\right]^{1/N}}{2^{1/N}} \quad . \quad \text{(A.13)}$$

By reinterpreting Equation (A.10) in terms of a combined exponential and logarithmic expression similar to that of Section A.2,

$$\lim_{N\downarrow 0} B_{ij} = \lim_{N\downarrow 0} \exp\left(\ln\left\{B_{ij}\right\}\right) = \lim_{N\downarrow 0} \exp\left(\ln\left\{\frac{\left[B_i^N + B_j^N\right]^{1/N}}{2^{1/N}}\right\}\right)$$

$$= \exp\left(\lim_{N\downarrow 0} \ln\left\{\frac{\left[B_i^N + B_j^N\right]^{1/N}}{2^{1/N}}\right\}\right) \quad . \qquad \text{(A.14)}$$

Here, the limit inside the exponential term of Equation (A.14) may be rearranged as

$$\exp\left(\lim_{N\downarrow 0} \ln\left\{\frac{\left[B_i^N + B_j^N\right]^{1/N}}{2^{1/N}}\right\}\right) = \exp\left(\lim_{N\downarrow 0} \ln\left\{\frac{\left[B_i^N + B_j^N\right]}{2}\right\}^{1/N}\right)$$

$$= \exp\left(\lim_{N\downarrow 0} \frac{1}{N} \ln\left\{\frac{\left[B_i^N + B_j^N\right]}{2}\right\}\right) = \exp\left(\lim_{N\downarrow 0} \frac{1}{N} \ln\left\{\frac{1}{2}\left[B_i^N + B_j^N\right]\right\}\right)$$

$$= \exp\left(\lim_{N\downarrow 0} \frac{\ln\left\{\frac{1}{2}\left[B_i^N + B_j^N\right]\right\}}{N}\right)$$

. . (A.15)

Second, the partial derivative of a constant p raised to the power of a variable x as presented by Salas and Hille (p. 261, 1978; p. 271, 1982; p. 362, 1986) becomes

$$\frac{d}{dx}\left(p^x\right) = p^x \ln p \quad . \qquad \text{(A.16)}$$

In similar fashion, the partial derivative of Equation (A.16) may be applied to the terms B_i^N and B_j^N in the form of

$$\frac{d}{dN}\left(B_i^N\right) = B_i^N \ln B_i \tag{A.17}$$

and

$$\frac{d}{dN}\left(B_j^N\right) = B_j^N \ln B_j \tag{A.18}$$

Third, in applying L'Hospital's rule, the term on the far right-hand side of Equation (A.15) becomes

$$\exp\left(\lim_{N\downarrow 0}\frac{\ln\left\{\frac{1}{2}\left[B_i^N + B_j^N\right]\right\}}{N}\right) \overset{*}{=} \exp\left(\lim_{N\downarrow 0}\frac{\frac{d}{dN}\ln\left\{\frac{1}{2}\left[B_i^N + B_j^N\right]\right\}}{\frac{d}{dN}N}\right)$$

$$= \exp\left(\lim_{N\downarrow 0}\frac{\frac{d}{dN}\ln\left\{\frac{1}{2}\left[B_i^N + B_j^N\right]\right\}}{1}\right) = \exp\left(\lim_{N\downarrow 0}\frac{\frac{d}{dN}\left\{\frac{1}{2}\left[B_i^N + B_j^N\right]\right\}}{\frac{1}{2}\left[B_i^N + B_j^N\right]}\right)$$

$$= \exp\left(\lim_{N\downarrow 0}\frac{\frac{1}{2}\left[\frac{d}{dN}\left(B_i^N\right) + \frac{d}{dN}\left(B_j^N\right)\right]}{\frac{1}{2}\left[B_i^N + B_j^N\right]}\right) . \tag{A.19}$$

Here, the insertion of Equations (A.17) and (A.18) into the far right-hand side of Equation (A.19) yields

$$\exp\left(\lim_{N\downarrow 0}\frac{\frac{1}{2}\left[B_i^N \ln\left(B_i\right) + B_j^N \ln\left(B_j\right)\right]}{\frac{1}{2}\left[B_i^N + B_j^N\right]}\right) , \tag{A.20}$$

while the application of the limit in Equation (A.20) results in

$$\exp\left(\frac{\frac{1}{2}\left[B_i^0 \ln\left(B_i\right)+B_j^0 \ln\left(B_j\right)\right]}{\frac{1}{2}\left[B_i^0+B_j^0\right]}\right)=\exp\left(\frac{\frac{1}{2}\left[(1)\ln\left(B_i\right)+(1)\ln\left(B_j\right)\right]}{\frac{1}{2}[1+1]}\right)$$

$$=\exp\left(\frac{\frac{1}{2}\left[\ln\left(B_i\right)+\ln\left(B_j\right)\right]}{\frac{1}{2}[2]}\right)=\exp\left(\frac{\frac{1}{2}\left[\ln\left(B_i\right)+\ln\left(B_j\right)\right]}{1}\right)=\exp\left(\frac{1}{2}\left[\ln\left(B_i\right)+\ln\left(B_j\right)\right]\right)$$

$$=\exp\left(\frac{1}{2}\left[\ln\left(B_iB_j\right)\right]\right)=\exp\left(\ln\left(B_iB_j\right)^{\frac{1}{2}}\right)=\left(B_iB_j\right)^{\frac{1}{2}} \quad . \qquad \text{(A.21)}$$

$$\therefore \lim_{N\downarrow 0}\frac{\left[B_i^N+B_j^N\right]^{1/N}}{2^{1/N}}=\sqrt{B_iB_j} \quad . \qquad \text{(A.22)}$$

Equation (A.22) thus represents the geometric combining rule of Equation (4.3) in Chapter 4 as a limiting case of Wenzel et al.'s (Juris, 1970; Juris and Wenzel, 1974) GSR as N approaches zero.

A.3.2 Derivation of the Halsey-Fender Combining Rule

The derivation of the Halsey-Fender (Fender, 1962) combining rule of Equation (4.5) in Chapter 4 arises as a limiting case of Wenzel et al.'s (Juris, 1970; Juris and Wenzel, 1974) GSR. In this case, the symmetric parameter N of the GSR is set equal to negative one $(N=-1)$ in Equation (A.12), thereby resulting in

$$B_{ij}=\frac{\left[B_i^{-1}+B_j^{-1}\right]^{1/-1}}{2^{1/-1}}=\frac{\left[B_i^{-1}+B_j^{-1}\right]^{-1}}{2^{-1}} \quad . \qquad \text{(A.23)}$$

Rearranging the right-hand side of Equation (A.23) then yields

$$B_{ij} = \frac{2}{\left[B_i^{-1} + B_j^{-1}\right]} = \frac{2}{\left[\frac{1}{B_i} + \frac{1}{B_j}\right]} = \frac{2}{\left[\left(\frac{B_j}{B_j}\right)\frac{1}{B_i} + \left(\frac{B_i}{B_i}\right)\frac{1}{B_j}\right]}$$

$$= \frac{2}{\left[\frac{B_j}{B_i B_j} + \frac{B_i}{B_i B_j}\right]} = \frac{2}{\left[\frac{B_i + B_j}{B_i B_j}\right]} = \frac{2B_i B_j}{\left(B_i + B_j\right)} \quad . \qquad \text{(A.24)}$$

$$\therefore B_{ij} = \frac{2B_i B_j}{\left(B_i + B_j\right)} \quad . \qquad \text{(A.25)}$$

In the above simple algebraic manipulations, Equation (A.25) represents the Halsey-Fender (Fender, 1962) combining rule of Equation (4.5) in Chapter 4 as a limiting case of Wenzel et al.'s (Juris, 1970; Juris and Wenzel, 1974) GSR with $(N = -1)$. Indeed, this particular derivation provides a sharp contrast to the more complicated derivation of the geometric combining rule presented in Section A.3.1.

A.4 Limiting Cases of the Generalized Asymmetric Rule (GAR)

A.4.1 Derivation of Asymmetric-Geometric Combining-Rule Forms

This section describes the derivation of the generalized asymmetric form of the geometric combining rule as a limiting case of the GAR invented by the author for this work. In analogous fashion to Section A.2.1, this derivation originates from a similar application of L'Hospital's rule in the detailed derivation of Section A.2.

First, in repeating the second-virial expression of the GAR from Equation (4.10) of Chapter 4,

$$\text{GAR:} \qquad B_{ij} = \frac{B_i^{\alpha} B_j^{-\alpha} \left[\gamma B_i^N + (2-\gamma) B_j^N \right]^{1/N}}{2^{1/N}} \quad . \qquad \text{(A.26)}$$

Taking the limit of Equation (A.26) as N approaches zero yields

$$\lim_{N \downarrow 0} B_{ij} = \lim_{N \downarrow 0} \frac{B_i^{\alpha} B_j^{-\alpha} \left[\gamma B_i^N + (2-\gamma) B_j^N \right]^{1/N}}{2^{1/N}}$$

$$= B_i^{\alpha} B_j^{-\alpha} \lim_{N \downarrow 0} \frac{\left[\gamma B_i^N + (2-\gamma) B_j^N \right]^{1/N}}{2^{1/N}} \quad . \qquad \text{(A.27)}$$

Here, it should be noted that since the term $B_i^{\alpha} B_j^{-\alpha}$ does not constitute a function of N, it may be treated as a constant and thus placed outside of the limit while evaluating the other terms inside Equation (A.27) inside the limit. Next, by reinterpreting the terms inside the limit (of the far right-hand side) of Equation (A.27) in terms of a combined exponential and logarithmic expression similar to that of Section A.2,

$$B_i^{\alpha} B_j^{-\alpha} \lim_{N \downarrow 0} \frac{\left[\gamma B_i^N + (2-\gamma) B_j^N \right]^{1/N}}{2^{1/N}} = B_i^{\alpha} B_j^{-\alpha} \lim_{N \downarrow 0} \exp\left(\ln\left\{ \frac{\left[\gamma B_i^N + (2-\gamma) B_j^N \right]^{1/N}}{2^{1/N}} \right\} \right)$$

$$= B_i^{\alpha} B_j^{-\alpha} \exp\left(\lim_{N \downarrow 0} \ln\left\{ \frac{\left[\gamma B_i^N + (2-\gamma) B_j^N \right]^{1/N}}{2^{1/N}} \right\} \right) \quad . \qquad \text{(A.28)}$$

Here, the limit inside the exponential term of Equation (A.28) may be rearranged as

$$B_i^{\alpha} B_j^{-\alpha} \exp\left(\lim_{N \downarrow 0} \ln\left\{ \frac{\left[\gamma B_i^N + (2-\gamma) B_j^N \right]^{1/N}}{2^{1/N}} \right\} \right)$$

$$= B_i^{\alpha} B_j^{-\alpha} \exp\left(\lim_{N \downarrow 0} \ln\left\{ \frac{\left[\gamma B_i^N + (2-\gamma) B_j^N \right]}{2} \right\}^{1/N} \right)$$

$$= B_i^{\alpha} B_j^{-\alpha} \exp\left(\lim_{N \downarrow 0} \frac{1}{N} \ln\left\{ \frac{\left[\gamma B_i^N + (2-\gamma) B_j^N \right]}{2} \right\} \right)$$

$$= B_i^{\alpha} B_j^{-\alpha} \exp\left(\lim_{N \downarrow 0} \frac{1}{N} \ln\left\{ \frac{1}{2} \left[\gamma B_i^N + (2-\gamma) B_j^N \right] \right\} \right)$$

$$= B_i^{\alpha} B_j^{-\alpha} \exp\left(\lim_{N \downarrow 0} \frac{\ln\left\{ \frac{1}{2} \left[\gamma B_i^N + (2-\gamma) B_j^N \right] \right\}}{N} \right) \quad . \qquad \text{(A.29)}$$

Second, the partial derivative of a constant p raised to the power of a variable x as presented by Salas and Hille (p. 261, 1978; p. 271, 1982; p. 362, 1986) becomes

$$\frac{d}{dx}\left(p^x\right) = p^x \ln p \quad . \qquad \text{(A.30)}$$

In similar fashion, the partial derivative of Equation (A.30) may be applied to the terms B_i^N and B_j^N in the form of

$$\frac{d}{dN}\left(B_i^N\right) = B_i^N \ln B_i \tag{A.31}$$

and

$$\frac{d}{dN}\left(B_j^N\right) = B_j^N \ln B_j \tag{A.32}$$

Third, in applying L'Hospital's rule, the term on the far right-hand side of Equation (A.29) becomes

$$B_i^{\alpha} B_j^{-\alpha} \exp\left(\lim_{N \downarrow 0} \frac{\ln\left\{\frac{1}{2}\left[\gamma B_i^N + (2-\gamma) B_j^N\right]\right\}}{N} \right)$$

$$\overset{*}{=} B_i^{\alpha} B_j^{-\alpha} \exp\left(\lim_{N \downarrow 0} \frac{\frac{d}{dN}\ln\left\{\frac{1}{2}\left[\gamma B_i^N + (2-\gamma) B_j^N\right]\right\}}{\frac{d}{dN}N} \right)$$

$$= B_i^{\alpha} B_j^{-\alpha} \exp\left(\lim_{N \downarrow 0} \frac{\frac{d}{dN}\ln\left\{\frac{1}{2}\left[\gamma B_i^N + (2-\gamma) B_j^N\right]\right\}}{1} \right)$$

$$= B_i^{\alpha} B_j^{-\alpha} \exp\left(\lim_{N \downarrow 0} \frac{\frac{d}{dN}\left\{\frac{1}{2}\left[\gamma B_i^N + (2-\gamma) B_j^N\right]\right\}}{\frac{1}{2}\left[\gamma B_i^N + (2-\gamma) B_j^N\right]} \right)$$

$$= B_i^{\alpha} B_j^{-\alpha} \exp\left(\lim_{N \downarrow 0} \frac{\frac{1}{2}\left[\gamma \frac{d}{dN}\left(B_i^N \right) + (2-\gamma) \frac{d}{dN}\left(B_j^N \right) \right]}{\frac{1}{2}\left[\gamma B_i^N + (2-\gamma) B_j^N \right]} \right) \qquad \text{(A.33)}$$

