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

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The methods used to evaluate excess enthalpy 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 enthalpy; heat of mixing.

Contents

1. Introduction

This paper is the first in a series of evaluation reports on excess enthalpy (H^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 volume (V^E) and vapor-liquid equilibrium (VLE) data. Each of these three lead papers present the specific evaluation methods used for the given property, and then apply 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 H^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 H^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 H^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 H^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 avail-

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

able 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 H^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 identified. For benzene(1) + cyclohexane(2) at 298.15 and 323.15 K, it is possible to identify individual sets of H^E data which probably lie 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 users. 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 H^E data are much more limited than those for vapor-liquid equilibrium data. The Gibbs-Duhem equation does not apply to H^E data because H^E is not a partial molar property. If one differentiates an H^E versus x_1 data set in some correct manner to obtain $\bar{H}_i^E$ values, those values must satisfy the Gibbs-Duhem equation by definition regardless of the accuracy of the original data. The Gibbs-Helmholtz equation applies but is not useful. It relates H^E to the temperature derivative of G^E in the following way,

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

The last term is so small numerically that the relationship

$$\left[\frac{d(G^E/T)}{d(1/T)} \right]_x \doteq (H^E)_x \qquad (2)$$

is completely adequate to check the consistency of the vapor-liquid equilibrium data with the H^E data. A plot of G^E/T versus $1/T$ at constant composition must have a slope equal to the H^E value at the given temperature and composition. That is a sensitive test for the relative location of the G^E/T points from the various sets of vapor-liquid equilibrium data. On the other hand, the slope of the curve through the G^E/T points is too sensitive to small discrepancies in the G^E values to provide a useful check on the experimental H^E values.

In the absence of any thermodynamic consistency test, the evaluator must rely on subjective methods. One can test the scatter of each reported H^E data set, and one can com-

pare 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 incor-

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 $M^E/x_1 x_2$ 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 $M^E/x_1 x_2$ 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 $M^E/x_1 x_2$ 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 $\ln(\gamma_1^\infty/\gamma_2^\infty)$ vs. x_1 may appear worthy of a G rating but the $M^E/x_1 x_2$ 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 $M^E/x_1 x_2$ or $\ln(\gamma_1^\infty/\gamma_2^\infty)$ 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.

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Two plots are used in the assignment of a scatter rating to a set of H^E data—the H^E versus x_1 plot, and either the H^E/x_1x_2 or the x_1x_2/H^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 H^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 H^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 H^E curve, and the N (none) category was defined for those sets.

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 H^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 7 show examples of scatter ratings based on the definitions in table 1. The data set in figure 1

FIGURE 2. Another excellent scatter rating example. Data of Murakami and Benson at 298.15 K. MRL 942. Ordinate values run from 3120 to 3680.

FIGURE 1. Excellent scatter rating example. Data of Elliot and Wormald at 298.15 K, second series. MRL 40319. Ordinate values run from 3120 to 3680.
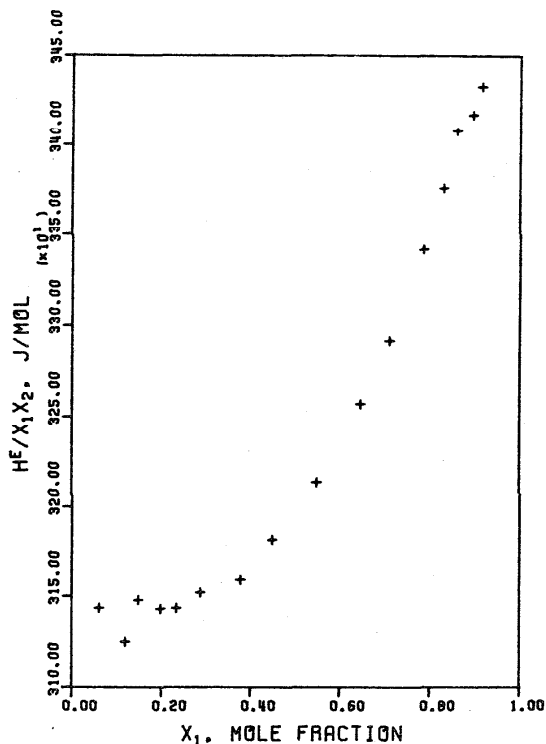
FIGURE 3. Good scatter rating example. Data of Elliot and Wormald at 298.15 K, first series. MRL 40319. Ordinate values run from 3100 to 3450.
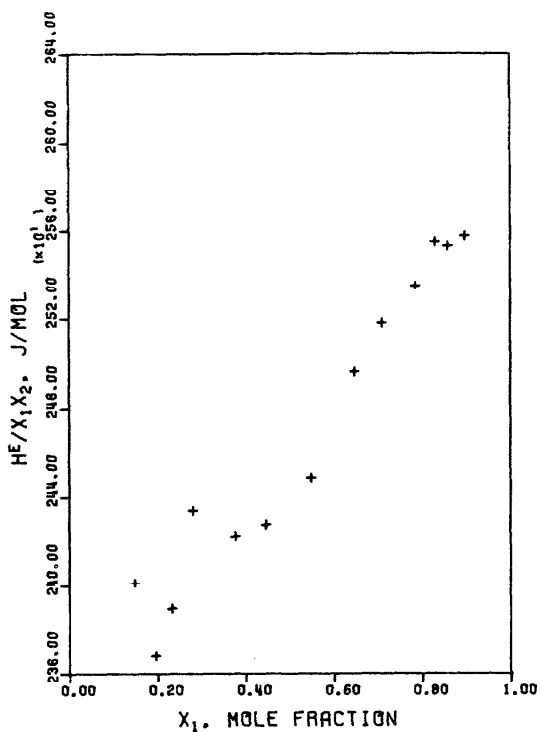
FIGURE 4. Another good scatter rating example. Data of Elliot and Wormald at 373.15 K. MRL 40319. Ordinate values run from 2360 to 2640.
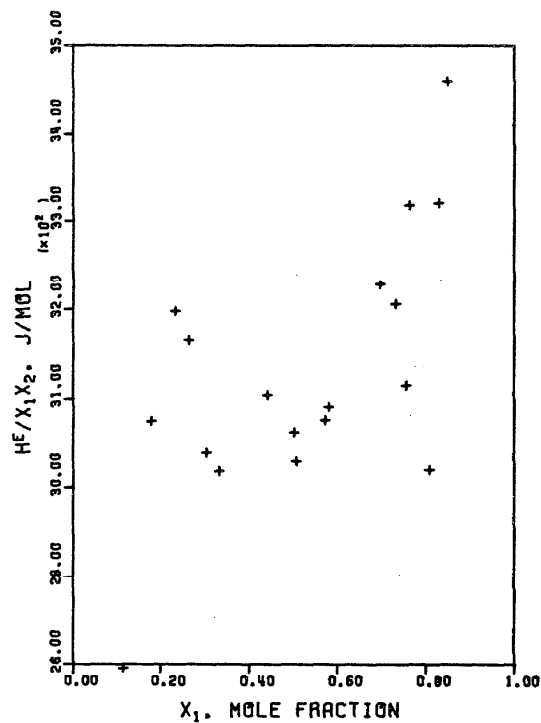
FIGᵀᵀ 6. Marginal scatter rating example. Data of Noordtzig at 303.15 K. MRL 178. Ordinate values run from 2800 ᵗᵒ ³⁵⁰⁰

