Evaluation of Binary Excess Volume Data for C_6 Hydrocarbons. Benzene + Cyclohexane

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The methods used to evaluate excess volume data are described. The evaluation results for the benzene + cyclohexane system are presented. The needs for new experimental data are defined.

Key words: benzene; cyclohexane; evaluation procedures; excess volume; volume change of mixing.

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1. Introduction

This paper is the first in a series of evaluation reports on excess volume (V^E) data for binary mixtures of nonelectrolyte liquids. It is accompanied by two parallel papers [1, 2][1] each of which is the lead paper in similar series for excess enthalpy (H^E) and *PTxy* vapor-liquid equilibrium (VLE) data. Each of these three lead papers presents the specific evaluation methods used for the given property, and then applies those methods to the first binary system to be reported—the benzene(1) + cyclohexane(2) system.

These three papers have been preceded by another paper [3] which described those Laboratory procedures which 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 data bank in order to make good compound data 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 mixture class contains three binaries—benzene + cyclohexane, benzene + hexane, cyclohexane + hexane—for which a large number of V^E 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 being covered first. The remaining binaries in the $C_6 + C_6$ hydrocarbon class will be covered in a single report.

The benzene(1) + cyclohexane(2) system is well established as a test system for experimental V^E measurement devices. However, its value as a test system has been diminished by the lack of a thorough, critical evaluation of the available data to identify recommended values which can be widely accepted as the most accurate approximation of the true values. In the past, workers reporting new V^E values have always been able to find one or more literature sets which agree with their new values even when their new values were not correct. This paper will attempt to rectify that situation.

An attempt will be made in these papers to establish selected values of V^E at mole fractions of 0.25, 0.50, and 0.75 for each temperature at which data appear in the literature. Because of the large amount of data available at 298.15 K for the benzene(1) + cyclohexane(2) system, the selected values at 298.15 will be fairly certain in this paper. At the other temperatures, the selected values will be much less firm but probably closer to the truth than any given set of data available at the given temperature.

The determination of selected values at three mole fractions will hopefully discourage the practice of comparing results only at the midpoint. As any experimenter or correlater knows, one can reproduce someone else's V^E curve exactly at one or more points but deviate from it at all other mole fraction values. The use of three mole fraction points, while not completely satisfactory in the comparison of experimental or correlation results, will certainly shed more light than the use of the midpoint alone.

Whenever possible, recommended data sets will be

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[1] Figures in brackets indicate literature references at the end of this paper.

identified. For benzene(1) + cyclohexane(2) at 298.15, it is possible to identify one set of V^E data which probably lies very close to the truth. At the other temperatures for which benzene + cyclohexane data appear, it is possible only to identify the best sets. Some obvious conclusions about the needs for new experimental data can be drawn.

2. 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 data sets 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.

The evaluation methods available for V^E data are more limited than those for vapor-liquid equilibrium data. The Gibbs-Duhem equation does not apply to V^E data because V^E is not a partial molar property. If one differentiates a V^E versus x_1 data set in some correct manner to obtain $\overline{V}_i^E$ values, those values must satisfy the Gibbs-Duhem equation by definition regardless of the accuracy of the original V^E data. The Gibbs-Helmholtz equation applies but is not useful. It relates V^E to the partial derivative of G^E with respect to pressure at constant temperature and composition but, for a binary system, it is not possible to obtain the pressure derivative while holding both T and x_i constant.

In the absence of any thermodynamic consistency test, the evaluation must rely on subjective methods. One can test the scatter of each reported V^E data set, and one can compare each set to other published data sets—if there are other data sets. Otherwise, the evaluator has only his opinion concerning the probable accuracy of the experimental apparatus and techniques used.

2.1. 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 property 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.

Two plots are used in the assignment of a scatter rating to a set of V^E data—the V^E versus x_1 plot, and either the V^E/x_1x_2 or the x_1x_2/V^E versus x_1 plot. The latter is the much more sensitive test and will often exhibit anomalies in the data set which are not apparent on the V^E versus x_1 plot.

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 V^E versus x_1 curve. 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 V^E curve, and the N (none) category was defined for those sets.

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 $\leq$ 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 $\leq$ 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 $\pm$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.

It can be seen from the definitions in 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 magnitude and slope of the V^E versus x_1 curve 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.

2.1.1. Scatter Rating Examples

Figures 1 through 11 show examples of scatter ratings based on the definitions in table 1. The data set in figure 1 was assigned an excellent scatter rating because all the points fall within a $\pm$ 0.5% band, the point pattern has the correct shape, and there is no gap in mole fraction greater than 0.1. Also, the data set does not exhibit the "hook" which often appears at one or both ends of the composition range.

The data set in figure 2 was given a good rather than excellent scatter rating because a mole fraction gap greater than 0.1 occurs at four different places across the composition range. The data set in figure 3 exhibits the correct point pattern, has an adequate point distribution, but exhibits too much scatter to receive an excellent scatter rating.

Comparison of figure 3 with figure 4 illustrates the difference between the good and fair scatter ratings. Figure 5 shows that the scatter is sometimes (but not always) apparent on the V^E versus x_1 plot also for systems with a fair scatter rating. Figure 6 shows a data set which would receive an excellent scatter rating based on the six points reported, but which falls in the fair category because of the large mole fraction gaps.

Figures 7 and 8 show a marginal scatter rating example. The shapes of both plots are not correct but one can get an approximate idea of the direction and magnitude of the deviation from the ideal solution model from the V^E versus x_1 plot. Figure 9 shows a smoothed data set which has been assigned the marginal rating because of the shape of the V^E/x_1x_2 plot even though the V^E plot in figure 10 appears normal. The smoothing operation appears to have produced some "nondata" which are not accurate for the system for which it was reported. That is a common occurrence in smoothed data sets.

Figure 11 is an example of an unacceptable scatter rating. Usually the nature of these data sets is obvious from the V^E plot alone.

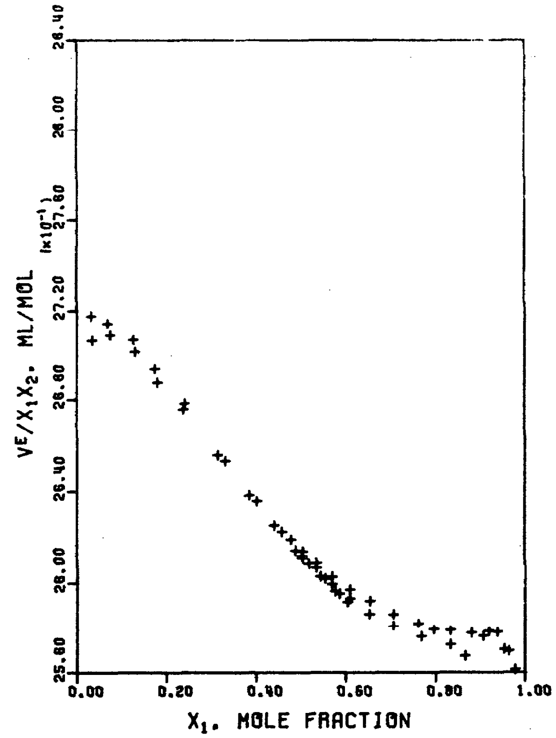

FIGURE 1. Excellent scatter rating example. Data of Tanaka, Kiyohara, D'Arcy, and Benson at 298.15 K. MRL 19026. Ordinate values run from 2.50 to 2.84.

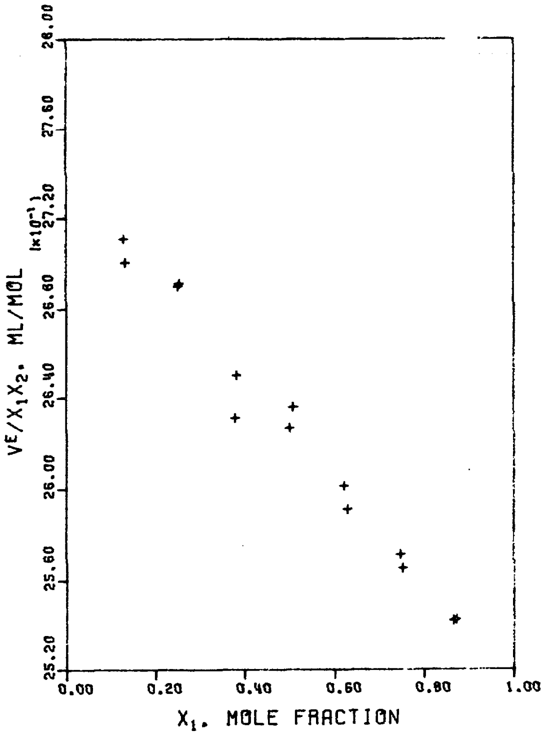

FIGURE 2. Good scatter rating example. Gaps greater than 0.10 in mole fraction. Data of Wood and Austin at 303.15 K. MRL 221. Ordinate values run from 2.52 to 2.80.

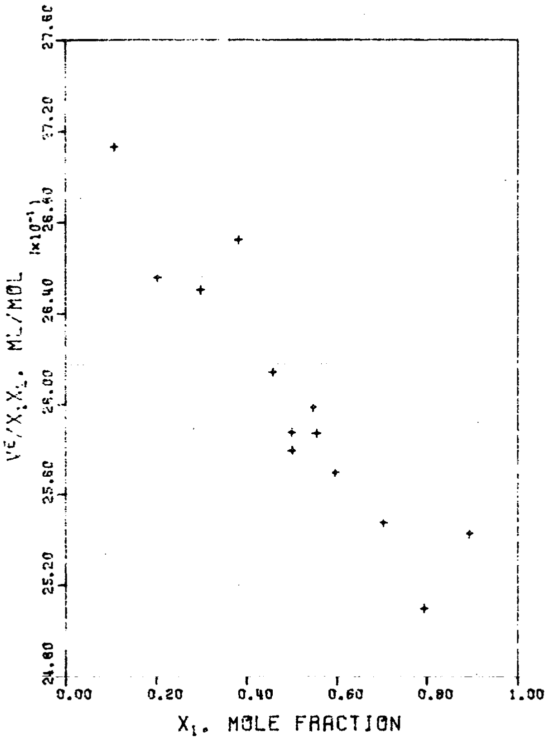

FIGURE 3. Good scatter rating example. Data of Stookey, Sallak, and Smith at 298.15 K. MRL 581. Ordinate values run from 2.48 to 2.76.