Here, the insertion of Equations (A.31) and (A.32) into the far right-hand side of Equation (A.33) yields

$$B_i^{\alpha} B_j^{-\alpha} \exp\left(\lim_{N \downarrow 0} \frac{\frac{1}{2}\left[\gamma B_i^N \ln\left(B_i \right) + (2-\gamma) B_j^N \ln\left(B_j \right) \right]}{\frac{1}{2}\left[\gamma B_i^N + (2-\gamma) B_j^N \right]} \right), \qquad \text{(A.34)}$$

while the application of the limit in Equation (A.34) results in

$$B_i^{\alpha} B_j^{-\alpha} \exp\left(\frac{\frac{1}{2}\left[\gamma B_i^0 \ln\left(B_i \right) + (2-\gamma) B_j^0 \ln\left(B_j \right) \right]}{\frac{1}{2}\left[\gamma B_i^0 + (2-\gamma) B_j^0 \right]} \right)$$

$$= B_i^{\alpha} B_j^{-\alpha} \exp\left(\frac{\frac{1}{2}\left[\gamma(1) \ln\left(B_i \right) + (2-\gamma)(1) \ln\left(B_j \right) \right]}{\frac{1}{2}\left[\gamma(1) + (2-\gamma)(1) \right]} \right)$$

$$= B_i^{\alpha} B_j^{-\alpha} \exp\left(\frac{\frac{1}{2}\left[\gamma \ln\left(B_i \right) + (2-\gamma) \ln\left(B_j \right) \right]}{\frac{1}{2}\left[\gamma + (2-\gamma) \right]} \right)$$

$$= B_i^{\alpha} B_j^{-\alpha} \exp\left(\frac{\frac{1}{2}\left[\ln\left(B_i \right)^{\gamma} + \ln\left(B_j \right)^{(2-\gamma)} \right]}{\frac{1}{2}\left[\gamma + 2 - \gamma \right]} \right)$$

$$= B_i^{\alpha} B_j^{-\alpha} \exp\left(\frac{\frac{1}{2}\left[\ln\left(B_i^{\gamma} B_j^{(2-\gamma)} \right) \right]}{\frac{1}{2}[2]} \right) = B_i^{\alpha} B_j^{-\alpha} \exp\left(\frac{\frac{1}{2} \ln\left[B_i^{\gamma} B_j^{(2-\gamma)} \right]}{[1]} \right)$$

$$= B_i^{\alpha} B_j^{-\alpha} \exp\left(\frac{1}{2} \ln\left[B_i^{\gamma} B_j^{(2-\gamma)} \right] \right) = B_i^{\alpha} B_j^{-\alpha} \exp\left(\ln\left[B_i^{\gamma} B_j^{(2-\gamma)} \right]^{\frac{1}{2}} \right)$$

$$= B_i^{\alpha} B_j^{-\alpha} \exp\left(\ln\left[B_i^{\gamma/2} B_j^{(2-\gamma)/2} \right] \right) = B_i^{\alpha} B_j^{-\alpha} B_i^{\gamma/2} B_j^{(2-\gamma)/2}$$

$$= B_i^{\alpha} B_j^{-\alpha} B_i^{\frac{\gamma}{2}} B_j^{1-\frac{\gamma}{2}} = B_i^{\left(\alpha+\frac{\gamma}{2}\right)} B_j^{\left(1-\alpha-\frac{\gamma}{2}\right)} \quad . \qquad \text{(A.35)}$$

$$\therefore \lim_{N \downarrow 0} \frac{B_i^{\alpha} B_j^{-\alpha} \left[\gamma B_i^N + (2-\gamma) B_j^N \right]^{1/N}}{2^{1/N}} = B_i^{\left(\alpha+\frac{\gamma}{2}\right)} B_j^{\left(1-\alpha-\frac{\gamma}{2}\right)}$$

. (A.36)

Equation (A.36) thus represents the generalized asymmetric form of the geometric combining rule shown in Equation (4.3) of Chapter 4 as a limiting case of the GAR invented by the author for this work. As seen in Equation (A.36), the two parameters α and $\frac{\gamma}{2}$ can give rise to a wide variety of asymmetric forms of the standard geometric combining rule. Moreover, the geometric combining rule of Equation (4.3) also serves as a limiting case of Equation (A.36) both when $\left(\alpha + \frac{\gamma}{2}\right) = \frac{1}{2}$ and as N approaches zero. Finally, the implications of this limiting case in terms of modeling aspects considered for this work are discussed in Section 5.2.

A.4.2 Derivation of Asymmetric Halsey-Fender Combining-Rule Forms

This section describes the derivation of the generalized asymmetric form of the Halsey-Fender (Fender, 1962) combining rule as a limiting case of the GAR invented by the author for this work. Here, the symmetric parameter, N, of the GAR is set equal to negative one ($N = -1$) in Equation (A.26), thereby resulting in

$$B_{ij} = \frac{B_i^{\alpha} B_j^{-\alpha}\left[\gamma B_i^{-1} + (2-\gamma)B_j^{-1}\right]^{1/-1}}{2^{1/-1}} = \frac{B_i^{\alpha} B_j^{-\alpha}\left[\gamma B_i^{-1} + (2-\gamma)B_j^{-1}\right]^{-1}}{2^{-1}} \quad . \tag{A.37}$$

Rearranging the right-hand side of Equation (A.27) then yields

$$B_{ij} = \frac{2B_i^{\alpha} B_j^{-\alpha}}{\left[\gamma B_i^{-1} + (2-\gamma)B_j^{-1}\right]} = \frac{2B_i^{\alpha} B_j^{-\alpha}}{\left[\frac{\gamma}{B_i} + \frac{(2-\gamma)}{B_j}\right]} = \frac{2B_i^{\alpha} B_j^{-\alpha}}{\left[\left(\frac{B_j}{B_j}\right)\frac{\gamma}{B_i} + \left(\frac{B_i}{B_i}\right)\frac{(2-\gamma)}{B_j}\right]}$$

$$= \frac{2B_i^{\alpha} B_j^{-\alpha}}{\left[\frac{\gamma B_j}{B_i B_j} + \frac{(2-\gamma)B_i}{B_i B_j}\right]} = \frac{2B_i^{\alpha} B_j^{-\alpha}}{\left[\frac{(2-\gamma)B_i + \gamma B_j}{B_i B_j}\right]} = \frac{2B_i^{\alpha} B_j^{-\alpha} B_i B_j}{\left[(2-\gamma)B_i + \gamma B_j\right]} = \frac{2B_i^{(1+\alpha)} B_j^{(1-\alpha)}}{\left[(2-\gamma)B_i + \gamma B_j\right]} \quad . \tag{A.38}$$

$$\therefore B_{ij} = \frac{2B_i^{(1+\alpha)} B_j^{(1-\alpha)}}{\left[(2-\gamma)B_i + \gamma B_j\right]} \quad . \tag{A.39}$$

In the above algebraic manipulations, Equation (A.39) represents the generalized asymmetric form of the Halsey-Fender (Fender, 1962) combining rule of Equation (4.5) in Chapter 4. Both viewed as a limiting case of the GAR invented by

the author for this work and seen in Equation (A.39), the two parameters α and γ can give rise to a wide variety of asymmetric forms of the standard Halsey-Fender combining rule. Moreover, the Halsey-Fender combining rule of Equation (4.5) also serves as a limiting case of Equation (A.36) when $\alpha = 0$, $\gamma = 1$, and $(N = -1)$. Finally, as with the Halsey-Fender equation as a limiting case of Wenzel et al.'s (Juris, 1970; Juris and Wenzel, 1974) GSR in Section A.3.2, this particular derivation also provides a contrast to the more complicated derivation of the geometric combining rule from the GAR presented in Section A.4.1.

APPENDIX B

REARRANGEMENT OF THE LORENTZ MIXING RULE AND RELATED IMPLICATIONS

B.1 Overview

This appendix details the derivations necessary for the rearrangement of the Lorentz mixing rule as only briefly mentioned by Beattie (p. 266, 1955). Here, Beattie presented the Lorentz mixing rule for the parameter, B_0, in the Beattie-Bridgeman (1927) equation of state. Consequently, Section B.2 presents the full derivation for rearrangement of the Lorentz mixing rule in second-virial form.

In addition, the rearranged Lorentz mixing rule presents related implications that merit further discussion for modeling of binary and multicomponent vapor-liquid equilibrium (VLE) systems. First, Section B.3 outlines these implications with consideration towards future modeling with both the generalized symmetric rule (GSR) and generalized asymmetric rule (GAR) presented in Chapter 4.

Second, Section B.4 outlines other implications in terms of a mixture concept conceived by the author and designated herein as the mixing-rule conjunction (MRC). Altogether, the MRC offers various options of mixture modeling through an equation of state (EOS) in terms of both statistical mixture considerations as well as the GSR and GAR. These considerations may prove helpful to future mixture research.

B.2 Rearrangement of the Lorentz Mixing Rule

To begin with, the Lorentz combining rule of Equation (4.4) of Chapter 4,

$$B_{ij} = \frac{\left(B_i^{1/3} + B_j^{1/3}\right)^3}{8} \quad , \tag{B.1}$$

may be inserted into the second-virial mixture expression, B_x, of Equation (4.13)

$$B_x = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j B_{ij} \quad . \tag{B.2}$$

This insertion yield then results in the mixture relation

$$B_x = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \frac{\left(B_i^{1/3} + B_j^{1/3}\right)^3}{8} \quad , \tag{B.3}$$

where the fraction $\frac{1}{8}$ may be factored out of the summations, resulting in

$$B_x = \frac{1}{8} \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \left(B_i^{1/3} + B_j^{1/3}\right)^3 \quad . \tag{B.4}$$

Equation (B.4) may, however, be expanded into

$$B_x = \frac{1}{8} \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \left(B_i^{1/3} + B_j^{1/3}\right)\left(B_i^{1/3} + B_j^{1/3}\right)^2$$

$$= \frac{1}{8} \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \left(B_i^{1/3} + B_j^{1/3}\right)\left(B_i^{2/3} + 2B_i^{1/3}B_j^{1/3} + B_j^{2/3}\right)$$

$$= \frac{1}{8} \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \left(B_i + 2B_i^{2/3}B_j^{1/3} + B_i^{1/3}B_j^{2/3} + B_i^{2/3}B_j^{1/3} + 2B_i^{1/3}B_j^{2/3} + B_j\right)$$

$$= \frac{1}{8} \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \left(B_i + B_j + 3B_i^{2/3}B_j^{1/3} + 3B_i^{1/3}B_j^{2/3}\right)$$

$$= \frac{1}{8}\sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j B_i + \frac{1}{8}\sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j B_j$$

$$+ \frac{3}{8}\sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j B_i^{2/3} B_j^{1/3} + \frac{3}{8}\sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j B_i^{1/3} B_j^{2/3}$$

$$= \frac{1}{8}\sum_{i=1}^{n} x_i B_i \sum_{j=1}^{n} x_j + \frac{1}{8}\sum_{j=1}^{n} x_j B_j \sum_{i=1}^{n} x_i$$

$$+ \frac{3}{8}\sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j B_i^{2/3} B_j^{1/3} + \frac{3}{8}\sum_{j=1}^{n}\sum_{i=1}^{n} x_j x_i B_j^{2/3} B_i^{1/3}$$

$$= \frac{1}{8}\sum_{i=1}^{n} x_i B_i(1) + \frac{1}{8}\sum_{j=1}^{n} x_j B_j(1)$$

$$+ \frac{3}{8}\sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j B_i^{2/3} B_j^{1/3} + \frac{3}{8}\sum_{j=1}^{n}\sum_{i=1}^{n} x_j x_i B_j^{2/3} B_i^{1/3} \quad . \qquad \text{(B.5)}$$

$$\therefore B_x = \frac{1}{8}\sum_{i=1}^{n} x_i B_i + \frac{1}{8}\sum_{j=1}^{n} x_j B_j$$

$$+ \frac{3}{8}\sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j B_i^{2/3} B_j^{1/3} + \frac{3}{8}\sum_{j=1}^{n}\sum_{i=1}^{n} x_j x_i B_j^{2/3} B_i^{1/3} \quad . \qquad \text{(B.6)}$$

Here, it should be noted that the series subscripts i and j of Equations (B.1-B.6) follow identical limits, that is, they proceed from unity to n. Consequently, they may be interchanged, thereby leading to the alteration of the second term in Equation (B.6) into

$$\frac{1}{8}\sum_{j=1}^{n} x_j B_j = \frac{1}{8}\sum_{i=1}^{n} x_i B_i \qquad \text{(B.7)}$$

and the alteration of the fourth term in Equation (B.6) into

$$\frac{3}{8}\sum_{j=1}^{n}\sum_{i=1}^{n} x_j x_i B_j^{2/3} B_i^{1/3} = \frac{3}{8}\sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j B_i^{2/3} B_j^{1/3} \quad . \qquad \text{(B.8)}$$

Substituting Equations (B.7) and (B.8) into equation (B.6) results in

$$B_x = \frac{1}{8}\sum_{i=1}^{n} x_i B_i + \frac{1}{8}\sum_{i=1}^{n} x_i B_i$$

$$+\frac{3}{8}\sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j B_i^{2/3} B_j^{1/3} + \frac{3}{8}\sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j B_i^{2/3} B_j^{1/3}$$

$$= \frac{2}{8}\sum_{i=1}^{n} x_i B_i + \frac{6}{8}\sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j B_i^{2/3} B_j^{1/3} \quad . \qquad \text{(B.9)}$$

$$\therefore B_x = \frac{1}{4}\sum_{i=1}^{n} x_i B_i + \frac{3}{4}\sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j B_i^{2/3} B_j^{1/3} \quad . \qquad \text{(B.10)}$$

Combining Equations (B.4) and (B.10) then leaves the equivalent expressions

$$B_x = \frac{1}{8}\sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j \left(B_i^{1/3} + B_j^{1/3}\right)^3 = \frac{1}{4}\sum_{i=1}^{n} x_i B_i + \frac{3}{4}\sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j B_i^{2/3} B_j^{1/3}$$

. (B.11)

Alternatively, the i and j terms in the second-virial expression of Equation (B.10) may be separated into each of their respective series, leading to

$$B_x = \frac{1}{4}\sum_{i=1}^{n} x_i B_i + \frac{3}{4}\left(\sum_{i=1}^{n} x_i B_i^{2/3}\right)\left(\sum_{j=1}^{n} x_j B_j^{1/3}\right) \quad . \qquad \text{(B.12)}$$

The substitution of Equation (B.12) into the right-hand side of Equation (B.11) then yields

$$B_x = \frac{1}{8}\sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j \left(B_i^{1/3} + B_j^{1/3}\right)^3 = \frac{1}{4}\sum_{i=1}^{n} x_i B_i + \frac{3}{4}\left(\sum_{i=1}^{n} x_i B_i^{2/3}\right)\left(\sum_{j=1}^{n} x_j B_j^{1/3}\right)$$

. (B.13)

Furthermore, the *j* subscripts in the last summation on the right-hand side of Equation (B.13) may be replaced by an *i* subscript to yield

$$B_x = \frac{1}{8}\sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j \left(B_i^{1/3} + B_j^{1/3}\right)^3 = \frac{1}{4}\sum_{i=1}^{n} x_i B_i + \frac{3}{4}\left(\sum_{i=1}^{n} x_i B_i^{2/3}\right)\left(\sum_{i=1}^{n} x_i B_i^{1/3}\right) \quad . \qquad \text{(B.14)}$$

Equation (B.14) coincides with the relation presented by Williams (p. 27, 1962) as taken from Beattie's (p. 266, 1955) presentation of the Lorentz mixing rule for the Beattie-Bridgeman equation-of-state parameter, B_0.