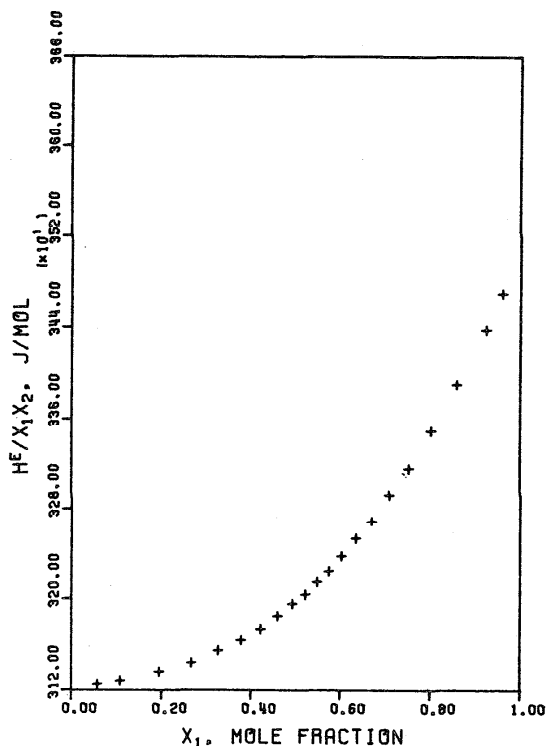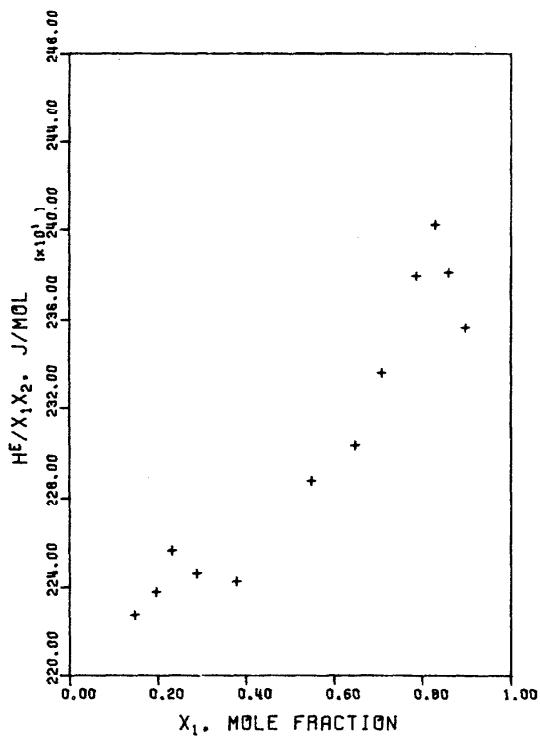FIGURE 5. Fair scatter rating example. Data of Elliot and Wormald at 393.15 K. MRL 40319. Ordinate values run from 2200 to 2480.
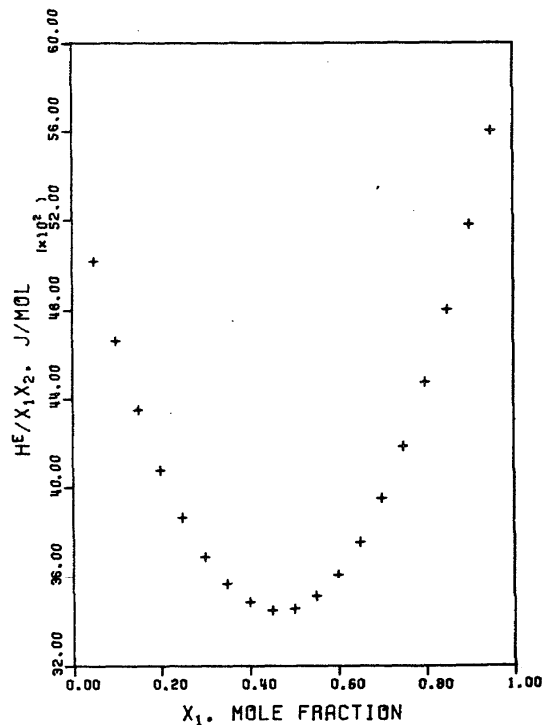
FIGURE 7. Marginal scatter rating example for a set of smoothed data. Data of Kauer, Kirchner, Haupt, and Bittrich at 293.15 K. MRL 5993. Ordinate values run from 3200 to 6000.

plots perfectly and obviously is worthy of an excellent scatter rating. Figure 2 shows more scatter but the points fall within a 0.5% band and an excellent scatter rating was assigned. Figures 3 and 4 illustrate the limits on the good scatter rating with the data set in figure 3 being close to an excellent rating while the one in figure 4 is close to a fair rating. (The data set in figure 3 probably would have received an excellent rating if there had not been a gap in the mole fraction greater than 0.1). The example of a fair scatter rating in figure 5 appears at first glance to be similar to figure 4 but that is due to the difference in the ordinate scale factors. Figures 6 and 7 illustrate the marginal scatter rating, the first one due to excessive scatter in the data points and the second due to an incorrect shape of the smoothed data. In both cases, the H^E versus x_1 plot gives the approximate magnitude of the deviation from ideality. When the approximate deviation from nonideality cannot be determined, an unacceptable scatter rating is given. No example is shown from the unacceptable rating.

2.2. Comparison Test

The comparison test uses a plot of H^E values versus $1/T$ at a specified mole fraction. A plot is made for each of the following x_1 values: 0.25, 0.50, and 0.75. The best curve is then drawn on each plot by the evaluator, and the pei ntage deviation of each data set's value from that best i rve is calculated using

$$\frac{H^E_{exp} - H^E_{curve}}{H^E_{curve}}(100).$$ (3)

Before drawing the best H^E versus $1/T$ curve for a given mole fraction, the H^E values from all the 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 later.

The H^E values are plotted versus $1/T$ instead of T in order to make the plot more useful in the Gibbs-Helmholtz test applied to vapor-liquid equilibrium data. The sign of the slope of the $1/T$ plot indicates whether the G^E/T versus $1/T$ plot must be concave upward or concave downward.

The H^E versus $1/T$ plot is illustrated in figure 8 for $x_1 = 0.50$. 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 values at 298.15 and 323.15 K. That could not be done with the same level of certainty at any other temperature. Fortunately, the data of Elliot and Wormald (MRL 40319) probably define the location of the best curve quite accurately above 323.15 K. Their point at 280.15 K (extreme point at right end of the plot) falls slightly below the straight line drawn as the best curve, but the straight line agrees so well with all their other five points that it did not seem reasonable to put a bend in the curve below 298.15 K.

Due care must be taken to use H^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,

$$H^E/x_1x_2 = \sum_{k=0}^{D} A_k(x_1 - x_2)^k$$ (4a)

or

$$x_1x_2/H^E = \sum_{k=0}^{D} A_k(x_1 - x_2)^k$$ (4b)

where the degree D used can be 1, 2, 3, 4, or 5. Reliable H^E values at any specified mole fraction will be provided by such a fit only if the data points are very smooth and well distributed. Hence, it is necessary to inspect the H^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 frac-
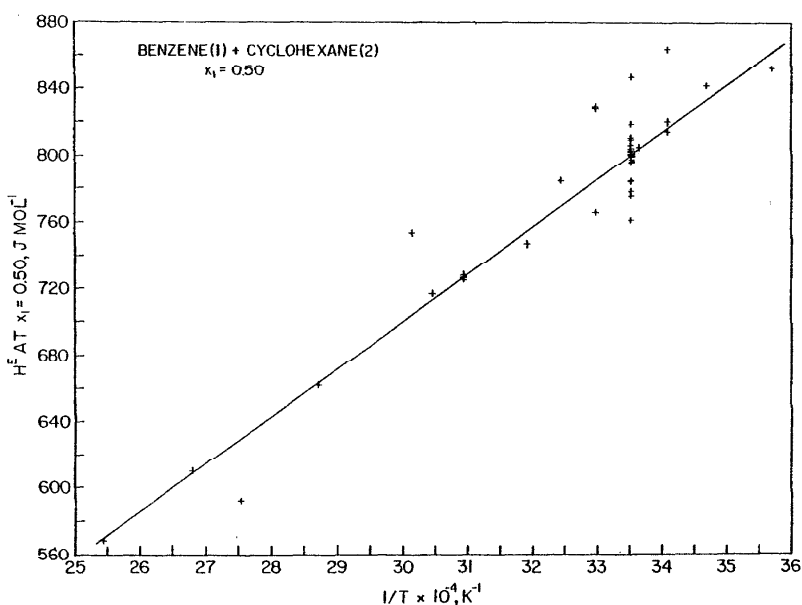
FIGURE 8. The comparison plot at $x_1 = 0.5$ for the H^E data sets for the benzene(1) + cyclohexane(2) system.

tions. Also, the computer program used to make the fits 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 an H^E value with any certainty at a given mole fraction; no data point appears on the H^E versus $1/T$ plot for such data sets. Whenever there is some slight uncertainty as to the most representative value, the question is resolved by choosing that possible value which favors the data set on the comparison 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 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 as-

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

Quality Rating	Scatter Rating	Minimum Required Test Results Deviation from Best H^E vs. 1/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

signed. 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 low 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 table 27. 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 enthalpy data for the benzene(1) + cyclohexane(2) system

