

Evaluation of Binary PT_{xy} Vapor–Liquid Equilibrium Data for C_6 Hydrocarbons. Benzene+Cyclohexane

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Evaluation of Binary $PTxy$ Vapor-Liquid Equilibrium Data for C_6 Hydrocarbons. Benzene + Cyclohexane

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The methods used to evaluate subcritical binary $PTxy$ vapor-liquid equilibrium data are described. The evaluation results for the benzene + cyclohexane system are presented. The needs for new experimental data are defined.

Key words: activity coefficients; benzene; cyclohexane; evaluation procedures; excess Gibbs function; vapor-liquid equilibrium.

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1. Introduction

This paper is the first in a series of evaluation reports on P, T, x, y vapor-liquid equilibrium (VLE) data for miscible subcritical binary mixtures of nonelectrolyte liquids. It is accompanied by two parallel papers [1, 2] each of which is the lead paper in similar series for excess enthalpy (H^E) and excess volume (V^E) data. It precedes another parallel paper to be published in the future as the lead paper in a series of evaluation reports on P, T, x (total-pressure) VLE data. Each of these lead papers presents the specific evaluation methods used for the given property and then applies those methods to the first binary system to be covered—the benzene-(1) + cyclohexane(2) system.

These lead papers have been preceded by another paper [3] which described those Laboratory procedures that are not specific to one of the three mixture properties being covered. Items covered there include the literature document retrieval methods, the computer program libraries developed for the pure compound and mixture evaluation projects, the methods used to evaluate pure compound data and store it in a computer where it is readily available to the mixture programs, and the way equations of state are used to model the vapor-phase behavior in the VLE data sets evaluated.

The C_6 hydrocarbon + C_6 hydrocarbon mixture class has been chosen as the first one to be processed. That mix-

ture class contains three binaries—benzene + cyclohexane, benzene + hexane, cyclohexane + hexane—for which a large number of VLE data sets have been measured. Because of the amount of data available, those three binaries will be covered in separate reports with the benzene + cyclohexane system covered first. The remaining binaries in the $C_6 + C_6$ hydrocarbon class will be covered in a single report.

An attempt will be made in these papers to establish selected values of G^E/T at mole fractions of 0.25, 0.50 and 0.75 for each temperature at which data appear in the literature. Whenever possible, recommended data sets will be identified.

The benzene + cyclohexane system is well established as a test system for experimental H^E and V^E measurement devices. Unfortunately, the use of test systems to verify the accuracy of experimental apparatuses and techniques is not as common for VLE data as for H^E and V^E data. The benzene + cyclohexane should be a good candidate for a test system for both P, T, x, y and P, T, x VLE devices. It is hoped that this paper will be useful in the evaluation of the benzene + cyclohexane system for that purpose.

2. Equations

The experimental P, T, x, y VLE data were reduced to liquid-phase activity coefficients with the equation

$$\gamma_i = \frac{y_i P \hat{\phi}_{i,P}}{x_i P_i' \phi_{i,P_i'} \exp[V_i^L(P - P_i')/RT]} \quad (1)$$

which uses the pure liquid i at the mixture temperature and pressure as the standard state. The excess Gibbs function is related to the γ_i by

$$G^E = RT \sum_i x_i \ln \gamma_i. \quad (2)$$

The term,

$$\frac{1}{RT} \int_{P_i'}^P V_i^L dP \quad (3)$$

which appears in approximate form in eq 1 represents the effect of pressure on the fugacity of the pure liquid i . It involves the pure liquid volume V_i^L which must always be an hypothetical quantity for the more volatile component in a binary liquid mixture. For those systems where the Poynting term is numerically significant, it is sometimes best to use an activity coefficient referred to the pure liquid i at its vapor pressure at the mixture temperature; that activity coefficient is defined by

$$\gamma_i' = \frac{y_i P \hat{\phi}_{i,P}}{x_i P_i' \phi_{i,P_i'}}. \quad (4)$$

The gas-phase nonideality is represented by the two fugacity coefficients. It is always assumed that those fugacity coefficients can be predicted with sufficient accuracy by an assumed equation of state. The equations of state available to the data reduction program, and the logic used to select the best possible equation of state for a given mixture, are described in a previous paper [3].

3. Evaluation Procedures

The evaluation procedures are designed to satisfy two different kinds of user. A person doing design or correlation work needs an identification of the best sets of data available for a system of interest, plus some overall quality rating for each of those best sets so that the appropriate safety factors can be used to allow for probable error. On the other hand, the person developing an experimental apparatus needs recommended property values at some commonly used test temperature so that he can verify the accuracy of his equipment and techniques.

A much more powerful array of evaluation tools are available for vapor-liquid equilibrium (VLE) data than for heat of mixing (H^E) and volume change of mixing (V^E) data. Four will be applied in this report: the scatter test, the end-point test, the Gibbs-Duhem consistency test, and the Gibbs-Helmholtz consistency test. The first three of these tests are internal tests, i.e., they involve only the given set of VLE data plus the associated pure compound data. The Gibbs-Helmholtz test is an external test in that it involves other VLE data sets plus whatever H^E sets are available for the given system. If H^E data are not available, the Gibbs-Helmholtz test becomes a comparison test similar to the ones used for H^E and V^E data.

If all four tests can be performed—as they can be for the benzene + cyclohexane system—the characterization of the

accuracy of a data set is quite reliable, and does not depend as heavily on subjective methods as does the evaluation of H^E and V^E data.

3.1. Scatter Tests

As used here, the word “scatter” denotes the deviation of a reported experimental point from the correct experimental value, and not just from some arbitrary smoothing curve. Before assigning ratings to the literature data sets, an attempt is made to identify the correct shape or configuration for the system on whatever plots are useful. The scatter rating assigned to a set reflects how well the data set agrees with that established shape, as well as how much the experimental points “scatter” relative to each other. This procedure permits the assignment of poor scatter ratings to data sets which have been smoothed but are obviously incorrect.

Table 1. Definition of scatter ratings

Symbol	Definition
S	Smoothed data. This rating is assigned automatically instead of the E, G, or F ratings when only smoothed data (tabular or in equation form) are available. The S rating is not used for sets of data which belong to the M or U categories; such sets must be assigned a Marginal or Unacceptable rating even though the data have been smoothed.
E	Excellent scatter. The data are very smooth and the various curves have the typical shapes established for the system. For titration apparatuses, the mismatch in the overlap region must be $\leq 0.5\%$, and most of the points must fall within a $\pm 0.5\%$ band for H^E and V^E data and within a $\pm 1.0\%$ band for G^E data on the M^E/x_1x_2 vs. x_1 plot. There must be at least ten mixture points and the largest gap in the reported mole fractions must be ≤ 0.1 .
G	Good scatter. The data show a small amount of scatter with most points falling within a $\pm 1.0\%$ band for H^E and V^E data and within a $\pm 2.5\%$ band for G^E data on the M^E/x_1x_2 vs. x_1 plot. The typical shape established for the system must be clearly exhibited. The largest gap in the mole fractions reported must be ≤ 0.15 .
F	Fair scatter. The data show considerable scatter, particularly on the M^E/x_1x_2 vs. x_1 plot, but the general trend of the data points with respect to x_1 reflects that of the typical shape established for the system. The M^E vs. x_1 or the $\ln(\gamma_1^*/\gamma_2^*)$ vs. x_1 may appear worthy of a G rating but the M^E/x_1x_2 vs. x_1 plot exhibits scatter considerably greater than the ± 1.0 or 2.5% band relative to the G rating. There must be at least six data points.
U	Unacceptable scatter. The data points are so scattered or their locations are so erroneous that the approximate magnitude and possibly even the direction of the deviation from nonideality cannot be determined. The U rating can be assigned to data sets with any number of points, even to sets with a single point if that point has the wrong sign or is obviously of the wrong magnitude. The rating can be assigned to smoothed data.
M	Marginal scatter. This category is used for data sets which fall between the F and U categories. The M rating is used when the data appear to be accurate enough to give an approximate idea of the magnitude and direction of the nonideality on the M^E vs. x_1 plot, but the typical shape established for the system is not exhibited by the M^E/x_1x_2 or $\ln(\gamma_1^*/\gamma_2^*)$ plots and possibly not by the M^E plot. The rating can be assigned to smoothed data. The M rating is assigned to sets which are smooth enough to warrant an E, G or F rating if one or more of the following criteria are satisfied: (a) the number of mixture points is less than 6, or (b) there is a gap in the reported mole fractions > 0.25 .
N	No scatter rating. The data point or points are so poorly distributed that the approximate magnitude of the deviation over the composition range is not illustrated. An example would be a set of data where the author was trying to establish the slope at infinite dilution and measured only a few points near the ends of the binary composition range.

Three plots are used in the assignment of a scatter rating to a set of VLE data: $\ln \gamma'_1/\gamma'_2$ vs x_1 , G^E/x_1x_2 vs x_1 and G^E vs x_1 . A scatter rating is first assigned to each type of plot individually and then the worst of the three ratings is used for the set of data.

The $\ln \gamma'_1/\gamma'_2$ plot is very sensitive to scatter in the reported liquid and vapor mole fractions, but is relatively insensitive to scatter in the temperatures and very insensitive to scatter in the pressure values. The reasons for this behavior are apparent if eq (4) is written for both compounds and the two equations ratioed to give

$$\frac{\gamma'_1}{\gamma'_2} = \frac{y_1x_2P'_2\phi_{2,P}'\hat{\phi}_{1,P}}{y_2x_1P'_1\phi_{1,P}'\hat{\phi}_{2,P}} \quad (5)$$

The pressure P cancels and the effect of pressure enters only in the $\hat{\phi}_{i,P}$ terms. The primary effect of temperature scatter is on the P'_i terms but the fact that they are ratioed reduces the sensitivity.

The G^E/x_1x_2 and G^E plots are much more sensitive to scatter in the temperature and pressure variables than is the $\ln \gamma'_1/\gamma'_2$ plot, and must be inspected along with the $\ln \gamma'_1/\gamma'_2$ plot to cover all four variables adequately. The G^E/x_1x_2 plot is always much more sensitive to scatter than is the G^E plot and is usually the controlling one of the two.

The symbols and definitions for the scatter ratings used are given in table 1. The E (excellent), G (good), F (fair), U (unacceptable), and M (marginal) ratings apply to those data sets where the original experimental values are reported, and enough points are reported to establish the general shape and magnitude of the curves. Unfortunately, it is quite common for data sets to be reported only in smoothed form (either in tabular or equation form), and it was necessary to define the S (smoothed) category for that kind of data set. Also, some published data sets include an insufficient number of points to establish the curve, and the N (none) category was defined for those sets.

It can be seen from table 1 that three factors are considered in the assignment of a scatter rating—the smoothness of the plot, the shape of the plot, and the spacing of the experimental points. It is important that the experimental points establish the magnitudes and slopes of the curves over the entire binary composition range. That requires a certain minimum number of experimental points and a reasonable distribution of those data points across the composition range.

3.1.1. Scatter Rating Examples

Figures 1 through 15 show examples of scatter ratings based on the definitions in table 1. The data set in figures 1 and 2 would have been assigned an excellent scatter except for a mole fraction gap greater than 0.1. Nevertheless, those figures illustrate the characteristic curve shapes for the benzene + cyclohexane system.

The upper limit on the good scatter rating range is illustrated by figure 3 where many of the points fall within a $\pm 1.0\%$ band. The lower limit is illustrated by figure 4 where three of the points fall outside the $\pm 2.5\%$ band. Figure 5 shows that the $\ln \gamma'_1/\gamma'_2$ plot for the figure 4 data set is still quite smooth.

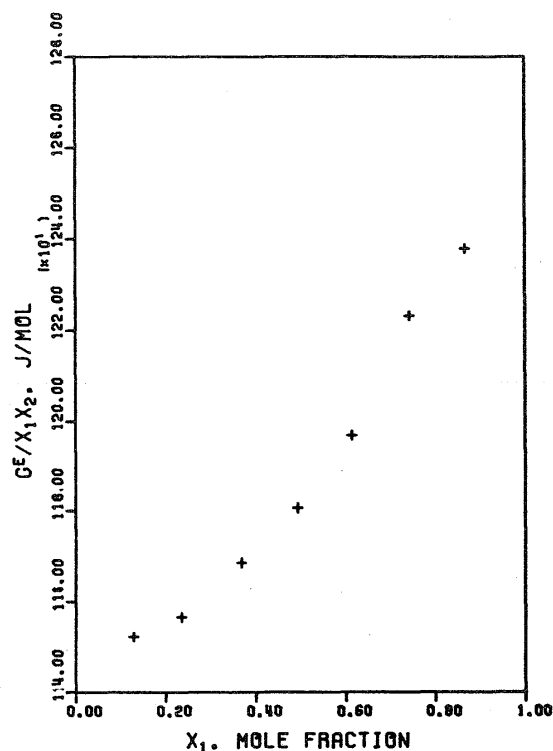


FIGURE 1. A data set downgraded from an excellent to a good scatter rating due to a mole fraction gap greater than 0.1. Data of Scatchard, Wood and Mochel at 39.997 °C. MRL 193. Ordinate values run from 1140 to 1280.

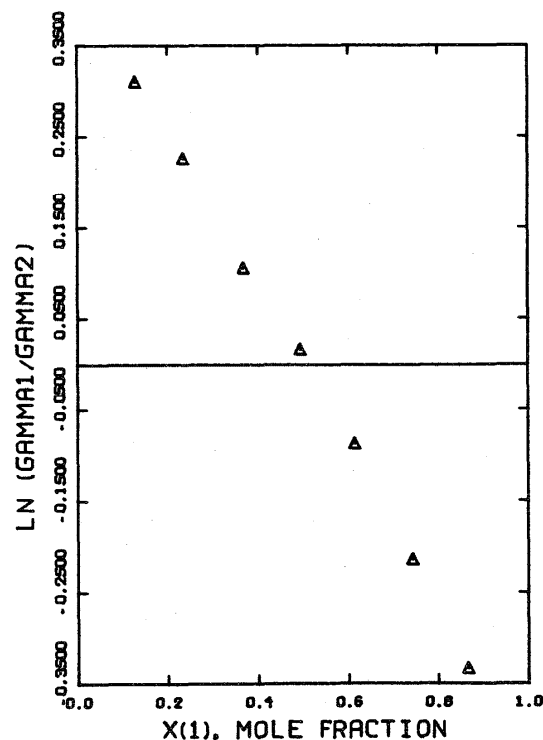


FIGURE 2. Characteristic shape of the $\ln \gamma'_1/\gamma'_2$ plot for the benzene(1) + cyclohexane(2) system. Same data as in figure 1.

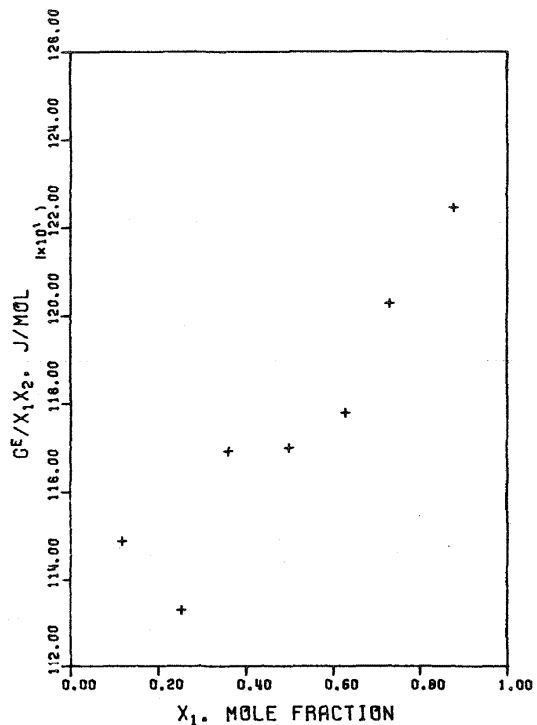


FIGURE 3. A good scatter rating which is close to an excellent rating. Data of Inoue, Azumi and Suzuki at 40°C. MRL 40032. Ordinate values run from 1120 to 1260.

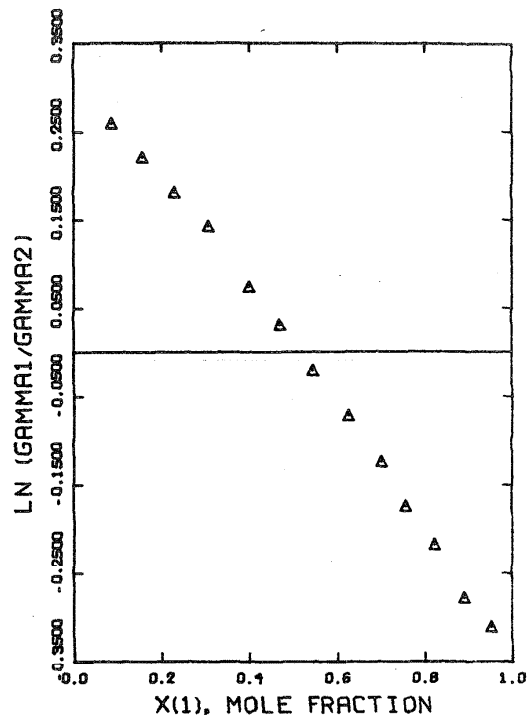


FIGURE 5. The $\ln \gamma_1/\gamma_2$ plot for the set of data in figure 4.

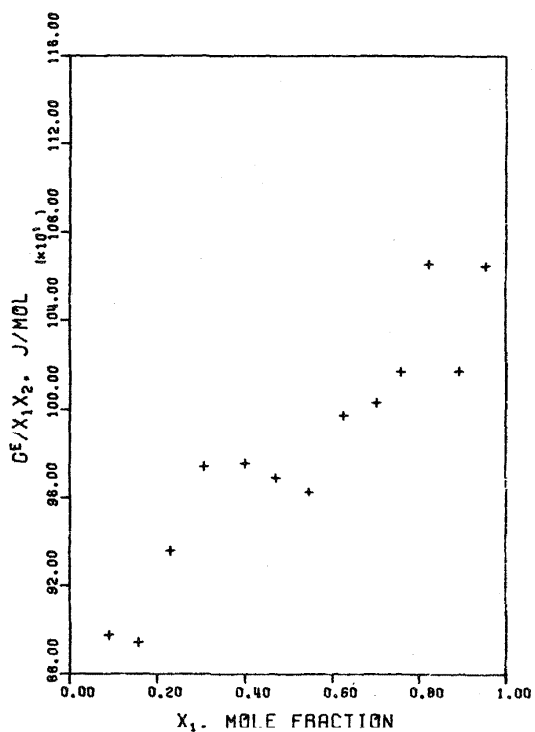


FIGURE 4. A good scatter rating which is close to a fair rating. Data of Chao and Hougén at 760 mm Hg. MRL 234. Ordinate values run from 880 to 1160.