In all, several investigators have followed Beattie's (ibid.) use of the Lorentz mixing rule for the equation-of-state parameter, B_0. First, Benedict et al. (1942) compared mixture predictions obtained between the linear and Lorentz combining rules for B_0 in the Benedict-Webb-Rubin (BWR) EOS (Benedict et al., 1940). Benedict et al. (1942) compared both combining rules in the prediction of binary pressure-volume-temperature (PVT) mixture data consisting of methane paired with ethane, propane, and n-butane. For all three binary mixtures, these investigators found the Lorentz combining rule slightly more accurate than the linear one. Nevertheless, while they concluded that near-equivalent results could be obtained with either combining rule, they did recommend use of the linear combining rule for its simplicity in calculations, a recommendation of importance before the widespread use of computers at that time. In addition, it should be noted that the mixture results

reported by Benedict et al. (1942) employed combining rules without binary interaction parameters (BIPs).

Second, three studies conducted through the Institute of Gas Technology (IGT) supported the findings of Benedict et al. (1942). These include work performed by (a) Bloomer et al. (1953) on methane-ethane PVT mixtures, (b) Bloomer et al. (1955) on methane-nitrogen PVT mixtures, and (c) Eakin et al. (1955) on ethane-nitrogen mixtures. The mixture predictions in all three of these cases also utilized combining rules without BIPs.

B.3 Related Implications of the Lorentz Mixing Rule

Overall, related implications of the Lorentz mixing rule may be drawn from the equivalent expressions of Equations (B.11), (B.13), and (B.14). To begin with, first-virial mixing definitely comprises a portion of second-virial mixing. Obviously, both first- and second-virial mixing in turn constitute relative portions of third-virial mixing, and so on. Here, the question arises: Which of these mixture forms proves superior in mixture predictions for an equation of state (EOS)?

Typically, mixture models for binary systems include first-, second-, or third-virial mixing for each unlike-interaction parameter (UIP). Interestingly enough, the Benedict-Webb-Rubin (BWR) EOS (Benedict et al., 1940) of Section 2.2.1 of Chapter 2, the Benedict-Webb-Rubin-Starling (BWRS) EOS (Starling, 1971) of Section 2.2.2, and the BWRS extensions by Nishiumi et al. in Section 2.4.1 employ each of the three virial-mixing forms for different UIPs. In addition, Benedict et al.

(1940) employed the Lorentz mixing rule as an alternative to the first-virial mixing rule for the mixture parameter, B_0, but realized the same accuracy for hydrocarbon mixtures with either rule. Furthermore, Wenzel et al. (Juris, 1970; Juris and Wenzel, 1974) employed the same value of N for their GSR in all mixture parameters of the Martin-Hou equation of state to predict Joule-Thomson coefficients of freon mixtures. The optimal choice of a given virial-mixing rule for any UIP, may, however, not be readily determined when using several UIPs to model a binary mixture.

As a whole, virial mixing involves consideration of combining rules, which in turn relate virial-mixture expressions to one another. Section B.3.1 therefore discusses the generalization of the Lorentz mixing rule in terms of simultaneous first- and second-virial mixing. Subsequently, Second B.3.2 expands this generalization to include any number of second-virial combining rules of choice. Altogether, both the GSR and GAR eliminate the need for more than one combining rule for each second- and higher-virial mixture expression, which greatly simplify the expressions found in second- and higher-virial mixture forms.

B.3.1 Generalization of the Lorentz Mixing Rule

For example, if the mixture molecular-energy parameter, $\frac{\varepsilon_x}{k}$, of the Khan-Chung-Lee-Starling (KCLS) EOS (Khan, 1983; Chung et al., 1984) was calculated through the Lorentz mixing rule of Equation (B.10), it would look like

$$\frac{\varepsilon_x}{k} = \frac{1}{4}\sum_{i=1}^{n} x_i \frac{\varepsilon_i}{k} + \frac{3}{4}\sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j \left(\frac{\varepsilon_i}{k}\right)^{2/3}\left(\frac{\varepsilon_i}{k}\right)^{1/3} \quad . \qquad \text{(B.15)}$$

Multiplication of Equation (B.15) by the Boltzmann constant, k, yields

$$\varepsilon_x = \frac{1}{4}\sum_{i=1}^{n} x_i \varepsilon_i + \frac{3}{4}\sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j \varepsilon_i^{2/3}\varepsilon_j^{1/3} \quad . \qquad \text{(B.16)}$$

If, however, varying proportions of first- and second-virial mixing were employed, Equation (B.16) could take the form

$$\varepsilon_x = P^{(1\varepsilon)}\sum_{i=1}^{n} x_i \varepsilon_i + P^{(2\varepsilon)}\sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j \varepsilon_i^{2/3}\varepsilon_j^{1/3} \quad . \qquad \text{(B.17)}$$

Here, $P^{(1\varepsilon)}$ represents the proportion of first-virial mixing and $P^{(2\varepsilon)}$ the proportion of second-virial mixing. Of course, both proportions must sum to unity according to the relation

$$P^{(1\varepsilon)} + P^{(2\varepsilon)} = 1 \quad . \qquad \text{(B.18)}$$

Equation (B.17) then represents a limiting case of Equation (B.16) under the conditions

$$P^{(1\varepsilon)} = \frac{1}{4}, \quad P^{(2\varepsilon)} = \frac{3}{4} \quad . \qquad \text{(B.19)}$$

B.3.2 Expansion of the Generalized, Second-Virial Lorentz Mixing Rule

This section discusses the expansion of the generalized, second-virial Lorentz mixing rule of Equation (B.16) in the above section. In Section 4.2 of Chapter 4, several second-virial combining rules (i.e., proportions of ε_i and ε_j) exist apart from

the two-thirds/one-third combining rule of Equation (B.16). The existence of so many combining rules then leads to the problem of either selecting and/or regressing their respective proportions. Consequently, the second-virial proportion of Equation (B.17) may be generalized into

$$\varepsilon_x = P^{(1\varepsilon)} \sum_{i=1}^{n} x_i \varepsilon_i + P^{(2\varepsilon)} \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \varepsilon_{ij} \quad , \qquad \text{(B.20)}$$

or more simply

$$\varepsilon_x = P^{(1\varepsilon)} \varepsilon_x^{(1)} + P^{(2\varepsilon)} \varepsilon_x^{(2)} \quad , \qquad \text{(B.21)}$$

where $\varepsilon_x^{(1)}$ constitutes the first-virial mixture sum and $\varepsilon_x^{(2)}$ the second-virial mixture sum.

Moreover, the generalized second-virial mixture portion could also contain different proportions of various second-virial combining rules. If, then, the total mixture expression for ε_x consisted of second-virial mixing only, i.e.,

$$P^{(1\varepsilon)} = 0, \quad P^{(2\varepsilon)} = 1 \quad , \qquad \text{(B.21)}$$

then the second-virial mixture expression

$$\varepsilon_x = P^{(2\varepsilon)} \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \varepsilon_{ij} \qquad \text{(B.22)}$$

could contain proportions of several second-virial combining rules. By itself, Equation (B.22) could be expanded into the expression

$$\varepsilon_x = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \left[P_{(1)}^{(2\varepsilon)} \varepsilon_{ij(1)} + P_{(2)}^{(2\varepsilon)} \varepsilon_{ij(2)} + P_{(3)}^{(2\varepsilon)} \varepsilon_{ij(3)} + \ldots \right]$$

$$,\qquad \text{(B.23)}$$

subject to

$$p^{(2\varepsilon)} = \sum_{l=1}^{ncr} P_{(l)}^{(2\varepsilon)} \qquad \text{(B.24)}$$

and

$$\varepsilon_{ij} = \sum_{l=1}^{ncr} \varepsilon_{ij(l)} \qquad . \qquad \text{(B.25)}$$

Here, *ncr* represents the total number of combining rules for any virial form, in this case a second-virial form. The insertion of Equations (B.24-B.25) into Equation (B.23) yields the **mixing-rule expression**

$$\varepsilon_x = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \sum_{l=1}^{ncr} P_{(l)}^{(2\varepsilon)} \varepsilon_{ij(l)} \qquad \text{(B.26)}$$

that contains the **combining-rule expression**

$$\varepsilon_{ij} = \sum_{l=1}^{ncr} P_{(l)}^{(2\varepsilon)} \varepsilon_{ij(l)} \qquad . \qquad \text{(B.27)}$$

Equations (B.26-B.27) can contain any given number of second-virial combining rules in various proportions. For example, if **combining rule one** of Equations (B.23-B.27) comprises the geometric combining rule of Equation (4.3) in Chapter 4 and **combining rule two** comprises the linear combining rule of Equation (4.2), then

$$\varepsilon_{ij(1)} = \sqrt{\varepsilon_i \varepsilon_j} \qquad \text{(B.28)}$$

and

$$\varepsilon_{ij(2)} = \frac{\left(\varepsilon_i + \varepsilon_j\right)}{2} \quad . \qquad \text{(B.29)}$$

Next, the proportions of each of these two combining rules might arbitrarily be set equal to each other as

$$P_{(1)}^{(2\varepsilon)} = P_{(2)}^{(2\varepsilon)} = \frac{1}{2} \quad . \qquad \text{(B.30)}$$

In this example, the insertion of Equation (B.30) into Equation (B.24) results in the assignment of $ncr = 2$, leading to the expression

$$P^{(2\varepsilon)} = \sum_{l=1}^{2} P_{(l)}^{(2\varepsilon)} = P_{(1)}^{(2\varepsilon)} + P_{(2)}^{(2\varepsilon)} = \frac{1}{2} + \frac{1}{2} = 1 \quad , \qquad \text{(B.31)}$$

which obeys the assignment of second-virial mixing only in Equation (B.21). In addition, Equations (B.28-30) now transform Equation (B.27) into

$$\varepsilon_{ij} = \sum_{l=1}^{2} P_{(l)}^{(2\varepsilon)} \varepsilon_{ij(l)} = \left[P_{(1)}^{(2\varepsilon)} \varepsilon_{ij(1)} + P_{(2)}^{(2\varepsilon)} \varepsilon_{ij(2)} \right]$$

$$= \left[\frac{1}{2}\sqrt{\varepsilon_i \varepsilon_j} + \left(\frac{1}{2}\right)\frac{\left(\varepsilon_i + \varepsilon_j\right)}{2} \right] \quad . \qquad \text{(B.32)}$$

Furthermore, this example may be more easily understood through the calculation of an actual mixture value. Here, the substitution of values

$$\varepsilon_i = 4 \ , \ \varepsilon_j = 9 \qquad \text{(B.33)}$$

into the combining-rule summation of Equation (B.32) amounts to

$$\varepsilon_{ij} = \left[\frac{1}{2}\sqrt{4 \cdot 9} + \left(\frac{1}{2}\right)\frac{(4+9)}{2} \right] = \left[\frac{1}{2}\sqrt{36} + \left(\frac{1}{2}\right)\frac{(13)}{2} \right] = \left[\frac{1}{2}(6) + \left(\frac{1}{2}\right)(6.5) \right] = 6.25$$

(B.34)

Interestingly enough, a result identical to that of Equation (B.34) may instead be obtained through the GSR of Section 4.3 in Chapter 4. Repeating Equation (4.1) for ε,

$$\text{GSR:} \qquad \varepsilon_{ij} = \frac{\left[\varepsilon_i^N + \varepsilon_j^N\right]^{1/N}}{2^{1/N}} \quad . \qquad \text{(B.35)}$$

As discussed in Section 4.2, the geometric combining rule constitutes a limiting case of $N = 0$, while the linear combining rule constitutes $N = 1$. Here, the equal proportions of both geometric and linear combining rules imply that

$$N = \frac{1}{2}(0) + \frac{1}{2}(1) = 0 + \frac{1}{2} = \frac{1}{2} \quad , \qquad \text{(B.36)}$$

or

$$\text{GSR:} \qquad \varepsilon_{ij} = \frac{\left[\varepsilon_i^{1/2} + \varepsilon_j^{1/2}\right]^2}{2^2} \quad . \qquad \text{(B.37)}$$

The substitution of the values in Equation (B.33) into Equation (B.37) results in

$$\varepsilon_{ij} = \frac{\left[4^{1/2} + 9^{1/2}\right]^2}{2^2} = \frac{[2+3]^2}{4} = \frac{[5]^2}{4} = \frac{25}{4} = 6.25 \quad , \qquad \text{(B.38)}$$

a result identical to that of Equation (B.34). Equations (B.35-38) thereby prove that the GSR comprises not only a generalization of symmetric combining rules, but also a

generalization of their proportions. These generalizations lead to the combination of Equations (B.27) and (B.35), which form the second-virial GSR relation, GSR:

$$\varepsilon_{ij} = \frac{\left[\varepsilon_i^{1/2} + \varepsilon_j^{1/2}\right]^2}{2^2} = \sum_{l=1}^{ncr} P_{(l)}^{(2\varepsilon)} \varepsilon_{ij(l)} \quad . \qquad \text{(B.39)}$$

The GSR can therefore represent any sum of proportions of second-virial symmetric combining rules. In addition, the GSR's extension to asymmetric mixing could be accomplished through the use of binary interaction parameters (BIPs), m_{ij} and m_{ji}, to form the second-virial-only mixture expression from Equation (B.22) in the form of

$$\varepsilon_x = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j m_{ij} \frac{\left[\varepsilon_i^N + \varepsilon_j^N\right]^{1/N}}{2^{1/N}} \quad . \qquad \text{(B.40)}$$

Finally, the GAR (of Section 4.3 in Chapter 4) can accomplish this same feat for asymmetric mixing **without** BIPs. As a result, the GAR may be viewed as a generalization of **both** symmetric and asymmetric combining rules as well as a generalization of their proportions. The substitution of the GAR in Equation (4.10) of Chapter 4 for ε,

$$\text{GAR:} \qquad \varepsilon_{ij} = \frac{\varepsilon_i^{\alpha} \varepsilon_j^{-\alpha} \left[\gamma \varepsilon_i^N + (2-\gamma)\varepsilon_j^N\right]^{1/N}}{2^{1/N}} \quad , \qquad \text{(B.41)}$$

thus results in a non-BIP expression analogous to Equation (B.40) in the form of

$$\varepsilon_x = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j \frac{\varepsilon_i^{\alpha}\varepsilon_j^{-\alpha}\left[\gamma\varepsilon_i^N + (2-\gamma)\varepsilon_j^N\right]^{1/N}}{2^{1/N}} \quad . \qquad \text{(B.42)}$$

B.4 The Mixing-Rule Conjunction (MRC)

This section presents the development of the mixing-rule conjunction (MRC) as originally conceived by the author of this work. Simply put, the MRC represented the sum of any proportions of combining rules for all virial forms of mixing. Although the MRC initially comprised the focus of this dissertation[1], the innovation of the GAR herein simplified the MRC to one combining rule for each second- and higher-virial mixture term containing an EOS UIP. Since the GAR holds so much potential in the area of thermodynamic research, the author changed the dissertation focus to the GAR alone. Nevertheless, the MRC still presents certain advantages and might therefore prove of interest to future investigators.