LITERATURE REFERENCE	T, K	P, MPA	QUALITY RATING	SCATTER RATING	% DEVIATION FROM HE VS. 1/T CURVE		
					X(1)=0.25	X(1)=0.50	X(1)=0.75
BENZENE(1) + CYCLOHEXANE(2)							
40319	280.150	0.1013	B	G	-1.2	-1.2	-0.8
01558	283.150	0.1013	DE	M	-	-	-
00921	288.150	0.1013	D	M	6.0	1.0	5.7
00057	293.150	0.1013	D	M	-	-0.3	-
00770	293.150	0.1013	E	M	-13.6	-	-2.3
01325	293.150	0.1013	D	M	-	0.5	-0.2
05993	293.150	0.1013	E	M	20.4	5.8	23.9
10417	297.039	0.1013	D	M	-0.5	0.1	-2.3
00053	298.150	0.1013	C	F	0.1	0.1	-0.3
00063	298.150	0.1013	D	M	-	2.3	-
00066	298.150	0.1013	C	F	-0.6	-0.4	-0.2
00069	298.150	0.1013	C	F	0.1	0.2	-0.7
00917	298.150	0.1013	D	M	-0.3	1.3	1.5
00921	298.150	0.1013	D	M	-	-4.9	-5.1
00942	298.150	0.1013	A	E	0.0	0.1	0.1
01028	298.150	0.1013	C	G	-2.4	-2.0	-1.9
01065	298.150	0.1013	A	E	-0.2	-0.1	-0.0
01555	298.150	0.1013	D	M	-5.8	-2.8	-3.9
01558	298.150	0.1013	C	F	-2.7	0.7	-0.0
01616	298.150	0.1013	A	S	-0.1	-0.1	-0.1
01616	298.150	0.1013	A	S	-0.3	-0.1	0.1
03647	298.150	0.1013	D	M	1.5	0.4	0.9
03990	298.150	0.1013	A	E	-0.5	0.0	0.4
04882	298.150	0.1013	C	F	0.4	-0.1	0.1
05308	298.150	0.1013	A	E	0.2	0.3	0.5
05308	298.150	0.1013	A	E	0.4	0.5	0.5
05349	298.150	0.1013	C	G	1.0	1.1	2.6
05936	298.150	0.1013	D	M	1.5	0.2	1.9
05993	298.150	0.1013	E	M	14.9	5.8	16.9
08388	298.150	0.1013	D	M	-2.3	-0.3	-0.5
10317	298.150	0.1013	B	G	0.0	0.5	-0.2
10643	298.150	0.1013	B	G	-0.1	-0.6	-0.3
18301	298.150	0.1013	C	F	1.6	0.0	0.9
18302	298.150	0.1013	C	F	0.3	0.2	-0.2
19177	298.150	0.1013	A	S	0.0	0.1	0.2
40043	298.150	0.1013	C	F	-2.0	-2.1	-1.2
40172	298.150	0.1013	D	M	-	-3.1	-
40307	298.150	0.1013	C	F	0.8	0.0	-0.2
40319	298.150	0.1013	B	G	0.2	-0.1	0.1
40319	298.150	0.1013	A	E	-0.1	-0.1	0.0
40365	298.150	0.1013	A	E	-0.1	-0.1	0.1
40439	298.150	0.1013	C	F	1.0	0.0	0.8
40451	298.150	0.1013	B	G	-1.0	-0.5	-0.6
40920	298.150	0.1013	B	G	0.0	0.3	0.4
40966	298.150	0.1013	B	E	-1.0	-0.1	-1.7
00149	303.150	0.1013	DE	M	-	-	-
00178	303.150	0.1013	D	M	2.8	-2.4	-1.4
04983	303.150	0.1013	DE	M	-	-	-
05022	303.150	0.1013	D	F	5.2	5.5	5.1
05993	303.150	0.1013	E	M	9.1	5.6	9.6
16357	303.150	0.1013	N	N	-	-	-
00051	308.150	0.1013	E	M	12.3	17.2	22.2
00062	308.150	0.1013	D	M	-2.7	-	-3.8
00921	308.150	0.1013	DE	M	-	-	-
05349	308.150	0.1013	B	G	1.7	1.9	0.9
00062	313.150	0.1013	D	M	-4.1	-	-2.2
00066	313.150	0.1013	D	F	-3.8	-1.0	-5.0
00062	318.150	0.1013	D	M	-5.7	-	-4.7
00053	323.150	0.1013	C	F	-0.3	0.1	1.1
00904	323.150	0.1013	A	S	-0.1	-0.1	-0.4
03633	323.150	0.1013	C	F	-0.0	-0.3	-0.9
04983	323.150	0.1013	DE	M	-	-	-
40319	323.150	0.1013	B	G	-0.1	-0.0	-0.3
00066	328.150	0.1013	C	F	0.2	0.5	-1.7
00062	331.550	0.1013	E	M	0.6	7.0	-0.1
40319	348.150	0.1013	B	G	0.5	-0.2	-0.6
00048	363.150	0.1013	E	M	-16.1	-6.0	-11.8
40319	373.150	0.2026	B	G	-0.3	0.2	0.4
40319	393.150	0.3040	C	F	-0.3	-0.3	0.0

4. Selected Point Values at 298.15 K

Tables 5, 6, and 7 show the H^E values at $x_1 = 0.25, 0.50$, and 0.75 for the various data sets at 298.15 K listed in the order of increasing magnitude. The literature source for each H^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 9, 10, and 11 show graphically the variation of the H^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 H^E values were selected:

Mole fraction benzene	Selected value, J mol^{-1}
0.25	590.0 ± 2.95
0.50	800.0 ± 4.00
0.75	621.5 ± 3.11

One major factor in the choice of these particular values was

Table 5. Magnitude listing of H^E 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 enthalpy J/mol
1555	M	01	Diaz Pena, Fernandez Martin	1963	555.9
1558	F	06	Woycicki, Sadowska	1968	574.3
1028	G	06	Schnaible	1955	575.9
8388	M	01	Mattingley, Fenby	1975	576.7
40043	F	08	Meyer, Giusti, Vincent, Meyer	1977	578.4
40451	G	05	Gracia	1977	584.0
40966	E	05	Obbink, Miltenburg, Berg	1978	584.0
66	F	04	Sabinin, Belousov, Morachevskii	1966	586.7
3990	E	05	Tanaka, Murakami, Fujishiro	1972	587.0
1616	S	05	Ewing, Marsh, Stokes, Tuxford	1970	588.0
917	M	06	Ridgway, Butler	1967	588.2
1065	E	05	Stokes, Marsh, Tomlins	1969	589.1
40319	E	09	Elliott, Wormald	1976	589.2
40365	E	05	Nagata, Kazuma	1977	589.2
1616	S	05	Ewing, Marsh, Stokes, Tuxford	1970	589.2
10643	G	05	Touhara, Ikeda, Nakanishi, Watanabe	1975	589.7
40920	G	05	Nicolaides, Eckert	1978	590.0
10317	G	07	Hsu, Clever	1975	590.0
942	E	05	Murakami, Benson	1969	590.1
19177	S	07	Tanaka, D'Arcy, Benson	1975	590.2
53	F	04	Lundberg	1964	590.5
69	F	04	Watson, McLure, Bennett, Benson	1965	590.7
40319	G	09	Elliott, Wormald	1976	591.0
5308	E	05	Savini	1963	591.1
18302	F	03	Bares, Soulie, Metzger	1973	592.0
4882	F	02	Vesely, Pick	1969	592.4
5308	E	05	Savini	1963	592.6
40307	F	11	Coomber, Wormald	1976	595.0
40439	F	08	Grolier	1976	596.0
5349	G	05	Mrazek	1960	596.0
5936	M	01	Cabani, Ceccanti	1973	598.8
3647	M	04	Grolier, Viallard	1970	599.0
18301	F	03	Abello	1973	599.5
5993	M	06	Kauer, Kirchner, Haupt, Bittrich	1972	678.0

Table 6. Magnitude listing of H^E values at 298.15 K 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 enthalpy J/mol
921	M	04	Goates, Sullivan, Ott	1959	761.0
40172	M	01	Yang, Gomez-Ibanez	1976	775.1
1555	M	01	Diaz Pena, Fernandez Martin	1963	778.0
40043	F	08	Meyer, Giusti, Vincent, Meyer	1977	783.5
1028	G	06	Schnaible	1955	784.2
10643	G	05	Touhara, Ikeda, Nakanishi, Watanabe	1975	795.3
40451	G	05	Gracia	1977	796.3
66	F	04	Sabinin, Belousov, Morachevskii	1966	797.0
8388	M	01	Mattingley, Fenby	1975	797.4
40365	E	05	Nagata, Kazuma	1977	799.0
40966	E	05	Obbink, Miltenburg, Berg	1978	799.1
1616	S	05	Ewing, Marsh, Stokes, Tuxford	1970	799.3
40319	G	09	Elliott, Wormald	1976	799.3
1616	S	05	Ewing, Marsh, Stokes, Tuxford	1970	799.3
4882	F	02	Vesely, Pick	1969	799.3
40319	E	09	Elliott, Wormald	1976	799.4
1065	E	05	Stokes, Marsh, Tomlins	1969	799.5
40307	F	11	Coomber, Wormald	1976	800.0
3990	E	05	Tanaka, Murakami, Fujishiro	1972	800.0
18301	F	03	Abello	1973	800.4
40439	F	08	Grolier	1976	800.4
53	F	04	Lundberg	1964	800.5
19177	S	07	Tanaka, D'Arcy, Benson	1975	800.6
942	E	05	Murakami, Benson	1969	800.7
18302	F	03	Bares, Soulie, Metzger	1973	801.9
69	F	04	Watson, McLure, Bennett, Benson	1965	801.9
5936	M	01	Cabani, Ceccanti	1973	802.0
40920	G	05	Nicolaides, Eckert	1978	802.3
5308	E	05	Savini	1963	802.5
3647	M	04	Grolier, Viallard	1970	802.9
10317	G	07	Hsu, Clever	1975	803.7
5308	E	05	Savini	1963	803.7
1558	F	06	Woycicki, Sadowska	1968	805.7
5349	G	05	Mrazek	1960	809.0
917	M	06	Ridgway, Butler	1967	810.2
63	M	04	Kokalos	1963	818.4
5993	M	06	Kauer, Kirchner, Haupt, Bittrich	1972	846.3