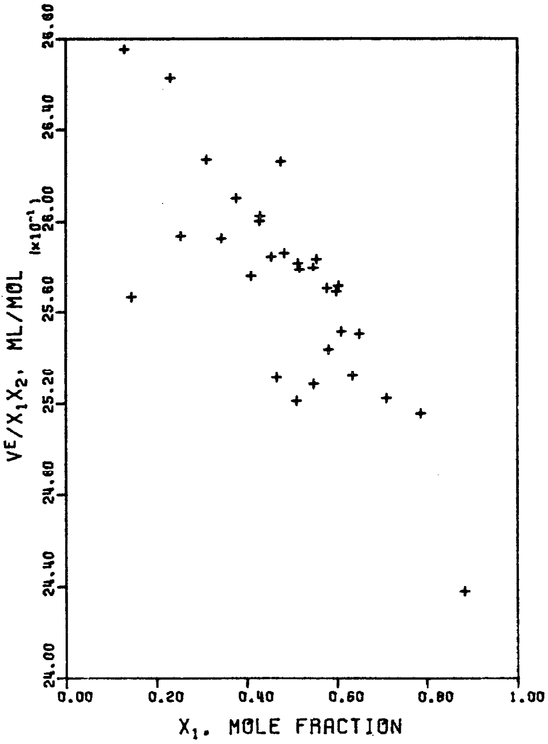

FIGURE 4. Fair scatter rating example. Data of Beath, O'Neill, and Williamson at 298.15 K. MRL 1060. Ordinate values run from 2.40 to 2.68.

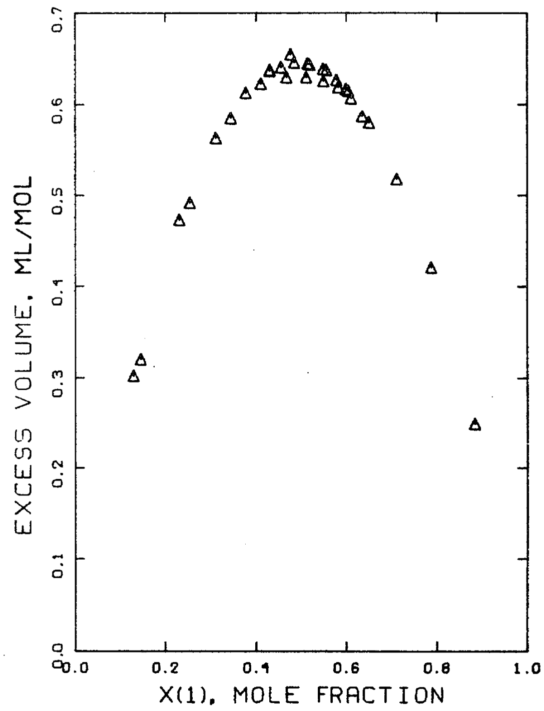

FIGURE 5. Fair scatter rating example. Data of Beath, O'Neill, and Williamson at 298.15 K. MRL 1060.

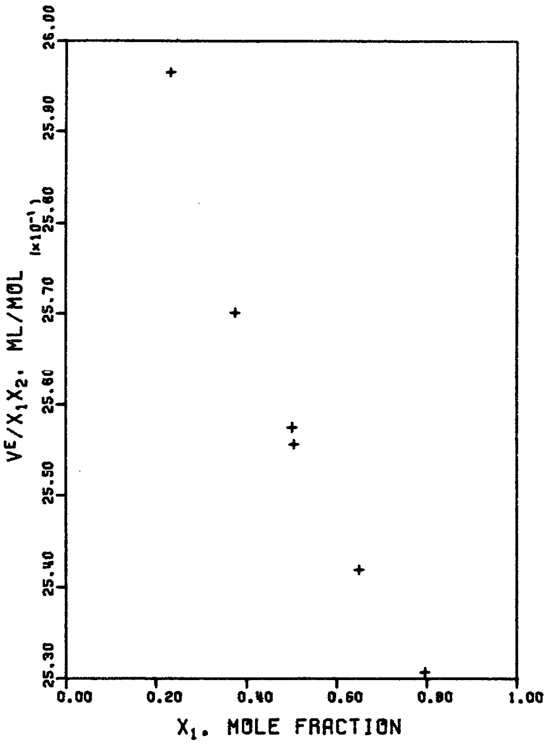

FIGURE 6. Fair scatter rating example. Data of Powell and Swinton at 298.15 K. MRL 748. Ordinate values run from 2.53 to 2.60.

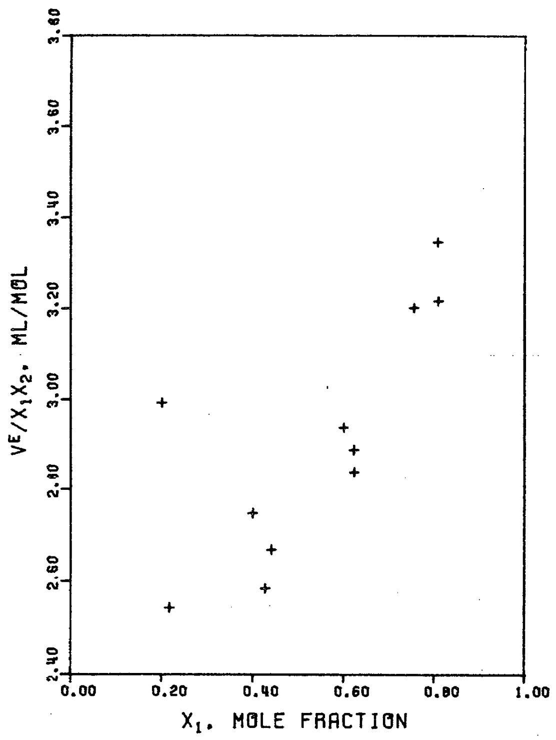

FIGURE 7. Marginal scatter rating example. Data of Konobeev and Lyapin at 313.15 K. MRL 15650.

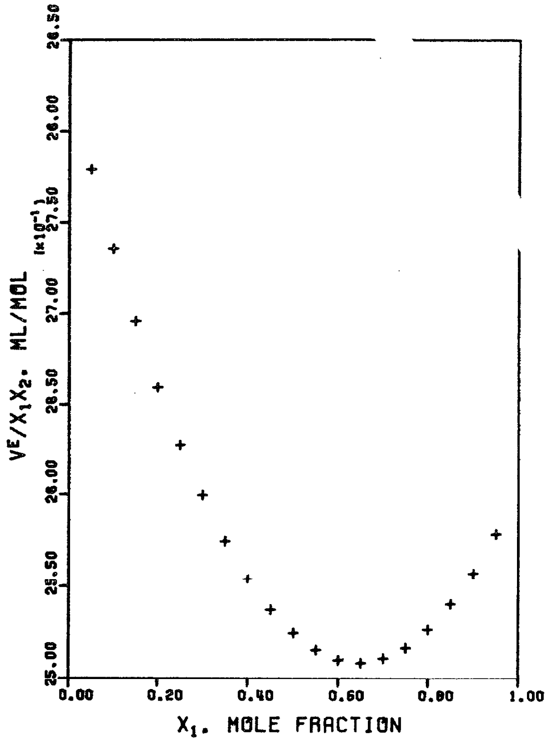

FIGURE 9. Marginal scatter rating example. Smoothed data set with wrong shape. Data of Janssens and Ruel at 298.15 K. MRL 4510. Ordinate values run from 2.50 to 2.85.

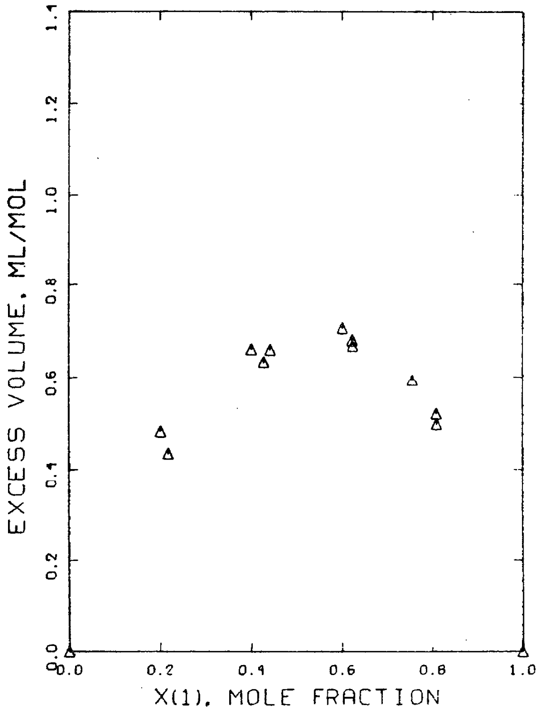

FIGURE 8. Marginal scatter rating example. Data of Konobeev and Lyapin at 313.15 K. MRL 15650.

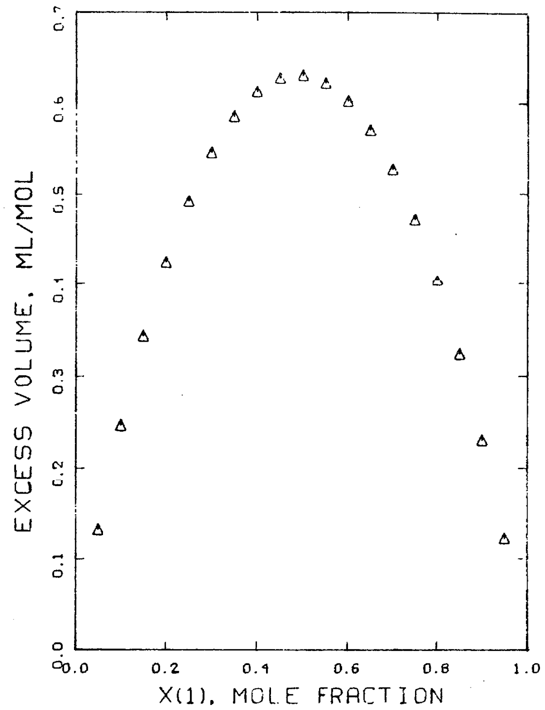

FIGURE 10. Marginal scatter rating example. The V^E plot appears normal but the V^E/x_1x_2 plot in figure 9 has the wrong shape. Data of Janssens and Ruel at 298.15 K. MRL 4510.