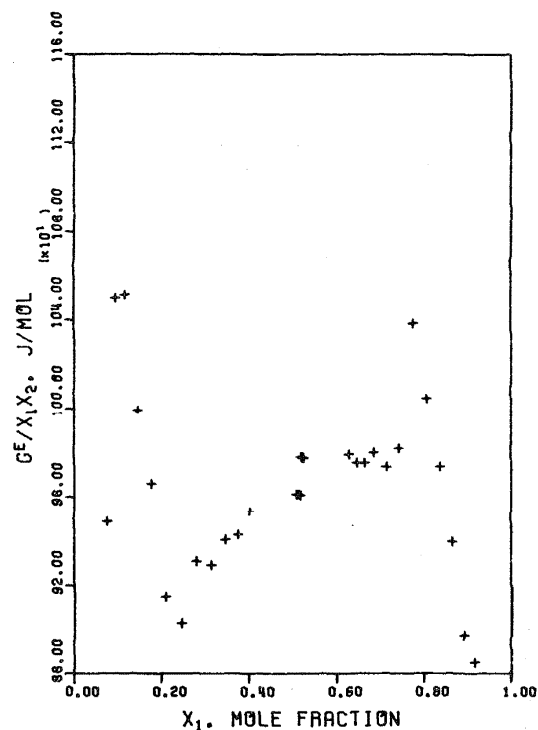


FIGURE 6. Fair scatter rating example. Data of Ridgway and Butler at 760 mm Hg. MRL 917. Ordinate values run from 880 to 1160.

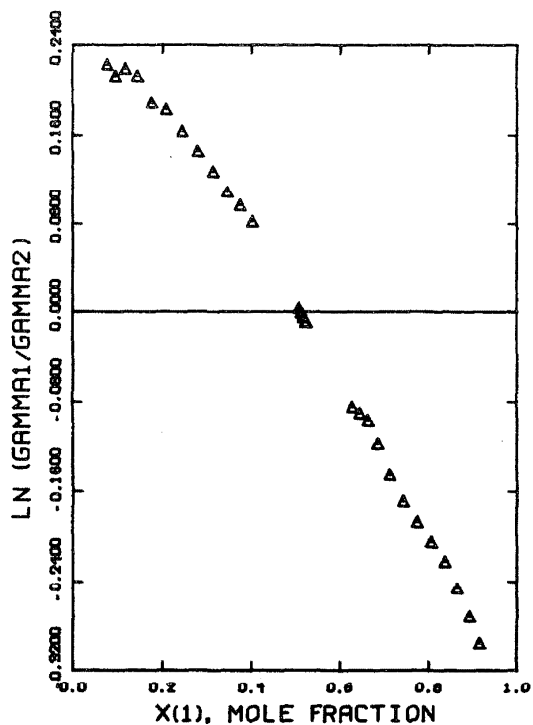
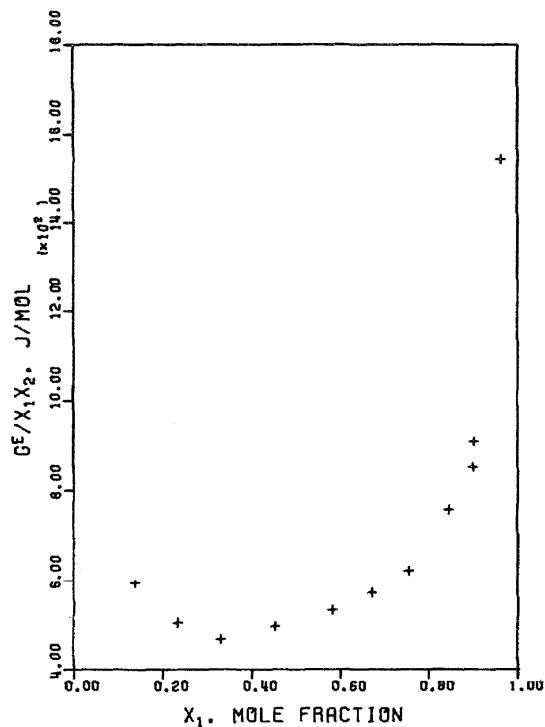
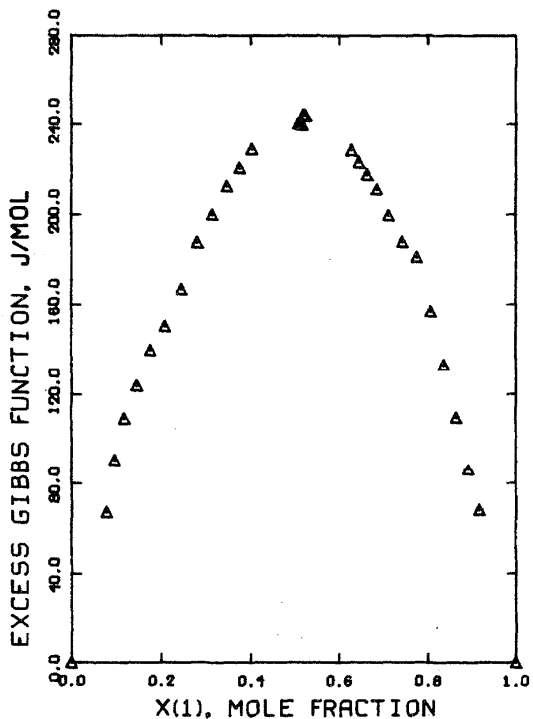
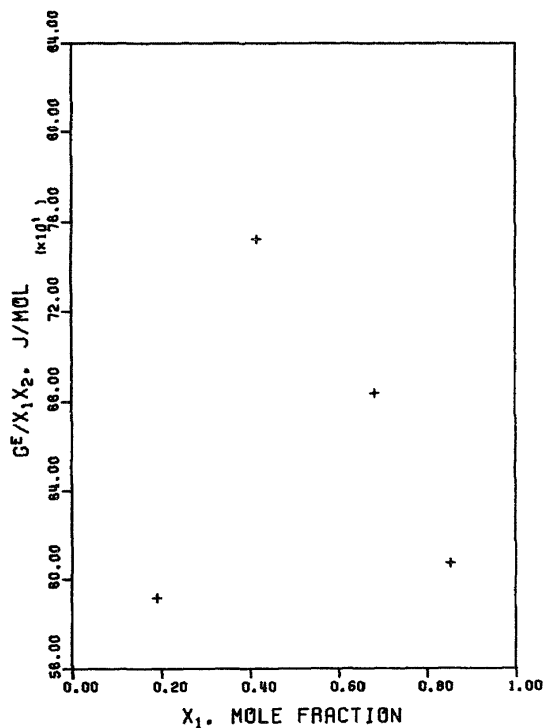
FIGURE 7. The $\ln \gamma_1/\gamma_2$ plot for the data set in figure 6.

FIGURE 9. A fair scatter rating which is close to a marginal rating due to the uncharacteristic shape. Data of Tao at 20.0 atm. MRL 334. Ordinate values run from 400 to 1800.

FIGURE 8. The G^E plot for the data set in figure 6.FIGURE 10. Marginal scatter rating due to shape of the G^E/x_1x_2 plot and a number of points less than six. Data of Kortum and Freier at 119.3 °C. MRL 269. Ordinate values run from 560 to 840.

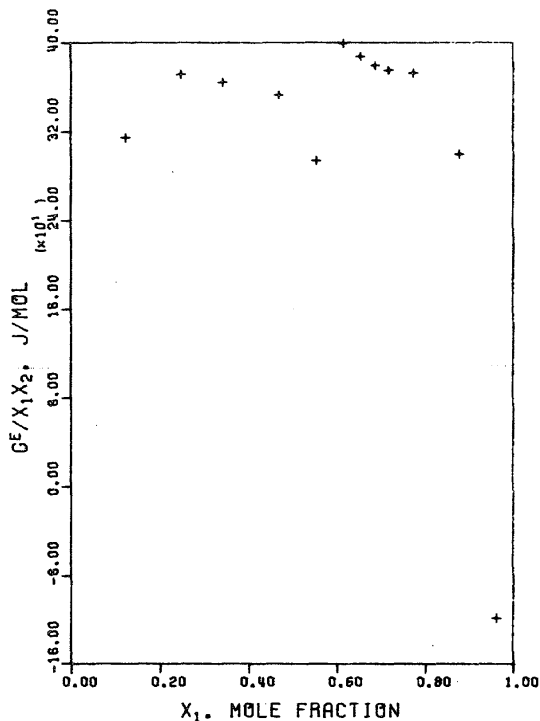


FIGURE 11. Marginal scatter rating example. Data of Kumarkrishna Rao, Swami and Narasinga Rao at 268.7 psi. MRL 271. Ordinate values run from -160 to 400.

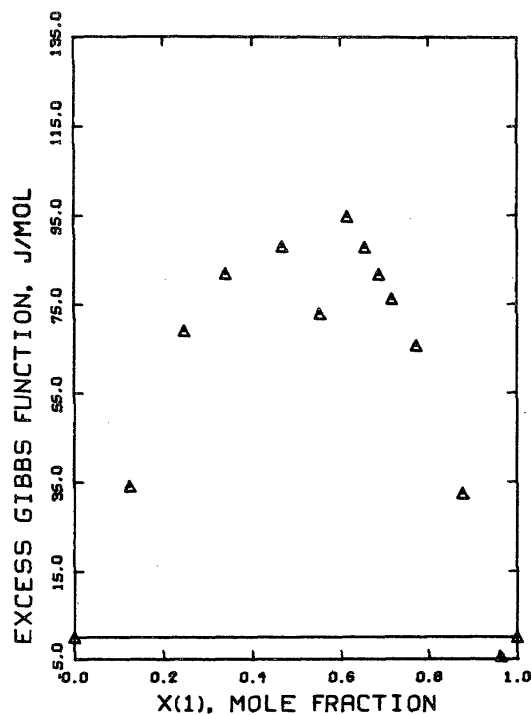


FIGURE 13. The G^E plot for the data set in figure 11.

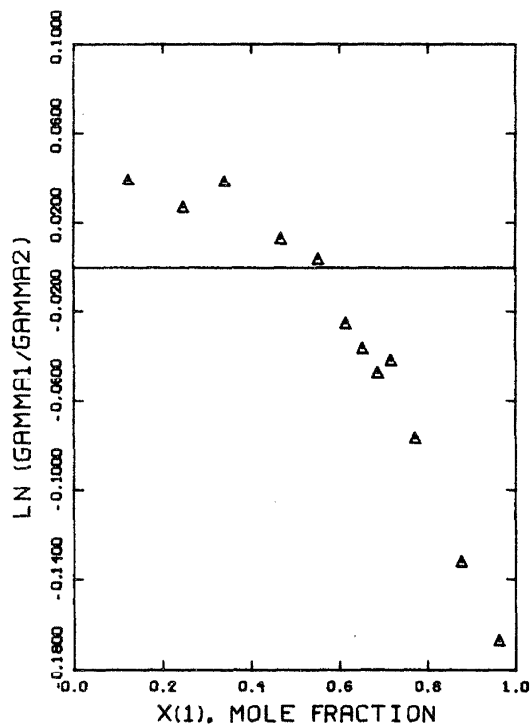


FIGURE 12. The $\ln \gamma_1/\gamma_2$ plot for the data set in figure 11.

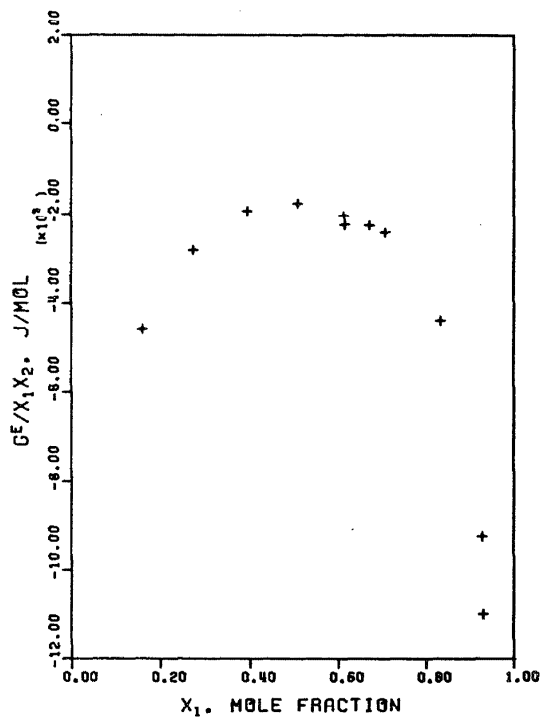


FIGURE 14. An unacceptable scatter rating example. Data of Weck and Hunt at 760 mm Hg. MRL 315. Ordinate values run from -12,000 to 2000.

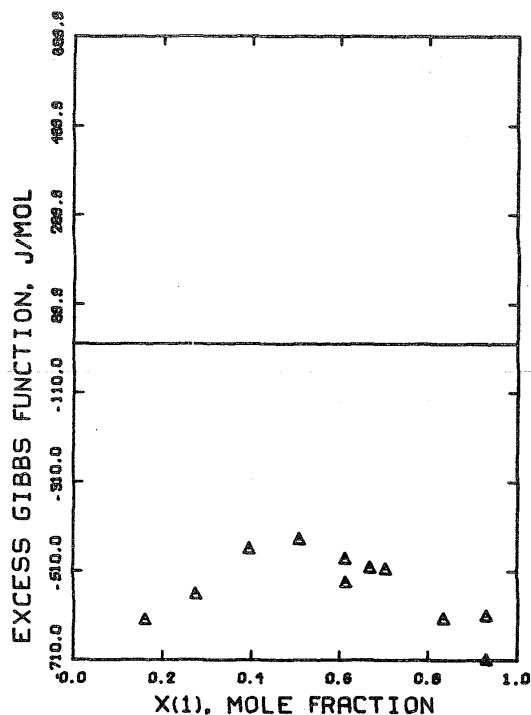


FIGURE 15. The G^E plot for the data set in figure 14.

Figures 6, 7, and 8 show a data set which is somewhat removed from the good scatter rating range. Figure 6 approaches the marginal rating range, but figures 7 and 8 do not deviate widely from the characteristic shapes for this system and they do not exhibit excessive scatter. Hence, a fair scatter rating was assigned. Figure 9 is another example of a data set which approaches a marginal rating because of the uncharacteristic shape of the G^E/x_1x_2 curve, but a fair rating was assigned due to the $\ln \gamma'_1/\gamma'_2$ and G^E plots (not shown).

Figure 10 is an example of a marginal scatter rating due to the shape of the G^E/x_1x_2 plot plus the fact that fewer than six data points were reported; the $\ln \gamma'_1/\gamma'_2$ plot is normal for that data set but the G^E curve is skewed. Figures 11, 12 and 13 show a data set which received a marginal rating because of the shapes and point locations of all three plots.

Figures 14 and 15 show an unacceptable rating example. The negative values are not characteristic of this system. Note the large scale factor used in figure 14. Surprisingly, the $\ln \gamma'_1/\gamma'_2$ plot for this system was not abnormal which indicates the temperature or pressure values are in error.

3.2. Endpoint Test

The endpoint test compares the endpoint ($x_1 = 0.0$ and $x_1 = 1.0$) pressures reported by the experimenter as part of his P, T, x, y data set to the selected pure compound vapor pressure values obtained from the pure compound data bank CDATA1. The procedures used to identify, retrieve, evaluate, correlate and store the vapor pressure data in CDATA1 have been described in a previous publication [3].

The endpoint errors are calculated with

$$P'_i \text{Error} = \frac{(P - P'_i)100}{P'_i} \quad (6)$$

where P is the system pressure reported in the literature document and P'_i is the selected vapor pressure value from CDATA1. If the literature document does not report P values at $x_1 = 0.0$ and $x_1 = 1.0$, the data set pressure or temperature curve may be extrapolated to provide values of the system pressure at the endpoints. Extrapolation is done only if the extrapolation is less than 0.1 mole fraction, i.e., there must be experimental values within the 0.0 to 0.1, or the 0.9 to 1.0, mole fraction range. Even then, extrapolation is done only if the shape of the P versus x_1 , or the T versus x_1 , curve permits reliable extrapolation.

Failure of the endpoint experimental pressure values to agree with the selected vapor pressure values from CDATA1 usually indicates the experimenter did not use pure compounds. It also can mean there is something wrong with either the reported T or P values, or both.

Another possibility, of course, is that the selected P' values stored in CDATA1 are not accurate. The endpoint values from the VLE data set were included in the input vapor pressure values to the vapor pressure data evaluation and correlation steps which provided the CDATA1 values. However, choices between disagreeing data points are always part of the evaluation and selection process, and there is always the possibility that the choice made disagrees with the P' values from the VLE data. Obviously, anyone evaluating mixture data must first make sure he has the best possible selected pure compound vapor pressure values.

3.3. Gibbs-Duhem Consistency Test

The integral form of the Gibbs-Duhem equation is used. The form used for isobaric VLE data is

$$\int_{x_1=0}^{x_1=1} \ln(\gamma'_1/\gamma'_2) dx_1 - \int_{x_1=0}^{x_1=1} \frac{H^E}{RT^2} dT = 0 \quad (7)$$

where the primes on the activity coefficients indicate the Poynting term has been eliminated by using the vapor pressure of i at the mixture temperature as the standard state pressure. The excess enthalpy in eq (7) is actually the one defined by

$$H^E = H^L - x_1 H_{1,P_1}^L - x_2 H_{2,P_2}^L \quad (8)$$

but the effect of the pressure on the liquid H_i values is so small that the use of H^E values calculated from

$$H^E = H^L - x_1 H_{1,P}^L - x_2 H_{2,P}^L \quad (9)$$

has a completely negligible effect on the results obtained.