Table 7. Magnitude listing of H^E 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 enthalpy J/mol
921	M	04	Goates, Sullivan, Ott	1959	590.0
1555	M	01	Diaz Pena, Fernandez Martin	1963	597.5
1028	G	06	Schnaible	1955	609.4
40966	E	05	Obbink, Miltenburg, Berg	1978	611.0
40043	F	08	Meyer, Giusti, Vincent, Meyer	1977	614.0
69	F	04	Watson, McLure, Bennett, Benson	1965	616.8
40451	G	05	Gracia	1977	617.6
8388	M	01	Mattingley, Fenby	1975	618.1
53	F	04	Lundberg	1964	619.3
10643	G	05	Touhara, Ikeda, Nakanishi, Watanabe	1975	619.5
18302	F	03	Bares, Soulie, Metzger	1973	620.0
40307	F	11	Coomber, Wormald	1976	620.0
10317	G	07	Hsu, Clever	1975	620.3
66	F	04	Sabinin, Belousov, Morachevskii	1966	620.4
1616	S	05	Ewing, Marsh, Stokes, Tuxford	1970	621.1
1065	E	05	Stokes, Marsh, Tomlins	1969	621.2
1558	F	06	Woycicki, Sadowska	1968	621.4
40319	E	09	Elliott, Wormald	1976	621.6
942	E	05	Murakami, Benson	1969	622.1
40319	G	09	Elliott, Wormald	1976	622.2
1616	S	05	Ewing, Marsh, Stokes, Tuxford	1970	622.3
40365	E	05	Nagata, Kazuma	1977	622.4
4882	F	02	Vesely, Pick	1969	622.4
19177	S	07	Tanaka, D'Arcy, Benson	1975	622.6
40920	G	05	Nicolaides, Eckert	1978	624.0
3990	E	05	Tanaka, Murakami, Fujishiro	1972	624.2
5308	E	05	Savini	1963	624.3
5308	E	05	Savini	1963	624.6
40439	F	08	Grolier	1976	626.4
3647	M	04	Grolier, Viallard	1970	627.3
18301	F	03	Abello	1973	627.3
917	M	06	Ridgway, Butler	1967	630.8
5936	M	01	Cabani, Ceccanti	1973	633.2
5349	G	05	Mrazek	1960	637.4
5993	M	06	Kauer, Kirchner, Haupt, Bittrich	1972	726.8

Table 8. Codes and symbols denoting equipment type

| Code	Symbol	Equipment Type
01	O	McGlashan batch vessel; no inlet or exit mass flow; vented fixed volume with no vapor space; mixed by rocking; semi-isothermal; external temperature sensors; internal calibration heater; internal control heater; no cooler; no reference cell; heat capacity needed. H^E obtained from the electrical energy input.
02	△	Scatchard batch vessel; no inlet or exit mass flow; vented fixed volume with no vapor space; mixed by rocking; non-isothermal; external temperature sensor; external calibration heater; no control heater; no cooler; reference cell may be used; heat capacity needed. H^E obtained from temperature rise of mixed liquids.
03	+	CRMT or Tian-Calvet batch vessel; no inlet or exit mass flow; vented fixed volume with no vapor space; mixed by rocking; semi-isothermal; no temperature sensor; internal calibration heater or chemical calibration; thermoelectric control heater; thermoelectric cooler; no reference cell; heat capacity not needed. H^E obtained from the energy flux across the thermopile as indicated by the voltage produced.
04	X	Miscellaneous batch vessels.
05	◇	Van Ness semi-batch vessel; one intermittent inlet mass flow, no exit mass flow; variable volume with no vapor space; stirred mixing; isothermal; internal temperature sensor; no calibration heater; internal control heater; thermoelectric cooler may or may not be used; no reference cell; heat capacity not needed. H^E obtained from the electrical energy input.
06	⟁	Miscellaneous semi-batch vessels.
07	⋈	Wadsö plug-flow vessel; two continuous inlet mass flows, one exit mass flow; fixed volume with no vapor space; flow mixing; semi-isothermal; no temperature sensor; external calibration heater; thermoelectric heater; thermoelectric cooler; reference cell sometimes used; heat capacity not needed. H^E obtained from the energy flux across the thermopile as indicated by the voltage produced. (This code covers the commercial models by LKB and the Beckman Instrument Co. based on the prototype developed by Monk and Wadso, Acta Chem. Scand., 22, 1842 (1968).
08	Z	Picker plug-flow vessel; two continuous inlet mass flows, one exit mass flow, fixed volume with no vapor space; flow mixing; semi-isothermal or nonisothermal; external temperature sensor; external calibration heater; no control heater; convective cooling; reference cell; heat capacity needed for system studied only when non-isothermal mode is used. In semi-isothermal mode, H^E is obtained from the temperature rise of the coolant stream. In nonisothermal mode, H^E is obtained from the temperature rise of the mixed liquids.
09	Y	Wormald plug-flow vessel; two continuous inlet mass flows, one exit mass flow; fixed volume with no vapor space; flow mixing; isothermal; external temperature sensor; no calibration heater; internal control heater; no cooler; reference cell; heat capacity not needed. H^E obtained from the electrical energy input. (Despite the absence of cooling, this calorimeter can handle both endothermic and exothermic systems.)
10	□	Miscellaneous plug-flow reactors.
11	✻	Wormald backmix vessel; two continuous inlet mass flows, one exit mass flow; fixed volume with no vapor space; stirred mixing; isothermal; internal temperature sensor; no calibration heater; internal control heater; no cooler; no reference cell; heat capacity not needed. H^E obtained from the electrical energy input.
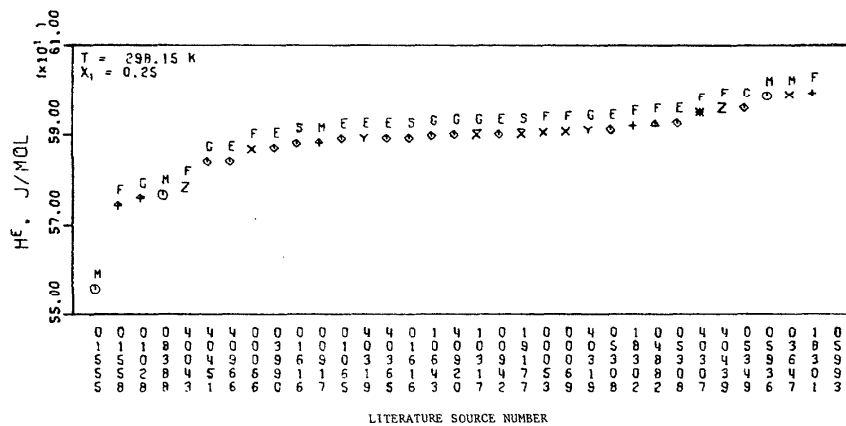
FIGURE 9. Magnitude comparison plot for H^E values at $x_1 = 0.25$ and 298.15 K. Ordinate values run from 550 to 610.
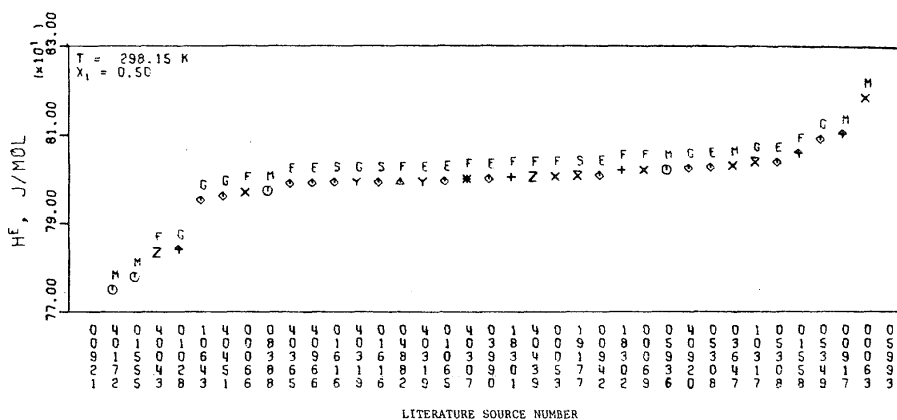
FIGURE 10. Magnitude comparison plot for H^E values at $x_1 = 0.50$ and 298.15 K. Ordinate values run from 770 to 830.
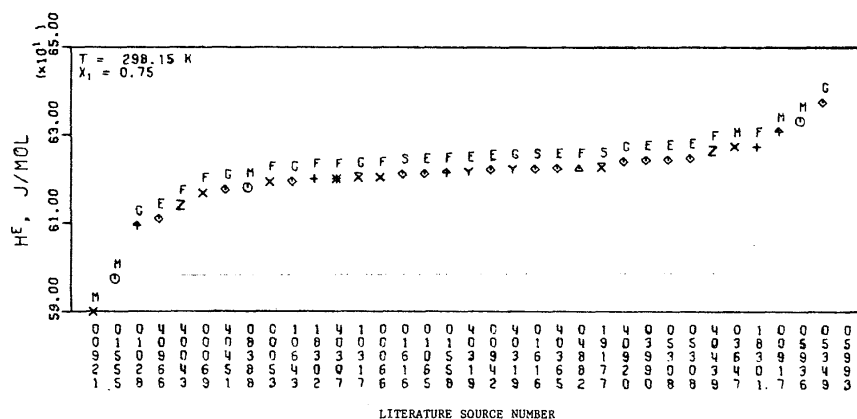
FIGURE 11. Magnitude comparison plot for H^E values at $x_1 = 0.75$ and 298.15 K. Ordinate values run from 590 to 650.

the desire to include as many of the E (excellent) and G (good) scatter rating sets as possible in the $\pm 0.5\%$ band around the selected values.

4.1. Effect of Equipment Type

An attempt has been made in table 8 to characterize with a string of descriptors some of the apparatuses which have had a major impact on the development of heat-of-mixing calorimeters. That list covers only those instruments which have been used to measure publishable H^E data for the benzene + cyclohexane system.

The large number of devices which have been used made it impractical to assign a separate code number to every apparatus. Only the more important representatives of each general type are described separately with the rest of the devices within each type being lumped together under a Miscellaneous code number for that type.

A complete, specific and accurate description of heat-of-mixing calorimeters is difficult to achieve for three reasons. First, an amazing variety of apparatuses have been developed and a very long list of descriptors would be necessary to cover all aspects of construction and operation.