The following section discuss the theoretical reasoning applied throughout this appendix that illustrates various implications of the MRC in mixture modeling. First, Section B.4.1 describes the conceptualization of the MRC from the implications of the Lorentz mixing rule presented in Section B.3. Second, Section B.4.2 presents statistical relations analogous to the MRC found in experimental-design modeling that might find use in thermodynamic mixture modeling. Third, Section B.4.3

[1]The proposed dissertation title would have read "The Mixing-Rule Conjunction: The Optimization of Mixing Rules in a Noncubic Equation of State."

outlines the simplifications to the MRC through both the GSR and the GAR. Fourth, Section B.4.4 discusses the variation of proportions of first-virial mixing rules through two mixture-modeling options. Finally, Section B.4.5 describes the usage of third-virial mixing when predicting binary VLE systems. Altogether, these five sections reveal potential for the MRC that might yield greater insight into and predictive accuracy for mixture equations of state.

B.4.1 Conceptualization

The conceptualization of the MRC by the author of this work arose from consideration of the equations presented in Sections B.2-B.3. To begin with, the proportional first- and second-virial mixing in Equation (B.20) may be viewed through the combining-rule expression of Equation and (B.27) as

$$\varepsilon_x = \sum_{i=1}^{n} x_i \sum_{l=1}^{ncr} P_{(l)}^{(1\varepsilon)} \varepsilon_{i(l)} + \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \sum_{l=1}^{ncr} P_{(l)}^{(2\varepsilon)} \varepsilon_{ij(l)} \quad . \qquad \text{(B.43)}$$

Equation (B.43) may be extended to include all higher forms of virial mixing as well according to

$$\varepsilon_x = \sum_{i=1}^{n} x_i \sum_{l=1}^{ncr} P_{(l)}^{(1\varepsilon)} \varepsilon_{i(l)} + \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \sum_{l=1}^{ncr} P_{(l)}^{(2\varepsilon)} \varepsilon_{ij(l)}$$

$$+ \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{k=1}^{n} x_i x_j x_k \sum_{l=1}^{ncr} P_{(l)}^{(3\varepsilon)} \varepsilon_{ijk(l)} + \ldots \quad . \qquad \text{(B.44)}$$

Equation (B.44) thus constituted the overall MRC relation that comprised the mixture effect of any symmetric/asymmetric combining rule of choice in selected and/or regressed proportions.

B.4.2 Analogous Statistical Relations to the MRC: Experimental-Design Models

The MRC of Equation (B.44) resembles to analogous statistical relations used to model experimental mixture designs. Specifically, these designs inspired the use of varying proportions of mixing/combining rules for the MRC, and may therefore generate future interest in thermodynamic mixture modeling. Cornell (1981) reviews several of these design models in their application to mixture data, some of which are reviewed and compared to thermodynamic mixing rules as follows.

First, Cornell (1981, p. 9) presents the relation

$$\eta = \phi\left(x_1, x_2, \ldots, x_n\right) \quad , \qquad \text{(B.45)}$$

where a response value, η, follows some functional relationship, ϕ, of the proportions, x_i, of a total of n components. Here, the response value corresponds to the energy mixture, ε_x, while the proportions relate to molar compositions. Second, Cornell (1981, p. 9, 20-22) presents various functional relationships through polynomial expressions, including the first-degree polynomial,

$$\eta = \sum_{i=1}^{n} \beta_i x_i \quad , \qquad \text{(B.46)}$$

and the second-degree polynomial,

$$\eta = \sum_{i=1}^{n} \beta_i x_i + \sum \sum_{i<j}^{n} \beta_{ij} x_i x_j \quad . \qquad \text{(B.47)}$$

Obviously, the **first-degree** polynomial of Equation (B.46) corresponds to the **first-virial** mixture expression in Equation (B.20) for ε_x with

$$P^{(1\varepsilon)} = 1, \qquad P^{(2\varepsilon)} = 0 \qquad , \qquad \text{(B.48)}$$

while the **second-degree** polynomial of Equation (B.47) corresponds to the **second-virial** mixture expression in Equation (B.20) according to Equation (B.21). The terms in Equations (B.46-B.47) remain unscaled in the sense that they do not comprise proportional values of the response value, η. Consequently, the parameter β_i roughly corresponds to $P_{(l)}^{(1\varepsilon)} \varepsilon_{i(l)}$ in Equation (B.43) and the parameter β_{ij} to $P_{(l)}^{(2\varepsilon)} \varepsilon_{ij(l)}$, although the subscript *l* now reflects a different designation for <u>each</u> parameter *i* and *ij*, respectively. Moreover, not all parameters β_i and β_{ij} need to have nonzero values.

Next, Equations (B.46-B.47) may be generalized (ibid., p. 20) to a ***Wth*-degree** polynomial of the form

$$\eta = \sum_{i=1}^{n} \beta_i x_i + \sum \sum_{i<j}^{n} \beta_{ij} x_i x_j + \sum \sum_{i<j}^{n} \delta_{ij} x_i x_j \left(x_i - x_j \right)$$

$$+ \sum \sum_{i<j<k}^{n} \beta_{ijk} x_i x_j x_k + \ldots \qquad . \qquad \text{(B.49)}$$

With the exception of the third summation term, Equation (B.49) corresponds to the MRC expression of Equation (B.44); the third term can, however, be removed (ibid., p. 22) for a more direct analogy between these two equations. Moreover, limiting cases of Equation (B.49) also exist, including the special cubic model of Scheffe',

$$\eta = \sum_{i=1}^{3} \beta_i x_i + \sum \sum_{i<j}^{3} \beta_{ij} x_i x_j + \beta_{123} x_1 x_2 x_3 \qquad , \qquad \text{(B.50)}$$

for three components. Equation (B.50) thus shows a simple third-degree relationship

between these three components.

Lastly, Cornell (1981, p. 212-213) also discusses the inclusion of inverse-mixture terms that may be added to experimental mixture-design models. For example, the addition of these terms to Equation (B.47) results in

$$\eta = \sum_{i=1}^{n} \beta_i x_i + \sum_{i<j}^{n} \beta_{ij} x_i x_j + \sum_{i=1}^{n} \beta_{-i} x_i^{-1} \quad . \qquad \text{(B.51)}$$

As Cornell (ibid., p. 212-213) notes, inverse terms, like the one on the right-hand side of Equation (B.51), are added to account for extreme response changes as any proportion x_i approaches zero. Cornell (ibid.) then discusses the avoidance of undefined (i.e., division by zero) values in the inverse-mixture terms through the application of pseudocomponent relations

$$x_i' = x_i\left(1 - \sum_{i=1}^{n} c_i\right) + c_i \quad , \qquad \text{(B.52)}$$

where x_i' represents the pseudocomponent proportion for component *i*, and each c_i consists of a small, positive number for component *i*. The inverse-mixture terms thus comprise first-virial alternatives to additive first-virial mixing alone.

B.4.3 Simplification of the MRC

This section presents simplifications that can be made to the MRC through both the GSR and the GAR. At first, it was hoped that the virial combining-rule proportions, $P_{(l)}^{(1\varepsilon)}$, $P_{(l)}^{(2\varepsilon)}$, $P_{(l)}^{(3\varepsilon)}$, etc., would replace BIPs, m_{ij}, as unlike-

interaction mechanisms for binary-mixture interpretations. In Section B.3, however, this replacement proved unnecessary since the GSR can represent any proportion of second-virial combining rules, a result that could be extended to all second- and higher-virial forms of symmetric mixing.

Moreover, Section B.3 also showed that the GAR extension to asymmetric mixing could be accomplished through the use of BIPs. This extension simplifies the expression of Equation (B.44) to

$$\varepsilon_x = \sum_{i=1}^{n} x_i \sum_{l=1}^{ncr} P_{(l)}^{(1\varepsilon)} \varepsilon_{i(l)} + P^{(2\varepsilon)} \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \varepsilon_{ij}$$

$$+ P^{(3\varepsilon)} \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{k=1}^{n} x_i x_j x_k \varepsilon_{ijk} + \ldots \quad , \qquad \text{(B.53)}$$

or more simply,

$$\varepsilon_x = P^{(1\varepsilon)} \varepsilon_x^{(1)} + P^{(2\varepsilon)} \varepsilon_x^{(2)} + P^{(3\varepsilon)} \varepsilon_x^{(3)} + \ldots \quad , \qquad \text{(B.54)}$$

where $\varepsilon_x^{(1)}$ represents all first-virial mixing, $\varepsilon_x^{(2)}$ represents all second-virial mixing, $\varepsilon_x^{(3)}$ represents all third-virial mixing, etc. Obviously, the GAR can accomplish this same task for asymmetric mixing without BIPs. In either case, the GSR or GAR greatly simplified the MRC as a modeling tool.

Furthermore, the GSR/GAR simplifications still allow for any virial-mixing terms of choice. In Sections (B.2-B.3), the choice of value for the symmetric parameter, *N*, for second-virial mixing influences the proportion of first-virial mixing used to calculate ε_x. Logically, then, a third-virial mixture expression with a fixed

value of N would contain certain proportions of first- and second-virial mixing as well, with the same trend occurring for all higher-virial forms. Nevertheless, these proportions with fixed values of N may be altered through the assignment of various values of $P_{(I)}^{(1\varepsilon)}$, $P_{(I)}^{(2\varepsilon)}$, $P_{(I)}^{(3\varepsilon)}$, etc. In fact, Juris (1970) discusses higher-virial forms for Joule-Thomson coefficients.

In addition, Section 2.2.3 of Chapter 2 noted the older practice reviewed by Juris (1970) and Juris and Wenzel (1974) of using different values of N in the GAR for various mixture parameters of the Martin-Hou (1955) EOS. This practice implies a reformulation of the mixing rules designated for each mixture parameter, which in turn bears analogy to the MRC choices of selecting and/or regressing different proportions of virial-mixing rules for each parameter. Nevertheless, the choice of either second- or third-virial mixing should predict mixture parameters with near equivalent accuracy, with the same result probably applying to higher-virial mixture forms.

B.4.4 The Variation of Proportions of First-Virial Mixing Rules

In contrast, the variation of proportions of first-virial mixing rules pose at least two options in mixture modeling. To begin with, Equation (B.53) shows that the first-virial mixture term still contains more than one type of mixing rule despite the insertion of either the GSR of the GAR. For example, the mixture expression for ε_x could solely consist of first-virial mixing, i.e.,

$$\varepsilon_x = \sum_{i=1}^{n} x_i \sum_{l=1}^{ncr} P_{(l)}^{(1\varepsilon)} \varepsilon_{i(l)} \quad , \qquad \text{(B.55)}$$

with

$$P^{(1\varepsilon)} = 1, \quad P^{(2\varepsilon)} = 0, \text{ and } P^{(3\varepsilon)} = 0 \quad . \qquad \text{(B.56)}$$

Since first-virial mixing does not contain various forms of combining rules, it instead contains various forms of mixing rules. Consequently, the mixture composition, x_i, might be placed with the second summation of Equation (B.55), thereby yielding

$$\varepsilon_x = \sum_{i=1}^{n} \sum_{l=1}^{ncr} P_{(l)}^{(1\varepsilon)} x_{i(l)} \varepsilon_{i(l)} \quad . \qquad \text{(B.57)}$$

Equation (B.57) may in turn be arbitrarily expanded into two first-virial mixing rules as

$$\varepsilon_x = \sum_{i=1}^{n} P_{(1)}^{(1\varepsilon)} x_{i(1)} \varepsilon_{i(1)} + \sum_{i=1}^{n} P_{(2)}^{(1\varepsilon)} x_{i(2)} \varepsilon_{i(2)}$$

$$= P_{(1)}^{(1\varepsilon)} \sum_{i=1}^{n} x_{i(1)} \varepsilon_{i(1)} + P_{(2)}^{(1\varepsilon)} \sum_{i=1}^{n} x_{i(2)} \varepsilon_{i(2)} \quad . \qquad \text{(B.58)}$$

For any three components, the first of these two mixing rules could comprise the simple additive mixing rule,

$$P_{(1)}^{(1\varepsilon)} \sum_{i=1}^{3} x_{i(1)} \varepsilon_{i(1)} = P_{(1)}^{(1\varepsilon)} \left(x_1 \varepsilon_1 + x_2 \varepsilon_2 + x_3 \varepsilon_3 \right) \quad , \qquad \text{(B.59)}$$

while the second mixing rule could constitute a sum of terms analogous to the inverse-mixing rule of Equation (B.51):

$$P_{(2)}^{(1\varepsilon)} \sum_{i=1}^{3} x_{i(2)} \varepsilon_{i(2)} = P_{(2)}^{(1\varepsilon)} \sum_{i=1}^{3} \frac{\varepsilon_i}{x_i} = P_{(2)}^{(1\varepsilon)} \left(\frac{\varepsilon_1}{x_1} + \frac{\varepsilon_2}{x_2} + \frac{\varepsilon_3}{x_3} \right) \quad . \tag{B.60}$$

Obviously, Equation (B.60) would provide a greater overall contribution to ε_x as one or more of the values for x_i approach zero. This circumstance may, however, prove advantageous when simulating binary VLE systems that contain a wide degree of phase separation as noted in Section 7.3.2. In other words, the inverse-mixture term of Equation (B.60) might "fine-tune" the mixture parameters to minuscule amounts of a component in a given phase.

Although the inverse-mixing rule of Equation (B.60) would alter the mixture expression -- in the sense that all mixture terms would not directly sum to that of a pure component -- it should be noted that BIPs technically alter the mixture expression in similar fashion. The past success achieved with BIPs thus lends support to this empirical method of predicting indirect mixture summations. (In contrast, mixture terms containing GARs do sum to a pure component in the technical sense).

Second, the fugacity derivatives entailed in first-virial mixing present different alternatives than higher forms of virial mixing. For example, the fugacity derivative of Equation (B.59) with respect to component *i*,

$$\frac{\partial}{\partial n_i} \left[P_{(1)}^{(1\varepsilon)} \sum_{i=1}^{3} x_{i(1)} \varepsilon_{i(1)} \right] = P_{(1)}^{(1\varepsilon)} \frac{\partial}{\partial n_i} \left[\sum_{i=1}^{3} x_{i(1)} \varepsilon_{i(1)} \right] = \varepsilon_{i(1)} = \varepsilon_i \quad , \tag{B.61}$$

consists solely of the pure-component parameter (PCP), in this case ε_i.