The integral form of the Gibbs-Duhem equation for isothermal VLE data is

$$\int_{x_1=0}^{x_1=1} \ln(\gamma_1/\gamma_2) dx_1 + \frac{1}{RT} \int_{x_1=0}^{x_1=1} V^E dP = 0 \quad (10)$$

when the mixture pressure is used as the standard state pressure for the pure liquid i . Switching to the vapor pressure standard state gives

$$\int_{x_1=0}^{x_1=1} \ln(\gamma'_1/\gamma'_2) dx_1 + \frac{1}{RT} \int_{x_1=0}^{x_1=1} V^L dP = 0. \quad (11)$$

The price paid for elimination of the Poynting term from the calculation of the activity coefficients is the presence of V^L instead of V^E in the correction integral. However, since

$$V^L = x_1 V_{1,P}^L + x_2 V_{2,P}^L + V^E \quad (12)$$

eq (11) can be rewritten as

$$\int_{x_1=0}^{x_1=1} \ln(\gamma'_1/\gamma'_2) dx_1 + \frac{x_1 V_1^L + x_2 V_2^L}{RT} (P_1 - P_2) + \frac{1}{RT} \int_{x_1=0}^{x_1=1} V^E dP = 0 \quad (13)$$

where the V_i^L values have been assumed independent of pressure over the range covered by the last integral.

If experimental V^L data are reported at the VLE data conditions (as it is sometimes for data near the critical point), eq (11) is the preferred form. If experimental V^L data are not given, then eq (13) is used. Equation (13) is normally used for data sets far removed from the critical point.

A convenient way to quantify the degree of agreement by a given set of VLE data with the Gibbs-Duhem equation is by the use of an area ratio. The positive and negative terms in eqs (7), (11), and (13) are summed separately. The smaller sum is divided by the larger and the sign is dropped. The result is a number which ranges from 0.0 to 1.0 with a 1.0 indicating perfect agreement with the Gibbs-Duhem equation. In the calculation of this area ratio, the $\ln(\gamma'_1/\gamma'_2) dx_1$ integral contributes both a positive and a negative area. The $V^L dP$, $V^E dP$ and $H^E/RT^2 dT$ integrals can be either positive or negative, while the middle term in eq (13) is always positive when the more volatile material is chosen as component 1.

If H^E or V^E data are available for the system, two area ratios are reported on the VLE tabulations when eq (7) or (13) is used. The following formats are used for isobaric and isothermal data sets, respectively:

AREA RATIO. 0.87 (0.90 with H^E)

AREA RATIO. 0.76 (0.75 with V^E)

The number in parentheses is the corrected area ratio and is obtained using all the terms in eq (7) or (13). The number outside the parentheses is the uncorrected area ratio obtained when the $H^E/RT^2 dT$ integral in eq (7), or the $V^E dP$ integral in eq (13), is omitted. If V^E or H^E data are not available the material in parentheses does not appear.

If eq (11) is used for a data set, an uncorrected area ratio is not calculated.

The accurate calculation of the various terms in eqs (7), (11) and (13) is essential if the area ratio is to be significant. The $\ln(\gamma'_1/\gamma'_2)$ versus x_1 points for each set of data are plotted by a CalComp plotter. The evaluator lays all the plots for a given system side by side and decides upon a characteristic shape of the curve for that system. Curves with that characteristic shape (insofar as is feasible) are then drawn by the evaluator through the points for each set of data. When all the curves have been carefully located, values of $\ln(\gamma'_1/\gamma'_2)$ are read off at x_1 increments of 0.05, including the extrapolated values at $x_1 = 0.0$ and 1.0 . The x_1 value at the crossover point where $\ln(\gamma'_1/\gamma'_2) = 0$ is also determined. The positive and negative areas are then calculated by the computer using

Simpson's rule.

Along with the $\ln(\gamma'_1/\gamma'_2)$ values, the evaluator tells the computer which sets of H^E data (for isobaric VLE data) or V^L or V^E data (for isothermal VLE data) are to be used for the last integral in eq (7), (11) or (13). That is done by giving the computer the sequence number of the first card image of each of the selected data sets in the disk data file created in the H^E or V^E data processing. Up to three sets of H^E and V^E or V^L data can be specified for each set of VLE data. When two or three sets are available, the computer interpolates or extrapolates those sets with respect to temperature and composition to provide the V^E or V^L versus P , or the H^E/RT^2 versus T , values necessary to evaluate the last integral in eq (7), (11), or (13) using the trapezoidal rule. Simpson's rule cannot be used because the P or T values associated with the x_1 values in the VLE data set are not evenly spaced.

The necessary pure compound values necessary to evaluate the second term in eq (13) are obtained directly from the pure compound data bank CDATAI.

It is essential that the evaluator draw the $\ln(\gamma'_1/\gamma'_2)$ curves for each set of VLE data. A least squares fit of the points with an equation which would then be plotted through the points by the CalComp plotter is not feasible. Just one wild point will distort such a fit. Also, many sets of data have some widely-scattered points at low and high x_1 values which cause erratic fits unless intelligent weightings are applied. The weights used must be a function of composition (the percent error in the measured x and y values increases rapidly as $x_1 = 0$ and $x_1 = 1.0$ are approached), and also a function of the temperature or pressure level. The most appropriate weightings will also vary from system to system. Hence, it is not possible to give the computer a set of general weighting rules which will give the best location of each $\ln(\gamma'_1/\gamma'_2)$ curve. The evaluator would have to adjust the weights, point by point, until he achieves curves which are adequate representations of the individual data sets. Those final curves can be achieved much more easily by simply drawing them manually. Also, the fact that different systems have different characteristic shapes requires the direct involvement of an experienced evaluator in the drawing of the $\ln(\gamma'_1/\gamma'_2)$ curves.

3.3.1. Alternate Method for Gibbs-Duhem Test

The use of the integral form of the Gibbs-Duhem equation to test VLE data for thermodynamic consistency is often criticized for lack of sensitivity in distinguishing between good sets of data. A more sensitive test for some systems is provided by calculating y values from the reported P , T , x values using one of the various data reduction procedures available for reducing total pressure (PTx) VLE data. The calculated y values are then compared to the experimental y values and the degree of thermodynamic consistency is judged on the basis of how well the experimental values agree with the consistent calculated values. Sets of data which appear to be about the same insofar as the area ratio test is concerned will sometimes respond differently when the alternate approach is used. That is particularly true for the more nonideal systems.

The y -comparison method has some major disadvantages.

tages. If one uses an indirect data reduction method on the P , T , x values, the calculated y values will depend upon the analytical form assumed for the G^E versus x_1 relationship. For data with considerable scatter, several analytical forms may all reproduce the experimental P versus x_1 isotherm within the experimental accuracy while giving y and γ values which differ appreciably. If one uses a direct data reduction method, the experimental P versus x_1 values must first be fitted in some way to provide smooth, evenly-spaced P values; slight changes in the closeness of the fit often cause appreciable changes in the calculated y and γ values. In any case, the thermodynamically consistent y values (consistent with the reported P , T , x values) are a function of the data reduction method. The calculated y values are also functions of the equation of state used to calculate the vapor-phase fugacity coefficients.

After one calculates the y values and compares them to the experimental values, some measure of the degree of thermodynamic consistency must be developed. The method does not provide a simple result which can be used to characterize large numbers of system conveniently, whereas the area ratio approach gives a single number which must lie between 0.0 and 1.0, and which can be easily related to the general level of accuracy of the data.

Another factor is processing costs. Two data reduction algorithms—one for isothermal and one for isobaric data sets—are necessary for the y -comparison method. The area ratio test is more economical for large numbers of systems.

For the above reasons, the integral form of the Gibbs-Duhem equation is used for the internal thermodynamic consistency test. It is a necessary test (data sets which do not satisfy it cannot be accurate), the degree of consistency can be represented by a single number which must fall between 0.0 and 1.0, it is more reliable in that it is not influenced by an arbitrary choice of some fitting function, and it can be performed economically on large numbers of data sets. However, once those sets of data which survive the integral Gibbs-Duhem test (plus the other evaluation tests) have been identified, it may be worthwhile at some time in the future to subject those good sets to the y -comparison thermodynamic consistency test. The number of sets for which that additional test will be justified will be less than one in ten of the total number of VLE sets in the literature.

3.4. Gibbs-Helmholtz Test

The Gibbs-Helmholtz test is an external test in that it involves another property besides those calculated from VLE data, and involves more than one set of VLE data. It tests for mutual thermodynamic consistency between two or more sets of VLE data and one or more sets of H^E data measured in the same range of temperature as the VLE data.

The three excess properties at constant composition are related by

$$\left[\frac{d(G^E/T)}{d(1/T)} \right]_x = (H^E)_x - (V^E)_x \left[\frac{dP}{d \ln T} \right]_x \quad (14)$$

A restriction of constant pressure eliminates the last term but is not possible to hold both pressure and composition constant for a binary system while varying the temperature. Fortunately, the $V^E(dP/d \ln T)$ term is so small numerically

that the relationship

$$\left[\frac{d(G^E/T)}{d(1/T)} \right]_x \cong (H^E)_x \quad (15)$$

is completely adequate to check the mutual consistency of binary VLE and H^E data sets at some specified composition. Equation (15) shows that a plot of G^E/T values at some composition versus $1/T$ must have a slope at a given temperature which equals the value of H^E at that temperature and composition. The effect of neglecting the $V^E(dP/d \ln T)$ term is inconsequential compared to the uncertainties involved in determining a slope graphically.

The midpoint G^E/T values from the various sets of VLE data for the system tend to scatter and the location of the best curve through the points requires considerable judgment. Further guidance is obtained by differentiating eq (15) with respect to $1/T$ to give

$$\left[\frac{d^2(G^E/T)}{d(1/T)^2} \right]_x \cong \left[\frac{dH^E}{d(1/T)} \right]_x \quad (16)$$

The midpoint H^E values from the available sets of data for the system are plotted versus $1/T$. If the slope of the H^E versus $1/T$ curve is positive, the G^E/T versus $1/T$ plot must be concave upward; if the H^E slope is negative, the G^E/T curve is concave downward. If the H^E versus $1/T$ plot passes through zero, the G^E/T curve must exhibit a maximum or a minimum at that temperature.

When making the G^E/T and the H^E versus $1/T$ plots, the results of the other evaluation tests for the VLE data and the H^E data are inspected and more weight is given to those points which rank highest on the other tests. The evaluator utilizes that information to locate the "best" curve through the midpoint G^E/T points for each system with two or more sets of VLE data and at least one set of H^E data in the temperature range covered by the VLE data. When dealing with a group of systems where one component is common to all (e.g., the alcohol + water systems), all the systems are evaluated simultaneously because family similarity usually helps locate the best curve for each system.

Once the best curve is located for each system, the deviation of each set of data from that best curve is evaluated from

$$\% \text{ Deviation} = \frac{(G^E/T)_{\text{exp}} - (G^E/T)_{\text{curve}}}{(G^E/T)_{\text{curve}}} (100) \quad (17)$$

That number represents the Gibbs-Helmholtz test results in the determination of the quality rating assigned to each set of VLE data.

When making the G^E/T and H^E versus $1/T$ plots, it is imperative that the points used for each data set represent that data set accurately. First, G^E and H^E values at a given mole fraction are obtained from a least-squares fit of the Redlich-Kister equation,

$$\frac{M^E}{x_1 x_2} = \sum_{k=0}^D A_k (x_1 - x_2)^k \quad (18a)$$

or

$$\frac{x_1 x_2}{M^E} = \sum_{k=0}^D A_k (x_1 - x_2)^k \quad (18b)$$

to the data set. The D value used can be 1, 2, 3, 4, or 5. The

x_1x_2/M^E form sometimes works better for highly nonideal systems. Regardless of the form or the degree of the equation used, the data set often has enough scatter to make the G^E or H^E fits unreliable insofar as the interpolation of values at specified mole fractions is concerned. Hence it is necessary for the evaluator to inspect the G^E and H^E plots and to read values which can be compared to the equation-generated values. Also, the fitting program tabulates the experimental and calculated values and that tabulation must be inspected to see if the fit was running high or low in the region of concern. It is often necessary to replace the equation-generated values with manually-read G^E or H^E values in order to use values in the Gibbs-Helmholtz test which accurately represent the experimental data sets. Whenever there is some slight uncertainty as to the most representative G^E or H^E value, the question is resolved by choosing that possible value which favors the data set in the test. In some data sets, it is not possible to establish a G^E or H^E value at a given mole fraction with any certainty; no data point appears on the H^E or G^E/T versus $1/T$ plots for such cases.

The Gibbs-Helmholtz test was initially applied only to the midpoint ($x_1 = 0.5$) data points. It quickly became apparent that a test at only one mole fraction was not sufficient to characterize the accuracy of the various data sets. Ideally, the test should be made at nine points ($x_1 = 0.1, 0.2, \dots$) across the binary composition range but that would involve considerable additional expense. A good compromise is to use three points: $x_1 = 0.25, 0.50$ and 0.75 .

3.5. Comparison Test

If good H^E data are not available for a system, the G^E/T versus $1/T$ plots are still made if three or more sets of VLE data exist. The "best" curve is located despite the fact that H^E values are not available to determine the necessary slopes and shapes of the G^E/T curves. Without H^E data, the plot is simply a way of comparing the available VLE data sets. A percent deviation from the best curve is calculated as in the Gibbs-Helmholtz test using eq (17).

3.6. Criteria for Quality Ratings

The results of all the evaluation tests applied to a set of data are summarized in a single letter quality rating—A, B, C, D or E. Those ratings are defined in table 2 and are designed primarily for the person doing design or correlation work.

The criteria used to relate the quality rating to the var-

Table 2. Definition of quality ratings

Symbol	Definition
A	Very good data; suitable for any use.
B	Good data; can be used with considerable confidence in close designs and in correlation work.
C	Fair data; can be used in designs where high accuracy is not essential but should be used with caution in both design and correlation work.
D	Poor data; should be used with extreme caution.
E	Bad data; probably better to estimate the behavior of the system by other means.

ious evaluation test results for the benzene + cyclohexane system are given in table 3. It is possible to specify different percent deviation criteria at the three mole fractions, but it was not deemed necessary to do so for the almost symmetrical benzene + cyclohexane system. Minimum required test results for the comparison test have been listed in table 3 even though that test is not used because of the availability of H^E data for the benzene + cyclohexane system. That has been done to show that the percent deviation criteria specified for the comparison test are usually looser than for the Gibbs-Helmholtz test. If H^E data are not available, the "best" curve cannot be located with as much certainty and the criteria should not be as exacting.

The worst test result controls the quality rating assigned. For example, a P' error of 0.3% at just one endpoint will trigger a B quality rating even though all the other test results satisfy the A rating criteria. Or, if a data set receives a marginal scatter rating, the quality rating can be no higher than a D even though all the other test results are good enough for a C or higher rating.

The quality rating criteria have two characteristics worthy of comment. First, it should be noted that each class of systems will require its own set of criteria. For example, the area ratio ranges given in table 3 for the benzene + cyclohexane system are too tight for light hydrocarbon systems and too loose for highly nonideal system. Second, the criteria used are inevitably influenced by the quality of the available data despite the best intentions of the evaluator. A mixture class which happens to have a large amount of good data will tend to have tighter criteria than a class where the available

Table 3. Quality rating criteria for the VLE data for the benzene(1) + cyclohexane(2) system

Quality Rating	Scatter Rating	Maximum P' Error, %	Gibbs-Duhem Area Ratio	Minimum Required Test Results					
				Deviation from Best G^E/T vs. $1/T$ Curve, %					
				Gibbs-Helmholtz			Comparison		
			0.25	0.50	0.75	0.25	0.50	0.75	
A	Excellent	0.25	0.95 - 1.00	<3	<3	<3	<5	<5	<5
B	Good	0.50	0.90 - 0.95	<6	<6	<6	<10	<10	<10
C	Fair	1.00	0.80 - 0.90	<12	<12	<12	<15	<15	<15
D	Marginal	2.00	0.70 - 0.80	<18	<18	<18	<20	<20	<20
E	Unacceptable	>2.00	<0.70	>18	>18	>18	>20	>20	>20

data are of lower quality, despite the evaluator's efforts to make the ratings as "absolute" as possible. Despite these shortcomings, the quality ratings do classify all the available data sets within a mixture class according to their relative qualities, and they do that as objectively as possible due to their definition in terms of basic thermodynamic tests whenever possible.

3.6.1. Smoothed Data Sets

Those sets receiving the S (smoothed) scatter rating are assigned quality ratings based on the other test results besides the scatter rating. If other test results are available for the set of data, the quality rating assigned can be anything from A to E depending upon those other results.

If no other test results are available, the quality rating assigned to a smoothed data set will be ABC. In the absence of any other information, the smoothed scatter rating does exclude the D and E quality ratings but cannot distinguish between the A, B and C quality ratings.

3.6.2. Other Multiple-Letter Quality Ratings

Multiple letter quality ratings occur in situations other than the one described above for the smoothed scatter rating. In general, if one of the regular scatter ratings (E, G, F, M, and U) is assigned and there are no other evaluation test results, the first letter of the quality rating assigned will be the one corresponding to the scatter rating and will be followed by the letters for the next two lower quality ratings. For example, if the only evaluation test result available is a good scatter rating, the assigned quality rating will be BCD.

It should be noted, however, that the probability of the scatter rating being the only available test result is much lower for VLE data than for H^E or V^E data sets.

A multiple letter rating can be used in other situations where the evaluator believes it to be more informative than a single letter rating. For example, an isobaric data set could satisfy all the criteria in table 3 for a B quality rating except for the uncorrected area ratio which is 0.88. No H^E data are available to evaluate the correction but, if it were available, the corrected area ratio might well be 0.90 or higher. Consequently, a BC quality rating would be assigned to indicate that the set could go either way if all the needed information were available.

3.6.3. No Quality Rating

When the available information is insufficient to define a quality rating, the letter N (for no quality rating) will appear in place of a quality rating.