Second, a device often will fall between two obvious descriptors and it is necessary to invent a word to indicate that in-between status. Third, many devices are not described clearly in the literature. Often, no description is given in the document reporting the data of interest; instead, the reader is referred to one or more previously-published documents. Sometimes those previously-published documents describe multiple versions of the apparatus and the technique used, and it is often impossible to determine with complete certainty just how the data were measured. In view of these difficulties, we apologize for any incorrect descriptions of apparatuses, and we request correction by any researchers who may object to the way their apparatuses have been described and classified.

4.1.1. Definition of Descriptors

The equipment types listed in table 8 are divided into four groups based on the mass flow pattern used: batch, semi-batch, plug-flow, and backmix. A batch vessel has no inlet or exit mass flows during the time period when the heat of mixing is being measured. A semi-batch vessel has one inlet stream but no exit stream; these vessels are commonly

termed dilution vessels because one component is initially charged to the vessel and then diluted by addition of the second component. A plug-flow vessel is a tubular device with two continuous feeds and one continuous exit stream; the two inlet streams are merged and flow through the vessel in the mixed state but there is no attempt to achieve complete axial mixing. A backmix vessel is also a continuous flow device with one or two continuous feeds and one continuous exit stream, but there is complete axial mixing.

The inlet feed streams may be none, one, or two, and they may be intermittent or continuous.

Three descriptors are used to describe the reaction vessel volume. The semi-batch vessel must have a variable volume if a vapor space is to be avoided. A flow vessel will have a fixed volume. A batch vessel must have a vented fixed volume to avoid a vapor space; the "vent" is usually a capillary tube in which the height of the vessel liquid can vary as the volume change of mixing occurs.

Vessels are described as having a vapor space or no vapor space. No attempt is made to distinguish between large and small vapor spaces.

Three types of mixing are recognized: mixing by rocking, stirred mixing, and flow mixing. Flow mixing is accomplished by forcing the liquid through constricted flow passages or over flow obstructions to create turbulence.

An accurate description of the vessel temperature mode is not possible with just "isothermal" and "adiabatic". No vessel is completely isothermal or adiabatic; they all fall somewhere between those two extremes. However, the departure from isothermal operation can be easily characterized by the temperature change which occurs; it is not so easy to characterize the departure from adiabatic operation. The descriptors finally selected for use are isothermal, semi-isothermal, and nonisothermal. A vessel was classified as isothermal if it contained control mechanisms which could keep the departure from the set temperature below 0.01 K. A semi-isothermal vessel is one which brings the liquids back to the set point eventually but makes no serious attempt to keep the temperature excursion below 0.01 or even 0.1 K. A non-isothermal vessel is one where adiabatic behavior is approached and no attempt is made to return the vessel temperature to the set temperature immediately.

Temperature sensors are described as being internal or external. An internal sensor is one immersed in the vessel liquids in a manner which permits the accurate sensing of the liquid temperature. An external sensor is one which is separated from the mixing liquids by the vessel wall, i.e., there is a large heat transfer resistance between the sensor and the liquid in the vessel. Sometimes when the sensor is in a glass or metal well which extends into the mixed liquids far enough to permit an accurate measurement, it has been classified as an internal sensor.

A calibration heater is used to determine the response of the vessel and its contents to an accurately measured energy input. The descriptors used are none, internal, and external. An external calibration heater is one mounted on the outside of the vessel wall. Usually the energy released by an external heater can flow to regions other than the vessel contents, and the calibration factors obtained are dependent upon the flow regime and the liquid transport properties inside the vessel.

A control heater is used to maintain the mixing vessel at the set temperature. As in the case of a calibration heater, the descriptors used are none, internal, and external. An external control heater is subject to the same kinds of problems as an external calibration heater. Sometimes the same heater serves as both a control heater and a calibration heater.

A cooler is used to remove energy from the mixing vessel. The descriptors are none, conduction, convective, and thermoelectric. A conduction cooler is a thermopile with one junction in thermal contact with the mixing vessel and other in contact with the heat sink; the metal connectors conduct heat from the vessel and the amount of energy transferred is monitored by the voltage produced. A convective cooler uses a flowing liquid to remove energy by heat transfer from the cell. A thermoelectric cooler is similar in principle to a conduction cooler but a fixed voltage is imposed in order to create a fixed ΔT between the junctions and cause a constant rate of heat transfer from the vessel.

A reference cell which is a duplication of the mixing cell (vessel) is sometimes used to cancel out all energy effects (stirring, energy dissipation due to viscous forces, etc.) except the heat of mixing.

The heat capacity of the mixed liquids plus the mixing vessel is required whenever the vessel contents are not returned to the temperature which existed before mixing. Often the heat capacity is not determined per se. Instead, the temperature response of the vessel to a known energy input is determined and used in the calculation of the H^E in a manner analogous to the use of the actual heat capacity. The descriptor "heat capacity needed" is used for that technique also.

After the string of descriptors for each equipment-type code in table 8, the basic phenomenon used to measure the heat of mixing is given. Other qualifying material may appear also.

4.1.2. Equipment Performance

The Van Ness semi-batch vessel (code 05) has been the most popular design with thirteen sets of data reported. (Two of those sets were reported by the same author (MRL 5308, Savini, Ph.D. Dissertation, 1963).) Of those thirteen sets, the numbers of sets falling within the $\pm 0.5\%$ bands around the selected values at $x_1 = 0.25, 0.50,$ and 0.75 are 10, 11, and 10, respectively. Obviously, the Van Ness vessel is a very reliable device.

Four sets of data measured with a McGlashan batch vessel (code 01) have been reported but H^E values at $x_1 = 0.25$ and 0.75 are available only from three of those sets. Two of the sets fall with the $\pm 0.5\%$ band at $x_1 = 0.50$ but none do at the other two mole fractions.

One set of data from a Scatchard batch vessel (code 02) was available and it fell within the $\pm 0.5\%$ band at all three mole fractions.

Two sets from a CRMT or Tian-Calvet type batch vessel (code 03) have been reported and both fall within the $\pm 0.5\%$ band at $x_1 = 0.50$. Only one set falls within the band at $x_1 = 0.25$ and 0.75.

Other batch vessels (code 04, Miscellaneous Batch Vessels) produced six sets of data. (Only four of those six sets
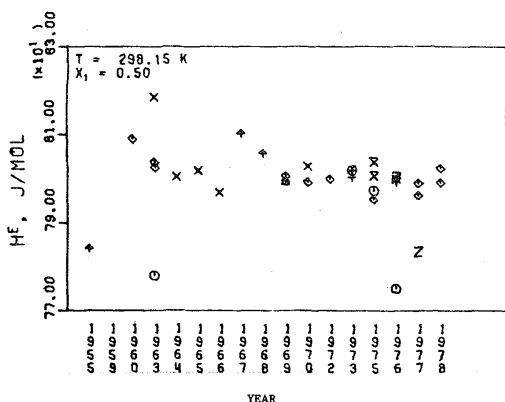
FIGURE 12. Chronological comparison plot for H^E values at $x_1 = 0.50$ and 298.15 K. Ordinate values run from 770 to 830.

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

t, °C	T, K	$1/T \times 10^2$	Best Curve Value $x_1 = 0.25$	$x_1 = 0.50$	$x_1 = 0.75$
7.0	280.15	0.3570	634.5	861.7	669.8
15.0	288.15	0.3470	613.9	833.5	647.7
20.0	293.15	0.3411	601.7	816.3	634.3
23.9	297.04	0.3367	592.7	804.0	624.3
25.0	298.15	0.3354	590.0	800.0	621.5
30.0	303.15	0.3299	578.8	784.8	609.6
35.0	308.15	0.3245	567.7	769.5	597.6
40.0	313.15	0.3193	556.8	754.7	585.8
45.0	318.15	0.3143	546.3	740.5	574.8
50.0	323.15	0.3095	536.8	727.0	564.0
55.0	328.15	0.3047	526.7	713.3	553.2
58.4	331.55	0.3016	520.0	704.3	546.3
75.0	348.15	0.2872	490.7	663.5	514.2
90.0	363.15	0.2754	465.9	629.9	487.8
100.0	373.15	0.2680	450.8	608.5	471.2
120.0	373.15	0.2544	422.6	570.3	441.0

provided values at $x_1 = 0.25$.) Four sets fell within the $\pm 0.5\%$ band at $x_1 = 0.5$ but only two sets fell within the band at the other two mole fractions.

Another semi-batch vessel (code 06, Miscellaneous Semi-Batch Vessels) besides the Van Ness vessel produced one set of data which fell within the $\pm 0.5\%$ band at $x_1 = 0.25$ and 0.75 but not at 0.50.

The Wadsö plug-flow vessel (code 07) has been used for two sets of data and both fall within the $\pm 0.5\%$ band at all three mole fractions.

Two sets of measurements have been reported from the Picker plug-flow vessel (code 08). All the points fall outside the $\pm 0.5\%$ band except for the value at $x_1 = 0.50$ for one set.

MRL 40319 reports two sets of measurements with a Wormald plug-flow vessel (code 09). Both fall within the $\pm 0.5\%$ band at all three mole fractions.

The Wormald backmix vessel (code 11) was used for one set of data. The values at $x_1 = 0.50$ and 0.75 fell within the $\pm 0.5\%$ band but the $x_1 = 0.25$ value did not.

Figure 12 plots the midpoint H^E values reported by the various sources as a function of the date of publication. (The point symbols are related to the equipment type in table 8.) The reliability of the Van Ness semi-batch vessel over a long period of time is illustrated by that figure.