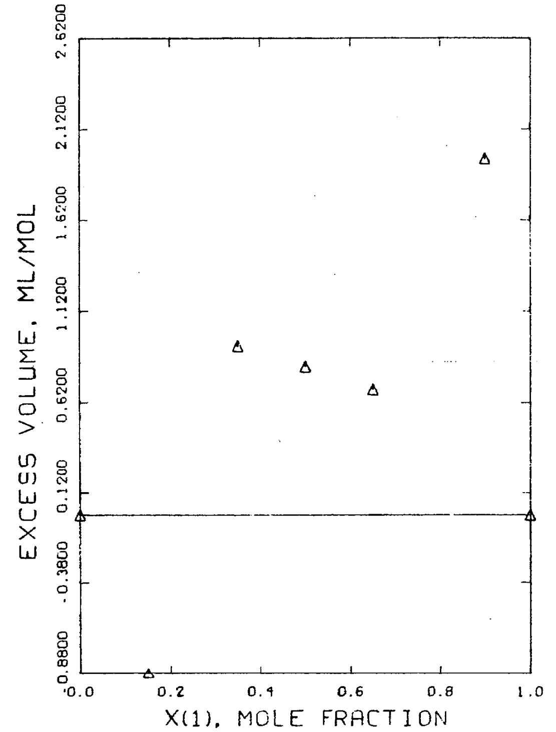

FIGURE 11. Unacceptable scatter rating. Data of Iguchi at 298.15 K. MRL 18179.

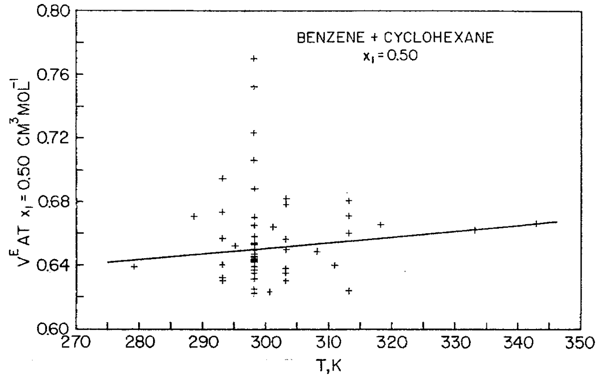

FIGURE 12. The comparison plot at $x_1 = 0.5$ for the V^E data sets for the benzene(1) + cyclohexane(2) system.

2.2. Comparison Test

The comparison test involves all the data sets available for a system regardless of their temperature. The test is made at three x_1 values: 0.25, 0.50, and 0.75. V^E values at the specified composition from all the available data sets are plotted versus temperature. The best curve through the points is then drawn by the evaluator and the percentage deviation of each data set from that best curve is calculated using

$$\frac{(V^E_{\text{exp.}} - V^E_{\text{curve}})}{V^E_{\text{curve}}}(100) \tag{1}$$

Before drawing the best V^E versus T curve, the V^E values for data sets at a given temperature are carefully inspected in order to establish a selected value at that temperature if possible. The techniques used to identify the selected values at individual temperatures are described in the section on Selected Point Values at 298.15 K.

The V^E versus T plot is illustrated in figure 12. The plots at $x_1 = 0.25$ and 0.75 were very similar to the one shown. On all three plots, it was possible to establish with considerable certainty the selected value at 298.15 K. That could not be done at the same level of certainty at any other temperature. In such a case, the isolated points at the extreme temperatures assume more weight than they would have if several other values were available at their temperatures. Fortunately, it was possible at all three mole fractions to draw a straight line which passed through the firm point at 298.15 K, passed close to the extreme points, and which "split" about as well as possible the better sets at the other temperatures. There was no justification for any more complicated temperature dependence than the linear one assumed.

Due care must be taken to use V^E values at $x_1 = 0.25$, 0.50, and 0.75 which represent each data set as well as possible. First, each set is fitted one or more times with the Redlich-Kister equation,

$$V^E/x_1x_2 = \sum_{k=0}^{D} A_k(x_1 - x_2)^k \tag{2a}$$

or

$$x_1x_2/V^E = \sum_{k=0}^{D} A_k(x_1 - x_2)^k \tag{2b}$$

where the degree D used can be 1, 2, 3, 4, or 5. Reliable V^E values at any specified mole fraction can be obtained from such a fit of a data set only if the data points are very smooth and well distributed, regardless of the degree of the equation used. Hence, it is necessary to inspect the V^E versus x_1 plot for each set of data and modify the equation values at $x_1 = 0.25$, 0.50 and 0.75 as necessary to conform with the experimental data points in the regions of those mole fractions. Also, the fitting program tabulates the experimental and the calculated values as a function of the mole fraction, and that tabulation must be inspected for each data set to determine whether the fit is running high or low in the region of the given mole fraction.

In some cases, it is not possible to establish a V^E value with any certainty at a given mole fraction; no data point appears on the V^E versus T plot for such data sets. Whenever there is some slight uncertainty as to the most representative V^E value, the question is resolved by choosing that possible value which favors the data set on the V^E versus x_1 plot.

2.3. Quality Ratings

The results of the scatter and comparison tests are used to assign a quality rating to each set of data. 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 scatter and comparison test results for the benzene(1) + cyclohexane(2) system are given in table 3. Note that it is possible to specify different percent deviation criteria at the three

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.

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

	Minimum Required Test Results			
Quality Rating	Scatter Rating	Deviation from Best V^E vs. T Curve, %		
		$x_1 = 0.25$	$x_1 = 0.50$	$x_1 = 0.75$
A	Excellent	1.0	1.0	1.0
B	Good	2.0	2.0	2.0
C	Fair	4.0	4.0	4.0
D	Marginal	6.0	6.0	6.0
E	Unacceptable	> 8.0	> 8.0	> 8.0

mole fractions, but it was not deemed necessary to do so for the almost symmetrical benzene(1) + cyclohexane(2) system.

The worst test result controls the quality rating assigned. For example, a data set with an excellent scatter rating and with percent deviations below 1.0 at both $x_1 = 0.25$ and 0.5 will receive a D quality rating if the percent deviation at $x_1 = 0.75$ falls between 4.0 and 6.0. Or, if a set receives a fair scatter rating, it will be assigned a C quality rating even though all the percent deviations are below 1.0.

2.3.1. Smoothed Data Sets

Those sets receiving the S (smoothed) scatter rating are assigned quality ratings based solely on the percent deviation at $x_1 = 0.25$, 0.50 and 0.75—if any of those quantities are available. Depending upon the deviation values, the quality rating assigned can be anything from A to E.

If no percent deviation values are available, the scatter 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.

2.3.2. 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. No more than three letters are ever included in a multiple-letter rating. For example, if the only evaluation test result available is a good scatter rating, the assigned quality rating will be BCD. Or, if a marginal scatter rating is the only evaluation test result, the assigned quality rating will be DE.

2.3.3. No Quality Rating

When the scatter rating is N (for none), the quality rating is determined solely by the available deviation values. If the comparison test cannot be made and no deviation values are available, an N (for no quality rating) is assigned to the data set.

3. Summary of Evaluation Results

Table 4 lists the evaluation results for all the data sets evaluated for the benzene(1) + cyclohexane(2) 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 data sets are ordered with respect to temperature. Use of these data sets should be restricted to those sets with quality ratings of A, B and C with C sets used only if no A or B sets are available.

Table 4. Summary list for excess volume data for the benzene(1) + cyclohexane(2) system

LITERATURE REFERENCE	T, K	P, MPA	QUALITY RATING	SCATTER RATING	% DEVIATION FROM VE VS. T CURVE		
					X(1)=0.25	X(1)=0.50	X(1)=0.75
BENZENE(1) + CYCLOHEXANE(2)							
20113	279.150	0.1013	C	F	-0.9	-0.7	-2.1
00228	283.150	0.1013	N	N	-	-	-
00922	288.706	0.1013	D	M	-	3.7	1.4
00159	293.150	0.1013	DE	M	-	-	-
00966	293.150	0.1013	D	F	-1.0	-2.5	-4.8
01408	293.150	0.1013	CDE	F	-	-	-
01570	293.150	0.1013	C	F	-3.0	-1.2	-0.7
12097	293.150	0.1013	C	F	-3.3	-2.8	-2.3
15650	293.150	0.1013	E	M	-7.6	3.9	25.2
21121	293.150	0.1013	C	F	3.5	1.4	1.2
21133	293.150	0.1013	E	F	17.9	7.2	0.4
00184	295.150	0.1013	D	M	-1.9	0.6	0.0
01559	295.150	0.1013	E	U	-	-	-
12507	296.150	0.1013	DE	M	-	-	-
10417	297.039	0.1013	DE	M	-	-	-
00069	298.150	0.1013	C	S	-2.5	-1.6	-2.3
00126	298.150	0.1013	DE	M	-	-	-
00165	298.150	0.1013	D	M	-4.0	-2.3	4.6
00234	298.150	0.1013	C	F	-3.1	-0.8	-0.3
00241	298.150	0.1013	E	F	16.0	15.8	4.2
00272	298.150	0.1013	D	F	-2.4	-3.8	-4.2
00581	298.150	0.1013	B	G	-0.1	-0.1	-1.1
00748	298.150	0.1013	C	F	-2.8	-1.7	-1.1
00917	298.150	0.1013	E	F	-6.0	-4.3	-6.3
01060	298.150	0.1013	C	F	-1.9	-0.9	-2.0
01502	298.150	0.1013	A	E	-0.5	-0.0	0.0
01558	298.150	0.1013	C	F	-0.8	-0.7	-2.0
01791	298.150	0.1013	C	F	-1.4	3.1	-2.8
04510	298.150	0.1013	D	M	-1.5	-2.9	-1.8
05069	298.150	0.1013	C	G	-4.0	-1.1	-2.4
05112	298.150	0.1013	A	E	0.0	0.5	0.0
05642	298.150	0.1013	B	G	0.1	0.6	1.2
05893	298.150	0.1013	C	F	-0.6	0.0	0.5
05992	298.150	0.1013	E	M	46.3	11.2	4.1
10296	298.150	0.1013	C	F	-1.6	0.0	1.0
10302	298.150	0.1013	C	F	0.7	2.3	-1.3
10616	298.150	0.1013	B	S	-1.1	-1.0	-0.7
11999	298.150	0.1013	E	M	18.0	8.6	8.2
12517	298.150	0.1013	E	M	26.0	18.5	-
18092	298.150	0.1013	C	S	-3.1	-2.0	-2.3
18179	298.150	0.1013	E	U	-	-	-
19026	298.150	0.1013	A	E	0.3	0.5	0.7
19572	298.150	0.1013	E	M	12.0	5.8	2.0
40006	298.150	0.1013	D	M	0.2	0.0	-0.5
40344	298.150	0.1013	C	F	-1.1	-1.2	-1.3
40563	298.150	0.1013	B	G	1.3	1.2	0.4
40564	298.150	0.1013	A	E	-0.1	-0.1	0.0
40591	298.150	0.1013	C	F	-0.9	0.6	0.8
40902	298.150	0.1013	C	F	-1.3	-1.1	-0.4
40944	298.150	0.1013	D	M	-	-1.0	-
41131	298.150	0.1013	B	G	-1.1	-0.4	-1.1
41226	298.150	0.1013	B	G	0.0	0.5	-0.2
00076	300.650	0.1013	E	M	-10.2	-4.2	-13.8
00271	301.150	0.1013	D	M	4.7	2.0	-
00193	303.150	0.1013	C	F	1.0	-0.3	0.6
00221	303.150	0.1013	B	G	0.1	0.7	-0.0
00985	303.150	0.1013	E	M	3.2	4.6	6.6
01408	303.150	0.1013	CDE	F	-	-	-
05328	303.150	0.1013	C	F	0.6	-2.6	-1.4
05338	303.150	0.1013	C	F	-2.4	-2.1	-3.1
12097	303.150	0.1013	D	F	-3.7	-3.3	-4.5
21121	303.150	0.1013	D	F	3.1	4.0	1.7
00779	308.150	0.1013	C	S	1.1	-0.7	-3.2
00922	310.928	0.1013	D	M	-4.4	-2.2	-4.9
00748	313.150	0.1013	D	F	-4.2	-4.8	-0.9
00779	313.150	0.1013	D	M	-3.2	0.8	-2.4
05992	313.150	0.1013	E	S	43.5	27.1	14.3
15650	313.150	0.1013	E	M	0.5	3.9	22.6
21121	313.150	0.1013	C	F	2.6	2.4	1.2
00779	318.150	0.1013	D	M	-4.0	1.3	0.5
00228	333.150	0.1013	N	N	-	-	-
05328	333.150	0.1013	C	F	-0.7	-0.0	-1.0
05992	333.150	0.1013	E	S	48.6	34.0	20.8
15650	333.150	0.1013	DE	M	-	-	-
05328	342.950	0.1013	C	F	0.0	0.0	0.0