4. Summary of Evaluation Results

Table 4 lists the evaluation results for all the data sets evaluated for the benzene + cyclohexane system. Each set of data is represented by a single line. The literature references are the Laboratory's Master Reference List (MRL) numbers which were assigned to the individual documents when they were retrieved. The literature citation for a given MRL number can be found in the Bibliography. The MRL number also appears on the tabulation of each set of data. The isothermal data sets are ordered with respect to temperature, and the isobaric data sets are ordered with respect to pressure. The

Table 4. Summary list for PTxy vapor-liquid equilibrium data for the benzene(1) + cyclohexane(2) system

LITERATURE REFERENCES	SYSTEM T OR P	QUALITY RATING	SCATTER RATING	P' ERROR, %		GIBBS-DUHEM AREA RATIO	% DEVIATION FROM GE/T VS. 1/T CURVE		
				X1=0	X1=1		X1=0.25	X1=0.50	X1=0.75
BENZENE(1) + CYCLOHEXANE(2)									
00228	283.14 K	B	G	-0.1	-0.0	0.98(0.98)	-0.0 H	1.7 H	0.9 H
00193	303.13 K	D	M	-0.2	-0.5	0.77(0.77)	-	-	-
00193	313.14 K	B	G	-0.0	-0.1	0.94(0.94)	0.7 H	0.1 H	0.3 H
40032	313.15 K	B	G	-0.0	-0.1	0.93(0.93)	-0.2 H	-0.9 H	-0.9 H
00193	323.13 K	D	M	0.0	0.0	0.94(0.94)	-	-	-
00277	323.14 K	E	M	-0.9	-0.9	0.85(0.85)	22.2 H	7.3 H	-7.0 H
00193	333.09 K	D	M	0.0	0.0	0.94(0.94)	-	-	-
00228	333.14 K	B	G	-0.1	-0.1	0.96(0.96)	1.6 H	1.6 H	1.5 H
00193	343.12 K	C	G	0.0	-0.0	0.87(0.87)	-0.5 H	0.1 H	-0.4 H
00028	343.14 K	E	S	0.4	0.0	0.94(0.94)	-21.7 H	-7.8 H	-6.3 H
01792	343.14 K	B	G	0.0	0.0	0.97(0.97)	0.9 H	-1.3 H	0.5 H
00269	392.46 K	E	M	-0.2	--	0.98(0.98)	-18.9 H	-9.2 H	-24.9 H
00277	40.00 KPA	E	M	-0.5	-0.8	0.83(0.83)	22.1 H	6.2 H	-1.3 H
00128	98.66 KPA	E	U	-6.6	0.1	0.40(0.40)	-	-	-
00186	101.19 KPA	D	F	0.2	-0.0	0.77(0.77)	3.6 H	2.7 H	-2.4 H
00026	101.32 KPA	D	M	-0.2	-0.1	0.71(0.71)	13.4 H	1.1 H	-13.8 H
00031	101.32 KPA	E	M	0.1	-0.0	0.77(0.77)	-16.1 H	-0.4 H	-19.0 H
00044	101.32 KPA	C	F	0.1	-0.0	0.92(0.92)	-7.5 H	-2.9 H	-6.2 H
00234	101.32 KPA	B	G	0.1	-0.0	0.99(0.99)	-2.6 H	-2.8 H	-1.4 H
00241	101.32 KPA	C	F	--	-0.3	0.84(0.84)	5.5 H	5.2 H	9.7 H
00272	101.32 KPA	C	F	0.1	-0.0	0.99(0.99)	-0.9 H	4.0 H	3.3 H
00277	101.32 KPA	D	M	-0.2	0.1	0.79(0.79)	-8.5 H	-6.1 H	-10.7 H
00297	101.32 KPA	C	F	-0.1	-0.2	0.97(0.97)	-10.6 H	-3.5 H	-5.6 H
00310	101.32 KPA	D	F	0.4	0.3	0.94(0.94)	-13.9 H	-3.6 H	-7.7 H
00315	101.32 KPA	E	U	--	--	0.80(0.80)	-	-	-
00334	101.32 KPA	C	F	0.1	-0.0	0.82(0.82)	4.4 H	4.0 H	-0.9 H
00917	101.32 KPA	C	F	0.0	-0.0	0.86(0.86)	-3.7 H	-2.8 H	-5.4 H
00271	459.88 KPA	E	M	3.3	0.3	0.90(0.90)	-	-	-
00271	803.24 KPA	D	M	2.0	-1.1	0.87(0.87)	-	-	-
00334	1013.25 KPA	D	F	-1.6	0.7	0.97(0.97)	3.6 H	0.7 H	-4.0 H
00271	1143.84 KPA	E	M	0.9	-0.6	0.64(0.64)	-21.7 H	-27.8 H	-35.0 H
00271	1143.84 KPA	E	M	0.9	-0.6	0.64(0.64)	-25.2 H	-29.8 H	-36.6 H
00271	1496.16 KPA	E	M	1.2	-0.9	0.63(0.63)	-	-	-
00271	1852.62 KPA	E	M	-0.1	-1.1	0.46(0.46)	-30.1 H	-32.7 H	-38.6 H
00334	2026.50 KPA	D	F	-1.0	1.1	0.92(0.92)	-4.3 H	-1.6 H	5.4 H
00334	3039.75 KPA	E	U	0.1	2.4	0.92(0.92)	9.2 H	7.6 H	5.8 H

isothermal data sets precede the isobaric ones.

The quality rating and the scatter rating symbols are defined in tables 2 and 1, respectively. The P' errors were calculated with eq (6), and the Gibbs-Duhem area ratios were calculated with eq (7) or (13). The % deviations in the last three columns of table 4 were obtained with eq (17); the H after each deviation indicates it was derived from the Gibbs-Helmholtz test rather than a simple comparison test.

5. Selected G^E/T Values at $x_1 = 0.25, 0.50,$ and 0.75

The selected G^E/T value at any given temperature and composition must be found in one of the following two ways. When a large number of very high quality data sets are available at the given temperature, it may be possible to identify the selected values at $x_1 = 0.25, 0.50$ and 0.75 from a consideration of only the data at that temperature; that approach was possible at 298.15 K in the two parallel papers for the V^E and H^E data for benzene + cyclohexane. When the data sets at the given temperature are in disagreement and the selected values cannot be identified from the data at that temperature alone, then the selected G^E/T values must be obtained from the best G^E/T versus $1/T$ curve based on the data sets at all temperatures. The latter approach must be used for the VLE data for benzene + cyclohexane.

Before the best G^E/T versus $1/T$ curve can be drawn, it is necessary to identify those sets which are probably the most reliable and should be given the most weight when drawing the G^E/T curve. All the evaluation test results except the Gibbs-Helmholtz results are available at this point and can be used to characterize an individual point or rank multiple measurements at any given temperature.

Multiple isobaric measurements have been reported at only one pressure; twelve sets of data (including one at 759 mm Hg) at one atmosphere are available. Two sets of isothermal data have been reported at 40 °C, including the one at 39.997 °C. There are two sets of isothermal data at 50 °C and at 60 °C but one set at each temperature reports only one mixture point. Three sets of data have been reported at 70 °C, including one at 69.985 °C. All the other sets of data are lone sets, i.e., they are the only one at their stated conditions.

5.1. Isothermal Data Sets

5.1.1 313.15 K

The MRL 193 set (Scatchard, Wood and Mochel, 1939) at 39.997 °C (313.14 K) is shown in figure 1. There are fewer than ten mixture points and there are several mole fraction gaps greater than 0.1. Otherwise, the shape of the plots and the scatter shown would have justified an excellent scatter rating. As shown in table 4, the endpoint P' errors are -0.04 and 0.10% and the area ratio is 0.94 . Based on these results alone, the set would receive a B quality rating.

As shown in figure 3, the MRL 40632 set (Inoue, Azumi and Suzuki, 1975) does not plot as well as the Scatchard et al. set but is obviously worthy of a good scatter rating. The endpoint P' errors are -0.01 and -0.14% and the area ratio is 0.93 , which would give the set a B quality rating.

The G^E/T values for the Scatchard et al. set at $x_1 = 0.25, 0.50,$ and 0.75 are $0.6938, 0.9444,$ and 0.7302 . The

values for the Inoue et al. set are $0.6879, 0.9331,$ and 0.7201 . Hence the two points fall very close to each other on the G^E/T versus $1/T$ plot at $1/T = 0.00319$ with the Scatchard et al. points slightly above the Inoue et al. points. The two points together provide a firm anchor point for the location of the G^E/T versus $1/T$ curve.

5.1.2. 343.14 K

The three sets at 70 °C have been reported by the following authors: MRL 28 (Susarev and Shu-Tzu, 1963), MRL 193 (Scatchard, Wood and Mochel, 1939), and MRL 1792 (Diaz Pena and Cheda, 1970). The evaluation results obtained so far for these three sets are as follows:

MRL	Scatter rating	P' Error, %		Area ratio
		$x_1 = 0$	$x_1 = 1$	
28	S	0.41	0.04	0.94
193	G	0.00	-0.01	0.87
1792	G	0.03	0.03	0.97

The relative locations of these data sets on the G^E/T versus $1/T$ plots are shown by the following tabulation:

MRL	T, K	G^E/T		
		$x_1 = 0.25$	$x_1 = 0.50$	$x_1 = 0.75$
28	343.14	0.4296	0.6881	0.5432
193	343.12	0.5465	0.7465	0.5778
1792	343.14	0.5537	0.7361	0.5829

The MRL 193 and 1792 sets agree quite well but the MRL 28 set falls considerably below the other two. The latter set is a smoothed data set and evidently used impure cyclohexane (P' error = 0.41% at $x_1 = 0$); either fault could cause the G^E/T values to be wrong.

Based on the evaluation results available so far, the MRL 1792 set would receive a B rating and the MRL 193 set a C rating. However, the G^E/x_1x_2 plot for the MRL 1792 set is somewhat suspect (as will be discussed later) and, in location of the G^E/T versus $1/T$ curve, equal weight was given the two sets.

5.1.3. Other Temperatures

MRL 228 (Boublick, 1963) reports sets at 283.14 and 333.14 K. Both received good scatter ratings, the P' errors for both were all below 0.08% , and the area ratios were 0.98 and 0.96 . Both sets fall generally in line with the best sets at 313.15 and 343.14 discussed above. Consequently, both were useful points in the location of the G^E/T versus $1/T$ curves.

The MRL 277 set (Morachevskii and Zharov, 1963) at 323.14 K agreed very well on the G^E/T plot with the 300 mm Hg set reported by the same authors. However, both sets received a marginal scatter rating, both have high P' errors (-0.92 and -0.89% for the isothermal set, and -0.53 and -0.79% for the isobaric set), and the G^E/x_1x_2 plots have the wrong shape. Little weight was given to those sets in the location of the G^E/T curve.

The MRL 269 set (Kortum and Freier, 1954) at 392.46 K has a good area ratio (0.98) but that is based on only four points and is therefore suspect. As shown in figure 10, the G^E/x_1x_2 plot also makes the data set suspect. The authors reported a pure compound vapor pressure only for cyclohexane and it differed from our selected value by 0.25% . Consequently, this data set could not be used as a guide in the location of the G^E/T curve.

5.2. Isobaric Data Sets

5.2.1. 101.325 kPa

Tables 5, 6, and 7 show the G^E/T values at $x_1 = 0.25$, 0.50, and 0.75 listed in the order of increasing magnitude for the twelve sets of data reported at a nominal pressure of one atmosphere. (One of these sets, MRL 186, reported a pressure of 759 mm Hg.) Figure 16 plots those G^E/T values versus MRL number in the order of increasing magnitude. The

MRL (Master Reference List) numbers relate the data sets to their literature citations in the Bibliography.

The results for all the evaluation tests except the Gibbs-Helmholtz test are shown in tables 5, 6, and 7 along with the G^E/T values. Only one set (MRL 234, Chao and Hougen, 1958) received a good scatter rating. Four other sets have area ratios above 0.90 and fair scatter ratings. One of those four sets (MRL 310, Thornton and Garner, 1951) has relatively large P' errors of 0.4 and 0.3%; the other three sets all

Table 5. Magnitude listing of G^E/T values at $x_1 = 0.25$ and 101.325 kPa

MRL	S	AR	P' Error, %		Authors	T, K	G^E	G^E/T
			$x_1=0$	$x_1=1$				
31	M	0.77	0.1	-0.0	Darmois, Darmois	351.9	151.8	0.4313
310	F	0.94	0.4	0.3	Thornton, Garner	351.8	156.0	0.4435
297	F	0.97	-0.1	-0.2	Sieg	351.7	162.0	0.4606
277	M	0.79	-0.2	0.1	Morachevski, Zharov	351.7	166.0	0.4720
44	F	0.92	0.1	-0.0	Nataraj, Raja Rao	351.6	167.8	0.4772
917	F	0.86	0.0	-0.0	Ridgway, Butler	351.5	175.0	0.4979
234	G	0.99	0.1	-0.0	Chao, Hougen	351.6	177.0	0.5035
272	F	0.99	0.1	-0.0	Nagata	351.5	180.0	0.5121
186	F	0.77	0.2	-0.0	Richards, Hargreaves	351.6	188.0	0.5347
334	F	0.82	0.1	-0.0	Tao	351.4	190.0	0.5407
241	F	0.84	-	-0.3	Donald, Ridgway	351.4	192.0	0.5464
26	M	0.71	-0.2	-0.1	Susarev, Lyzlova	351.2	206.8	0.5888

Note. S = scatter rating. AR = area ratio.

Table 6. Magnitude listing of G^E/T values at $x_1 = 0.50$ and 101.325 kPa

MRL	S	AR	P' Error, %		Authors	T, K	G^E	G^E/T
			$x_1=0$	$x_1=1$				
277	M	0.79	-0.2	0.1	Morachevski, Zharov	350.8	231.5	0.6598
310	F	0.94	0.4	0.3	Thornton, Garner	350.8	238.0	0.6784
297	F	0.97	-0.1	-0.2	Sieg	350.8	238.2	0.6791
44	F	0.92	0.1	-0.0	Nataraj, Raja Rao	350.8	239.5	0.6826
234	G	0.99	0.1	-0.0	Chao, Hougen	350.7	240.0	0.6843
917	F	0.86	0.0	-0.0	Ridgway, Butler	350.7	240.0	0.6843
31	M	0.77	0.1	-0.0	Darmois, Darmois	350.8	246.0	0.7013
26	M	0.71	-0.2	-0.1	Susarev, Lyzlova	350.6	249.8	0.7125
186	F	0.77	0.2	-0.0	Richards, Hargreaves	350.6	254.3	0.7254
272	F	0.99	0.1	-0.0	Nagata	350.6	257.0	0.7330
334	F	0.82	0.1	-0.0	Tao	250.6	257.0	0.7330
241	F	0.84	-	-0.3	Donald, Ridgway	350.7	260.0	0.7414

Note. S = scatter rating. AR = area ratio.

Table 7. Magnitude listing of G^E/T values at $x_1 = 0.75$ and 101.325 kPa

MRL	S	AR	P' Error, %		Authors	T, K	G^E	G^E/T
			$x_1=0$	$x_1=1$				
31	M	0.77	0.1	-0.0	Darmois, Darmois	351.4	156.0	0.4439
26	M	0.71	-0.2	-0.1	Susarev, Lyzlova	351.4	166.0	0.4724
277	M	0.79	-0.2	0.1	Morachevski, Zharov	351.3	172.0	0.4896
310	F	0.94	0.4	0.3	Thornton, Garner	351.2	178.0	0.5069
44	F	0.92	0.1	-0.0	Nataraj, Raja Rao	351.2	180.6	0.5142
917	F	0.86	0.0	-0.0	Ridgway, Butler	351.2	182.0	0.5182
297	F	0.97	-0.1	-0.2	Sieg	351.2	182.0	0.5183
186	F	0.77	0.2	-0.0	Richards, Hargreaves	351.0	188.0	0.5357
234	G	0.99	0.1	-0.0	Chao, Hougen	351.1	190.0	0.5412
334	F	0.82	0.1	-0.0	Tao	351.0	191.0	0.5441
272	F	0.99	0.1	-0.0	Nagata	351.0	199.0	0.5670
241	F	0.84	-	-0.3	Donald, Ridgway	350.6	212.0	0.6046

Note. S = scatter rating. AR = area ratio.

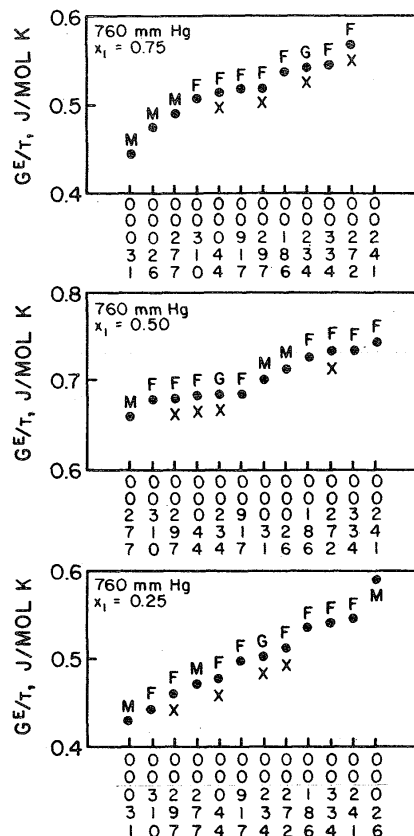


FIGURE 16. Magnitude comparison plots for the G^E/T values at $x_1 = 0.25$, 0.50 and 0.75 and 101.325 kPa.

have P' errors less than 0.2%.

The four data sets with a fair or good scatter rating, an area ratio above 0.9, and P' errors of 0.2% or less are marked with X's below their respective points in figure 16. Unfortunately, the plots are not very helpful in the identification of the selected values at 101.325 kPa. The MRL 234 set (Chao and Hougen, 1958) is probably the best set with the MRL 272 set (Nagata, 1962) a close second. Those two sets do not agree closely in their G^E/T values at all three temperatures, hence it was not possible to pick a firm point at 101.325 kPa through which the G^E/T versus $1/T$ curve must pass. That curve should come close to the MRL 234 and 272 set values, but there was freedom to adjust the curve to also agree well with the reliable data sets identified at other $1/T$ values.