5. Selected Point Values at Other Temperatures

The summary listing in table 4 shows H^E data are available at seventeen temperatures ranging from 280.15 to 393.15 K. Multiple measurements are available at six temperatures: 293.15 (4 sets), 298.15 (37 sets), 303.15 (6 sets), 308.15 (4 sets), 313.15 (2 sets), and 323.15 (5 sets). The number of data sets at each of these temperatures which received an excellent (E), good (G), fair (F) or smoothed (S) scatter

rating is as follows: 293.15 (none), 298.15 (28 sets), 303.15 (1 set), 308.15 (1 set), 313.15 (1 set), and 323.15 (4 sets).

As can be seen from table 4 and from figure 8, the 323.15 K ($1/T = 0.003095$) sets show remarkable agreement. That cluster of points plus the selected values at 298.15 K ($1/T = 0.003354$) were the anchor points used to locate the "best curves" drawn on the comparison plots at $x_1 = 0.25, 0.50$, and 0.75. The selected values at 323.15 can be read from those best curves. Those selected values plus the probable best values at all the other temperatures are listed in table 9.

The remarkable agreement of the high temperature data sets (348.15, 373.15 and 393.15 K) measured by Elliot and Wormald (MRL 40319) with a straight line drawn through the selected values at 298.15 and 323.15 K support the validity of the straight-line best curves drawn on the comparison plots such as figure 8. The lowest-temperature data set of Elliot and Wormald falls slightly below the straight-line best curves (see table 4 and figure 8) which may indicate that the best curve may show some curvature at low temperatures.

6. Recommended Data Sets

The selection of a recommended data set can be done with considerable certainty at 298.15 and 323.15 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.

It is possible also to identify some recommended data sets at temperatures where only one set of data is available.

6.1. Temperatures Other than 298.15 K

The temperatures other than 298.15 at which multiple measurements are available are 293.15, 303.15, 308.15, 313.15, and 323.15 K.

6.1.1. 293.15 K

All four sets at 293.15 received marginal scatter ratings and two of those sets (MRL 770 and 4993) received E quality ratings because of very large percent deviations from the best curves. The two sets with a D quality rating (MRL 57 and MRL 1325) both have only four points. For the MRL 57 set, a comparison could be made with the best curve at only $x_1 = 0.50$. Comparisons at only $x_1 = 0.50$ and 0.75 could be made for the MRL 1325 set.

The two sets with a D quality rating are shown in tables 10 and 11 and in figures 13 and 14. The MRL 57 set (Grosse-Wortman, Jost, and Wagner, 1966) plots more smoothly while the MRL 1325 set (Scatchard, Ticknor, Goates, and McCartney, 1952) covers a slightly wider composition range. Both agree well with the best curves where comparisons can be made (see table 4).

Table 10.   One of the two best sets at 293.15 K

SYSTEM. Benzene(1) + Cyclohexane(2)

TEMPERATURE. 293.15 K   PRESSURE. 0.1013 MPa

QUALITY RATING. D   SCATTER. Marginal

DEVIATION FROM HE VS. 1/T CURVE AT x(1) = 0.25.   -- %

DEVIATION FROM HE VS. 1/T CURVE AT x(1) = 0.50.   -0.3 %

DEVIATION FROM HE VS. 1/T CURVE AT x(1) = 0.75.   -- %

REFERENCE. Grosse-Wortmann, H., Jost, W., Wagner, H. G.,
            Zeitschrift fuer Physikalische Chemie (Frankfurt
            am Main), 49, 74 (1966). (MRL 57)

x(1) mole fraction	EXCESS ENTHALPY J/mol	x(1) mole fraction	EXCESS ENTHALPY J/mol
0.3418	719.1	0.6069	786.0
0.4882	813.1	0.7392	646.6

Table 11.   One of the two best sets at 293.15 K

SYSTEM. Benzene(1) + Cyclohexane(2)

TEMPERATURE. 293.15 K   PRESSURE. 0.1013 MPa

QUALITY RATING. D   SCATTER. Marginal

DEVIATION FROM HE VS. 1/T CURVE AT x(1) = 0.25.   -- %

DEVIATION FROM HE VS. 1/T CURVE AT x(1) = 0.50.   0.5 %

DEVIATION FROM HE VS. 1/T CURVE AT x(1) = 0.75.   -0.2 %

REFERENCE. Scatchard, G., Ticknor, L. B., Goates, J. R.,
            McCartney, E. R., Journal of the American
            Chemical Society, 74, 3721 (1952).
            (MRL 1325)

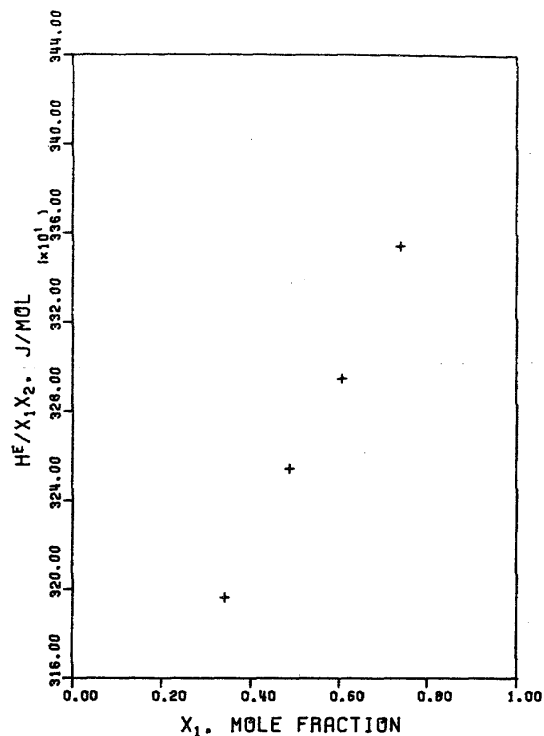| x(1) mole fraction	EXCESS ENTHALPY J/mol	x(1) mole fraction	EXCESS ENTHALPY J/mol
0.3057	675.5	0.5679	805.0
0.5246	828.2	0.8081	526.7

FIGURE 13. One of the two best sets of data at 293.15 K. Grosse-Wortman, Jost, and Wagner, 1966. MRL 57. Ordinate values run from 3160 to 3440.
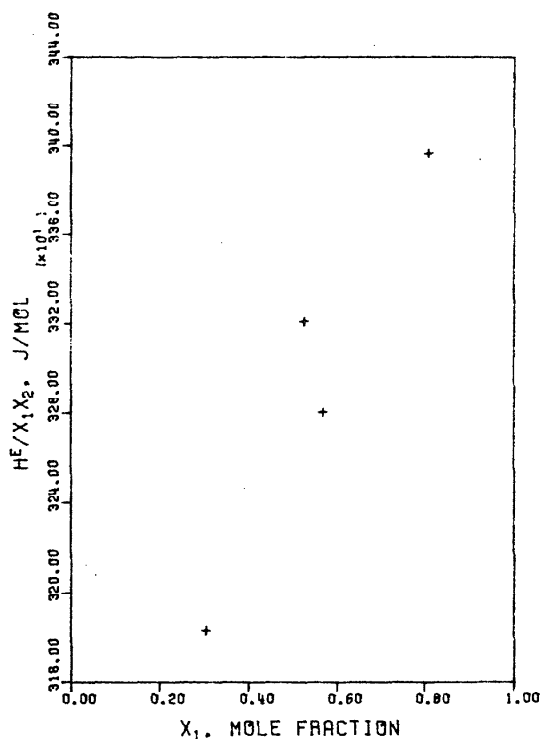

FIGURE 14. One of the two best sets of data at 293.15 K. Scatchard, Ticknor, Goates, and McCartney, 1952. MRL 1325. Ordinate values run from 3160 to 3440.

Table 12. The best set of data at 303.15 K

SYSTEM. Benzene(1) + Cyclohexane(2)

TEMPERATURE. 303.15 K   PRESSURE. 0.1013 MPa

QUALITY RATING. D   SCATTER. Marginal

DEVIATION FROM HE VS. 1/T CURVE AT x(1) = 0.25.   2.8 %

DEVIATION FROM HE VS. 1/T CURVE AT x(1) = 0.50. -2.4 %

DEVIATION FROM HE VS. 1/T CURVE AT x(1) = 0.75. -1.4 %

REFERENCE. Noordtzij, R. M. A., Helvetica Chimica Acta, 39, 637 (1956). (MRL 178)

x(1) mole fraction	EXCESS ENTHALPY J/mol	x(1) mole fraction	EXCESS ENTHALPY J/mol
0.1150	284.5	0.5720	753.1
0.1790	451.9	0.5800	753.1
0.2340	573.2	0.6970	682.0
0.2640	615.0	0.7330	627.6
0.3050	644.3	0.7570	573.2
0.3320	669.4	0.7640	598.3
0.4420	765.7	0.8080	468.6
0.5020	765.7	0.8300	468.6
0.5070	757.3	0.8490	443.5

6.1.2. 303.15 K

The best scatter rating assigned to a 303.15 K data set was the fair (F) rating given the MRL 5022 set (Sosnkowska-Kehiaian and Woycicki, 1965). However, that set had percent deviations of 5.2, 5.5, and 5.1% from the best curves which downgraded it to a D quality rating. One other set (MRL 178, Noordtzij, 1956) also received a D quality rating because, based on the plot shown in figure 6, it received only a marginal (M) scatter rating. However, the percent deviations for the Noordtzij set are only 2.8, − 2.4, and − 1.4. Based on the lower percent deviations and on the H^E versus x_1 plots (not shown), the Noordtzij set appears to be closer to the truth than the Sosnkowska-Kehiaian set. Table 12 lists the Noordtzij data points and figure 6 shows the H^E/x_1x_2 versus x_1 plot.