4. Selected Point Values at 298.15 K

Tables 5, 6, and 7 show the V^E values at $x_1 = 0.25, 0.50, 0.75$ for the various data sets at 298.15 K listed in the order of increasing magnitude. The literature source for each V^E value is identified by the MRL (Master Reference List) number in the first column. (The MRL numbers are related to the literature citations in the Bibliography.) The scatter rating assigned to each set of data is shown in the S column. (See table 1 for the definition of the scatter rating symbols.) The equipment-type code is shown in the ET column; those codes are defined in table 8.

Figures 13, 14, and 15 show graphically the variation of the V^E values listed in tables 5, 6, and 7. The literature sources are shown on the abscissa. The scatter rating assigned is shown above the symbol for each set of data, and the symbol itself denotes the equipment type as defined in table 8.

Based on these tables and plots, and the scatter ratings assigned, the following V^E values were selected:

Mole fraction benzene	Selected value cm^3 mol^{-1}
0.25	0.4998 ± 0.0025
0.50	0.6500 ± 0.0032
0.75	0.4804 ± 0.0024

One major factor in the choice of these particular values was the desire to include as many of the E (excellent) and G (good) scatter rating sets as possible in the ±0.5% band around the selected values.

Table 5. Magnitude listing of excess volume values at 298.15 K and x(1) = 0.25. The S and ET codes refer to the scatter rating and equipment type respectively. Benzene + cyclohexane.

MRL number	Codes S	ET	Authors	Year	Excess volume ml/mol
917	F	01	Ridgway, Butler	1967	0.4700
165	M	01	Mathieson, Thynne	1956	0.4800
5069	G	01	Diaz Pena, Rodriquez Cheda	1970	0.4800
234	F	01	Chao, Hougen	1958	0.4845
18092	S	05	Chareyron, Clechet	1971	0.4846
748	F	04	Powell, Swinton	1968	0.4861
69	S	05	Watson, McLure, Bennett, Benson	1965	0.4877
272	F	01	Nagata	1962	0.4880
1060	F	05	Beath, O'Neill, Williamson	1969	0.4905
10296	F	04	Letcher	1975	0.4918
4510	M	05	Janssens, Ruel	1972	0.4927
1791	F	01	Weck	1948	0.4930
40902	F	04	Brennan, Hill, Swinton	1978	0.4936
10616	S	05	Dickinson, Hunt, McLure	1975	0.4943
40344	F	04	Radojkovic, Tasic, Djordjevic, Grozdanic	1976	0.4946
41131	G	04	Kowalski, Boniecka, Orszagh	1978	0.4946
40591	F	01	Oba, Murakami, Fujishiro	1977	0.4953
1558	F	01	Woycicki, Sadowska	1968	0.4960
5893	F	02	Grolier, Ballet, Viallard	1974	0.4970
1502	E	05	Stokes, Levien, Marsh	1970	0.4973
40564	E	05	Kumaran, McGlashan	1977	0.4996
581	G	04	Stookey, Sallak, Smith	1973	0.4997
5112	E	02	Kiyohara, Benson	1973	0.5000
41226	G	02	Goates, Ott, Grigg	1979	0.5002
5642	G	03	Weeks, Benson	1973	0.5003
40006	M	02	Meyer, Giusti, Meyer, Vincent	1975	0.5010
19026	E	05	Tanaka, Kiyohara, D'Arcy, Benson	1975	0.5015
10302	F	04	Gracia, Otin, Gutierrez Losa	1975	0.5035
40563	G	02	Goates, Ott, Moellmer	1977	0.5064
19572	M	01	Tojo, Arce, Bao, Quintela	1975	0.5600
241	F	01	Donald, Ridgway	1958	0.5800
11999	M	01	Rodwin, Harpst, Lyons	1965	0.5900
12517	M	01	Fort, Moore	1965	0.6300
5992	M	01	Sanni, Hutchison	1973	0.7313

Table 6. Magnitude listing of excess volume values at 298.15 and x(1) = 0.50. The S and ET codes refer to the scatter rating and equipment type respectively. Benzene + cyclohexane.

MRL number	Codes S	ET	Authors	Year	Excess volume ml/mol
917	F	01	Ridgway, Butler	1967	0.6222
272	F	01	Nagata	1962	0.6250
4510	M	05	Janssens, Ruel	1972	0.6312
165	M	01	Mathieson, Thynne	1956	0.6350
18092	S	05	Chareyron, Clechet	1971	0.6370
748	F	04	Powell, Swinton	1968	0.6391
69	S	05	Watson, McLure, Bennett, Benson	1965	0.6393
40344	F	04	Radojkovic, Tasic, Djordjevic, Grozdanic	1976	0.6420
5069	G	01	Diaz Pena, Rodriquez Cheda	1970	0.6427
40902	F	04	Brennan, Hill, Swinton	1978	0.6428
40944	M	04	Dixon, Hewitt	1978	0.6433
10616	S	05	Dickinson, Hunt, McLure	1975	0.6435
1060	F	05	Beath, O'Neill, Williamson	1969	0.6443
234	F	01	Chao, Hougen	1958	0.6450
1558	F	01	Woycicki, Sadowska	1968	0.6456
41131	G	04	Kowalski, Boniecka, Orszagh	1978	0.6471
40564	E	05	Kumaran, McGlashan	1977	0.6494
581	G	04	Stookey, Sallak, Smith	1973	0.6495
1502	E	05	Stokes, Levien, Marsh	1970	0.6499
5893	F	02	Grolier, Ballet, Viallard	1974	0.6500
10296	F	04	Letcher	1975	0.6500
40006	M	02	Meyer, Giusti, Meyer, Vincent	1975	0.6500
41226	G	02	Goates, Ott, Grigg	1979	0.6530
5112	E	02	Kiyohara, Benson	1973	0.6531
19026	E	05	Tanaka, Kiyohara, D'Arcy, Benson	1975	0.6531
40591	F	01	Oba, Murakami, Fujishiro	1977	0.6536
5642	G	03	Weeks, Benson	1973	0.6540
40563	G	02	Goates, Ott, Moellmer	1977	0.6580
10302	F	04	Gracia, Otin, Gutierrez Losa	1975	0.6650
1791	F	01	Weck	1948	0.6700
19572	M	01	Tojo, Arce, Bao, Quintela	1975	0.6880
11999	M	01	Rodwin, Harpst, Lyons	1965	0.7060
5992	M	01	Sanni, Hutchison	1973	0.7230
241	F	01	Donald, Ridgway	1958	0.7525
12517	M	01	Fort, Moore	1965	0.7700

Table 7. Magnitude listing of excess volume values at 298.15 K and x(1) = 0.75. The S and ET codes refer to the scatter rating and equipment type respectively. Benzene + cyclohexane.

MRL number	Codes S	ET	Authors	Year	Excess volume ml/mol
917	F	01	Ridgway, Butler	1967	0.4500
272	F	01	Nagata	1962	0.4600
1791	F	01	Weck	1948	0.4670
5069	G	01	Diaz Pena, Rodriquez Cheda	1970	0.4689
69	S	05	Watson, McLure, Bennett, Benson	1965	0.4694
18092	S	05	Chareyron, Clechet	1971	0.4695
1060	F	05	Beath, O'Neill, Williamson	1969	0.4706
1558	F	01	Woycicki, Sadowska	1968	0.4706
4510	M	05	Janssens, Ruel	1972	0.4719
10302	F	04	Gracia, Otin, Gutierrez Losa	1975	0.4740
40344	F	04	Radojkovic, Tasic, Djordjevic, Grozdanic	1976	0.4743
581	G	04	Stookey, Sallak, Smith	1973	0.4750
748	F	04	Powell, Swinton	1968	0.4751
41131	G	04	Kowalski, Boniecka, Orszagh	1978	0.4751
10616	S	05	Dickinson, Hunt, McLure	1975	0.4770
40006	M	02	Meyer, Giusti, Meyer, Vincent	1975	0.4780
40902	F	04	Brennan, Hill, Swinton	1978	0.4787
234	F	01	Chao, Hougen	1958	0.4788
41226	G	02	Goates, Ott, Grigg	1979	0.4795
1502	E	05	Stokes, Levien, Marsh	1970	0.4804
5112	E	02	Kiyohara, Benson	1973	0.4804
40564	E	05	Kumaran, McGlashan	1977	0.4804
40563	G	02	Goates, Ott, Moellmer	1977	0.4822
5893	F	02	Grolier, Ballet, Viallard	1974	0.4830
19026	E	05	Tanaka, Kiyohara, D'Arcy, Benson	1975	0.4839
40591	F	01	Oba, Murakami, Fujishiro	1977	0.4844
10296	F	04	Letcher	1975	0.4850
5642	G	03	Weeks, Benson	1973	0.4860
19572	M	01	Tojo, Arce, Bao, Quintela	1975	0.4902
5992	M	01	Sanni, Hutchison	1973	0.5000
241	F	01	Donald, Ridgway	1958	0.5004
165	M	01	Mathieson, Thynne	1956	0.5025
11999	M	01	Rodwin, Harpst, Lyons	1965	0.5200