5.2.2. Other Pressures

Two sources have reported isobaric data sets above 101.325 kPa. MRL 271 (Kumarkrishna Rao, Swami, and Narasinga Rao, 1957) reports data at 66.7, 116.5, 165.9, 217.0 and 268.7 pounds force per square inch. All of those data sets received marginal scatter ratings for the reasons illustrated by figures 11, 12 and 13. The $\ln(\gamma'_1/\gamma'_2)$ plot in figure 12 and the G^E plot in figure 13 are better than for the other four sets; the G^E versus x_1 curves were badly distorted in the $x_1 = 0.0$ to 0.5 range on the other four plots. The P' errors were large with at least one error in each data set being

one percent or higher. It was possible to read G^E at $x_1 = 0.25, 0.50$ and 0.75 with any degree of certainty only for two of the five sets. The area ratios were 0.90, 0.87, 0.64, 0.63, 0.46—declining as the pressure increased—but it was necessary to bias the $\ln(\gamma'_1/\gamma'_2)$ curve in the direction of the characteristic curve in order to get ratios that high. Obviously, the MRL 271 sets cannot be used as guides for the G^E/T versus $1/T$ curve.

MRL 334 (Tao, 1952) reports sets at 1, 10, 20 and 30 atm. The set at 30 atm received an unacceptable scatter rating because all the $\ln(\gamma'_1/\gamma'_2)$ values were negative and that curve plus the others for that set deviated widely from the characteristic shapes. The other three sets received fair scatter ratings. The sets at 10 and 20 atmospheres had good area ratios of 0.97 and 0.92 but showed large P' errors: -1.57 and 0.69% at 10 atm, and -1.05 and 1.14% at 20 atm. Despite the large P' errors, the 10 atm and 20 atm sets are the best sets available in the high temperature range to serve as guides for the G^E/T versus $1/T$ curve.

5.3. Selected H^E Values

Besides passing through or near the better VLE data set points, the G^E/T versus $1/T$ curve must have a slope at each point equal to the H^E value at that temperature. The needed H^E values were read from the best H^E versus $1/T$ curves at $x_1 = 0.25, 0.50$, and 0.75 established in the evaluation report for the benzene + cyclohexane H^E data [2]. Those values are shown in table 8. The slope of the H^E versus $1/T$ curve is positive at each x_1 value. As shown by equation 16, the second derivative of G^E/T with respect to $1/T$ is therefore positive which requires the G^E/T versus $1/T$ curve to be concave upward.

Table 8. Selected H^E values at evenly-spaced $1/T$ increments for the benzene + cyclohexane system

$1/T \times 10^4$	$x_1 = 0.25$	$x_1 = 0.50$	$x_1 = 0.75$
36	640.8	870.4	676.6
35	620.1	842.0	654.3
34	599.5	813.6	632.1
33	578.9	785.2	609.8
32	558.3	756.9	587.5
31	537.6	728.5	565.2
30	517.0	700.1	542.9
29	496.3	671.5	520.4
28	475.5	643.0	498.0
27	454.7	614.5	475.7
26	433.8	586.2	453.4
25	413.0	557.8	431.1
24 ^a	392.3	529.4	408.8
23 ^a	371.6	501.0	386.5
22 ^a	350.9	472.5	364.1
21 ^a	330.2	444.1	341.8
20 ^a	309.5	415.7	319.5
19 ^a	288.8	387.3	297.2

^a H^E values at these temperatures are extrapolated. The H^E versus $1/T$ plot was a straight line which facilitated extrapolation.

Table 9. Selected G^E values for benzene(1) + cyclohexane(2)

T, K	$x_1 = 0.25$		$x_1 = 0.50$		$x_1 = 0.75$	
	G^E/T	G^E	G^E/T	G^E	G^E/T	G^E
280	0.913	255.6	1.247	349.2	0.951	266.3
290	0.834	241.9	1.142	331.2	0.874	253.5
300	0.766	229.8	1.048	314.4	0.805	241.5
310	0.705	218.6	0.964	298.8	0.744	230.6
320	0.652	208.6	0.890	284.8	0.687	219.8
330	0.603	199.0	0.823	271.6	0.637	210.2
340	0.560	190.4	0.761	258.7	0.591	200.9
350	0.519	181.7	0.707	247.5	0.552	193.2
360	0.482	173.5	0.658	236.9	0.513	184.7
370	0.447	165.4	0.611	226.1	0.478	176.9
380	0.414	157.3	0.567	215.5	0.448	170.2
390	0.386	150.5	0.528	205.9	0.418	163.0
400	0.360	144.0	0.494	197.6	0.392	156.8
410	0.335	137.4	0.461	189.0	0.368	150.9
420	0.311	130.6	0.429	180.2	0.347	145.7
430	0.292	125.6	0.401	172.4	0.327	140.6
440	0.274	120.6	0.376	165.4	0.307	135.1
450	0.258	116.1	0.350	157.5	0.288	129.6
460	0.242	111.3	0.328	150.9	0.271	124.7
470	0.229	107.6	0.307	144.3	0.256	120.3
480	0.217	104.2	0.287	137.8	0.240	115.2
490	0.204	100.0	0.267	130.8	0.226	110.7
500	0.194	97.0	0.250	125.0	0.213	106.5
510	0.183	93.3	0.234	119.3	0.202	103.0
520	0.174	90.5	0.218	113.4	0.190	98.8

5.4. Best G^E/T Versus $1/T$ curve

Program COMPLT was used to plot the G^E/T versus $1/T$ values at $x_1 = 0.25, 0.50$ and 0.75 for all the VLE sets of data. Slope lines were established manually near the more reliable points and at appropriate intervals between. It was relatively easy to then establish smooth "best" curves on all three plots which satisfied the slope requirements and which passed close to those points selected as guide points in the

previous section. The only difficulty arose at the low temperature end of the $x_1 = 0.50$ curve. It was not possible to pass through the good points at 313.15 K (Scatchard et al., MRL 193; Inoue et al., MRL 40032) and at 343.14 K (Scatchard et al., MRL 193; Diaz Pena et al., MRL 1792), then turn the curve up sharply enough to pass through the 283.14 K point of Boublik (MRL 228) and at the same time satisfy the slope requirements imposed by the H^E data. Consequently, the curve at $x_1 = 0.50$ passes below the 283.14 K Boublik point whereas that set of data falls very close to the curves at $x_1 = 0.25$ and 0.75 .

The plots used to establish the best G^E/T versus $1/T$ curves were too large to reproduce satisfactorily. Instead, the best curves are presented in tabular form in table 9. The locations of each set of data relative to those curves are given by the percent deviations in the Gibbs-Helmholtz test columns in table 4. Those deviations are defined by eq (17).

6. Recommended Data Sets

As shown in table 4, none of the VLE data sets for benzene(1) + cyclohexane(2) received an A quality rating. Only one set—MRL 193; Scatchard, Wood and Mochel, 1939, at 39.997 °C—had a G^E/x_1x_2 versus x_1 plot which exhibited a scatter rating required by the A quality rating. Unfortunately, that set has fewer than ten mixture points and has several mole fraction gaps greater than 0.1 and those shortcomings resulted in a good scatter rating and a B quality rating. All the other better sets had plots worthy of only a good scatter rating which caused B to be the highest quality rating assigned.

6.1. Isothermal Data Sets

6.1.1. 283.14 K

Even though the G^E/T point at $x_1 = 0.5$ for the 10 °C data set of Boublik, 1963 (MRL 228) falls a little above the

Table 10. A recommended data set at 283.14 K

SYSTEM.		Benzene(1) + Cyclohexane(2)		C(6)H(6) + C(6)H(12)		PTXY							
RATING.	R	AREA RATIO.	0.98 (0.98 with VE)	P' ERRORS.	-0.1% and -0.0% at $x(1) = 0$ and 1	SCATTER.	Good						
DEVIATION FROM G^E/T VS. $1/T$ CURVE AT $x(1) = 0.25$.				-0.0%		INFINITE DILUTION ACTIVITY COEFFICIENTS.							
DEVIATION FROM G^E/T VS. $1/T$ CURVE AT $x(1) = 0.50$.				1.7%		1 = 1.82							
DEVIATION FROM G^E/T VS. $1/T$ CURVE AT $x(1) = 0.75$.				0.9%		2 = 1.92							
EQUATIONS OF STATE.		1 = Virial, C zero, B from Tsonopoulos.											
		2 = Virial, C zero, B from Tsonopoulos.											
REFERENCE. Boublik, T., Collection of Czechoslovak Chemical Communications, 28, 1771 (1963). (MRL 228)													
Mole Fraction $x(1)$	$y(1)$	T, K	P, kPa	Vapor Pressure, kPa		Liquid Molar Volume, ml/mol		$\frac{\theta(\text{mix}, P)}{\theta(\text{pure}, P')}$ $\exp(V(P-P')/RT)$		ln Gamma Ratio	Activity Coefficient		E G J/mol
				1	2	1	2	1	2				
0.0000	0.0000	283.145	6.34	6.07	6.35	87.80	106.82	0.9998	1.0000		1.0000	0.0	
0.0610	0.0953	283.145	6.58	6.07	6.35	87.80	106.82	0.9995	0.9998	0.5274	1.6946	1.0000	75.8
0.2149	0.2710	283.145	6.97	6.07	6.35	87.80	106.82	0.9992	0.9994	0.3501	1.4481	1.0203	224.5
0.3187	0.3600	283.145	7.13	6.07	6.35	87.80	106.82	0.9990	0.9992	0.2285	1.3267	1.0557	299.1
0.4320	0.4453	283.145	7.16	6.07	6.35	87.80	106.82	0.9990	0.9992	0.0981	1.2158	1.1022	328.9
0.5246	0.5106	283.145	7.21	6.07	6.35	87.80	106.82	0.9990	0.9991	-0.0120	1.1553	1.1692	353.2
0.6117	0.5735	283.145	7.13	6.07	6.35	87.80	106.82	0.9990	0.9992	-0.1142	1.1012	1.2344	331.3
0.7265	0.6626	283.145	6.97	6.07	6.35	87.80	106.82	0.9992	0.9994	-0.2580	1.0466	1.3546	273.2
0.8040	0.7312	283.145	6.84	6.07	6.35	87.80	106.82	0.9993	0.9995	-0.3667	1.0243	1.4781	225.8
0.8830	0.8200	283.145	6.61	6.07	6.35	87.80	106.82	0.9995	0.9997	-0.4608	1.0113	1.6033	153.4
0.8999	0.8382	283.145	6.55	6.07	6.35	87.80	106.82	0.9996	0.9998	-0.5072	1.0052	1.6693	131.8
1.0000	1.0000	283.145	6.07	6.07	6.35	87.80	106.82	1.0000	1.0003		1.0000		0.0

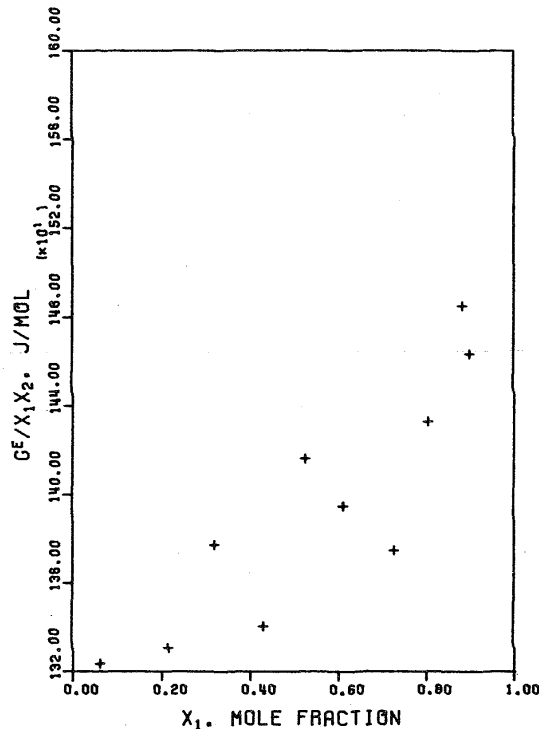


FIGURE 17. A recommended data set at 283.14 K. Data of Boublik, 1963. MRL 228. Ordinate values run from 1320 to 1600.

best curve, the data set is reliable and exceptionally valuable because it extends the temperature range beyond the next sets at 40 °C. The set is tabulated in table 10 and its G^E/x_1x_2 plot is shown in figure 17.

6.1.2. 313.15 K

There are two good sets of data of 40 °C—Scatchard, Wood and Mochel, 1963 (MRL 193) and Inoue, Azumi and

Table 11. The recommended data set at 313.15 K

SYSTEM.		C(6)H(6) + C(6)H(12)		PTXY									
RATING.	B	AREA RATIO.	0.94 (0.94 with VE)	P' ERRORS.	-0.0% and -0.1% at x(1) = 0 and 1	SCATTER.	Good						
DEVIATION FROM GE/T VS. 1/T CURVE AT x(1) = 0.25.				0.7%	INFINITE DILUTION ACTIVITY COEFFICIENTS.								
DEVIATION FROM GE/T VS. 1/T CURVE AT x(1) = 0.50.				0.1%	1 =	1.50							
DEVIATION FROM GE/T VS. 1/T CURVE AT x(1) = 0.75.				0.3%	2 =	1.62							
EQUATIONS OF STATE.		1 = Virial, C zero, B from Tsonopoulos.											
		2 = Virial, C zero, B from Tsonopoulos.											
REFERENCE.													
Scatchard, G., Wood, S. E., Mochel, J. M., Journal of Physical Chemistry, 43, 119 (1939). (MRL 193)													
Mole Fraction x(1)	y(1)	T, K	P, kPa	Vapor Pressure, kPa		Liquid Molar Volume, ml/mol		$\theta(\text{mix}, P)/\theta(\text{pure}, P')$ $\exp(V(P-P')/RT)$		ln Gamma Ratio	Activity Coefficient		E _G J/mol
				1	2	1	2	1	2		1	2	
0.0000	0.0000	313.136	24.60	24.37	24.61	91.09	110.79	0.9999	1.0000		1.0000		0.0
0.1282	0.1657	313.136	25.98	24.37	24.61	91.09	110.79	0.9991	0.9991	0.3105	1.3773	1.0097	128.8
0.2354	0.2766	313.136	26.75	24.37	24.61	91.09	110.79	0.9986	0.9986	0.2267	1.2882	1.0269	208.2
0.3685	0.3912	313.136	27.29	24.37	24.61	91.09	110.79	0.9983	0.9982	0.1064	1.1873	1.0674	272.0
0.4932	0.4950	313.136	27.48	24.37	24.61	91.09	110.79	0.9982	0.9981	0.0172	1.1299	1.1105	295.1
0.6143	0.5909	313.136	27.35	24.37	24.61	91.09	110.79	0.9982	0.9982	-0.0877	1.0780	1.1768	283.6
0.7428	0.6979	313.136	26.89	24.37	24.61	91.09	110.79	0.9985	0.9985	-0.2133	1.0355	1.2817	233.7
0.8656	0.8205	313.136	26.00	24.37	24.61	91.09	110.79	0.9990	0.9991	-0.3329	1.0106	1.4099	144.0
1.0000	1.0000	313.136	24.34	24.37	24.61	91.09	110.79	1.0000	1.0002		1.0000		0.0

Table 12. The second best set of data at 313.15 K

SYSTEM.		Benzene(1) + Cyclohexane(2)		C(6)H(6) + C(6)H(12)		PTXY	
RATING.	B	AREA RATIO.	0.93 (0.93 with VE)	P' ERRORS.	-0.0% and -0.1% at x(1) = 0 and 1	SCATTER.	Good
DEVIATION FROM GE/T VS. 1/T CURVE AT x(1) = 0.25.				-0.2%	INFINITE DILUTION ACTIVITY COEFFICIENTS.		
DEVIATION FROM GE/T VS. 1/T CURVE AT x(1) = 0.50.				-0.9%	1 =	1.48	
DEVIATION FROM GE/T VS. 1/T CURVE AT x(1) = 0.75.				-0.9%	2 =	1.56	
EQUATIONS OF STATE.		1 = Virial, C zero, B from Tsonopoulos.					
		2 = Virial, C zero, B from Tsonopoulos.					
REFERENCE.		Inoue, M., Azumi, K., Suzuki, N., Industrial and Engineering Chemistry, Fundamentals, 14(4), 312 (1975). (MRL 40032)					

Mole Fraction x(1) y(1)	T, K	P, kPa	Vapor Pressure, kPa		Liquid Molar Volume, ml/mol		$\frac{\theta(\text{mix}, P)}{\theta(\text{pure}, P')}$ $\exp(V(P-P')/RT)$		ln Gamma Ratio	Activity Coefficient		E G J/mol
			1	2	1	2	1	2		1	2	
0.0000 0.0000	313.150	24.61	24.38	24.62	91.09	110.79	0.9999	1.0000		1.0000	1.0000	0.0
0.1170 0.1500	313.150	25.88	24.38	24.62	91.09	110.79	0.9991	0.9992	0.2965	1.3599	1.0110	118.7
0.2540 0.2950	313.150	26.82	24.38	24.62	91.09	110.79	0.9986	0.9985	0.2162	1.2760	1.0280	214.7
0.3610 0.3840	313.150	27.29	24.38	24.62	91.09	110.79	0.9983	0.9982	0.1084	1.1887	1.0665	269.7
0.4980 0.5010	313.150	27.46	24.38	24.62	91.09	110.79	0.9982	0.9981	0.0220	1.1313	1.1067	292.5
0.6270 0.5990	313.150	27.29	24.38	24.62	91.09	110.79	0.9983	0.9982	-0.1081	1.0677	1.1895	275.5
0.7300 0.6860	313.150	26.94	24.38	24.62	91.09	110.79	0.9985	0.9985	-0.2031	1.0369	1.2704	237.1
0.8770 0.8350	313.150	25.88	24.38	24.62	91.09	110.79	0.9991	0.9992	-0.3329	1.0098	1.4088	132.1
1.0000 1.0000	313.150	24.34	24.38	24.62	91.09	110.79	1.0000	1.0002		1.0000		0.0

Suzuki, 1975 (MRL 40032). The MRL 193 set is tabulated in table 11 and plotted in figure 1. The MRL 40032 set appears in table 12 and figure 3.

Comparison of figures 1 and 3 indicates that the MRL 193 data set should be preferred.