In contrast, the fugacity derivative of Equation (B.60),

$$\frac{\partial}{\partial n_i}\left[P_{(2)}^{(1\varepsilon)}\sum_{i=1}^{3}\frac{\varepsilon_i}{x_i}\right]=P_{(2)}^{(1\varepsilon)}\frac{\partial}{\partial n_i}\left[\sum_{i=1}^{3}\frac{\varepsilon_i}{x_i}\right]=P_{(2)}^{(1\varepsilon)}\frac{\partial}{\partial n_i}\left[\sum_{i=1}^{3}\varepsilon_i\left(x_i\right)^{-1}\right]$$

$$=P_{(2)}^{(1\varepsilon)}\varepsilon_i\left(x_i\right)^{-2}=P_{(2)}^{(1\varepsilon)}\frac{\varepsilon_i}{x_i^2} \quad , \qquad \text{(B.62)}$$

contains the PCP ε_i divided by the square of the molar composition, x_i.

Finally, it remains unclear at this time how successfully different proportions of first-virial mixing rules could simulate binary systems, either with or without higher virial forms of mixing. In fact, little effort has been made to employ varying proportions of simple, additive mixing of Equation (B.59), and certainly no effort has been made in thermodynamics to employ the inverse mixing of Equation (B.60). Understandably, first-virial mixing comprises one-fourth of the second-virial Lorentz mixing rule of Section B.2, while other second- and higher-virial mixing rules will contain a portion of first-virial mixing as well. The alteration of these defined proportions of first-virial mixing could, however, introduce new functional relationships between molar compositions, x_i., into both the pressure and pure-component fugacity expressions of an EOS. Consequently, the use of either fixed and/or regressed proportions of these two mixing rules should be tested, perhaps with fixed proportions of the second-virial mixing rule as well. At any rate, the author recommends this type of simulation to future investigators.

B.4.5 Usage of Third-Virial Mixing to Predict Binary and Multicomponent VLE Systems

Aside from first- and second-virial mixing, consideration should also be given to the usage of third-virial mixing to predict binary VLE systems. With the simplifications to the MRC in Section B.4.3, both the GSR and GAR can provide third-virial relations for UIPs in mixture models for two components. The UIP relations for *ijk* interactions must, however, be designated differently when predicting three of more components through third-virial GSR/GAR relations.

For example, the energy parameter, ε_x, would exist as a limiting case of the MRC of Equation (B.53) according to

$$\varepsilon_x = \sum_{i=1}^{n}\sum_{j=1}^{n}\sum_{k=1}^{n} x_i x_j x_k \varepsilon_{ijk} \quad , \qquad \text{(B.63)}$$

with

$$P^{(1\varepsilon)} = 0, \quad P^{(2\varepsilon)} = 0, \text{ and } P^{(3\varepsilon)} = 1 \quad . \qquad \text{(B.64)}$$

The GSR would then represent ε_{ijk} in Equation (B.63) through the relation

$$\varepsilon_x = \sum_{i=1}^{n}\sum_{j=1}^{n}\sum_{k=1}^{n} x_i x_j x_k \frac{\left[\varepsilon_i^N + \varepsilon_j^N + \varepsilon_k^N\right]^{1/N}}{3^{1/N}} \quad . \qquad \text{(B.65)}$$

Here, attention should be paid to the fact that third-virial mixing always forces asymmetric mixing for binary systems in the sense that one of the two components must be counted twice. For example, if $k = i$, Equation (B.65) then becomes

$$\varepsilon_x = \sum_{i=1}^{n}\sum_{j=1}^{n}\sum_{k=1}^{n} x_i^2 x_j \frac{\left[2\varepsilon_i^N + \varepsilon_j^N\right]^{1/N}}{3^{1/N}} \quad . \tag{B.66}$$

Since third-virial asymmetry occurs for both the GSR and the GAR, varying proportions of first- and third-virial mixing might suffice to predict binary VLE systems.

In contrast, the GAR would represent third-virial, unlike interactions for Equation (B.63) in the form of

$$\varepsilon_{ijk} = \frac{\varepsilon_i^{\alpha}\varepsilon_j^{\beta}\varepsilon_k^{-\alpha-\beta}\left[\gamma\varepsilon_i^N + \delta\varepsilon_j^N + (3-\gamma-\delta)\varepsilon_k^N\right]^{1/N}}{3^{1/N}} \quad . \tag{B.67}$$

Of course, the third-virial form of the GAR includes five parameters, not all of which must be regressed over each binary system. Nevertheless, even if the symmetric parameter, N, were held equal to unity, the other four parameters would have to be held constant and/or regressed. In any case, the third-virial GAR would yield the following six combining-rule expressions for Equation (B.67):

(1) $$\varepsilon_{ijj} = \frac{\varepsilon_i^{\alpha}\varepsilon_j^{-\alpha}\left[\gamma\varepsilon_i^N + (3-\gamma)\varepsilon_j^N\right]^{1/N}}{3^{1/N}} \tag{B.68}$$

(2) $$\varepsilon_{jii} = \frac{\varepsilon_i^{-\alpha}\varepsilon_j^{\alpha}\left[(3-\gamma)\varepsilon_i^N + \gamma\varepsilon_j^N\right]^{1/N}}{3^{1/N}} \tag{B.69}$$

(3) $$\varepsilon_{jij} = \frac{\varepsilon_i^{\beta}\varepsilon_j^{-\beta}\left[\delta\varepsilon_i^N + (3-\delta)\varepsilon_j^N\right]^{1/N}}{3^{1/N}} \tag{B.70}$$

$$(4) \qquad \varepsilon_{iji} = \frac{\varepsilon_i^{-\beta}\varepsilon_j^{\beta}\left[(3-\delta)\varepsilon_i^N + \delta\varepsilon_j^N\right]^{1/N}}{3^{1/N}} \tag{B.71}$$

$$(5) \qquad \varepsilon_{iij} = \frac{\varepsilon_i^{\alpha+\beta}\varepsilon_j^{-\alpha-\beta}\left[(\gamma+\delta)\varepsilon_i^N + (3-\gamma-\delta)\varepsilon_j^N\right]^{1/N}}{3^{1/N}} \tag{B.72}$$

$$(6) \qquad \varepsilon_{jji} = \frac{\varepsilon_i^{-\alpha-\beta}\varepsilon_j^{\alpha+\beta}\left[(3-\gamma-\delta)\varepsilon_i^N + (\gamma+\delta)\varepsilon_j^N\right]^{1/N}}{3^{1/N}} \quad . \tag{B.73}$$

Equations (B.68-B.73) correspond to the two second-virial GARs in Equations (4.26-4.27) of Chapter 4. Moreover, the six third-virial combining rules in Equations (B.68-B.73) employ the three symmetric, unlike-interaction parameter relations

$$\alpha_{ijj} = \alpha_{jii} = \alpha_{jij} = \alpha_{iji} = \alpha_{iij} = \alpha_{jji} \quad , \tag{B.74}$$

$$N_{ijj} = N_{jii} = N_{jij} = N_{iji} = N_{iij} = N_{jji} \quad , \tag{B.75}$$

and

$$\gamma_{ijj} = \gamma_{jii} = \gamma_{jij} = \gamma_{iji} = \gamma_{iij} = \gamma_{jji} \quad . \tag{B.76}$$

The symmetrical, third-virial parameter relations of Equations (B.74-B.76) correspond to the symmetrical, second-virial parameter relations of Equations (4.28-4.30).

In contrast to Equations (B.74-B.76), the *ijk*, third-virial parameter relations must be assigned different functional values when predicting VLE mixtures of three

or more components. For example, α_{ijk} might be calculated from the symmetrical expression

$$\alpha_{ijk} = \frac{\alpha_{ij} + \alpha_{ik} + \alpha_{jk}}{3} \quad , \qquad \text{(B.77)}$$

with similar equations for the other five *ijk* UIPs. Obviously, the GAR could be used instead of Equation (B.77) to obtain asymmetric *ijk* averages that might provide greater insight into the relative weights of binary interactions in three- and higher-component systems.

In fact, either symmetric or asymmetric **third-virial** relations that stem from averaged **second-virial** UIP values of α could be compared to results obtained through direct regression of the *ijk* parameters themselves against ternary data of the three components involved. Hopefully, a comparison between these **averaged** versus **regressed** results might yield greater insight into the predictive accuracy of the EOS of interest. Of course, similar considerations would also apply to both N_{ijk} and γ_{ijk}.

Finally, the author suggests that the *ijk* parameters of the GAR could just as easily be applied to the option mentioned in Section 3.3.4.3 of regressing GAR parameters over pure-component and/or mixture property weights. Again, this application would provide a means of obtaining possible improvements in ternary- and multicomponent- property predictions.

APPENDIX C

LITERATURE REVIEW OF AVAILABLE BINARY AND MULTICOMPONENT VAPOR-LIQUID EQUILIBRIUM (VLE) DATA

The author consulted several literature sources for the binary vapor-liquid equilibrium (VLE) data simulated in this work. These sources were found to contain VLE data as well as several other forms of chemical mixture data, including vapor pressure, liquid-density, and enthalpy data. Typically, many of the literature sources exist in the form of monographic bibliographies that review most of the VLE data taken in the twentieth century; Table C.1 lists these in chronological order. In addition, some of the sources actually list the experimental data, many of which comprise several volumes of the DECHEMA data collection; Table C.2 presents several of these volumes in chronological order as well. Actually, the DECHEMA sources were assembled from several of the sources in Table 3.1, but possess a distinct advantage over some of the other sources in that they actually list the data referred to. Next, Table C.3 presents the sources utilized for all binary VLE simulations of this work, some of which were taken from the DECHEMA volume by Gmehling, Onken, and Arlt (1980).

In Table C.1, only seven out of the twenty sources report experimental data. Although the DECHEMA collection remains extensive (with more volumes than those in Table C.2), it does not prove entirely comprehensive. In fact, the methane-*ortho*-xylene data reported by Stepanova and Velikovskii (1969) were located through

Table C.1

Sources of Binary and Multicomponent Vapor-Liquid Equilibrium Data

(Various Sources)

Author(s)	Publisher	Source Type	Lists Actual Data?	Modeling Provided	Properties	Remarks
Chu et al. (1950)	Reinhold	Monograph	Yes	None	VLE	Lists ternary data
Chu et al. (1956)	J. W. Edwards	Monograph	Yes	None	VLE	Excellent source
Hala et al. (1958).	Pergamon Press	Distillation/ rectification text	No	None	VLE	Description of Apparatus
Malesinski (1965)	Interscience Publishers	Azeotropy Monograph	No	None	VLE	Solely refers to azeotropic systems
Hala et al. (1967).	Pergamon Press	Distillation/ rectification text	No	None	VLE	Description of Apparatus
Hala et al. (1968).	Pergamon Press	Monograph	Yes	Van Laar, Margules, Antoine Constants	VLE	Excellent source
CACHE (1972)	No publisher	Monograph	No	None	VLE, LLE, solubility, azeotropes	Refers to other sources

Table C.1

(Continued)

Wichterle et al. (1973)	Elsevier	Monograph Bibliography	No	None	VLE	Comprehensive source
Hirata (1975)	Elsevier	Monograph	Yes	Wilson, Antoine Constants	VLE	Comprehensive
Wichterle et al. (1976)	Elsevier	Monograph Bibliography	No	None	VLE	First Supplement to Wichterle (1973)
Fredenslund et al. (1977)	Elsevier	Simulation/ Application Monograph	No	UNIFAC	VLE	Scattered references; contains FORTRAN source code
McGlashan (1978)	The Chemical Society	Monograph on Mixture Modeling	No	None	G^E, H^E, P_c, T_c, V^E, VLE, x, y	Excellent source of many properties
Kojima and Tochigi (1979)	Elsevier	Simulation/ Application Monograph	Yes	ASOG	VLE	Scattered references; contains FORTRAN source code

Table C.1

(Continued)

Wichterle et al. (1979)	Elsevier	Monograph Bibliography	No	None	VLE	Second Supplement to Wichterle (1973)
Wichterle et al. (1982)	Elsevier	Monograph Bibliography	No	None	VLE	Third Supplement to Wichterle (1973)
Li (1984)	University of Oklahoma	MS thesis	No	Local Composition Model	VLE	Extensive modeling discussion
Wichterle et al. (1985)	Elsevier	Monograph Bibliography	No	None	VLE	Fourth Supplement to Wichterle (1973)
Ohe (1991)	Elsevier	Monograph	Yes	None	VLE	Electrolyte mixtures
Malanowski and Oracz (1997)	Thermo-dynamics Research Center	Index	Yes	None	C_p, G^E, H^E, LLE, P_c, SLE, T_c, V^E, VLE, x, y	Contains list of component pseudonyms
Skrzecz (1997)	IUPAC	Journal Article	No	None	VLE, solubility	Focuses on solubility rather than VLE

Table C.2

Sources of Binary and Multicomponent Vapor-Liquid Equilibrium Data

(DECHEMA only)

Author(s)	Publisher	Source Type	Lists Actual Data?	Modeling Provided	Properties	Remarks
Gmehling and Onken (1977a)	DECHEMA	Volume I	Yes	Margules, NRTL, Wilson, UNIQUAC	VLE	Includes Antoine parameters
Gmehling and Onken (1977b)	DECHEMA	Volume I Part 2a	Yes	Margules, NRTL, Wilson, UNIQUAC	VLE	Includes Antoine parameters
Gmehling, Onken, and Arlt (1978)	DECHEMA	Volume I Part 2b	Yes	Margules, NRTL, Wilson, UNIQUAC	VLE	Includes Antoine parameters
Gmehling, Onken, and Arlt (1979)	DECHEMA	Volume I Parts 3 + 4	Yes	Margules, NRTL, Wilson, UNIQUAC	VLE	Includes Antoine parameters

Table C.2

(Continued)

Gmehling, Onken, and Arlt (1980)	DECHEMA	Volume I Part 7	Yes	Margules, NRTL, Wilson, UNIQUAC	VLE	Includes Antoine parameters
Gmehling, Onken, and Arlt (1981)	DECHEMA	Volume I Part 1a	Yes	Margules, NRTL, Wilson, UNIQUAC	VLE	Includes Antoine parameters
Gmehling Onken, and Arlt (1982)	DECHEMA	Volume I Part 2c	Yes	Margules, NRTL, Wilson, UNIQUAC	VLE	Includes Antoine parameters
Gmehling, Onken, and Weidlich (1982)	DECHEMA	Volume I Part 2d	Yes	Margules, NRTL, Wilson, UNIQUAC	VLE	Includes Antoine parameters
Knapp et al. (1982)	DECHEMA	Volume VI	Yes	Margules, NRTL, Wilson, UNIQUAC	VLE	Includes Antoine parameters

Table C.2

(Continued)