6.1.3. 308.15 K

The MRL 5349 set (Mrazek, Ph.D. Dissertation, 1960) is obviously the best set at 308.15 K. It received a good (G) scatter rating and a B quality rating. However, as can be seen from table 4 and figure 8, the set does lie above the selected values at $x_1 = 0.25, 0.50,$ and 0.75. The MRL 5349 data set is shown in table 13 and figure 15.

Table 13. The best set of data at 308.15 K

SYSTEM. Benzene(1) + Cyclohexane(2)

TEMPERATURE. 308.15 K   PRESSURE. 0.1013 MPa

QUALITY RATING. B   SCATTER. Good

DEVIATION FROM HE VS. 1/T CURVE AT x(1) = 0.25.   1.7 %

DEVIATION FROM HE VS. 1/T CURVE AT x(1) = 0.50.   1.9 %

DEVIATION FROM HE VS. 1/T CURVE AT x(1) = 0.75.   0.9 %

REFERENCE. Mrazek, R. V., Ph.D. Thesis, Rensselaer Polytechnic Institute, Troy, New York, 1960. (MRL 5349)

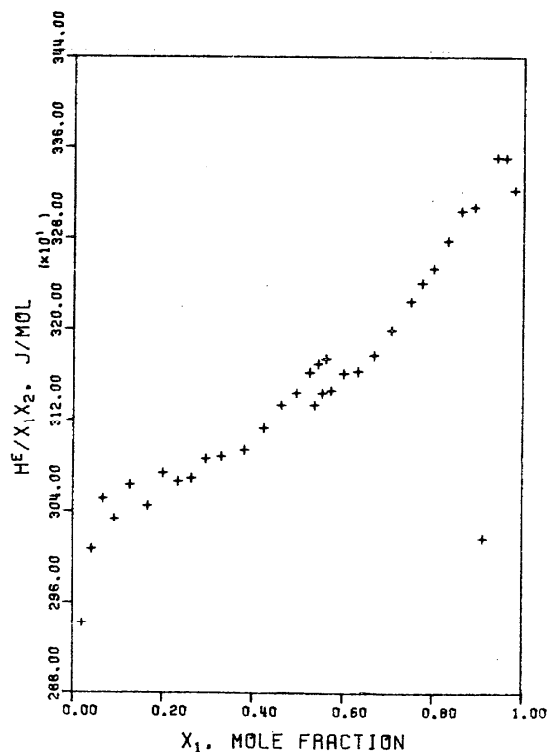| x(1) mole fraction	EXCESS ENTHALPY J/mol	x(1) mole fraction	EXCESS ENTHALPY J/mol
0.0210	60.5	0.3310	683.8
0.0420	121.0	0.3820	730.4
0.0670	190.7	0.4250	760.6
0.0930	255.9	0.4630	779.2
0.1280	341.9	0.4970	786.2
0.1680	425.7	0.5260	788.5
0.2020	495.4	0.5370	779.2
0.2350	551.3	0.5450	786.2
0.2650	597.8	0.5540	776.9
0.2970	644.3	0.5620	781.5
0.5730	769.9	0.8320	458.2
0.6010	758.3	0.8620	393.1
0.6330	735.0	0.8920	318.7
0.6680	704.8	0.9130	239.6
0.7070	662.9	0.9410	186.1
0.7500	604.8	0.9610	125.6
0.7750	565.2	0.9800	65.1
0.8010	518.7		

FIGURE 15. The best set of data at 308.15 K. Mrazek, Ph.D. Dissertation, 1960. MRL 5349. Ordinate values run from 2880 to 3440.

6.1.4. 313.15 K

Both available sets at 313.15 K—MRL 62 and MRL 66—received D quality ratings. The better of the two sets—the MRL 66 set—received a fair (F) scatter rating but was downgraded to a D quality rating by the fairly large deviations (− 3.8, − 1.0, and − 5.0%) from the best curves at $x_1 = 0.25$, 0.50, and 0.75. The MRL 62 set also has fairly large deviations at $x_1 = 0.25$ and 0.75 and, in addition, has a large gap in the middle composition range which prevented a comparison at $x_1 = 0.50$.

The MRL 66 set is tabulated in table 14 and plotted in figure 16.

Table 14. The best set of data at 313.15 K

SYSTEM. Benzene(1) + Cyclohexane(2)

TEMPERATURE. 313.15 K   PRESSURE. 0.1013 MPa

QUALITY RATING. D   SCATTER. Fair

DEVIATION FROM HE VS. 1/T CURVE AT x(1) = 0.25. -3.8 %

DEVIATION FROM HE VS. 1/T CURVE AT x(1) = 0.50. -1.0 %

DEVIATION FROM HE VS. 1/T CURVE AT x(1) = 0.75. -5.0 %

REFERENCE. Sabinin, V. E., Belousov, V. P., Morachevskii, A. G., Izvestiya Vysshikh Uchebnykh Zavedenii, Khimiya i, Khimicheskaya Teknologiya, 9, 382 (1966). (MRL 66)

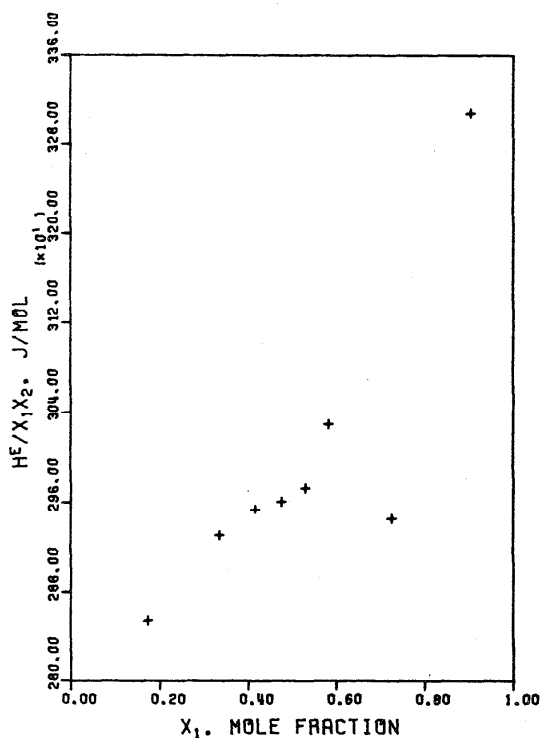| x(1) mole fraction	EXCESS ENTHALPY J/mol	x(1) mole fraction	EXCESS ENTHALPY J/mol
0.1740	410.0	0.5300	740.6
0.3350	652.7	0.5830	736.4
0.4160	717.6	0.7260	585.8
0.4760	738.5	0.9050	284.5

FIGURE 16. The best set of data at 313.15 K. Sabinin, Belousov, and Morachevskii, 1966. MRL 66. Ordinate values run from 2800 to 3360.

6.1.5. 323.15 K

One of the five sets listed at 323.15 K reported only two points near the midpoint and the comparison test could not be made for that set. The other four sets—MRL 53, 904, 3633, and 40319—all show good agreement with the best curves at all three mole fractions, but the MRL 904 and MRL 40319 sets have smaller deviations at $x_1 = 0.75$ than

Table 15. One of the two recommended data sets at 323.15 K

SYSTEM. Benzene(1) + Cyclohexane(2)

TEMPERATURE. 323.15 K   PRESSURE. 0.1013 MPa

QUALITY RATING. A   SCATTER. Smoothed

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

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

DEVIATION FROM HE VS. 1/T CURVE AT x(1) = 0.75. -0.4 %

REFERENCE. Savini, C. G., Winterhalter, D. R., Kovach, L. H., Van Ness, H. C., Journal of Chemical and Engineering Data, 11, 40 (1966). (MRL 904)

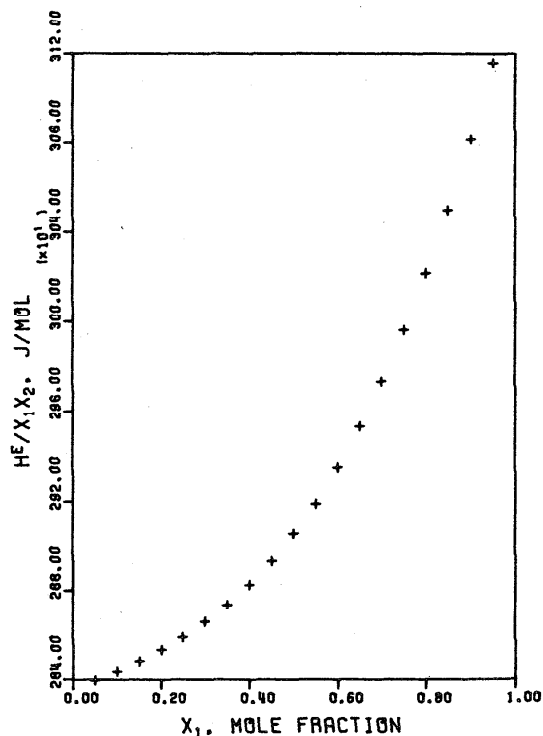| x(1) mole fraction	EXCESS ENTHALPY J/mol	x(1) mole fraction	EXCESS ENTHALPY J/mol
0.0500	134.9	0.5500	722.4
0.1000	255.9	0.6000	704.4
0.1500	363.1	0.6500	671.8
0.2000	456.5	0.7000	624.4
0.2500	536.0	0.7500	561.8
0.3000	601.8	0.8000	483.5
0.3500	653.7	0.8500	388.9
0.4000	691.8	0.9000	277.3
0.4500	716.0	0.9500	148.0
0.5000	726.3		

FIGURE 17. One of the two recommended data sets at 323.15 K. Savini, Winterhalter, Kovach, and Van Ness, 1966. MRL 904. Ordinate values run from 2840 to 3120.

do the other two.