6.1.3. 333.14 K

As shown in table 4, the 60 °C set of Boublik, 1963 (MRL 228) falls slightly above the best curves (1.6, 1.6, and 1.5%). Even though it does not agree exactly with the best

Table 13. A recommended data set at 333.14 K

SYSTEM.		Benzene(1) + Cyclohexane(2)		C(6)H(6) + C(6)H(12)		PTXY	
RATING.	B	AREA RATIO.	0.96 (0.96 with VE)	P' ERRORS.	-0.1% and -0.1% at x(1) = 0 and 1	SCATTER.	Good
DEVIATION FROM GE/T VS. 1/T CURVE AT x(1) = 0.25.				1.6%	INFINITE DILUTION ACTIVITY COEFFICIENTS.		
DEVIATION FROM GE/T VS. 1/T CURVE AT x(1) = 0.50.				1.6%	1 =	1.44	
DEVIATION FROM GE/T VS. 1/T CURVE AT x(1) = 0.75.				1.5%	2 =	1.53	
EQUATIONS OF STATE.		1 = Virial, C zero, B from Tsonopoulos.					
		2 = Virial, C zero, B from Tsonopoulos.					
REFERENCE.		Boublik, T., Collection of Czechoslovak Chemical Communications, 28, 1771 (1963). (MRL 228)					

Mole Fraction x(1) y(1)	T, K	P, kPa	Vapor Pressure, kPa		Liquid Molar Volume, ml/mol		$\frac{\theta(\text{mix}, P)}{\theta(\text{pure}, P')}$ $\exp(V(P-P')/RT)$		ln Gamma Ratio	Activity Coefficient		E G J/mol
			1	2	1	2	1	2		1	2	
0.0000 0.0000	333.140	51.84	52.20	51.89	93.46	113.68	1.0002	1.0000		1.0000	1.0000	0.0
0.0672 0.0912	333.140	53.41	52.20	51.89	93.46	113.68	0.9995	0.9992	0.3256	1.3879	1.0022	66.8
0.2261 0.2670	333.140	55.92	52.20	51.89	93.46	113.68	0.9983	0.9978	0.2148	1.2629	1.0187	185.8
0.3201 0.3526	333.140	56.72	52.20	51.89	93.46	113.68	0.9979	0.9974	0.1400	1.1944	1.0384	228.4
0.4320 0.4480	333.140	57.51	52.20	51.89	93.46	113.68	0.9975	0.9970	0.0593	1.1397	1.0740	268.7
0.5203 0.5203	333.140	57.61	52.20	51.89	93.46	113.68	0.9975	0.9970	-0.0057	1.1009	1.1071	273.8
0.6029 0.5895	333.140	57.41	52.20	51.89	93.46	113.68	0.9976	0.9971	-0.0613	1.0728	1.1406	262.0
0.7095 0.6770	333.140	56.97	52.20	51.89	93.46	113.68	0.9978	0.9973	-0.1586	1.0391	1.2176	233.8
0.7952 0.7563	333.140	56.08	52.20	51.89	93.46	113.68	0.9982	0.9978	-0.2298	1.0198	1.2833	184.8
0.8752 0.8386	333.140	54.92	52.20	51.89	93.46	113.68	0.9987	0.9984	-0.3057	1.0068	1.3667	124.3
0.8932 0.8600	333.140	54.61	52.20	51.89	93.46	113.68	0.9989	0.9986	-0.3144	1.0062	1.3778	110.0
1.0000 1.0000	333.140	52.17	52.20	51.89	93.46	113.68	1.0000	0.9999		1.0000		0.0

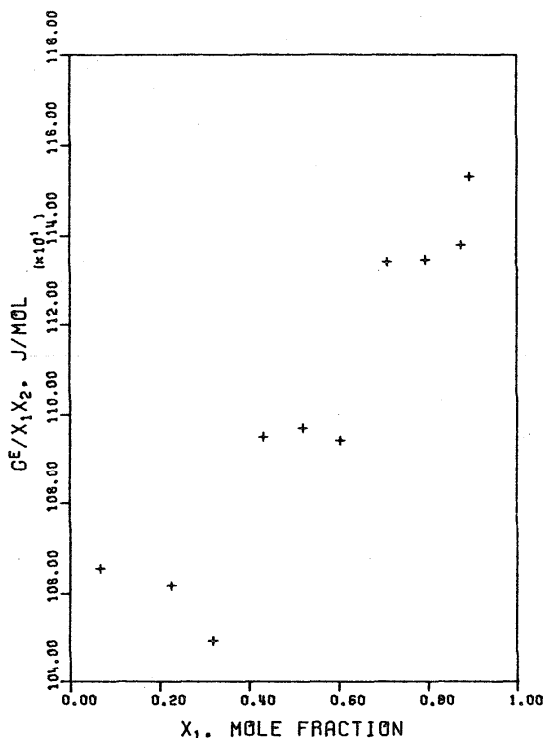


FIGURE 18. A recommended data set at 333.14 K. Data of Boublik, 1963. MRL 228. Ordinate values run from 1040 to 1180.

sets at 40 and 70 °C, the Boublik set is reliable. It is tabulated in table 13 and plotted in figure 18.

6.1.4. 343.14 K

The two best sets at this temperature are those reported by Scatchard, Wood and Mochel, 1939 (MRL 193) and by Diaz Pena and Cheda, 1970 (MRL 1972). The MRL 193 set has only an 0.87 area ratio which restricts it to a C quality rating. The MRL 1792 has a much better area ratio, 0.97,

and the set received a B quality rating. The MRL 193 set appears in table 14 and in figure 19, while the MRL 1792 set is shown in table 15 and in figure 20.

The G^E/x_1x_2 plot for the Diaz Pena and Cheda set (see figure 20) is close to a fair scatter rating, and that set would have received a C quality rating if the fair scatter rating had been assigned. The G^E/x_1x_2 plot for the Scatchard, Wood and Mochel data set (see figure 19) is much better and close to an excellent scatter rating, but that set has only an 0.87

Table 14. The recommended data set at 343.14 K

SYSTEM.		C(6)H(6) + C(6)H(12)		PTY									
RATING.	C	AREA RATIO.	0.87 (0.87 with VE)	P' ERRORS.	0.0% and -0.0% at x(1) = 0 and 1	SCATTER.	Good						
DEVIATION FROM GE/T VS. 1/T CURVE AT x(1) = 0.25.				-0.5%	INFINITE DILUTION ACTIVITY COEFFICIENTS.								
DEVIATION FROM GE/T VS. 1/T CURVE AT x(1) = 0.50.				0.1%	1 =	1.38							
DEVIATION FROM GE/T VS. 1/T CURVE AT x(1) = 0.75.				-0.4%	2 =	1.54							
EQUATIONS OF STATE.		1 = Virial, C zero, B from Tsonopoulos.											
		2 = Virial, C zero, B from Tsonopoulos.											
REFERENCE.													
Scatchard, G., Wood, S. E., Mochel, J. M., Journal of Physical Chemistry, 43, 119 (1939). (MRL 193)													
Mole Fraction		T, K	P, kPa	Vapor Pressure, kPa		Liquid Molar Volume, ml/mol		$\frac{\theta(\text{mix}, P)}{\theta(\text{pure}, P')}$		ln Gamma Ratio	Activity Coefficient		E G / J/mol
x(1)	y(1)			1	2	1	2	1	2		1	2	
0.0000	0.0000	343.122	72.47	73.41	72.47	94.70	115.21	1.0004	1.0000		1.0000	0.0	
0.1186	0.1486	343.122	75.67	73.41	72.47	94.70	115.21	0.9991	0.9985	0.2479	1.2904	1.0070	103.9
0.2409	0.2805	343.122	77.98	73.41	72.47	94.70	115.21	0.9981	0.9973	0.1936	1.2345	1.0171	181.6
0.3759	0.3982	343.122	79.48	73.41	72.47	94.70	115.21	0.9975	0.9966	0.0819	1.1440	1.0539	237.8
0.4945	0.4975	343.122	80.02	73.41	72.47	94.70	115.21	0.9972	0.9964	-0.0001	1.0937	1.0937	255.5
0.6180	0.6027	343.122	79.90	73.41	72.47	94.70	115.21	0.9973	0.9964	-0.0764	1.0586	1.1426	245.6
0.7248	0.6962	343.122	79.12	73.41	72.47	94.70	115.21	0.9976	0.9968	-0.1513	1.0328	1.2014	210.8
0.8659	0.8311	343.122	77.03	73.41	72.47	94.70	115.21	0.9985	0.9978	-0.2840	1.0056	1.3358	124.6
1.0000	1.0000	343.122	73.40	73.41	72.47	94.70	115.21	1.0000	0.9996		1.0000		0.0

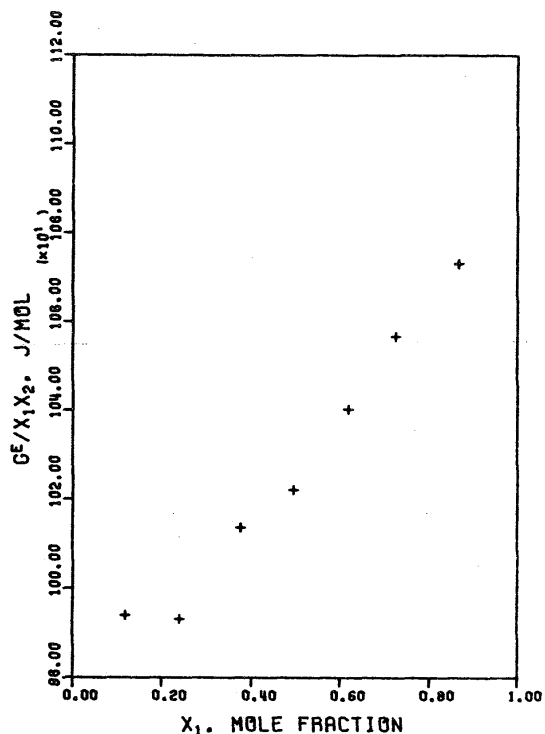


FIGURE 19. The recommended data set at 343.14 K. Data of Scatchard, Wood and Mochel, 1939. MRL 193. Ordinate values run from 980 to 1120.

area ratio compared to 0.97 for the Diaz Pena and Cheda set. However, the relatively low area ratio for an otherwise good set of data is due to the mislocation of the lowest concentration point (see figure 19). That point pulls down the $\ln \gamma'_1 / \gamma'_2$ versus x_1 curve at the left end and causes the left area to be

smaller than it should be. If that point were ignored, the area ratio for the MRL 193 set would be close to that obtained for the MRL 1792 set, and the MRL 193 set would obviously be the better set. Consequently, the Scatchard et al. set is selected as the recommended data set at 343.14 K.

Table 15. The second best set of data at 343.14 K

SYSTEM.	Benzene(1) + Cyclohexane(2)	C(6)H(6) + C(6)H(12)	PTXY
RATING.	B	AREA RATIO. 0.97 (0.97 with VE)	P' ERRORS. 0.0% and 0.0% at $x(1) = 0$ and 1 SCATTER. Good
DEVIATION FROM GE/T VS. 1/T CURVE AT $x(1) = 0.25$.	0.9%	INFINITE DILUTION ACTIVITY COEFFICIENTS. 1 = 1.42	
DEVIATION FROM GE/T VS. 1/T CURVE AT $x(1) = 0.50$.	-1.3%	2 = 1.49	
DEVIATION FROM GE/T VS. 1/T CURVE AT $x(1) = 0.75$.	0.5%		
EQUATIONS OF STATE.	1 = Virial, C zero, B from Tsonopoulos. 2 = Virial, C zero, B from Tsonopoulos.		
REFERENCE.	Diaz Pena, M., Rodriguez Cheda, D., Anales de Quimica, 66, 721 (1970). (MRL 1792)		

Mole Fraction $x(1)$	$y(1)$	T, K	P, kPa	Vapor Pressure, kPa		Liquid Molar Volume, ml/mol		$\frac{\theta(\text{mix}, P)}{\theta(\text{pure}, P')}$ $\exp(V(F-P)/RT)$		ln Gamma Ratio	Activity Coefficient		E G J/mol
				1	2	1	2	1	2				
0.0000	0.0000	343.141	72.54	73.46	72.52	94.70	115.21	1.0004	1.0000		1.0000	0.0	
0.1398	0.1770	343.141	76.25	73.46	72.52	94.70	115.21	0.9988	0.9982	0.2679	1.3127	1.0042	118.8
0.2309	0.2707	343.141	77.96	73.46	72.52	94.70	115.21	0.9981	0.9974	0.2000	1.2419	1.0167	179.2
0.3150	0.3476	343.141	79.11	73.46	72.52	94.70	115.21	0.9976	0.9968	0.1351	1.1856	1.0357	221.5
0.3936	0.4165	343.141	79.72	73.46	72.52	94.70	115.21	0.9974	0.9965	0.0830	1.1453	1.0541	243.5
0.4411	0.4591	343.141	79.85	73.46	72.52	94.70	115.21	0.9973	0.9965	0.0606	1.1284	1.0619	247.9
0.5004	0.5076	343.141	80.00	73.46	72.52	94.70	115.21	0.9972	0.9964	0.0167	1.1018	1.0834	252.6
0.5485	0.5376	343.141	80.06	73.46	72.52	94.70	115.21	0.9972	0.9964	-0.0560	1.0653	1.1265	252.4
0.5963	0.5760	343.141	79.95	73.46	72.52	94.70	115.21	0.9973	0.9964	-0.0958	1.0484	1.1537	245.2
0.6650	0.6452	343.141	79.77	73.46	72.52	94.70	115.21	0.9973	0.9965	-0.0998	1.0508	1.1609	236.6
0.7949	0.7609	343.141	78.28	73.46	72.52	94.70	115.21	0.9980	0.9972	-0.2093	1.0181	1.2550	173.6
0.8614	0.8287	343.141	77.32	73.46	72.52	94.70	115.21	0.9984	0.9977	-0.2628	1.0110	1.3148	135.2
0.9432	0.9231	343.141	75.38	73.46	72.52	94.70	115.21	0.9992	0.9987	-0.3369	1.0035	1.4054	64.6
1.0000	1.0000	343.141	73.47	73.46	72.52	94.70	115.21	1.0000	0.9996		1.0000		0.0

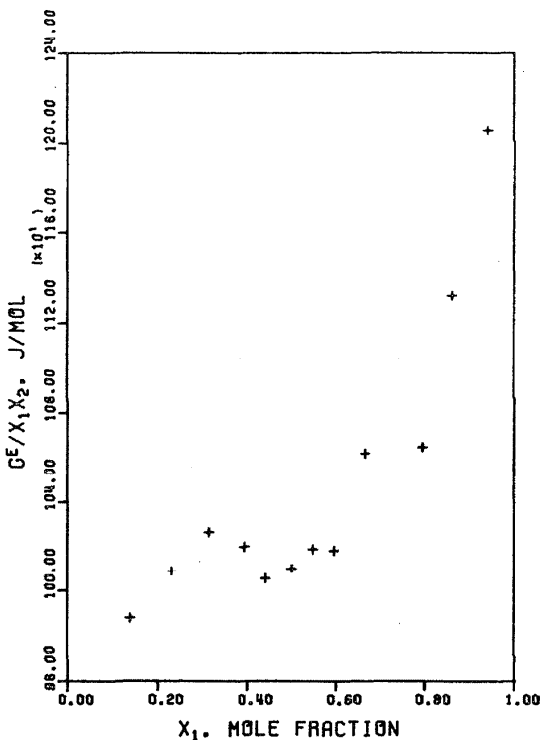


FIGURE 20. The second best set of data at 343.14 K. Data of Diaz Pena and Cheda, 1970. MRL 1792. Ordinate values run from 960 to 1240.

6.2. Isobaric Data Sets

6.2.1. 101.325 kPa

The two best sets of isobaric data at one atmosphere are the Chao and Hougen, 1958 (MRL 234) set and the Nagata,

1962 (MRL 272) set. Both have an area ratio of 0.99 and both have P' errors of 0.1% or less. However, the Nagata set received only a fair scatter rating while the Chao and Hougen set received a good scatter rating. As shown in figure 16, the G^E/T values agree well at $x_1 = 0.25$, poorly at 0.50, and

Table 16. The recommended data set at 101.325 kPa

SYSTEM. Benzene(1) + Cyclohexane(2)				C(6)H(6) + C(6)H(12)				PTXY					
RATING. B		AREA RATIO. 0.99 (0.99 with HE)		P' ERRORS. 0.1% and -0.0% at $x(1) = 0$ and 1		SCATTER. Good							
DEVIATION FROM GE/T VS. 1/T CURVE AT $x(1) = 0.25$. -2.6%				INFINITE DILUTION ACTIVITY COEFFICIENTS. 1 = 1.36									
DEVIATION FROM GE/T VS. 1/T CURVE AT $x(1) = 0.50$. -2.8%				2 = 1.43									
DEVIATION FROM GE/T VS. 1/T CURVE AT $x(1) = 0.75$. -1.4%													
EQUATIONS OF STATE. 1 = Virial, C zero, B from Tsonopoulos.				2 = Virial, C zero, B from Tsonopoulos.									
REFERENCE. Chao, K. C., Hougen, O. A., Chemical Engineering Science, 7, 246 (1958). (MRL 234)													
Mole Fraction		T, K	P, kPa	Vapor Pressure, kPa		Liquid Molar Volume, ml/mol		$\frac{\theta(\text{mix}, P)}{\theta(\text{pure}, P')}$ $\exp(\frac{V(P-P')}{RT})$		ln Gamma Ratio	Activity Coefficient		E G J/mol
x(1)	y(1)			1	2	1	2	1	2		1	2	
0.0000	0.0000	353.844	101.32	103.24	101.26	96.08	116.92	1.0008	1.0000		1.0000		0.0
0.0880	0.1130	352.844	101.32	100.11	98.25	95.95	116.75	0.9996	0.9986	0.2600	1.2991	1.0016	72.0
0.1560	0.1900	352.244	101.32	98.27	96.48	95.87	116.66	0.9989	0.9978	0.2208	1.2544	1.0058	117.7
0.2310	0.2680	351.644	101.32	96.45	94.73	95.79	116.56	0.9981	0.9971	0.1808	1.2165	1.0152	166.2
0.3080	0.3430	351.144	101.32	94.96	93.29	95.73	116.48	0.9975	0.9964	0.1428	1.1853	1.0275	207.6
0.4000	0.4220	350.843	101.32	94.08	92.44	95.69	116.43	0.9972	0.9960	0.0744	1.1331	1.0517	234.1
0.4700	0.4820	350.743	101.32	93.78	92.15	95.68	116.41	0.9971	0.9959	0.0316	1.1047	1.0702	241.4
0.5450	0.5440	350.743	101.32	93.78	92.15	95.68	116.41	0.9971	0.9959	-0.0205	1.0753	1.0974	238.7
0.6250	0.6120	350.743	101.32	93.78	92.15	95.68	116.41	0.9970	0.9959	-0.0716	1.0548	1.1330	233.8
0.7010	0.6780	350.943	101.32	94.37	92.72	95.70	116.45	0.9973	0.9962	-0.1241	1.0356	1.1723	210.3
0.7570	0.7270	351.144	101.32	94.96	93.29	95.73	116.48	0.9975	0.9964	-0.1736	1.0222	1.2158	187.1
0.8220	0.7910	351.443	101.32	95.86	94.15	95.77	116.53	0.9979	0.9968	-0.2160	1.0150	1.2596	155.9
0.8910	0.8630	352.043	101.32	97.66	95.89	95.85	116.62	0.9986	0.9976	-0.2780	1.0035	1.3249	98.8
0.9530	0.9380	352.644	101.32	99.49	97.66	95.92	116.72	0.9993	0.9984	-0.3107	1.0017	1.3665	47.7
1.0000	1.0000	353.244	101.32	101.35	99.45	96.00	116.82	1.0000	0.9992		1.0000		0.0

show only fair agreement at 0.75. The location of the best G^E/T versus $1/T$ curve resulted in percent deviations of -2.6, -2.8, and -1.4 for the Chao and Hougen set compared to -0.9, 4.0, 3.3 for the Nagata set.