Christensen et al. (1984)	DECHEMA	Volume III Part 1	Yes	Margules, NRTL, Wilson, UNIQUAC	VLE	Includes Antoine parameters
Stephan and Hildwein (1987)	DECHEMA	Volume IV Parts 1 + 2	Yes	P^{v}	P^{v}, VLE	Contains pure-component and mixture data
Gmehling, Onken, Rarey-Nies (1988a)	DECHEMA	Volume I Part 1b	Yes	Margules, NRTL, Wilson, UNIQUAC	VLE	Includes Antoine parameters
Gmehling, Onken, and Rarey-Nies (1988b)	DECHEMA	Volume I Part 2e	Yes	Margules, NRTL, Wilson, UNIQUAC	VLE	Includes Antoine parameters
Gmehling, Onken, and Rarey (1990)	DECHEMA	Volume I Part 2f	Yes	Margules, NRTL, Wilson, UNIQUAC	VLE	Includes Antoine parameters
Gmehling, Onken, and Rarey (1993)	DECHEMA	Volume I Part 3b	Yes	Margules, NRTL, Wilson, UNIQUAC	VLE	Includes Antoine parameters

Table C.3

Sources of Binary VLE Data Simulated for this Work

System	Number of Data Points	Temp. Range (°R)	Pressure Range (psia)	References
Benzene-*meta*-Xylene	9	536.67	0.57-1.72	Boublik and Benson (1969)
Benzene-*meta*-Xylene	13	558.27	0.43-2.91	Boublik and Benson (1969)
Benzene-*meta*-Xylene	13	581.67	0.82-4.92	Boublik and Benson (1969)
Benzene-*meta*-Xylene	9	655.27-716.31	14.696	Gultekin (1990)
Benzene-*meta*-Xylene (All data sets)	44	536.67-716.31	0.43-14.696	Boublik and Benson (1969); Gultekin (1990)
Benzene-*para*-Xylene (Single isobar only)	13	642.15-723.87	14.696	Michishita et al. (1971)
Toluene-*meta*-Xylene	15	672.48	5.12-10.33	Willman and Teja (1985)
Toluene-*meta*-Xylene	9	690.48	6.92-14.29	Willman and Teja (1985)
Toluene-*meta*-Xylene	9	708.66	9.42-18.60	Willman and Teja (1985)
Toluene-*meta*-Xylene	9	699.21-725.44	14.696	Gultekin (1990)
Toluene-*meta*-Xylene (All data sets)	42	672.48-725.44	5.12-18.60	Willman and Teja (1985); Gultekin (1990)
Toluene-*para*-Xylene (Single isotherm only)	12	653.67	4.04-6.28	Wichterle (1965)[1]

Table C.3

(Continued)

Benzene-Toluene	88	637.69-691.02	14.696	Kirschbaum and Gerstner (1939)[1]; Todd (1940); Rollet et al. (1956); Heertjes (1960)[1]; Kesselman et al. (1968); Meeboer (1969)[1]; Michishita et al. (1971); Gultekin (1990)
Benzene-Toluene	4	617.67	7.96-8.20	Arich and Tagliavini (1958)
Benzene-Toluene (All data sets)	92	617.67-691.02	7.96-14.696	Kirschbaum and Gerstner (1939)[1]; Todd (1940); Rollet et al. (1956); Arich and Tagliavini (1958); Heertjes (1960)[1]; Kesselman et al. (1968); Meeboer (1969)[1]; Michishita et al. (1971); Gultekin (1990)
Ethylbenzene-*ortho*-Xylene	15	671.67	3.90-4.91	Wisniewska (1996b)
Ethylbenzene-*ortho*-Xylene	13	594.99-606.87	0.97	Monton and Llopis (1994)
Ethylbenzene-*ortho*-Xylene	13	658.71-671.13	3.87	Monton and Llopis (1994)
Ethylbenzene-*ortho*-Xylene (All data sets)	41	594.99-671.67	0.97-4.91	Wisniewska (1996b); Monton and Llopis (1994)
Benzene-Ethylbenzene (Single isobar only)	11	637.63-735.23	14.696	Kesselman et al. (1968)
Toluene-Ethylbenzene	4	536.67	0.27-0.52	Arm et al. (1957)[1]
Toluene-Ethylbenzene	15	671.67	5.25-10.46	Wisniewska (1996a)

Table C.3

(Continued)

Toluene-Ethylbenzene (Both isotherms)	19	536.67-671.67	0.27-10.46	Arm et al. (1957)[1]; Wisniewska (1996a)
Methane-Benzene	13	609.67	100.00-4000.00	Elbishlawi and Spencer (1951)
Methane-Benzene	6	757.89	288.19-2949.19	Lin et al. (1979)
Methane-Benzene	5	831.33	438.23-2364.15	Lin et al. (1979)
Methane-Benzene	5	902.07	743.18-1982.34	Lin et al. (1979)
Methane-Benzene (All data sets)	29	609.67-902.07	100.00-4000.00	Elbishlawi and Spencer (1951); Lin et al. (1979)
Methane-Toluene	12	459.67	50.00-2500.00	Lin et al. (1978)
Methane-Toluene	11	499.67	50.00-2500.00	Lin et al. (1978)
Methane-Toluene	11	609.67	100.00-4000.00	Elbishlawi and Spencer (1951)
Methane-Toluene	6	760.41	293.19-2939.20	Lin et al. (1979)
Methane-Toluene	7	831.69	294.36-3341.43	Lin et al. (1979)
Methane-Toluene	6	901.35	292.45-2446.44	Lin et al. (1979)
Methane-Toluene	3	977.67	446.32-1022.40	Lin et al. (1979)
Methane-Toluene (All data sets)	56	459.67-977.67	50.00-4000.00	Elbishlawi and Spencer (1951); Lin et al. (1979)
Methane-*ortho*-Xylene (Single isotherm only)	10	599.67	142.23-4267.00	Stepanova and Velikovskii (1969)
Methane-n-Propylbenzene	7	564.48	739.70-5076.34	Richon et al. (1991)
Methane-n-Propylbenzene	4	706.86	1522.90-4394.66	Richon et al. (1991)

Table C.3

(Continued)

Methane-n-Propylbenzene (Both isotherms)	11	564.48-706.86	739.70-5076.34	Richon et al. (1991)
Methane-Water	6	600.66-932.94	192.47-935.64	Crovetto et al. (1982)
Methane-Water	17	559.67	200.00-10000.00	Culberson and McKetta, Jr. (1951)
Methane-Water	16	619.67	200.00-8000.00	Culberson and McKetta, Jr. (1951)
Methane-Water	17	679.67	200.00-9000.00	Culberson and McKetta, Jr. (1951)
Methane-Water	11	739.67	200.00-3500.00	Culberson and McKetta, Jr. (1951)
Methane-Water	12	799.67	200.00-4000.00	Culberson and McKetta, Jr. (1951)
Methane-Water (All Data sets)	79	559.67-932.94	192.47-10000.00	Culberson and McKetta, Jr. (1951); Crovetto et al. (1982)
Methane-Triethylene Glycol	9	536.67	16.46-2823.89	Jou et al. (1987)
Methane-Triethylene Glycol	9	581.67	16.06-2440.99	Jou et al. (1987)
Methane-Triethylene Glycol	11	626.67	15.84-2855.80	Jou et al. (1987)
Methane-Triethylene Glycol	10	671.67	16.37-2790.54	Jou et al. (1987)
Methane-Triethylene Glycol	10	716.67	18.46-2744.12	Jou et al. (1987)
Methane-Triethylene Glycol (All data sets)	49	536.67-716.67	15.84-2855.80	Jou et al. (1987)
Triethylene Glycol - Water (Single isotherm only)	15	859.67	18.53-76.04	Pimentel (1993)
Benzene - Triethylene Glycol (Single isobar only)	11	638.37-771.75	14.696	Gupta et al. (1989)

Table C.3

(Continued)

Toluene - Triethylene Glycol (Single isobar only)	10	693.45-796.59	14.696	Gupta et al. (1989)
Tetrafluoromethane-Trifluoromethane	14	309.67	10.68-68.20	Piacentini and Stein (1967)
Tetrafluoromethane-Trifluoromethane	18	359.67	26.78-218.82	Piacentini and Stein (1967)
Tetrafluoromethane-Trifluoromethane	14	404.67	89.86-489.70	Piacentini and Stein (1967)
Tetrafluoromethane-Trifluoromethane	9	459.67	283.28-703.71	Piacentini and Stein (1967)
Tetrafluoromethane-Trifluoromethane	12	509.67	519.56-753.46	Piacentini and Stein (1967)
Tetrafluoromethane-Trifluoromethane (All data sets)	67	309.67-509.67	10.68-753.46	Piacentini and Stein (1967)

[1]Source: Gmehling, Onken, and Arlt (1980)

the sources that appear in Table C.1 and not found in the sources of Table C.2.

Moreover, many interesting items appeared during the literature search for data. First, Onken et al. (1980) notes thirteen journals that comprised roughly fifty-five percent of the literature sources of VLE data of their Dortmund Data Bank through which the DECHEMA data books were assembled. Second, all of the DECHEMA monographs referred to in this work may be found at Oklahoma State University (OSU) in Stillwater, Oklahoma. Even though this particular geographic location may not prove accessible to all researchers, the OSU Edmon Low library catalog may be accessed through the Internet for a listing of the standard DECHEMA collection.

Finally, although many of the IGT monographs reviewed herein focused on mixture-density data, the first IGT report by Parent (1948) suggested a method of storage for natural gas in hydrate form (i.e., as a solid). This storage method was intended to provide a safer fuel supply than natural gas in liquid form, and may find use in future research.

APPENDIX D

CORRELATION BETWEEN PURE-COMPONENT PARAMETERS (PCPS) AND RELATED ASPECTS OF THERMODYNAMIC MODELING

D.1 Overview

Regardless of the equation of state (EOS) chosen to predict binary and/or multicomponent mixtures, the degree of correlation (DOC) between pure-component parameters (PCPs) bears consideration. To be sure, the DOC can affect the final values of the PCPs themselves, which can result in obscure trends in these values between pure components. This appendix therefore discusses correlation between PCPs along with related aspects of thermodynamic modeling observed throughout the preparation of this dissertation.

First, Section D.2 details a description of the PCP-correlation problem (Section D.2.1) along with a recommended procedure (Section D.2.2) to counteract correlation effects. Next, Section D.3 evaluates the relation between PCP correlation and multiproperty analysis (MPA). Finally, Section D.4 presents various considerations on the effect of correlation on the prediction of mixture properties.

D.2 Correlation between PCPs

D.2.1 Description of Correlation Problems

Correlation between PCPs may be described in terms of the regression process itself. First of all, the regression of PCPs in an EOS to a given set of data (e.g., vapor pressure and density) typically involves changes in the numerical values of at least a few of the initial parameter estimates. Commonly, these changes will most likely continue to occur throughout the iterative regression evaluations of the objective-function relationship chosen to relate the parameters regressed to the actual data simulated.

Unfortunately, the numerical values of some PCPs can remain unchanged with regard to their initial estimates. This occurrence then leaves the **changed** parameters highly correlated in terms of their becoming forced to numerically adjust to the **unchanged** parameters. In other words, the changed parameters follow some type of unknown correlational dependency of the unchanged parameters.

The author observed the effect of parameter correlation while attempting to duplicate the work of Nishiumi et al.. Specifically, this work involved regressing the PCPs in Equations (2.29-2.32) of Chapter 2, which comprised an extension of the Benedict-Webb-Rubin-Starling (BWRS) EOS (Starling, 1971). Moreover, the duplication of Nishiumi et al.'s work involved the regression of nineteen PCPs; this high number of parameters reflects the fact that the chances of correlation between parameters increases with the number of parameters regressed. (The author surmounted this DOC obstacle through the regression of only one polar parameter).

Consequently, the use of as few parameters as possible will most likely result in a lesser likelihood of correlated parameters.

In contrast, the Khan-Chung-Lee-Starling (KCLS) equation of state (EOS) formulated by Khan (1983) and Chung et al. (1984) contains only four PCPs. Although the fewer PCPs in the KCLS EOS presents an obvious advantage over a multiparameter EOS (in terms of a lesser DOC between them), some correlation does arise during their regression. As noted in Section 3.3.3.1 of Chapter 3, the author noticed a high degree of correlation when regressing the polar parameter, κ, in that the first estimate of κ typically did not change throughout the regression. Moreover, a similar degree of correlation also occurred to a far lesser, but noticeable, extent in the energy parameter, $\frac{\varepsilon}{k}$, with $\kappa = 0$. The high DOC with κ might, however, be avoided in the future through the following procedure.

D.2.2 Procedure to Counteract Correlation Effects

The solution in Section D.2.1. to counteract the effects of correlation between parameters in the extended-BWRS EOS of Nishiumi et al. may be applied to avoid the high DOC found in the KCLS polar parameter, κ. During the course of PCP regression outlined in Chapter 3, the author noticed that near-equal predictions of pure-component properties for polar substances could be attained by the initial assignment of $\kappa = 0$. As a result, the other three KCLS parameters (λ, $\frac{\varepsilon}{k}$, and V^*)

could be (1) regressed for each pure component and then followed by (2) the regression of κ alone.

The above two-step procedure for the KCLS EOS should "fine-tune" predictions of pure-component properties of interest. In addition, although the above two-step procedure would at first imply an assumption of nonpolarity for all components predicted, the author suggests that κ be reinterpreted to account for quadrupolar moments (found even in "nonpolar" hydrocarbons) as well as dipole moments (found in polar substances). Hopefully, the two-step procedure would also provide a clearer indication of trends between all component PCP in the KCLS EOS. Furthermore, the procedure could be applied to other pure-component equations of state as well, with due consideration given to the regression algorithm of choice.

D.3 Relation between PCP Correlation and Multiproperty Analysis (MPA)

Surprisingly, the high DOC with the KCLS polar parameter, κ, revealed a relation between PCP correlation and multiproperty analysis (MPA). This relation was noticed when determining all four KCLS PCPs for polar substances. As noted in Section 3.3.4 of Chapter 3, the MPA regression presented in this work consisted of regressing KCLS PCPs over the two thermodynamic properties of vapor pressure and liquid density. First of all, κ typically remained unchanged from its initial estimate; this phenomenon led to the procedure of (1) regressing all four PCPs with different initial values of κ, (2) observing the initial value of the objective function, and then

(3) choosing an initial estimate for κ that minimized the initial value of the objective function.

The above three-step procedure for the polar parameter, however, resulted in different values of the average absolute relative deviations (AARDs) of both thermodynamic properties. Specifically, it appeared that each property retained roughly the same AARD value for a certain range of initial values supplied for κ; in contrast, when a value outside of this range was chosen for either property, the AARD for that property increased dramatically. Nevertheless, a coincidental range of initial estimates for κ that yielded little change in the AARDs of both properties could always be ascertained for the ten pure components listed in Chapter 3.