Table 8. Codes and symbols denoting equipment type

Code	Symbol	Equipment type
01	○	Pycnometer
02	△	Mechanical oscillator densimeter
03	+	Magnetic float densimeter
04	×	Batch dilatometer
05	◊	Dilution dilatometer

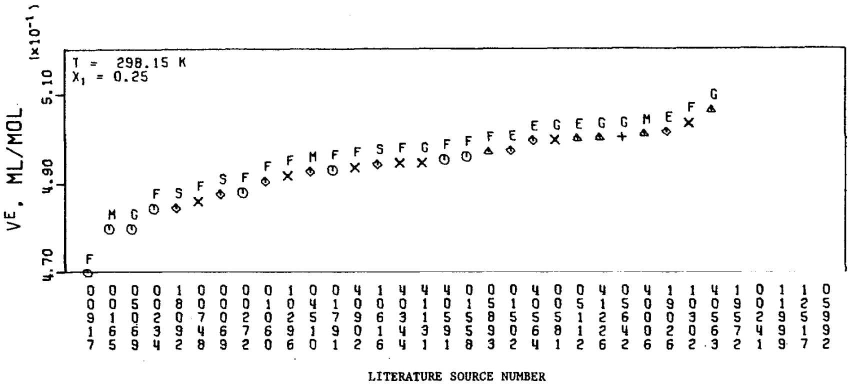

FIGURE 13. Magnitude comparison plot for V^E values at $x_1 = 0.25$ and 298.15 K. Ordinate values run from 0.47 to 0.51.

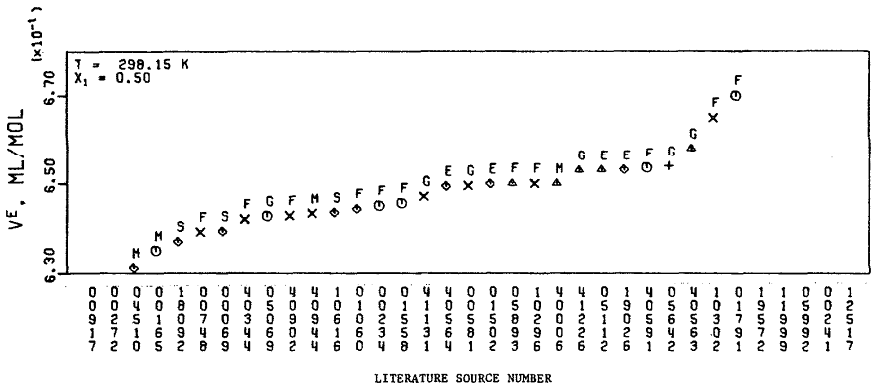

FIGURE 14. Magnitude comparison plot for V^E values at $x_1 = 0.50$ and 298.15 K. Ordinate values run from 0.63 to 0.67.

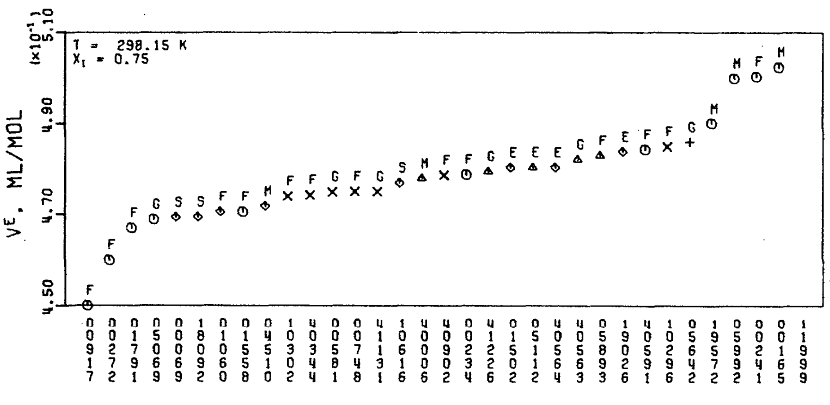

FIGURE 15. Magnitude comparison plot for V^E values at $x_1 = 0.75$ and 298.15 K. Ordinate values run from 0.45 to 0.51.

4.1. Effect of Equipment Type

All of the data sets whose points fell below or above the ordinate ranges covered by figures 13, 14, and 15 were obtained with pycnometers (code 01). In fairness to the pycnometer technique, it should be noted that most of the very bad V^E sets were calculated from mixture density data which had been measured for some purpose other than the determination of V^E data. Nevertheless, none of the pycnometer points fell within the $\pm 0.5\%$ band on the $x_1 = 0.25$ and 0.50 plots, and only one fell in that band on the 0.75 plot. Obviously, the pycnometer does not appear to be a good tool for the measurement of excess volumes.

The relatively new mechanical oscillator densimeter (code 02) performed better. Of the five data sets reported at 298.15 K for benzene(1) + cyclohexane(2), four out of five points fell within the ±0.5 band at two of the three mole fractions. It should be noted that the oscillator densimeters came into use after the correct values have been relatively well established for the benzene(1) + cyclohexane(2) system. It is possible that bad values obtained with that instrument were never published, and that we are now observing the salutary effect which a well-established test system can have on the quality of the newly-published experimental data.

Only one set of data measured with the magnetic float densimeter has been published. The result at $x_1 = 0.25$ was very close to the selected value but the 0.50 and 0.75 values fell slightly above the +0.5% band.

The basic difficulty in the measurement of excess volume by means of density measurements is the large number of significant digits which are necessary in the densities to provide three significant digits in the excess volume when the pure compound volumes are subtracted from the mixture volume,

$$V^E = V - x_1 V_1 - x_2 V_2. \tag{3}$$

The batch and dilution dilatometers avoid that problem by making a direct determination of V^E. In general, the dilatometer results have been more reliable than the pycnometer results; none of the results for the dilatometers fall outside the ordinate scale ranges in figures 13, 14, and 15. (Again, in fairness to the pycnometer method, anyone using a dilatometer was obviously interested in V^E values while most of the bad pycnometer data were obtained by workers who had no interest in the excess volume.) However, the dilatometers have their own set experimental problems. One important problem is the possible presence of very small but compressible air bubbles which cannot be easily detected visually but which have a large effect on the measured V^E values. Another one is the sensitivity to temperature fluctuations, particularly when a large amount of mercury is present.

For the results obtained with batch dilatometers, only one of the seven values available at $x_1 = 0.25$ and 0.75, and only three of the eight available values at $x_1 = 0.50$, fall within the ±0.5% error band. For the continuous dilatometers, three of eight values at $x_1 = 0.25$ and 0.50 and two of eight values at $x_1 = 0.75$ fall within the band. Based on these comparisons, the continuous dilatometers appear to perform better. Also, the continuous dilatometers may suffer in this comparison due to the fact that three of the eight reported data sets were reported in smoothed form. The vagaries of curve-fitting make it easy to degrade the experimental data by more than 0.5% at any given mole fraction. That problem will be discussed further in a following section.

The continuous dilatometer is a relatively new development, and the oscillator and float densimeters are quite recent. It is therefore interesting to plot the data sets in chronological order as shown in figure 16.

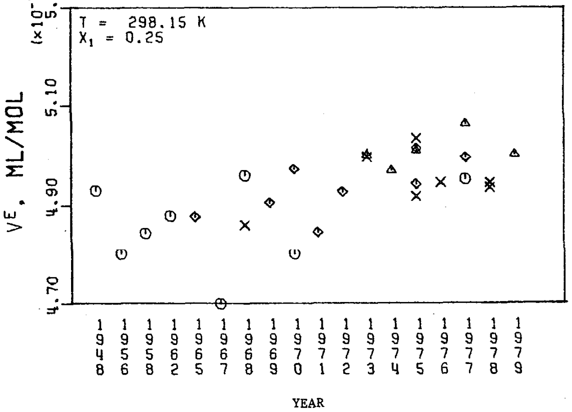

FIGURE 16. Chronological comparison plot for V^E values at $x_1 = 0.25$ and 298.15 K. Ordinate values run from 0.47 to 0.53.

5. Selected Point Values at Other Temperatures

As shown in table 4, V^E data are available at seventeen temperatures ranging from 279.15 to 342.95, but multiple measurements are available at only six temperatures: 293.15 (8 sets), 295.15 (2 sets), 298.15 (37 sets), 303.15 (8 sets), 313.15 (5 sets), and 333.15 (4 sets). One of the two 295.15 K sets received an Unacceptable scatter rating which means percent deviation values (comparison test) were not meaningful. Likewise, only one of the four sets at 333.15 K is useable; the comparison test was not feasible at any mole fraction for two of those sets, and one set had very large percent deviations. Hence, there are only four temperatures where selection between the available sets is necessary: 293.15, 298.15, 303.15, and 313.15.

For those four temperatures, tabulations and plots such as those shown in tables 5, 6, and 7 and in figures 13, 14, and 15 were effective only for the 298.15 K sets. No plateaus appeared in the tables and plots at the other temperatures, as can be seen by the distribution of points at those temperatures on figure 12. Consequently, it was not possible to identify selected point values at other temperatures by the procedures used in the previous section for the data sets at 298.15 K.

Table 9. Best curve values for the benzene(1) + cyclohexane(2) system

t, °C	T, K	Best Curve Values x_1=0.25	x_1=0.50	x_1=0.75
6.	279.15	0.4920	0.6433	0.4756
15.56	288.71	0.4960	0.6465	0.4781
20.	293.15	0.4978	0.6482	0.4793
22.	295.15	0.4987	0.6486	0.4798
25.	298.15	0.4998	0.6500	0.4804
27.5	300.65	0.5013	0.6505	0.4812
28.	301.15	0.5016	0.6508	0.4814
30.	303.15	0.5022	0.6518	0.4819
35.	308.15	0.5044	0.6536	0.4832
37.78	310.93	0.5058	0.6543	0.4838
40.	313.15	0.5066	0.6553	0.4844
45	318.15	0.5088	0.6571	0.4857
60	333.15	0.5158	0.6622	0.4897
69.8	342.95	0.5200	0.6660	0.4921

The best values at temperatures other than 298.15 K had to be obtained from the three comparison plots such as the one shown in figure 12 for $x_1 = 0.50$. The best value at 298.15 for each of the three mole fractions was first determined as explained in the previous section. With that one point established, a line was drawn which best represented the trend of the points with respect to temperature. In the absence of firm points at any other temperature besides 298.15, there was no justification for anything but a straight line on each of the three plots.