The Chao and Hougen set is tabulated in table 16 and

plotted in figure 4, while the Nagata set appears in table 17 and figure 21. Based on the G^E/x_1x_2 plots and the lower percent deviations of the Chao and Hougen set from the best G^E/T versus $1/T$ curve, the Chao and Hougen set is selected as the recommended data set at one atmosphere.

Table 17. The second best set at 101.325 kPa

SYSTEM.				C(6)H(6) + C(6)H(12)				PTXY							
RATING.				P' ERRORS.				SCATTER.							
Benzene(1) + Cyclohexane(2)				0.99 (0.99 with HE)				0.1% and -0.0% at $x(1) = 0$ and 1				Fair			
DEVIATION FROM G^E/T VS. $1/T$ CURVE AT $x(1) = 0.25$.				-0.9%				INFINITE DILUTION ACTIVITY COEFFICIENTS.				1 = 1.40			
DEVIATION FROM G^E/T VS. $1/T$ CURVE AT $x(1) = 0.50$.				4.0%								2 = 1.47			
DEVIATION FROM G^E/T VS. $1/T$ CURVE AT $x(1) = 0.75$.				3.3%											
EQUATIONS OF STATE.				1 = Virial, C zero, B from Tsonopoulos.											
				2 = Virial, C zero, B from Tsonopoulos.											
REFERENCE.				Nagata, I., Journal of Chemical and Engineering Data, 7, 461 (1962). (MRL 272)											
Mole Fraction $x(1)$	$y(1)$	T, K	P, kPa	Vapor Pressure, kPa		Liquid Molar Volume, ml/mol		$\theta(\text{mix}, P)/\theta(\text{pure}, P')$ $\exp(V(P-P')/RT)$		ln Gamma Ratio	Activity Coefficient		E G J/mol		
				1	2	1	2	1	2		1	2			
0.0000	0.0000	353.844	101.32	103.24	101.26	96.08	116.92	1.0008	1.0000		1.0000	1.0000	0.0		
0.1010	0.1310	352.644	101.32	99.49	97.66	95.92	116.72	0.9993	0.9984	0.2763	1.3200	1.0013	85.6		
0.1710	0.2110	352.043	101.32	97.66	95.89	95.85	116.62	0.9986	0.9976	0.2423	1.2784	1.0032	130.8		
0.2560	0.2930	351.543	101.32	96.15	94.44	95.78	116.54	0.9980	0.9969	0.1690	1.2037	1.0164	174.1		
0.3430	0.3760	350.943	101.32	94.37	92.72	95.70	116.45	0.9973	0.9961	0.1268	1.1738	1.0339	224.3		
0.4280	0.4450	350.643	101.32	93.49	91.87	95.66	116.40	0.9969	0.9958	0.0527	1.1234	1.0656	251.1		
0.5250	0.5290	350.543	101.32	93.20	91.59	95.65	116.38	0.9968	0.9956	-0.0003	1.0920	1.0922	256.8		
0.5710	0.5640	350.543	101.32	93.20	91.59	95.65	116.38	0.9968	0.9956	-0.0449	1.0705	1.1194	254.4		
0.6650	0.6450	350.743	101.32	93.78	92.15	95.68	116.41	0.9970	0.9959	-0.1050	1.0448	1.1604	230.4		
0.7590	0.7280	351.043	101.32	94.67	93.01	95.71	116.46	0.9974	0.9963	-0.1794	1.0239	1.2250	195.2		
0.8100	0.7770	351.343	101.32	95.56	93.86	95.75	116.51	0.9978	0.9967	-0.2187	1.0149	1.2628	164.4		
0.8630	0.8340	351.743	101.32	96.75	95.02	95.81	116.58	0.9982	0.9972	-0.2434	1.0102	1.2885	127.3		
0.9450	0.9260	352.444	101.32	98.88	97.07	95.90	116.69	0.9991	0.9982	-0.3347	1.0032	1.4019	63.2		
1.0000	1.0000	353.244	101.32	101.35	99.45	96.00	116.82	1.0000	0.9992		1.0000		0.0		

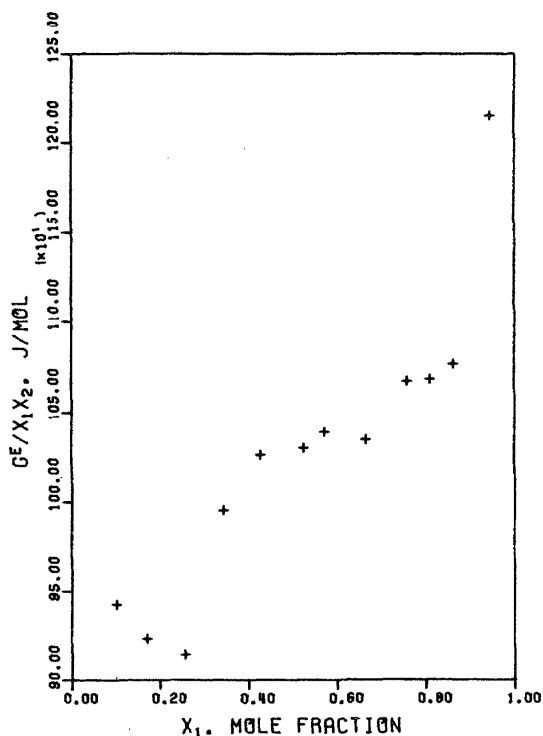


FIGURE 21. Second best set of data at 101.325 kPa. See figure 4 for the recommended set. Data of Nagata, 1962. MRI. 272. Ordinate values run from 900 to 1250.

6.2.2. Other Pressures

The 10 and 20 atmosphere data sets of Tao, 1952 (MRL 334) received fair scatter ratings, have area ratios of 0.97 and 0.92, respectively, and have P' errors of -1.57 and 0.69% at 10 atmospheres and of -1.05 and 1.14% at 20 atm. It was possible to draw all three G^E/T curves fairly close to these two data sets without straining the slope requirements seriously. However, all the firm points on that curve were at

pressures less than 1.0 atmosphere, hence the percent deviations of the 10 and 20 atmosphere points should not be given much weight in judging their quality.

The large P' errors prevent the selection of these two data sets as recommended data sets. However, they are the best available data at pressures above 1.0 atmosphere and for that reason the sets are tabulated in tables 18 and 19. Figures 22 and 9 show the G^E/x_1x_2 plots for those two data sets. Those plots give additional evidence as to why these sets should not be considered to be recommended data sets.

Table 18. One of the two best data sets at pressures above 101.325

SYSTEM. Benzene(1) + Cyclohexane(2)				C(6)H(6) + C(6)H(12)				PTXY					
RATING. D				AREA RATIO. 0.97 (0.97 with HE)				P' ERRORS. -1.6% and 0.7% at x(1) = 0 and 1		SCATTER. Fair			
DEVIATION FROM GE/T VS. 1/T CURVE AT x(1) = 0.25.				3.6%				INFINITE DILUTION ACTIVITY COEFFICIENTS.		1 = 1.15			
DEVIATION FROM GE/T VS. 1/T CURVE AT x(1) = 0.50.				0.7%						2 = 1.18			
DEVIATION FROM GE/T VS. 1/T CURVE AT x(1) = 0.75.				-4.0%									
EQUATIONS OF STATE.				1 = Virial, C zero, B from Tsonopoulos.									
				2 = Virial, C zero, B from Tsonopoulos.									
REFERENCE. Tao, L.-C., Ph.D. Dissertation, University of Wisconsin, Madison, Wisconsin, 1952. (MRL 334)													
Mole Fraction		T, K	P, kPa	Vapor Pressure, kPa		Liquid Molar Volume, ml/mol		$\theta(\text{mix}, P)/\theta(\text{pure}, P')$ $\exp(V(P-P')/RT)$		ln Gamma Ratio	Activity Coefficient		E G J/mol
x(1)	y(1)			1	2	1	2	1	2		1	2	
0.0000	0.0000	456.985	1013.24	1098.20	1029.44	114.17	140.33	1.0178	1.0038		1.0000	0.0	
0.2380	0.2670	452.683	1013.24	1018.79	956.00	113.12	138.96	1.0016	0.9863	0.1032	1.1175	1.0056	115.5
0.3290	0.3520	451.883	1013.24	1004.50	942.78	112.93	138.71	0.9985	0.9831	0.0523	1.0777	1.0204	143.3
0.4150	0.4340	451.383	1013.24	995.64	934.58	112.81	138.56	0.9966	0.9812	0.0278	1.0607	1.0292	155.0
0.4840	0.4990	451.082	1013.24	990.35	929.69	112.74	138.47	0.9955	0.9800	0.0101	1.0501	1.0371	159.1
0.5650	0.5710	450.983	1013.24	988.60	928.07	112.72	138.44	0.9951	0.9797	-0.0255	1.0307	1.0548	151.2
0.6310	0.6350	450.782	1013.24	985.09	924.82	112.67	138.37	0.9943	0.9789	-0.0327	1.0292	1.0609	149.9
0.7010	0.7000	450.782	1013.24	985.09	924.82	112.67	138.37	0.9943	0.9790	-0.0548	1.0212	1.0762	137.5
0.7700	0.7670	450.883	1013.24	986.84	926.44	112.69	138.40	0.9946	0.9795	-0.0671	1.0173	1.0852	119.9
0.8480	0.8400	450.983	1013.24	988.60	928.07	112.72	138.44	0.9950	0.9800	-0.1112	1.0101	1.1262	99.8
0.9210	0.9150	451.183	1013.24	992.12	931.32	112.76	138.50	0.9957	0.9809	-0.1304	1.0103	1.1482	76.2
1.0000	1.0000	451.983	1013.24	1006.28	944.43	112.95	138.74	0.9986	0.9842		1.0000		0.0

Table 19. One of the two best data sets at pressures above 101.325

SYSTEM. Benzene(1) + Cyclohexane(2)				C(6)H(6) + C(6)H(12)				PTXY					
RATING. D				AREA RATIO. 0.92 (0.92 with HE)				P' ERRORS. -1.0% and 1.1% at x(1) = 0 and 1		SCATTER. Fair			
DEVIATION FROM GE/T VS. 1/T CURVE AT x(1) = 0.25.				-4.3%				INFINITE DILUTION ACTIVITY COEFFICIENTS.		1 = 1.10			
DEVIATION FROM GE/T VS. 1/T CURVE AT x(1) = 0.50.				-1.6%						2 = 1.12			
DEVIATION FROM GE/T VS. 1/T CURVE AT x(1) = 0.75.				5.4%									
EQUATIONS OF STATE.				1 = Redlich-Kwong(Peng-Robinson modification.)									
				2 = Redlich-Kwong(Peng-Robinson modification.)									
REFERENCE. Tao, L.-C., Ph.D. Dissertation, University of Wisconsin, Madison, Wisconsin, 1952. (MRL 334)													
Mole Fraction		T, K	P, kPa	Vapor Pressure, kPa		Liquid Molar Volume, ml/mol		$\theta(\text{mix}, P)/\theta(\text{pure}, P')$ $\exp(V(P-P')/RT)$		ln Gamma Ratio	Activity Coefficient		E G J/mol
x(1)	y(1)			1	2	1	2	1	2		1	2	
0.0000	0.0000	501.203	2026.49	2202.68	2048.00	128.61	159.21	1.0325	1.0043		1.0000	0.0	
0.1380	0.1530	497.702	2026.49	2093.73	1947.71	127.10	157.25	1.0135	0.9844	0.0726	1.0876	1.0064	70.6
0.2340	0.2520	496.702	2026.49	2063.37	1919.75	126.69	156.71	1.0079	0.9789	0.0498	1.0661	1.0090	90.3
0.3310	0.3490	495.901	2026.49	2039.30	1897.59	126.36	156.28	1.0035	0.9746	0.0321	1.0514	1.0128	103.5
0.4530	0.4730	494.801	2026.49	2006.54	1867.43	125.92	155.71	0.9975	0.9688	0.0323	1.0519	1.0129	123.0
0.5810	0.5910	494.101	2026.49	1985.91	1848.42	125.65	155.35	0.9936	0.9653	-0.0071	1.0314	1.0331	129.7
0.6720	0.6760	493.800	2026.49	1977.10	1840.32	125.53	155.19	0.9919	0.9640	-0.0305	1.0228	1.0486	125.9
0.7550	0.7540	493.700	2026.49	1974.18	1837.62	125.49	155.14	0.9913	0.9638	-0.0545	1.0162	1.0672	115.2
0.8460	0.8430	493.700	2026.49	1974.18	1837.62	125.49	155.14	0.9912	0.9642	-0.0724	1.0138	1.0840	98.7
0.9000	0.8960	494.000	2026.49	1982.97	1845.72	125.61	155.30	0.9926	0.9661	-0.0938	1.0099	1.1031	76.8
0.9020	0.8980	493.900	2026.49	1980.04	1843.02	125.57	155.24	0.9921	0.9655	-0.0945	1.0109	1.1050	80.4
0.9610	0.9600	494.201	2026.49	1988.85	1851.13	125.68	155.40	0.9936	0.9675	-0.0770	1.0114	1.0863	57.9
1.0000	1.0000	494.701	2026.49	2003.58	1864.70	125.88	155.66	0.9961	0.9705		1.0000		0.0

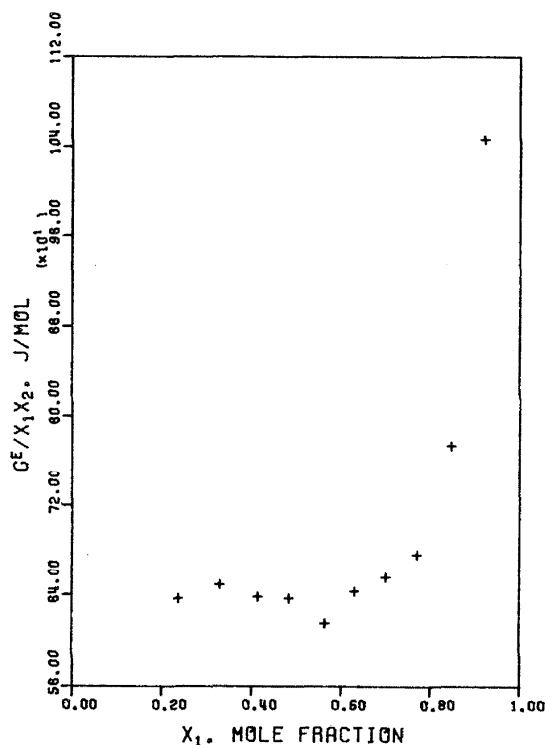


FIGURE 22. One of the two best available sets of data at pressures above one atmosphere. See figure 9 for the other set. Data of Tao, 1952. MRL 334. Ordinate values run from 560 to 1120.

7. Equipment Types

Table 20 lists the kinds of VLE apparatuses used to measure the *PTxy* vapor-liquid equilibrium data covered in this report. Brief descriptions of the equipment used in each literature document are given in table 21.

Table 20. Popularity of various types of apparatus

Apparatus	MRL numbers of user documents
Colburn still	44, 272 ^a
Colburn-Gillespie still	234 ^a
Fenske still	310
Gillespie still	228 ^a , 241, 1792 ^a
Griswold still	271
Kireyev still	26, 28
Othmer still	128, 186
Scatchard still	193 ^a , 297
Miscellaneous stills	31, 315, 334 ^a
Multi-stage Ellis stills	917
Static cell	269
Static cell, vapor circulation	40032 ^a

^aDocuments reporting data sets which were selected as recommended, best or second best data sets in the Recommended Data Sets section.