Moreover, the coincidental range of initial estimates for κ decreased with respect to the somewhat-larger ranges encountered for each property. In other words, MPA appeared to restrain the range of values for a correlated PCP (i.e., the polar parameter) more than the single-property analysis (SPA) of either vapor pressure of liquid density. This restriction not only suggests that (a) different ranges of optimal PCP values exist for each thermodynamic property of a given component, but that (b) the addition of each property in a MPA regression scheme tends to constrict PCP values to the point of singularity -- that is, a point where the PCP values can neither be improved upon nor altered.

Even if a MPA singularity were found not to exist, a near singular result might nonetheless be found. Of course, non-singularity would lead to different ranges and/or singularities of optimal PCP values for various groups of thermodynamic properties.

At the same time, each pure component would still retain a separate identity while similar components would comprise a common trend. In short, if either a singularity or a non-singularity condition were to prevail, MPA should still lead to the discovery of new methods that will help overcome the problem of incomplete data for one or more thermodynamic properties of any number of pure components.

D.4 Effect of Correlation on the Prediction of Mixture Properties

In Sections D.2-D.3, PCP correlation definitely affects pure-component properties. In addition, it can also affect the prediction of mixture properties as well. Section D.4.1 describes the indications that may belie PCP correlation in mixture-property simulations, while Section D.4.2 evaluates the significance of MPA in both pure-component- and mixture-property predictions. Finally, Section D.4.3 entails parameter correlation that can occur in GAR parameters. Hopefully, these three sections will aid future researchers in overcoming the problem of parameter correlation in regressing fewer parameters.

D.4.1 Indications of Correlation

This section discusses certain indications that may reflect correlation between PCPs in mixtures. To begin with, the work performed on the Martin-Hou (1955) EOS by Juris (1970) and Juris and Wenzel (1974) suggested using identical values of N for the generalized symmetric rules (GSRs) of all Martin-Hou mixture parameters in predicting binary Joule-Thomson mixtures. As noted in Section 2.2.3 of Chapter 2,

this GSR approach entailed the use of fewer unlike-interaction parameters (UIPs), thereby lowering the possibility of correlation between UIPs altogether.

Moreover, Juris (1970) and Juris and Wenzel (1974) mentioned the complexity of using a different value of N for **each** GSR of **each** mixture parameter. As these two authors (ibid.) note and summarize, different combining rules (i.e., values of N) had already been reported by several researchers at Lehigh University and elsewhere for Martin-Hou UIPs in various combinations. As also mentioned in Section 2.2.3, the "reshuffling" of mixture-parameter combining rules (to achieve near identical accuracy in mixture predictions) might indicate a certain degree of correlation in EOS PCPs. This indication of correlation, along with the PCP DOC (discussed in Section D.2.1) that occurred in following the work of Nishiumi et al. herein, leads the author to believe that the regression of UIPs for a mixture might tend to "mask" the correlational effect.

D.4.2 Significance of MPA in Pure-Component- and Mixture-Property Predictions

Next, although UIP regression might conceal PCP correlation, this concealment does not in any way reduce the significance of the application of MPA to the prediction of either pure-component and/or mixture properties. Since MPA can improve pure-component property predictions, it will logically provide a clearer understanding of the asymmetric role of each component in terms of its respective contributions to a mixture. Furthermore, it may serve to "sharpen" the fit of UIPs to

binary mixture data even when a high DOC cannot be avoided. Consequently, the question that arises should not concern whether the regression of UIPs can accurately predict single or multiple properties, but rather to what extent mixture predictions can "correct" for the DOC that occurs in PCPs.

At this time, the answer to this alternative question of extension remains to be discovered. Nevertheless, it might lie in the MPA of binary mixture systems, especially in systems that contain highly dissimilar components since any tendency of the PCPs to correlate should occur along different lines for each pure component. Obviously, the different ranges of **UIP** values that might occur when applying MPA to simulate mixture data could indicate how much correlation exists, especially when evaluating the effects of sequentially adding each pure-component property to the PCP regression process.

D.4.3 Implications of Parameter Correlation in the GAR

To begin with, the GAR parameters do not appear as highly correlated as the KCLS PCPs in the sense that their values do not tend to remain constant in the simulation of a binary vapor-liquid equilibrium (VLE) mixture. Nevertheless, when both of the asymmetric GAR parameters (α and γ) are regressed over binary VLE data, they do appear to show a different type of correlation: The two asymmetric parameters sometimes correlate with one another and "drive" each other to large values of opposite sign (i.e., positive and negative).

Most likely, this occasional situation of large GAR values probably reflects an effort of the two asymmetric parameters to "cancel out" their effects relative to the simulation. This situation may be seen in Table 7.13 in the GAR parameter values of -16.417 for $\alpha_{ij}(\lambda_i,\lambda_j)$ and 16.873 for $\gamma_{ij}(\lambda_i,\lambda_j)$ in the toluene-*meta*-xylene isotherm at 672.48 °R. In addition, this effect may carry over in the same system to the value of 23.540 for $\gamma_{ij}(V_i^*,V_j^*)$. Obviously, some correlation does occur between GAR parameters. Fortunately, this effect only occurred in a few of the toluene-*meta*-xylene systems and in the toluene-ethylbenzene system Table 7.15 at 536.67 °R.

The above situation of GAR parameter correlation may be appreciably reduced through different means. First, as noted in Section 7.4 of Chapter 7, the flexible tolerance (flexiplex) method of Himmelblau (1972) was used to constrain the GARs according to

$$0.5 \le \alpha_{ij} \le 0.5 \qquad \text{(D.1)}$$

and

$$3.0 \le \gamma_{ij} \le 3.0 \qquad \text{(D.2)}$$

Although the flexiplex method proved inadequate for the above two binary VLE isotherms, it did reveal that they should be defined either (a) in some sort of relationship to each other or (b) as a function of pure-component properties.

First, the asymmetric GAR parameters α_{ij} and γ_{ij} might be defined by a relationship between themselves. Since Equations (D.1-D.2) show different

constraints for these two parameters, perhaps one of them might be defined as a function of the other. Typically, the asymmetric-linear GAR parameter, γ_{ij}, should prove easier to regress than the asymmetric-geometric GAR parameter, α_{ij}. Consequently, these two GAR parameters might be related to one another through the general relation

$$\alpha_{ij} = \frac{1}{6}\gamma_{ij} \quad . \qquad \text{(D.3)}$$

Of course, some other proportionality may be introduced into Equation (D.3) other than one-sixth. In fact, the proportionality could be regressed as an alternative to α_{ij}, but could lead to the same problem mentioned of above of opposite-sign values for α_{ij} and γ_{ij}. At any rate, Equation (D.3) preserves the identical sign between both GAR parameters.

Second, α_{ij} and γ_{ij} might instead be defined as a function of pure-component properties. The pure-component properties of interest for a function could include critical temperature, pressure, volume, etc. For example, Twu et al. (1991) studied the Soave-Redlich-Kwong EOS (Soave, 1972; Walas, p. 53, 1985),

$$P = \frac{RT}{V-b} - \frac{a\alpha}{V(V+b)} \quad , \qquad \text{(D.4)}$$

in the form of

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)} \quad , \qquad \text{(D.5)}$$

where

$$a(T_c) = 0.427481 R^2 T_c^2 / P_c \quad , \quad \text{(D.6)}$$

$$b = 0.086641 R T_c / P_c \quad , \quad \text{(D.7)}$$

and

$$a(T) = \alpha(T) a(T_c) \quad . \quad \text{(D.8)}$$

Twu et al. (1991) then proposed a correlation for $\alpha(T)$ in the form of

$$\alpha(T) = T_r^{N(M-1)} \exp\left[L\left(1 - T_r^{NM}\right)\right] \quad \text{(D.9)}$$

as an extension (through the development of several intermediate equations) of Soave's (1972) relation

$$\alpha(T) = \left[1 + M\left(1 - T_r^{1/2}\right)\right]^2 \quad . \quad \text{(D.10)}$$

Moreover, Twu et al. (1991) developed Equations (D.5-D.10) for nine pure components in terms of the three PCPs *L*, *M*, and *N*. These parameters included ethylene glycol, diethylene glycol, and triethylene glycol.

Both Equations (D.9) and (D.10) show $\alpha(T)$ as a function of reduced temperature, T_r, according to the standard relation

$$T_r = T / T_c \quad . \quad \text{(D.11)}$$

A relationship of this type could be used for either asymmetric GAR parameter, especially since UIPs have long been known to depend on temperature.

Next, it should be noted that Equations (D.6-D.10) comprise equations for pure components. Twu et al. (1991) defined mixture relations for *a* and *b* in the same manner as Soave (1972), with

$$a_x = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j a_{ij} \quad , \tag{D.12}$$

$$b_x = \sum_{i=1}^{n} x_i b_i \quad , \tag{D.13}$$

$$a_{ij} = \sqrt{a_i a_j}\left[\left(1 - \frac{k_{ij}}{T}\right) + \left(\frac{H_{ij} G_{ij} x_j^2}{x_i + G_{ij} x_j}\right)\right], \tag{D.14}$$

$$H_{ij} = \frac{\left(k_{ji} - k_{ij}\right)}{T} \quad , \tag{D.15}$$

and

$$G_{ij} = \exp\left(-\beta_{ij} H_{ij}\right) \quad . \tag{D.16}$$

Equations (D.12-D.16) require the regression of the four UIPs k_{ij}, k_{ji}, β_{ij}, and β_{ji}. Obviously, the GAR with $N = 1$,

$$B_{ij} = \frac{B_i^{\alpha} B_j^{-\alpha}\left[\gamma B_i + (2-\gamma) B_j\right]}{2} \quad , \tag{D.17}$$

presents a much simpler relation, especially since it requires only two UIPs, α_{ij} and γ_{ij}. Furthermore, since many cubic EOS use relations as complex as Equations (D.14-D.16), the GAR holds potential in representing unlike interactions for cubic EOS as well as the noncubic EOS reviewed in Section 2.2 of Chapter 2.

In addition, critical volume might instead be used either to define and/or correlate α_{ij} and γ_{ij}. Definitions/correlations of this type could follow one of the

many functions of critical volume ratios for binary interaction parameters (BIPs) suggested by Nishiumi et al. and reviewed in Section 2.4.2, most notably the relation

$$m_{ij} = k_3 + k_4\left(\frac{V_{ci}}{V_{cj}}\right) + k_5\left(\frac{V_{ci}}{V_{cj}}\right)^2 \quad , \quad \left(\frac{V_{ci}}{V_{cj}}\right) \geq 1 \quad , \qquad \text{(D.18)}$$

where α_{ij} and/or γ_{ij} would replace m_{ij}. Hopefully, Equations (D.9), (D.10), and/or (D.18) will help to reduce the DOC between the two asymmetric GAR parameters α_{ij} and γ_{ij}.

NOMENCLATURE

Arabic Letters

a = pure-component/mixture parameter in BWR, BWRS, Nishiumi et al.-extended BWRS, Martin-Hou, and Soave-Redlich-Kwong equations of state (-)

A' = Helmholtz configurational free energy

A_o = pure-component/mixture parameter in Beattie-Bridgeman, BWR, BWRS, and Nishiumi et al.-extended BWRS equations of state (-)

A_i = universal constant for BWRS equation of state
or pure-component/mixture parameter (-) in Martin-Hou equation of state
or pure-component/mixture parameter (-) in 3PCS-MBWR equation of state
or pure-component/mixture parameter (-) in KCLS equation of state

A'_{kj} = Helmholtz unlike-interaction, configurational free energy between components k and j

b = pure-component/mixture parameter in Beattie-Bridgeman, BWR, BWRS, Nishiumi et al.-extended BWRS, Martin-Hou, and Soave-Redlich-Kwong equations of state (-)
or correlation parameter for binary interaction parameter m_{ij} in Nishiumi et al.-extended BWRS equations of state (-)

B = second-virial coefficient (-)

B_o = pure-component/mixture parameter in Beattie-Bridgeman, BWR, BWRS, and Nishiumi et al.-extended BWRS equations of state (-)

B_i = generic second-virial parameter for pure component i in a combining rule (e.g., GAR, GSR)
or universal constant for BWRS equation of state (-)
or pure-component/mixture parameter (-) in Martin-Hou equation of state
or pure-component/mixture parameter (-) in 3PCS-MBWR equation of state
or generic parameter (-) for pure component i in combining rule (e.g., GAR, GSR)

$B_i^{(0)}$ = isotropic (argon) universal constant for KCLS equation of state (-)

$B_i^{(p)}$ = anisotropic (perturbation) universal constant for KCLS equation of state (-)

B_{ii} = second-virial like interaction parameter between pure-component molecules i

B_{ij} = generic, second virial, unlike-interaction parameter for pure components i and j (-)

B_j = generic parameter (-) for pure component j (e.g., GAR, GSR)

B_{jj} = second-virial like interaction parameter between pure-component molecules j

B_x = generic, second virial mixture parameter (-)

c = pure-component/mixture parameter in Beattie-Bridgeman, BWR, BWRS, and Nishiumi et al.-extended BWRS equations of state (-)
or correlation parameter for binary interaction parameter m_{ij} in Nishiumi et al.-extended BWRS equations of state (-)
or generic constant (-)

c_i = small, positive number for experimental, mixture-design component i

C = third-virial coefficient (-)

C_o = pure-component/mixture parameter in BWR, BWRS, and Nishiumi et al.-extended BWRS equations of state (-)

C_{oi} = pure-component parameter in BWRS and Nishiumi et al.-extended BWRS equations of state for component i (-)

C_i = generic third-virial parameter for pure component i in a combining rule (e.g., GAR, GSR)

C_{ijk} = generic, third-virial, unlike-interaction parameter for pure components i, j, and k

C_j = generic third-virial parameter for pure component j in a combining rule (e.g., GAR, GSR)

C_k = generic third-virial parameter for pure component k in a combining rule (e.g., GAR, GSR)

C_p = heat capacity at constant pressure (BTU/lbmol)

d = pure-component parameter in BWRS and Nishiumi et al.-extended BWRS equations of state (-)

D = fourth-virial coefficient (-)
or polar parameter in KCLS equation of state $(^{\circ}R)^2$

D_o = pure-component/mixture parameter in BWRS and Nishiumi et al.-extended BWRS equations of state (-)

$D_{ij\cdots(n-1)n}$ = any higher-virial, unlike-interaction parameter for pure components i, j, ..., n-1 through n

e = pure-component/mixture parameter in Nishiumi et al.-extended BWRS equations of state (-)

E_o = pure-component/mixture parameter in BWRS and Nishiumi et al.-extended BWRS equations of state (-)

f = pure-component/mixture parameter in Nishiumi et al.-extended BWRS equations of state (-)

$\hat{f}_i$ = fugacity of component i in a mixture

F_{kj} = coordination volume characterization ratio between components k and j

g = pure-component/mixture parameter in Nishiumi et al.-extended BWRS equations of state (-)