Table 9 shows the values read from the best curve established on each of the three comparison plots. It is highly probable that the values shown there are closer to the true values than any of the reported data sets.

6. Recommended Data Sets

The selection of a recommended data set can be done with certainty only at 298.15 K. At the other temperatures where more than one useable set are available, it is possible only to identify those sets which deviate least from the selected values at $x_1 = 0.25$, 0.50, and 0.75.

6.1 Temperatures Other Than 298.15 K

The temperatures of interest are 293.15, 303.15, and 313.15.

6.1.1. 293.15 K

At 293.15 K, the best scatter rating assigned was F (fair) which means the best quality rating assigned was C. Of the three sets receiving a C rating, the two with the best percent deviations (see table 4) are the 1570 set (Pavlova, 1926) and the 21121 set (Nissema, 1970). The best curve on the comparison plots at $x_1 = 0.25$, 0.50, and 0.75 (see figure 12 for an example) splits those two sets with the Nissema points falling above and the Pavlova points falling below the curve. The tabulations for the two sets appear in tables 10 and 11, and the V^E/x_1x_2 plots appear in figures 17 and 18. The ordinate scale factor (cm^{3}mol^{-1} per inch) is four times as large in figure 18 as it is in figure 17 which makes the data appear more scattered in figure 17 than it would be if plotted on the same scale as used in figure 18. Also, the general configura-

Table 10. The best set of data at 293.15 K

SYSTEM. Benzene(1) + Cyclohexane(2)

TEMPERATURE. 293.15 K PRESSURE. 0.1013 MPa

MOLAR VOLUMES (ml/mol). 1 = 88.937 2 = 108.093

QUALITY RATING. C SCATTER. Fair

DEVIATION FROM VE VS. T CURVE AT x(1) = 0.25. -3.0 %

DEVIATION FROM VE VS. T CURVE AT x(1) = 0.50. -1.2 %

DEVIATION FROM VE VS. T CURVE AT x(1) = 0.75. -0.7 %

REFERENCE. Pavlova, G. S., Zhurnal Russkogo Fiziko - Khimicheskogo Obshchestva, Chast Khimicheskaya, 58, 1302 (1926). (MRL 1570)

x(1) mole fraction	EXCESS VOLUME ml/mol	x(1) mole fraction	EXCESS VOLUME ml/mol
0.0	0.0	0.5144	0.6414
0.0495	0.1199	0.5674	0.6255
0.1079	0.2472	0.6182	0.6027
0.1671	0.3573	0.6700	0.5611
0.2133	0.4390	0.7174	0.5094
0.2661	0.5051	0.7614	0.4593
0.3157	0.5618	0.8132	0.3835
0.3710	0.5978	0.8589	0.3040
0.3897	0.6124	0.9083	0.2094
0.4694	0.6389	0.9530	0.1148
1.0000	0.0		

Table 11. The second best set of data at 293.15 K

SYSTEM. Benzene(1) + Cyclohexane(2)

TEMPERATURE. 293.15 K PRESSURE. 0.1013 MPa

MOLAR VOLUMES (ml/mol). 1 = 88.904 2 = 108.072

QUALITY RATING. C SCATTER. Fair

DEVIATION FROM VE VS. T CURVE AT x(1) = 0.25. 3.5 %

DEVIATION FROM VE VS. T CURVE AT x(1) = 0.50. 1.4 %

DEVIATION FROM VE VS. T CURVE AT x(1) = 0.75. 1.2 %

REFERENCE. Nissema, A., Annales Academiae Scientiarum Fennicae, Series A2, 153, 1 (1970). (MRL 21121)

x(1) mole fraction	EXCESS VOLUME ml/mol	x(1) mole fraction	EXCESS VOLUME ml/mol
0.0	0.0	0.6010	0.5902
0.1030	0.2593	0.7049	0.5320
0.1989	0.4393	0.7940	0.4338
0.3033	0.5677	0.9034	0.2447
0.4019	0.6367	1.0000	0.0
0.5014	0.6573		

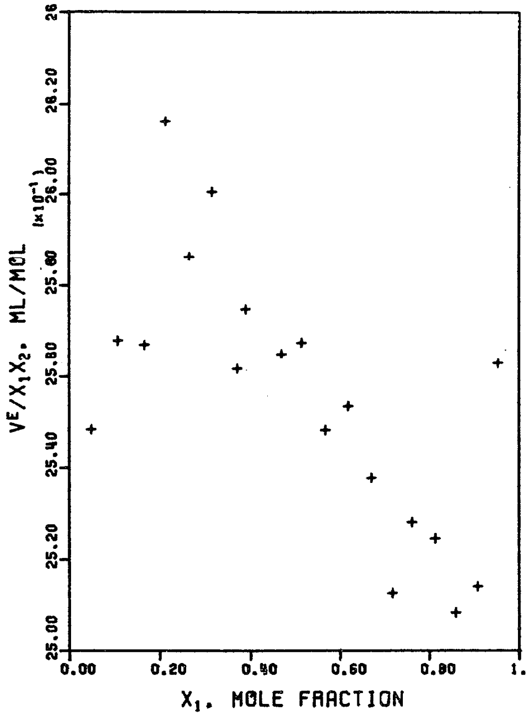

FIGURE 17. The best set of data at 293.15 K. Pavlova, 1926. MRL 1570. Ordinate values run from 2.50 to 2.64.

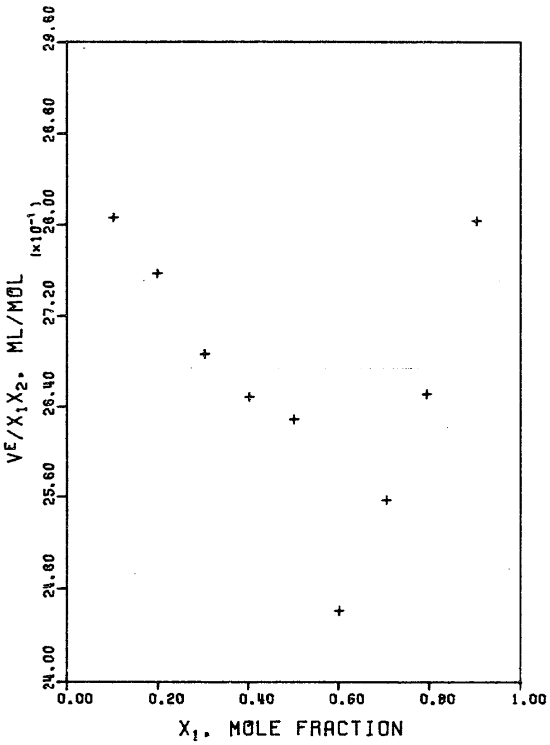

FIGURE 18. The second best set of data at 293.15 K. Nissema, 1970. MRL 21121. Ordinate values run from 2.40 to 2.96.

tion of the points in figure 17 is better in that it conforms better to the typical system configuration shown in figures 1, 2, and 3. Based on these considerations, plus the number of points reported, the Pavlova set is probably the better of the two sets. However, as shown by their positions relative to the best curve on the comparison plot, an average of the Pavlova and the Nissema sets would probably lie closer to the truth than does either set.

6.1.2. 303.15 K

The best set of data at 303.15 K is the MRL 221 set (Wood and Austin, 1945). That set received a G (good) scatter rating and a B quality rating. The data set is tabulated in table 12 and plotted in figure 2. The set would have received an E (excellent) scatter rating if there had not been gaps in the mole fraction greater than 0.1.

Another reliable data set is that of Scatchard, Wood and Mochel, 1939 (MRL 193). It agrees with the selected values at $x_1 = 0.25$, 0.50, and 0.75 within 1.0% and, as shown in figure 19, would have received a G (good) scatter rating if the excessive scatter at high x_1 values had not occurred. As can be seen on figure 12, the best curve lies between the MRL 193 and 221 sets.

Table 12. The best set of data at 303.15 K

SYSTEM. Benzene(1) + Cyclohexane(2)

TEMPERATURE. 303.15 K PRESSURE. 0.1013 MPa

MOLAR VOLUMES (ml/mol). 1 = 89.945 2 = 109.431

QUALITY RATING. B SCATTER. Good

DEVIATION FROM VE VS. T CURVE AT x(1) = 0.25. 0.1 %

DEVIATION FROM VE VS. T CURVE AT x(1) = 0.50. 0.7 %

DEVIATION FROM VE VS. T CURVE AT x(1) = 0.75. -0.0 %

REFERENCE. Wood, S. E., Austin, A. E., Journal of the American Chemical Society, 67, 480 (1945). (MRL 221)

x(1) mole fraction	EXCESS VOLUME ml/mol	x(1) mole fraction	EXCESS VOLUME ml/mol
0.0	0.0	0.5084	0.6588
0.1286	0.3038	0.6206	0.6125
0.1333	0.3120	0.6290	0.6047
0.2521	0.5072	0.7484	0.4842
0.2548	0.5110	0.7511	0.4796
0.3803	0.6201	0.8651	0.2967
0.3832	0.6263	0.8710	0.2857
0.5007	0.6567	1.0000	0.0

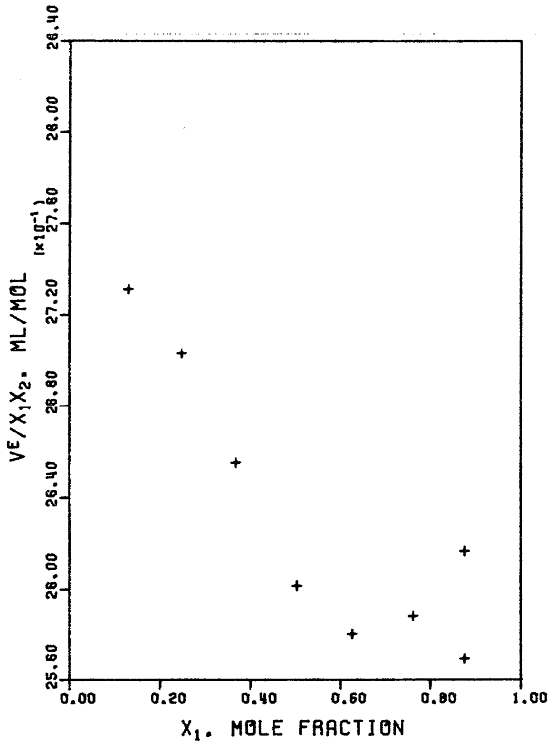

FIGURE 19. Second best set of data at 303.15 K. Scatchard, Wood, and Mochel, 1939. MRL 193. Ordinate values run from 2.56 to 2.84.