Table 21. Description of VLE apparatuses

MRL Number	Major Characteristics of Apparatus
26	<i>PTxy</i> ; single-stage, modified Kireyev still; vapor circulated; condenser vented to a pressure regulator, no pressurizing gas used; no description of pressure measurement device; boiling temperatures determined in a separate ebullimeter; phase analyses by specific gravity; upper portion of boiling flask covered with an insulating hood.
31	<i>PTxy</i> ; single-stage; vapor circulation; condenser vented to atmosphere; temperature measured with a thermocouple which had one junction at the equilibrium liquid surface and the other junction in boiling benzene to compensate for atmospheric pressure fluctuations; phase analyses by refractive index; temperature-controlled air bath kept within 1 C of the boiling temperature.
43	<i>PTxy</i> ; multi-stage, six Ellis stills; vapor circulated; condensers vented to a common manifold connected to a manostat; no description of pressure measurement device; temperature measured with glass thermometer at Cottrell tube discharge just above liquid surface; phase analyses by refractive index; heated air bath with no thermostat; vapor disengaging section of still heated with electrical heater.
44	<i>PTxy</i> ; single-stage, modified Colburn still; vapor circulated; condenser vented to pressure-controlled surge chamber with air bleed for vacuum operation; pressure measured with mercury manometer; temperature of boiling liquid measured; phase analyses by refractive index; still heated by a temperature controlled liquid bath, with wound electrical heaters used on the vapor head and the condensate return line (flash boiler).
128 186	<i>PTxy</i> ; single-stage, Othmer still; vapor circulated; condenser vented to atmosphere; temperature measured by thermometer in vapor space; phase analyses by refractive index; no description of any external bath, insulation or heaters.
193	<i>PTxy</i> ; single-stage, Scatchard still; vapor circulated; condenser connected to a pressure-controlled tank with a "confining" gas bleed; pressure measured with precision barometer; temperature of mixed vapor and liquid measured with a twenty-junction thermocouple in a well at the outlet of a Cottrell pump; phase analyses from densities; the manostat tank was thermostated but not the still; some insulation at top of boiler to reduce condensation.
228	<i>PTxy</i> ; single-stage, modified Gillespie still; both vapor and liquid circulated; condenser connected to pressure-controlled flasks with an air bleed; pressure measured with a mercury manometer read with a cathetometer; temperature measured by a thermometer at Cottrell tube discharge; phase analyses by refractive index; no description of external bath, insulation or heaters.
234	<i>PTxy</i> ; single-stage, combination of Colburn and Gillespie stills; both vapor and liquid circulated; condenser connected to a pressure regulating device where pressure was controlled by bleeding compressed air through a nozzle immersed in water; no description of pressure measurement device; temperature measured with thermocouple at discharge of Cottrell tube; phase analyses by refractive index; insulation and external heaters used to ensure adiabatic operation of the equilibrium phase chambers of the still.
241	<i>PTxy</i> ; single-stage, modified Gillespie still; both vapor and liquid circulated; condenser connected to a surge volume maintained at 760 mm Hg pressure by adding or removing air; no description of pressure measurement device; temperature measured with a glass thermometer at Cottrell pump discharge; phase analyses by refractive index; the Cottrell lift was heated electrically, no other external heaters or insulation was described.
269	<i>PTxy</i> ; single static cell; cell connected to balance pressure manostat by capillary tube filled with equilibrium liquid; manostat pressure measured with a manometer and corrections were made for hydrostatic head difference; temperature measured by glass thermometer in the thermostated air bath surrounding the static cell; liquid phase analysis by refractive index, vapor phase composition obtained by mass balance.
271	<i>PTxy</i> ; single-stage, Griswold still; vapor circulated; pressure measured with a calibrated Bourdon gauge; temperature measured with thermocouples in a metal well in the liquid space; phase analysis by density; entire apparatus was insulated.
272	<i>PTxy</i> ; single-stage, modified Colburn still; vapor circulated; condenser vented to atmosphere; no description of pressure measuring device; temperature measured by thermocouple in a well in the liquid phase; phase analyses by refractive index; some compensating wound electrical heaters but no thermostated bath or insulation.
297	<i>PTxy</i> ; single-stage, modified Scatchard still; vapor circulated; condenser connected to a pressure regulator with an air bleed; no description of pressure measurement device; temperature measured with a glass thermometer; phase analyses by refractive index; no description of any special heaters, insulation or thermostated bath.
310	<i>PTxy</i> ; single-stage Fenske still; neither the vapor nor the liquid is circulated; condenser connected to an electrically operated barostat; no description of the pressure measuring device; temperature measured by a thermocouple at the discharge of a Cottrell-like boiling tube situated in the liquid phase; phase analyses by refractive index; vapor section of the still enclosed in a heated air bath.

Table 21. Description of VLE apparatuses—Continued

MRL Number	Major Characteristics of Apparatus
315	PTxy; single-stage still; vapor circulated; condenser connected to a pressure tank controlled by an air bleed through a nozzle immersed in water and set with an ebulliometer containing water; pressure measured with a mercury manometer; temperature measured with a glass thermometer immersed in the liquid; phase analyses by refractive index; liquid portion of still immersed in an oil bath, vapor portion heated electrically and with heating lamps.
334	PTxy; single-stage still; both vapor and liquid phases circulated; pressure controlled by venting vapor as necessary through a nitrogen loaded diaphragm valve; nitrogen pressure measured with a pressure gauge; temperature measured by thermocouple at point where vapor disengages from liquid surface; phase analyses by refractive index; adiabatic conditions provided by electrical heaters on vapor disengaging portion of still.
917	Same data as in MRL 43.
1792	PTxy; single-stage, modified Gillespie still; vapor and liquid circulated; condenser connected to vacuum system with air bleed; pressure measured by mercury manometer; temperature measured by thermocouple at discharge of Cottrell tube; phase analyses by density; an external heater wound around the boiler was used in addition to the internal heater, and the Cottrell tube and disengaging section was insulated.
40032	PTxy; single static cell; vapor circulated through sampling bulbs without condensation; a quartz Bourdon gauge was used as a nulling device between the vapor and a balance gas (argon); pressure of the balance gas measured with a thermostated mercury manometer; temperature measured in the temperature-controlled water bath containing the equilibrium cell; phase analyses by refractive index; equilibrium cell in a water bath controlled to ± 0.01 C, while the vapor sampling bulbs and the nulling device (quartz Bourdon gauge) were mounted in a temperature-controlled air bath regulated to ± 0.5 C at about 1 C above the water bath temperature.

It is surprising that all the workers reporting *PTxy* data for benzene + cyclohexane have used refractive index or density of the phase analyses. Large sample sizes are required for those analytical methods (relative to gas-liquid chromatography) and that requires some sort of circulating equilibrium device to provide phase samples of sufficient size.

7.1. Equilibrium Stills

The circulating equilibrium stills have been popular because they provide the large phase samples required by the refractive index and density analytical methods. Eight of the more widely used types—Colburn, Ellis, Fenske, Gillespie, Griswold, Kireyev, Othmer, and Scatchard—appear in table 20.

The documents which reported those data sets selected as recommended, best, or second best data sets in the Recommended Data Sets section have been marked with asterisks in table 20. Three of those documents—MRL 228, 234 and 1792—used some version of the Gillespie still.

Over the last three decades, the equilibrium stills have evolved to a form best typified by the Gillespie still. In that design, both the vapor and liquid phases are circulated and the equilibrium vapor and liquid samples are both collected outside the stillpot. The circulation starts in the stillpot which is the chamber to which energy is supplied to vaporize some liquid to form the vapor phase. The energy may come from an internal or external heat source, or it may come from a vaporized condensate stream which passes through a wound electrical heater as it flows from the vapor-phase sample collector back to the stillpot.

The vapor phase in the stillpot is channeled into a Cottrell pump and carries slugs of liquid with it up the Cottrell tube. At the discharge of the Cottrell tube, the two phases

must be in equilibrium if the data are to be accurate. The mixed phases impinge on the well holding the temperature sensor in the center of the phase separator chamber. The diameter of the separator is large enough to allow the two phases to disengage. The liquid falls to the bottom of the chamber from whence it flows to the liquid sample collector. The vapor flows out through a chilled condenser from which the condensate flows to the vapor sample collector. Both of the sample collectors have an over-flow pipe or weir which allows the materials to flow back to the stillpot when the collectors are full. Capillary tubes are often used for the return lines to control the rate of flow. As mentioned previously, the condensate return line may be heated in order to return a saturated or slightly super-heated vapor to the stillpot.

For isobaric operation the condenser is connected to a pressure control device of some kind. An "inert" gas bleed (usually nitrogen or air) must be used along with a vacuum pump to maintain an operating pressure other than ambient pressure. Precautions must be taken to minimize contamination of the vapor condensate with the inert gas.

The pressure measurement device measures the pressure in the pressure controlled region to which the condenser is vented. Precautions must be taken to make sure the pressure drop between the discharge point of the Cottrell tube and the pressure measurement device is essentially zero.

The phases are circulated (usually for an hour or more) until the still has reached steady-state at all points. The only "equilibrium" point is at the discharge of the Cottrell pump; the achievement of equilibrium at that point must be instantaneous. The equilibrium achieved there (as indicated by the temperature reading) will keep changing until the stillpot composition stops changing, and the stillpot composition will continue to change until the sample collectors have been flushed out. Hence, the need for a long period of operation to provide phase samples which correspond to the temperature recorded when the samples are taken.

The best set of data was taken with the Scatchard still (MRL 193). That still also collects its vapor and liquid samples outside the heated (stillpot) region but differs from the Gillespie design in that the phase separator also serves as the liquid sample collector.

The combination of the Colburn and Gillespie stills used by Chao and Hougen (MRL 234) had all the features described above for the Gillespie still. The Tao apparatus (MRL 334) also circulated both phases and sampled them both outside the stillpot.

Of those stills which produced data sets cited in the Recommended Data Set section, only the Colburn still used by Nagata (MRL 272) deviated markedly from the Gillespie circulation pattern. In the Colburn still, the stillpot serves as both the phase separator and the liquid sample collector, and also contains the temperature sensor. The energy input is to the returning condensate flowing from the vapor sample collector back to the stillpot. The condensate is completely vaporized and that vapor bubbles through the liquid in the stillpot before disengaging to rise and pass through the condenser.

It is easy to measure inaccurate data regardless of the still design, and the skill and patience of the operator is

usually the most important factor in the measurements. Nevertheless, the tabulation in table 20 indicates that the Gillespie design is the preferred one if a circulating equilibrium still is to be used.

One document (MRL 917) reported data obtained on a multistage apparatus using six Ellis stills in series. The multistage approach was an attempt to reduce the time required to obtain enough points to define the entire binary equilibrium curve. The data obtained received a C rating which means useful data were obtained. Nevertheless, the multistage scheme is not recommended because of the obvious difficulty in achieving steady-state in all the various liquid and vapor regions simultaneously.

7.2. Static Cells

The availability of gas-liquid chromatography units for the last two decades has eliminated the need for large phase samples. That development makes more attractive the use of static cells where equilibrium is the only consideration; one need not worry about steady state if phases are not circulated.

Two sets of benzene + cyclohexane data were obtained with static cells—MRL 269 and 40032. Only the data from MRL 40032 (Inoue, Azumi, and Suzuki) are useful; those data are similar in quality to the good MRL 193 data. Actually, the Inoue et al. cell was not a true static cell. Refractive index was used for the phase analyses which required the circulation of the equilibrium vapor from the equilibrium cell through two large glass sample bulbs in series. Those bulbs were kept slightly warmer than the equilibrium cell. The equilibrium cell was in a thermostated liquid bath while the vapor sample bulbs were in a thermostated air bath above the liquid bath.

The use of static cells depends upon the availability of nulling pressure transducers which can be mounted in the temperature controlled region and kept slightly warmer than the equilibrium cell. The nulling device is exposed to the equilibrium vapor on one side and a balance gas (such as nitrogen or argon) on the other side. When the nulling device reads zero, the balance gas pressure equals the equilibrium vapor pressure and that pressure can be measured outside the temperature-controlled region at ambient temperatures. Suitable nulling devices which can handle a wide range of temperatures, pressures, and chemicals have become available only within the last decade. That development, plus the availability of the gas-liquid chromatography unit with its ability to analyze very small samples, will make the static cell apparatuses more popular in the future. The static cell approach has a higher potential for reliability than does the circulating stills.

8. New Experimental Measurements Needed

The benzene + cyclohexane system has special value as a test system for new VLE apparatuses and for correlation procedures. Reliable or fairly reliable data sets are available only at the following conditions: 10 °C, 40 °C, 60 °C, 70 °C, and 1.0 atmosphere. The data sets at 10 and 60 °C are lone sets which should be checked by duplication. Multiple sets

are available at 40 °C, 70 °C, and 1.0 atm, but new measurements at 70 °C and 1.0 atm are needed to reach the level of certainty established by the Scatchard, Wood and Mochel data at 39.997 °C. Even the Scatchard et al. set needs some backup because that data set is hampered by an inadequate number of data points.

Better data are badly needed above 1.0 atm. Those new data sets should be isothermal data sets because isothermal data are much more useful than isobaric data. Temperatures of 90, 110, 130 and 150 °C are suggested. That would provide a 140 degree range for correlation purposes, and would cover adequately the range of conditions to which the benzene + cyclohexane binary might be exposed in petroleum and chemical processing units.

9. Pure Compound Values

The pure compound vapor pressure and liquid density values used by program PTXY2 to reduce the experimental P , T , x , y values to activity coefficient and excess Gibbs function values always come from the pure compound data bank CDATAI regardless of whether or not the authors reported pure compound values. A major effort has been made to store the best possible pure compound values in CDATAI and the use of those carefully selected values in itself constitutes a check on the accuracy of a VLE data set because it checks the purity of the components. For example, a data set may appear to be good because it plots well and it satisfies the Gibbs-Duhem consistency test when the authors' pure compound vapor pressures are used. However, that appearance of accuracy is deceiving if impure components were used because the data are not actually for the stated compounds. If impure components were used, the Gibbs-Helmholtz test will usually indicate something is wrong with the data—if the Gibbs-Helmholtz test can be made. Another, more reliable, way to test the data is to substitute well-established pure component vapor pressure values for those of the authors. If their VLE data are based on impure components, the end-point test and the Gibbs-Duhem test will then also indicate problems with the data set.

The VLE data sets evaluated for the benzene(1) + cyclohexane(2) system fell in the temperature range from 283 to 531 K. The vapor pressure data over that range for both benzene and cyclohexane were represented in CDATAI by the two Wagner equation fits given in table 22. The P_c and T_c values used were 4.898 MPa and 562.16 K for benzene and 4.075 MPa and 553.64 K for cyclohexane.

The benzene vapor pressure correlations are based on data (one or more points) from 90 primary literature sources; the data from another 50 primary literature documents were

Table 22. Pure compound vapor pressure data

$$\ln P_r = \frac{1}{T_r} \left[A(1-T_r) + B(1-T_r)^{1.5} + C(1-T_r)^3 + D(1-T_r)^6 \right]$$

	Benzene		Cyclohexane	
	278 to 374 K	333 to 563 K	279 to 374 K	333 to 354 K
A	-0.69650565D+01	-0.69755790D+01	-0.69647641D+01	-0.68713138D+01
B	0.12975649D+01	0.13234387D+01	0.13517692D+01	0.10128423D+01
C	-0.26030426D+01	-0.26475417D+01	-0.29164844D+01	-0.18311178D+01
D	-0.33168888D+01	-0.31913135D+01	-0.18325037D+01	-0.69946415D+01

totally excluded from the correlations. The low-range correlation fitted 268 selected data points with a RMSD of 0.04 kPa. The high range correlation used 176 selected points with a RMSD of 1.23 kPa. In the overlap region, the two correlations agree within 2.0 in the sixth digit.

The cyclohexane vapor pressure correlations are based on the data from 80 primary literature sources each of which contributed one or more data points. The data from another 38 primary literature documents were totally excluded. The low-range correlation fitted 212 selected data points with a RMSD of 0.056 kPa. The analogous numbers for the high-range correlation are 93 and 1.49 kPa. In the overlap region, the two correlations agree within 1.0 in the fourth digit.

The liquid density correlations in CDATA1 which provided values needed by program PTXY2 have been presented in a parallel paper [1] on the evaluation of the excess volume data for the benzene + cyclohexane system.

The actual vapor pressure and liquid density values used for each set of data are shown in columns 5 through 8 in the VLE tabulations. (See tables 10 through 19 for examples.)

The tabulations do not give the individual pure component fugacity coefficients. However the sources of those values, and the mixture fugacity coefficient values, are given under the Equation of State heading on each table. The fugacity coefficients are tabulated in the combined correction term

$$\frac{\phi(\text{mix}, P)}{\phi(\text{pure}, P')} \exp[V(P - P')/RT]$$

where

$$\phi(\text{mix}, P) = \hat{\phi}_{i,P} = \hat{f}_{i,P}/y_i P$$

$$\phi(\text{pure}, P') = \phi_{i,P'} = f_i/P'$$

10. Data Set Tabulations

Tabulation of all the data sets covered is not feasible in this paper due to their large number. Any person who wants a complete set of the tables should contact the Director, Thermodynamics Research Laboratory, Box 1144, Washington University, St. Louis, Missouri 63130. Copies of the VLE tables will be provided for \$1.00 per table plus \$5.00 for handling charges. An invoice will be mailed with the tables.

The tables will be provided only in a complete set for a given system, i.e., requests for tables for individual sets of data will not be processed.

11. Bibliography

Table 23 is the bibliography for P , T , x , y vapor-liquid equilibrium data for the benzene + cyclohexane system. The identifying number for each citation is the Laboratory's Master Reference List (MRL) number which was assigned to the cited document when its copy was retrieved. The MRL number relates the citation in table 23 to the data set tabulation, and to the various tables and figures used in this report. A few of the documents listed in table 23 reported the same data as some other document. When this occurred, a tabulation was prepared for only one of the two documents reporting the same data.

TABLE 23. Bibliography for $PTxy$ vapor-liquid equilibrium data

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|--------|---|
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12. Nomenclature

- A_k Empirical constants in Redlich-Kister equation.
 D Degree of Redlich-Kister equation.
 k Index in Redlich-Kister equation.
 M^E Any molar excess property.
MRL Acronym for Master Reference List.
 G^E Molar excess Gibbs function.
 H^L Molar enthalpy of a liquid mixture.
 $H_{i,P}^L$ Molar enthalpy of liquid component i at the system temperature and the pressure P .
 $H_{i,P'}^L$ Molar enthalpy of liquid component i at the system temperature and the component's vapor pressure.
 H^E Molar excess enthalpy.
 P Pressure.
 P'_i Component i vapor pressure.
 R Gas constant.
 T Absolute temperature.
 V^L Molar volume of a liquid mixture.
 $V_{i,P}^L$ Molar volume of liquid component i at the system temperature and pressure.
 $V_{i,P'}^L$ Molar volume of liquid component i at the system temperature and the component's vapor pressure.
 V^E Molar excess volume.
 x_i Liquid mole fraction of component i .
 y_i Vapor mole fraction of component i .
 γ_i Liquid-phase activity coefficient of component i referred to the total pressure standard state.
 γ'_i Liquid-phase activity coefficient of component i referred to the vapor-pressure standard state.
 $\hat{\phi}_{i,P}$ Vapor-phase fugacity, $\hat{f}_{i,P}/y_i P$, for component i in a

gaseous mixture at the system temperature and pressure.

$\phi_{i,P}$ Vapor-phase fugacity, f_i/P , of pure component i as a gas at its vapor pressure at the system T .

13. Acknowledgments

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