G = generalized, second-virial LCM parameter

g^E = excess-Gibbs property (BTU/lb)

G^E = excess-Gibbs property (BTU/lb)

G_{ij} = unlike-interaction parameter in Soave-Redlich-Kwong equation of state (-)

g_{jj} = energy of interaction between two identical molecules j

g_{kj} = energy of interaction between molecules k and j (-)

h = pure-component/mixture parameter in Nishiumi et al.-extended BWRS equations of state (-)

H = enthalpy (BTU/lb)

H^E = excess enthalpy (BTU/lb)

$H-H^\circ$ = residual (excess) enthalpy (BTU/lb)

H_{ij} = unlike-interaction parameter in Soave-Redlich-Kwong equation of state (-)

k = pure-component/mixture parameter in Martin-Hou equation of state (-) **or** Boltzmann constant in KCLS equation of state

k_i = correlation parameter for binary interaction parameter m_{ij} in Nishiumi et al.-extended BWRS equations of state (-)

k_{ij} = unlike-interaction parameter in BWR, BWRS and Soave-Redlich-Kwong equations of state (-)

L = intermolecular distance
or pure-component parameter for Soave-Redlich-Kwong equation of state (-)

L_{kj} = intermolecular distance between molecules k and j

m_{ij} = unlike-interaction parameter in Nishiumi et al.-extended BWRS equations of state (-)

M = pure-component parameter for Soave-Redlich-Kwong equation of state (-)

n = number of components (-)

N = symmetric unlike-interaction parameter for GAR and GSR for second- and higher-virial interactions (-)
or pure-component parameter for Soave-Redlich-Kwong equation of state (-)

N_c = number of binary, ternary, quaternary, etc., sets of data required to simulate a multicomponent VLE system

p = generic constant (-)
or generalized, second-virial LCM model coefficient

P = pressure (psia)

P_c = critical pressure (psia)

P_{kj} = unlike-interaction pressure exerted between components k and j (psia)

P^v = vapor pressure (psia)

P_v = vapor pressure (psia)

$P_{(l)}^{(1)}$ = first-virial mixing rule P-coefficient l

$P_{(l)}^{(2)}$ = second-virial mixing rule P-coefficient for combining rule l

$P_{(l)}^{(3)}$ = third-virial mixing rule P-coefficient for combining rule l

q = generalized, second-virial LCM model coefficient

Q = objective (fitting) function (-)

R = Gas constant, 10.7335 (ft^3·psia/lb-mole·°R)

$\overline{R}_i$ = partial derivative of molecular hard-core volume parameter V^* in KCLS equation of state

R_{jk} = experimental value of thermodynamic property jk

s_i = pure-component/mixture polar parameter in Nishiumi et al.-extended BWRS equations of state (-)

T = temperature (°R)

T^* = dimensionless temperature (-)

T_c = critical temperature (°R)

T_{ci} = critical temperature of component i (°R)

T_r = reduced temperature (-)

V = molar volume (ft^3/lb-mole)

V^* = molecular hard-core volume parameter in KCLS equation of state (ft^3/lb-mole)

V_c = critical volume (ft^3/lb-mole)

V_{ci} = critical volume of component i (ft^3/lb-mole)

V^E = excess volume (ft^3/lb-mole)

W = *Wth*-virial form

W_i = weighting factor in objective function for thermodynamic property i

x = liquid molar composition (-)
or any phase composition (-)
or dummy (-) variable (Section A.2)
or liquid composition (-)

x_i = molar composition of component i (-)
or proportions of components (-)

x_i' = pseudocomponent proportion for experimental, mixture-design component i (-)

x_j = molar composition of component i (-)

y = vapor composition (-)

z = compressibility (-)

z_{kj} = unlike-interaction compressibility found between components k and j (-)

Greek Letters

α = asymmetric-geometric GAR/GSR parameter for second- and higher-virial interactions (-)
or pure-component/mixture parameter in BWR, BWRS, Nishiumi et al.-extended BWRS, and Soave-Redlich-Kwong equations of state (-)
or generalized, second-virial LCM parameter

α' = generalized LCM coordination-number relation (-)

β = asymmetric-geometric GAR/GSR parameter for third- and higher-virial interactions (-)

β_{ij} = unlike-interaction parameter in Soave-Redlich-Kwong equation of state (-)

δ = asymmetric-geometric GAR/GSR parameter for third- and higher-virial interactions (-)

ε_x = mixture characteristic molecular-energy parameter in 3PCS-MBWR, KCLS equations of state (°R)

$\frac{\varepsilon}{k}$ = characteristic molecular-energy parameter in 3PCS-MBWR, KCLS equations of state (°R)

$\frac{\varepsilon'}{k}$ = temperature-dependent characteristic molecular-energy parameter in 3PCS-MBWR, KCLS equations of state (°R)

$\varepsilon_x^{(1)}$ = sum of first-virial mixing

$\varepsilon_x^{(2)}$ = sum of second-virial mixing

$\varepsilon_x^{(3)}$ = sum of third-virial mixing

ϕ = functional relationship between proportions and response value for experimental mixture-design models

γ = asymmetric-linear GAR/GSR parameter for second- and higher-virial interactions (-)
or pure-component/mixture parameter in BWR, BWRS, and Nishiumi et al.-extended BWRS equations of state (-)
or orientation/shape parameter in 3PCS-MBWR equation of state (-)

γ_i = activity coefficient for component *i*

η = response value for experimental mixture-design models

η_{jk} = calculated value of thermodynamic property *jk*

κ = polar parameter in KCLS equations of state $(°R)^2/(ft^3/lb\text{-}mole)^2$

λ = orientation/shape parameter in KCLS equation of state (-)

ρ = molar density ($lbmol/ft^3$)

ρ^* = dimensionless density (-)

ρ_{ci} = critical volume of component *i* (lb-mole/ ft^3)

ρ^L = liquid density (lbmol/ft^3)

σ^3 = characteristic molecular distance between a the molecules of a pure component in 3PCS-MBWR equation of state (ft/lb-mole)

τ = generalized, second-virial LCM parameter

ω = acentric factor (lb-mole/ ft^3)

ω_i = acentric factor of component *i* (lb-mole/ ft^3)

Ψ_A = pure-component/mixture polar parameter in Nishiumi et al.-extended BWRS equations of state (-)

Ψ_E = pure-component/mixture polar parameter in Nishiumi et al.-extended BWRS equations of state (-)

Ψ_s = pure-component/mixture polar parameter in Nishiumi et al.-extended BWRS equations of state (-)

Superscripts

(0) = isotropic (argon)

(1) = first-virial designation for a P-coefficient

(2) = second-virial designation for a P-coefficient

(3) = third-virial designation for a P-coefficient

BIP = binary interaction parameter

CALC = calculated

EXP = experimental

GAR = generalized asymmetric rule

k,p,u = powers for γ

l,q,v = powers for ε

L = liquid

m,r,w = power for σ

ncr = number of combining rules

ND = number of data points

NPh = total number of phases

NPr = total number of properties

(p) = anisotropic (perturbation)

V = vapor

* = dimensionless

Subscripts

i = pure component *i*

id = data point *i*

ii = second-virial like interaction between pure-component molecules *i*

ij = second-virial, unlike-interaction between pure components *i* and *j*

ijk = third-virial, unlike-interaction between pure components *i* , *j*, and *k*

j = pure component *j*
or thermodynamic property *j*

ji = second-virial, unlike-interaction between pure components *j* and *i*

jj = second-virial, like interaction between pure-component molecules *j*

k = pure component *k*
or thermodynamic phase *k*

kk = second-virial like interaction between pure-component molecules k

l = combining rule l

n = number of components

v = vapor

x = mixture

Abbreviations

AARD = average absolute relative deviation

AIChE = American Society of Chemical Engineers

API = American Petroleum Institute

ASHRAE= American Society of Heating, Refrigerating and Air-Conditioning Engineers, Inc.

ASOG = Analytical solution of groups

BIP = binary interaction parameter

BTEX = benzene-toluene-ethylbenzene-xylene

BTU = British thermal unit

BWR = Benedict-Webb-Rubin

BWRS = Benedict-Webb-Rubin-Starling

CALC = calculated

CSM = conformal solution model

DECHEMA= Deutsche Gesellschaft fur Chemisches Apparatewessen

DEG = diethylene glycol

DOC = degree of correlation

EG = ethylene glycol

EOS = equation(s) of state

EXP = experimental

FORTRAN = FORmula TRANslation programming language

ft^3 = cubic foot

GAR = generalized asymmetric rule

GSR = generalized symmetric rule

GPA = Gas Processors Association

GRI = Gas Research Institute

HSGC = Han-Starling generalized correlation

IGT = Institute of Gas Technology

IRPLS = include iteratively-reweighted partial-least squares

KCLS = Khan-Chung-Lee-Starling

lb = pound

LCM = local composition model

LLE = liquid-liquid equilibria

MPA = multiproperty analysis

MRC = mixing-rule conjunction

ND = number of data points

NPh = total number of phases

NPr = total number of properties

NRTL = nonrandom, two-liquid

OSU = Oklahoma State University

OU = Oklahoma University

PCP = pure-component parameter

3PCS-MBWR = three-parameter, corresponding-states, modified-Benedict-Webb-Rubin

PLS = partial-least squares

PR = Peng-Robinson

psia = pound per square inch absolute

P-T-x = data directly reported as liquid-phase molar fractions at various temperatures and pressures

PVT = pressure-volume-temperature

R = Refrigerant

°R degrees Rankine

SLE = solid-liquid equilibria

SPA = single-property analysis

SPE = Society of Petroleum Engineers

TEG = triethylene glycol

UIP = unlike-interaction parameter

UNIQUAC = universal quasi-chemical equation

VLE = vapor-liquid equilibria, vapor-liquid equilibrium

Operators

$\frac{d}{dN}$ = partial derivative with respect to N

e,exp = exponential function

$\lim_{N \downarrow 0}$ = limit as N approaches zero

ln = natural logarithm

$\sum$ = summation

$\prod$ = multiplication

Symbols

$\overset{*}{=}$ = partial derivative of numerator and denominator according to L'Hospital's rule

$=$ = "equal to"

$\neq$ = "not equal to"

$<$ = "less than"

$\leq$ = "less than or equal to"

$>$ = "greater than"

$\geq$ = "greater than or equal to"

$\therefore$ = "therefore"

! = factorial

IMAGE EVALUATION
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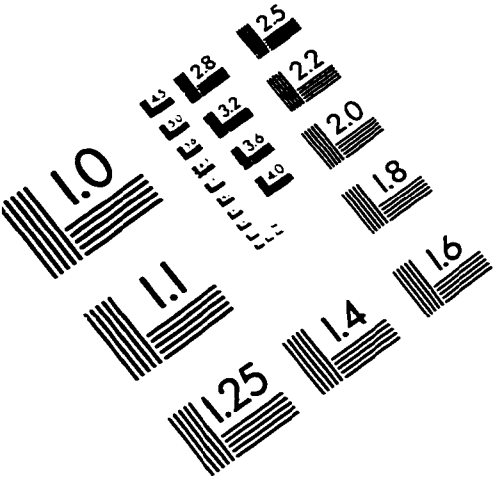

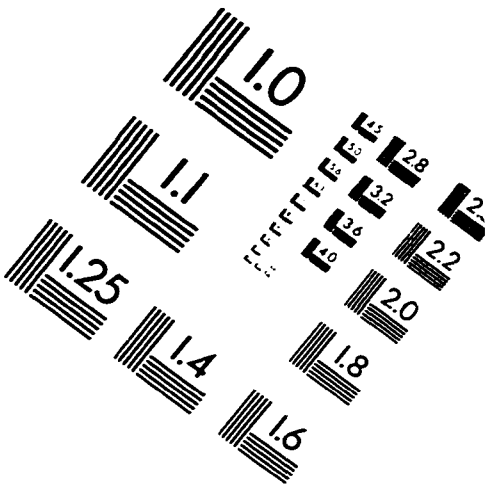

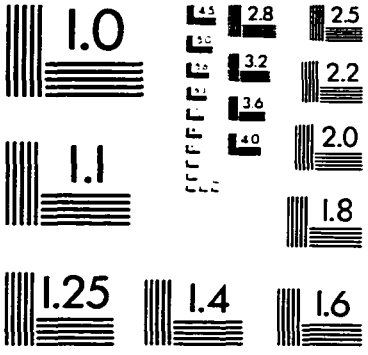

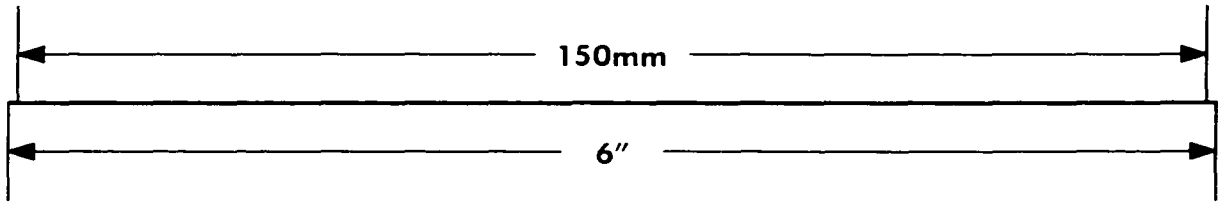

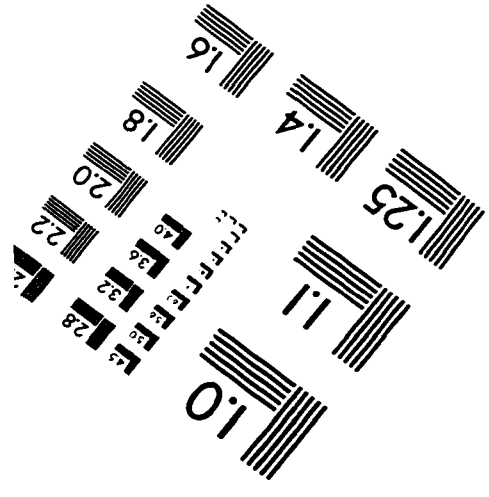

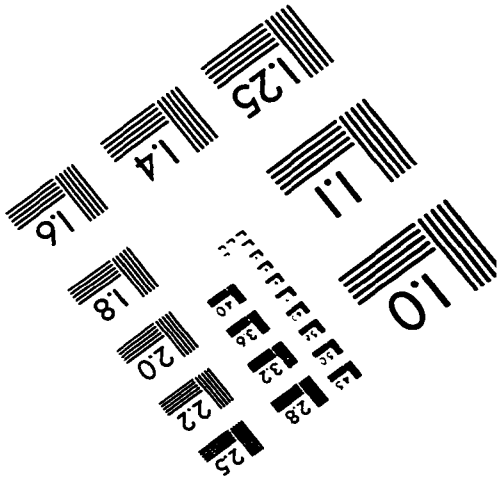

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