Table 13. The best set of data at 313.15 K

SYSTEM. Benzene(1) + Cyclohexane(2)

TEMPERATURE. 313.15 K PRESSURE. 0.1013 MPa

MOLAR VOLUMES (ml/mol). 1 = 91.111 2 = 110.764

QUALITY RATING. C SCATTER. Fair

DEVIATION FROM VE VS. T CURVE AT x(1) = 0.25. 2.6 %

DEVIATION FROM VE VS. T CURVE AT x(1) = 0.50. 2.4 %

DEVIATION FROM VE VS. T CURVE AT x(1) = 0.75. 1.2 %

REFERENCE. Nissema, A., Annales Academiae Scientiarum Fennicae, Series A2, 153, 1 (1970). (MRL 21121)

x(1) mole fraction	EXCESS VOLUME ml/mol	x(1) mole fraction	EXCESS VOLUME ml/mol
0.0	0.0	0.6010	0.6468
0.1030	0.2605	0.7049	0.5411
0.1989	0.4421	0.7940	0.4317
0.3033	0.5827	0.9034	0.2382
0.4019	0.6442	1.0000	0.0
0.5014	0.6707		

6.1.3. 313.15 K

The best of the five sets of data at 313.15 K is the MRL 21121 set (Nissema, 1970) which received an F (fair) scatter rating and a C quality rating. The set is tabulated in table 13 and plotted in figure 20. As shown in table 13, the deviations from the selected values at $x_1 = 0.25$, 0.50, and 0.75 are fairly large, but all the other available sets have D or E quality ratings.

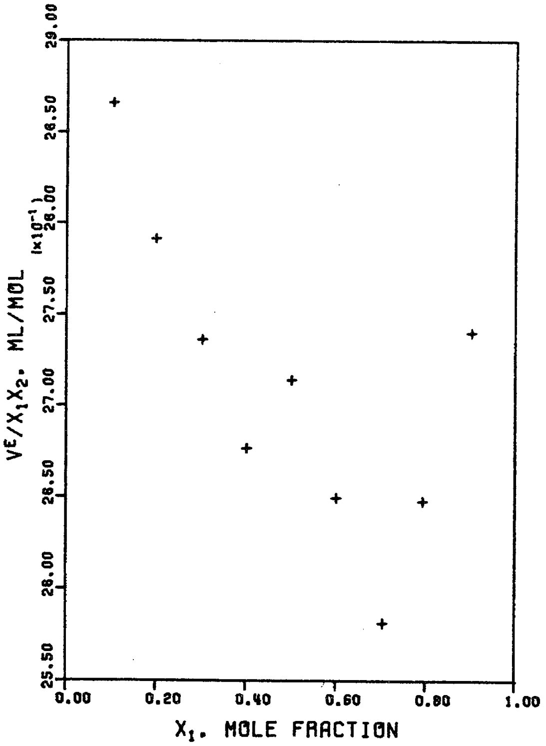

FIGURE 20. Best set of data at 313.15 K. Nissema, 1970. MRL 21121. Ordinate values run from 2.55 to 2.90.

Table 14. MRL numbers and scatter ratings for the data sets within 0.5% of the selected values at 298.15 K for benzene mole fractions of 0.25, 0.50 and 0.75

x_1 = 0.25	x_1 = 0.50	x_1 = 0.75
--	--	234 (F)
581 (G)	581 (G)	--
1502 (E)	1502 (E)	1502 (E)
5112 (E)	5112 (E)	5112 (E)
5642 (G)	--	--
--	5893 (F)	--
--	10296 (F)	--
--	--	--
19026 (E)	19026 (E)	--
40006 (M)	40006 (M)	40006 (M)
	--	40563 (G)
40564 (E)	40564 (E)	40564 (E)
--	--	40902 (F)
--	41131 (G)	--
41226 (G)	41226 (G)	41226 (G)

6.2. Data Sets at 298.15 K

Table 14 lists those sets at 298.15 K which agree within 0.5% with at least one of the selected values at $x_1 = 0.25$, 0.50, and 0.75. All those sets which fell within the 0.5% band at one or more of the three mole fractions had F (fair) or better scatter ratings with the exception of the data set from MRL 40006 (Meyer, Giusti, Meyer, Vincent, 1975). That document reports some high-quality data but there is a mole fraction gap greater than 0.25 in the reported data points, hence the M (marginal) scatter rating.

Seven of the data sets in table 14 were compared in one final way as an aid in the selection of the recommended data set. Each of those seven sets was fitted with the Redlich-Kister equation (eq (2a)) using D values of 1, 2, 3, 4, and 5. The results are shown in table 15. The root mean squared deviation (RMSD) used is defined by

$$\mathrm{RMSD} = \left[\frac{\sum_{i=1}^{N} (V^E_{\mathrm{exp}} - V^E_{\mathrm{calc}})^2_i}{N} \right]^{1/2} \tag{4}$$

where N is the number of experimental points reported. This RMSD provides a relative measure of the amount of scatter in the various data sets.

Table 15 illustrates two interesting points. First, note the smoothness of the data measured on a continuous dilatometer (MRL 1502, Stokes, Levien, and Marsh, 1970; MRL 19026, Tanaka, Kiyohara, D'Arcy, and Benson, 1975; MRL 40564, Kumaran and McGlashan, 1977) relative to data measured with batch dilatometers (MRL 581, Stookey, Sallak, and Smith, 1973) and with the mechanical oscillator densimeter (MRL 5112, Kiyohara and Benson, 1973; MRL 40563, Goates, Ott, and Moellmer, 1977; MRL 41226, Goates, Ott, and Grigg, 1979). The continuous dilatometer is a titration device while the other devices make discrete point measurements. Second, the change in the root mean

Table 15. Fitting results for some selected data sets at 298.15 K

Source	Equipment Type Code[a]	Root Mean Squared Deviation D=1[b]	D=2	D=3	D=4	D=5
581	04	0.0041[c]	0.0042	0.0038	0.0037	0.0036
1502	05	0.0020	0.0008[c]	0.0008	0.0008	0.0008
5112	02	0.0017	0.0016[c]	0.0016	0.0016	0.0016
19026	05	0.0023	0.0008	0.0006	0.0004[c]	0.0004
40563	02	0.0038	0.0022	0.0014[c]	0.0012	0.0012
40564	05	0.0025	0.0007[c]	0.0007	0.0006	0.0006
41226[d]	02	0.0036	0.0036	0.0036[c]	0.0033	0.0029

[a] Codes are defined in Table 8.

[b] The number of constants is one greater than the degree (D).

[c] Degree used by the authors reporting the experimental data.

[d] The RMSD values are based on V^E values calculated from the experimental density values. The V^E values listed by the authors are not consistent with their density values.

squared deviation with the degree of the fitting equation is very small above $D = 2$ (three constants) for six of the seven sets, and very small for all seven sets after $D = 3$ (four constants). Based on the RMSD alone, the results in table 15 indicate that it would not make much difference what equation degree is used to represent a set of data for the benzene + cyclohexane system as long as the degree is 2 or higher. However, as will be shown below, other factors besides the RMSD must be considered when a fitting equation is selected.

The data sets listed in table 15 are plotted in figures 21, 22, and 23 in a way which compares each set to the selected point V^E values at $x_1 = 0.25$, 0.50, and 0.75 and at the same time illustrates how well the literature sets agree with each

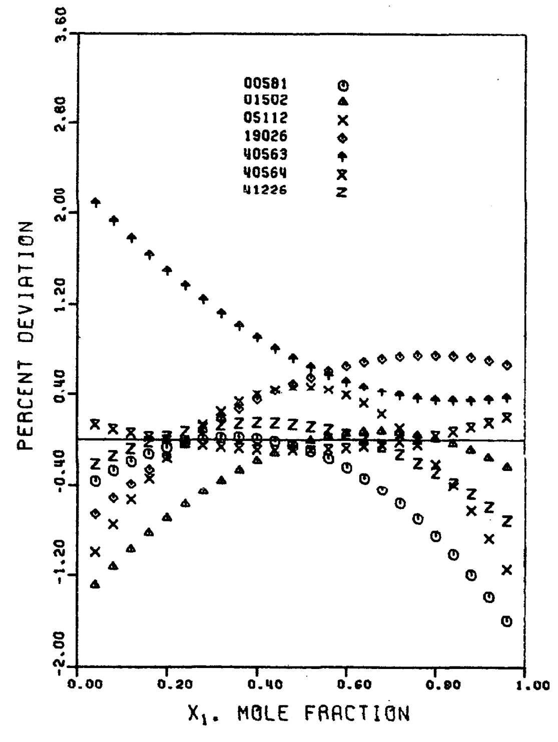

FIGURE 21. Comparison of the better sets of data at 298.15 K to a three-constant ($D = 2$) fit of the selected values at $x_1 = 0.25$, 0.50, and 0.75. The literature sets are represented by three-constant ($D = 2$) equations.

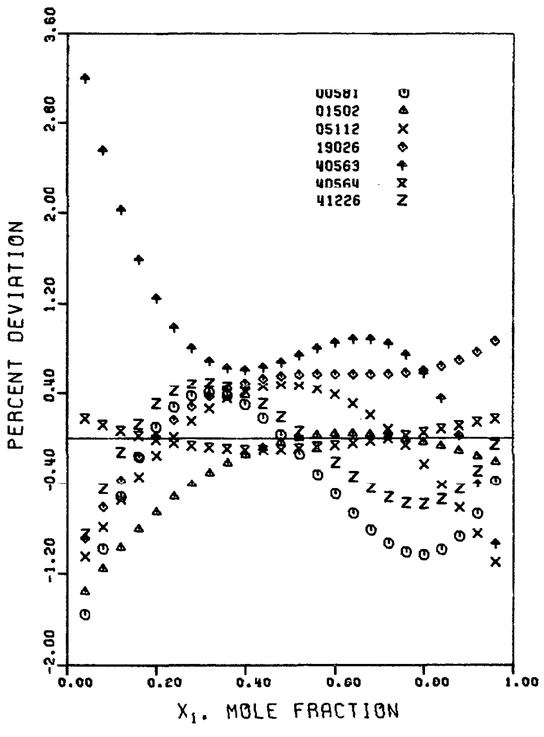

FIGURE 22. Comparison of the better sets of data at 298.15 K to a three-constant ($D = 2$) fit of the selected values at $x_1 = 0.25$, 0.50, and 0.75. The literature sets are represented by four-constant ($D = 3$) equations.

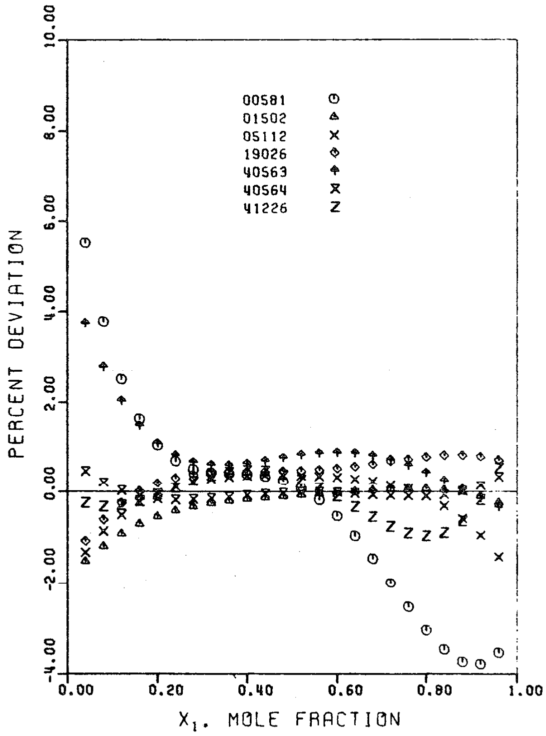

FIGURE 23. Comparison of the better sets of data at 298.15 K to a three-constant ($D = 2$) fit of the selected values at $x_1 = 0.25$, 0.50, and 0.75. The literature sets are represented by five-constant ($D = 4$) equations.

other. The percent deviations plotted were obtained from

$$\frac{V^E_{\text{set}} - V^E_{\text{ref}}}{V^E_{\text{ref}}}(100) \tag{5}$$

where V^E_{ref} was calculated from the three-constant equation

$$V^E/x_1x_2 = 2.59999847 - 0.10346699(x_1 - x_2) + 0.05546951(x_1 - x_2)^2 \tag{6}$$

obtained by fitting the three selected V^E values at $x_1 = 0.25$, 0.50, and 0.75. In each of the three figures, a different degree (ranging from 2 to 4) was used for the equations representing the literature data sets.

Figures 21, 22, and 23 illustrate that one often pays a price when the equation degree is increased to obtain the small reductions in the RMSD values shown in table 15. The very smooth sets of data obtained on the continuous dilatometers (MRL 1502, 19026, and 40564) are affected less than the other sets but, in general, the fitting equations tend to weave back and forth more relative to the fixed reference equation as the number of constants is increased. Obviously, the degree of equation used can have a large impact on how sets of data compare with each other.

Fortunately, in this case the effect of the equation degree used does not obscure the fact that the MRL 40564 set (Kumaran and McGlashan) appears to be the most representative set. That set of data is recommended as the one which most closely represents the true behavior of the benzene + cyclohexane system at 298.15 K. The set is tabulated in table 16 and plotted in figure 24.

Table 16. The recommended set of data at 298.15 K

SYSTEM. Benzene(1) + Cyclohexane(2)

TEMPERATURE. 298.15 K PRESSURE. 0.1013 MPa

MOLAR VOLUMES (ml/mol). 1 = 89.409 2 = 108.760

QUALITY RATING. A SCATTER. Excellent

DEVIATION FROM VE VS. T CURVE AT x(1) = 0.25. -0.1 %

DEVIATION FROM VE VS. T CURVE AT x(1) = 0.50. -0.1 %

DEVIATION FROM VE VS. T CURVE AT x(1) = 0.75. 0.0 %

REFERENCE. Kumaran, M. K., McGlashan, M. L., Journal of Chemical Thermodynamics, 9(3), 259 (1977). (MRL 40564)

x(1) mole fraction	EXCESS VOLUME ml/mol	x(1) mole fraction	EXCESS VOLUME ml/mol
0.0520	0.1356	0.3811	0.6189
0.0872	0.2164	0.3864	0.6208
0.1126	0.2719	0.4224	0.6380
0.1587	0.3594	0.4356	0.6425
0.2072	0.4398	0.4754	0.6492
0.2123	0.4465	0.4847	0.6501
0.2631	0.5162	0.5041	0.6495
0.2726	0.5274	0.5197	0.6471
0.3232	0.5761	0.5233	0.6471
0.3375	0.5902	0.5298	0.6461
0.5324	0.6455	0.6887	0.5507
0.5634	0.6368	0.7026	0.5359
0.5681	0.6335	0.7364	0.4972
0.5691	0.6346	0.7852	0.4311
0.5714	0.6331	0.7865	0.4286
0.6029	0.6186	0.8424	0.3385
0.6045	0.6175	0.8511	0.3228
0.6091	0.6147	0.8882	0.2540
0.6429	0.5918	0.9185	0.1914
0.6437	0.5908	0.9243	0.1792
0.9603	0.0981	0.9619	0.0933

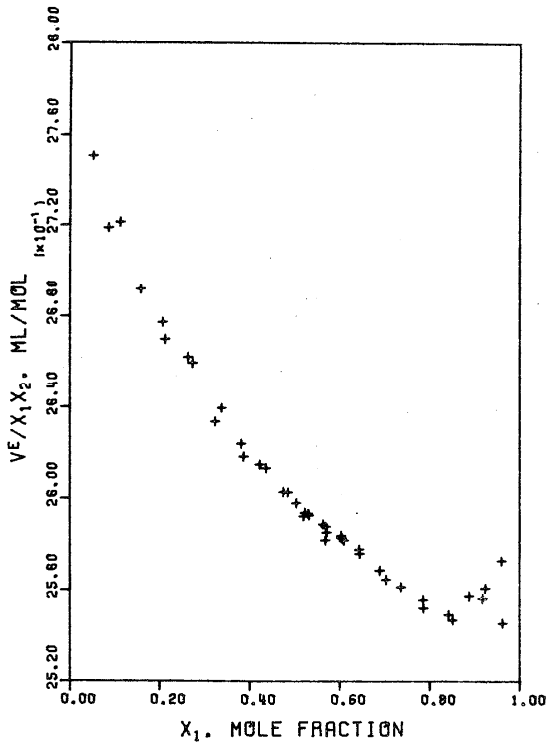

FIGURE 24. The recommended set of data at 298.15 K. Kumaran and McGlashan, 1977. MRL 40564. Ordinate values run from 2.52 to 2.80.

7. Experimental Measurements Needed

The only firm point available for the location of the best curve on the comparison plots at $x_1 = 0.25$, 0.50, and 0.75 was at 298.15. As shown by figure 12, there are no clusters of highly reliable measurements at any other temperature. The MRL 221 set at 303.15 (Wood and Austin, 1945) provided fairly reliable guidance but otherwise the best curve was drawn to split the better (but disagreeing) data sets at other multiple-measurement temperatures while staying fairly close to the single sets at the extreme temperatures. There was no justification for drawing anything but a straight line as the "best curve" on each of the three plots.

The temperatures of the V^E sets processed ranged from 279.15 to 342.95 K (6 to 69.8 °C). It would be helpful if those laboratories which have developed the capability of measuring highly-accurate V^E data would help establish other well-defined points besides 298.15 K within this temperature range. Temperatures of 323.15 and 348.15 K (50 and 75 °C) are obvious choices.

It will also be necessary to extend the temperature range upward. The Thermodynamics Research Laboratory has developed a correlation procedure whereby vapor-liquid equilibrium (VLE), excess enthalpy (H^E), and excess volume (V^E) data can be correlated simultaneously within experimental error and stored in a computer data bank in terms of four binary constants (4, 5, 6). The best correlation procedure is to determine the four binary constants from isothermal VLE and V^E data sets at the same temperatures. The correlation is then checked by the prediction of the available good H^E data to make sure it is reproduced within experimental accuracy. VLE and V^E data sets must be available at a minimum of two temperatures and preferably at three. The Laboratory has developed a reliable VLE-measurement device which can routinely measure VLE data at 298.15, 348.15, and 398.15 K (25, 75 and 125 °C). It will be very helpful to have V^E data available at the same three temperatures, or at least at the lower two.

8. Pure Compound Densities

Pure compound volume values are needed to calculate V^E values with eq (3) when mixture density or volume values are reported. The authors' pure compound values are always used if they are given. If not reported, the computer program VECON which converts the mixture or density data to V^E values accesses the pure compound data bank CDATA1 for the needed pure compound values. The general procedures used in selecting and correlating the pure compound liquid density data and storing it in CDATA1 have been described in the preceding paper [3].

The V^E data sets evaluated for the benzene + cyclohexane system fell in the 279 to 343 K temperature range. The pure component values used for each set of data are given on the tabulation for that set. (See tables 10 through 13 as examples.) When obtained from CDATA1, the benzene and cyclohexane density values were both calculated from correlations based on the Francis equation constants given in table 17. The benzene correlation shown there is based on a fit of 279 selected experimental data points with a RMSD of 0.00018 g cm^{-3}. The cyclohexane correlation fitted 148 selected data points with a RMSD of 0.00017.

Table 17. Pure compound liquid density data

$d = A - BT - C/(E - T)$ (T in kelvin)

	Benzene (280 to 374 K)	Cyclohexane (279 to 374 K)
A	0.11971445D+01	0.10512676D+01
B	0.96949888D-03	0.83394744D-03
C	0.11815362D+02	0.77268763D+01
E	0.64129077D+03	0.56643433D+03

The total experimental data base for the benzene liquid density correlations in CDATA1 came from 73 primary literature documents each of which contributed one or more data points. The data points reported by 19 other primary literature documents were totally excluded from the correlation. The analogous numbers for cyclohexane are 46 and 6.

9. Data Set Tabulations

Tabulation of all the data sets covered in this paper is not feasible due to their large number. Any person who wants a set of the tables should contact the Director, Thermodynamics Research Laboratory, Box 1144, Washington University, St. Louis, Missouri 63130. Copies of the V^E tables with the V^E/x_1x_2 versus x_1 plots on the back of the pages will be provided for $0.50 per set of data 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.

10. Bibliography

Table 18 is the bibliography for excess volume data for the benzene(1) + cyclohexane(2) 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. That MRL number relates the citation in table 18 to the various tables and figures used in the main body of the paper.

A few of the documents listed in table 18 report V^E data in a form which did not permit transcription and processing. In most of those cases, the data were presented only in graphical form. They have been included in the bibliography in order to provide complete coverage of the V^E literature for the benzene(1) + cyclohexane(2) system.

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11. Nomenclature

A_k	Empirical constants in Redlich-Kister equation.
D	Degree of Redlich-Kister equation.
k	Index in Redlich-Kister equation.
MRL	Acronym for Master Reference List.
RMSD	Acronym for root mean squared deviation. Defined by eq (4).
V	Liquid molar volume of mixture.
V_i	Liquid molar volume of component i.
V^{E}	Excess volume. Defined by eq (3).
x	Liquid mole fraction.

12. Acknowledgments

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