The MRL 53 and MRL 3633 sets received only fair (F) scatter ratings because of mole fraction gaps greater than 0.15 at low x_1 values; neither set contains any points below $x_1 = 0.20$. Otherwise, the scatter, point distribution, and curve shape were good enough to warrant a good (G) scatter rating.

The MRL 904 set was reported in smoothed form and, because of the small percent deviations from the best curves,

received an A quality rating. The MRL 40319 set was not reported in smoothed form; it was assigned a good (G) scatter rating which, along with the small percent deviations, gave it a B quality rating. The MRL 904 set was obtained with the Van Ness semi-batch vessel (code 05), and the MRL 40319 set was measured with the Wormald plug-flow vessel (code 09). The capability of both apparatuses to measure accurate data has been demonstrated by measurements at 298.15 K. Consequently, there is no apparent reason to choose between the two sets and both are selected as recommended sets at 323.15 K. The MRL 904 set (Savini, Winterhalter, Kovach, and Van Ness, 1966) is tabulated in table 15 and plotted in figure 17. The MRL 40319 set (Elliot and Wormald, 1976) is shown in table 16 and figure 18.

6.1.6. Other Temperatures

The best curves on the H^E versus $1/T$ comparison plots are defined primarily by the data sets of Elliot and Wormald

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Table 16. One of the two recommended data sets at 323.15 K

SYSTEM. Benzene(1) + Cyclohexane(2)

OTHER DATA SET INFORMATION. First series

TEMPERATURE. 323.15 K   PRESSURE. 0.1013 MPa

QUALITY RATING. B   SCATTER. Good

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

DEVIATION FROM HE VS. 1/T CURVE AT x(1) = 0.50. -0.0 %

DEVIATION FROM HE VS. 1/T CURVE AT x(1) = 0.75. -0.3 %

REFERENCE. Elliott, K., Wormald, C. J., Journal of Chemical
          Thermodynamics, 8, 881 (1976). (MRL 40319)

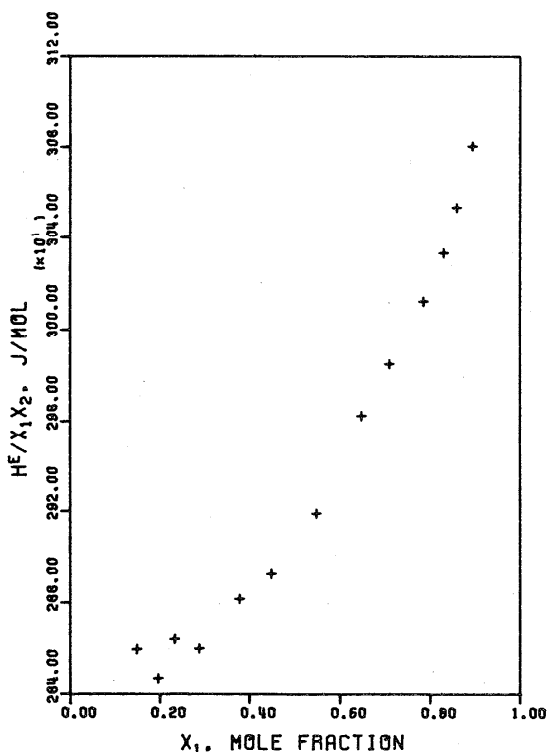| x(1) mole fraction	EXCESS ENTHALPY J/mol	x(1) mole fraction	EXCESS ENTHALPY J/mol
0.1488	362.2	0.6472	676.4
0.1960	448.6	0.7091	615.7
0.2331	512.0	0.7855	507.6
0.2881	586.6	0.8298	428.4
0.3776	677.3	0.8589	370.1
0.4477	715.3	0.8945	290.7
0.5484	722.9		

FIGURE 18. One of the two recommended data sets at 323.15 K. Elliot and Wormald, 1976. MRL 40319. Ordinate values run from 2840 to 3120.

Table 17. Recommended data set at 280.15 K

SYSTEM. Benzene(1) + Cyclohexane(2)

OTHER DATA SET INFORMATION. First series

TEMPERATURE. 280.15 K   PRESSURE. 0.1013 MPa

QUALITY RATING. B   SCATTER. Good

DEVIATION FROM HE VS. 1/T CURVE AT x(1) = 0.25. -1.2 %

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

DEVIATION FROM HE VS. 1/T CURVE AT x(1) = 0.75. -0.8 %

REFERENCE. Elliott, K., Wormald, C. J., Journal of Chemical
          Thermodynamics, 8, 881 (1976). (MRL 40319)

x(1) mole fraction	EXCESS ENTHALPY J/mol	x(1) mole fraction	EXCESS ENTHALPY J/mol
0.1483	422.2	0.6475	794.1
0.1963	524.7	0.7095	726.5
0.2880	687.4	0.7853	600.1
0.3776	791.1	0.8296	509.6
0.4478	837.7	0.8597	438.6
0.5482	849.4	0.8954	343.6

Table 18. Recommended data set at 348.15 K

SYSTEM. Benzene(1) + Cyclohexane(2)

OTHER DATA SET INFORMATION. First series

TEMPERATURE. 348.15 K   PRESSURE. 0.1013 MPa

QUALITY RATING. B   SCATTER. Good

DEVIATION FROM HE VS. 1/T CURVE AT x(1) = 0.25. 0.5 %

DEVIATION FROM HE VS. 1/T CURVE AT x(1) = 0.50. -0.2 %

DEVIATION FROM HE VS. 1/T CURVE AT x(1) = 0.75. -0.6 %

REFERENCE. Elliott, K., Wormald, C. J., Journal of Chemical
          Thermodynamics, 8, 881 (1976). (MRL 40319)

x(1) mole fraction	EXCESS ENTHALPY J/mol	x(1) mole fraction	EXCESS ENTHALPY J/mol
0.1493	328.1	0.6471	614.0
0.1955	411.4	0.7096	558.2
0.2336	464.3	0.7854	461.5
0.2880	536.9	0.8301	390.5
0.3781	615.6	0.8588	337.6
0.4474	651.6	0.8943	261.4
0.5483	658.4		

at 280.15, 298.15, 323.15, 348.15, 373.15, and 393.15 K. The 298.15 data are analyzed in the next section, and the 323.15 data are shown in table 16 and figure 18. The sets at 280.15, 348.15, 373.15, and 393.15 K are shown in tables 17 through 20 and in figures 19, 20, 4, and 5, respectively. The sets at 280.15, 348.15, and 373.15 all received good (G) scatter ratings and B quality ratings. The highest temperature set (393.15 K) showed more scatter and received a fair (F) scatter rating which restricted it to a C quality rating. Despite the C quality rating for the 393.15 K set, and despite the fact that the 280.15. 280.15 K set falls slightly below the straight line defined by the other five sets, all six of the Elliot and Wormald sets are presented as recommended data sets. Their apparent accuracy and the fact that they cover a 113 K temperature range make them a very important experimental contribution.

Table 19. Recommended data set at 373.15 K

SYSTEM. Benzene(1) + Cyclohexane(2)

OTHER DATA SET INFORMATION. First series

TEMPERATURE. 373.15 K   PRESSURE. 0.2026 MPa

QUALITY RATING. B   SCATTER. Good

DEVIATION FROM HE VS. 1/T CURVE AT x(1) = 0.25.   -0.3 %

DEVIATION FROM HE VS. 1/T CURVE AT x(1) = 0.50.   0.2 %

DEVIATION FROM HE VS. 1/T CURVE AT x(1) = 0.75.   0.4 %

REFERENCE. Elliott, K., Wormald, C. J., Journal of Chemical
           Thermodynamics, 8, 881 (1976). (MRL 40319)

x(1) mole fraction	EXCESS ENTHALPY J/mol	x(1) mole fraction	EXCESS ENTHALPY J/mol
0.1493	305.0	0.6472	570.1
0.1960	373.2	0.7098	518.7
0.2333	427.4	0.7863	426.0
0.2814	492.2	0.8300	360.5
0.3773	569.2	0.8588	309.6
0.4474	600.2	0.8967	236.9
0.5489	606.3		

Table 20. Recommended data set at 393.15 K

SYSTEM. Benzene(1) + Cyclohexane(2)

OTHER DATA SET INFORMATION. First series

TEMPERATURE. 393.15 K   PRESSURE. 0.3040 MPa

QUALITY RATING. C   SCATTER. Fair

DEVIATION FROM HE VS. 1/T CURVE AT x(1) = 0.25.   -0.3 %

DEVIATION FROM HE VS. 1/T CURVE AT x(1) = 0.50.   -0.3 %

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

REFERENCE. Elliott, K., Wormald, C. J., Journal of Chemical
           Thermodynamics, 8, 881 (1976). (MRL 40319)

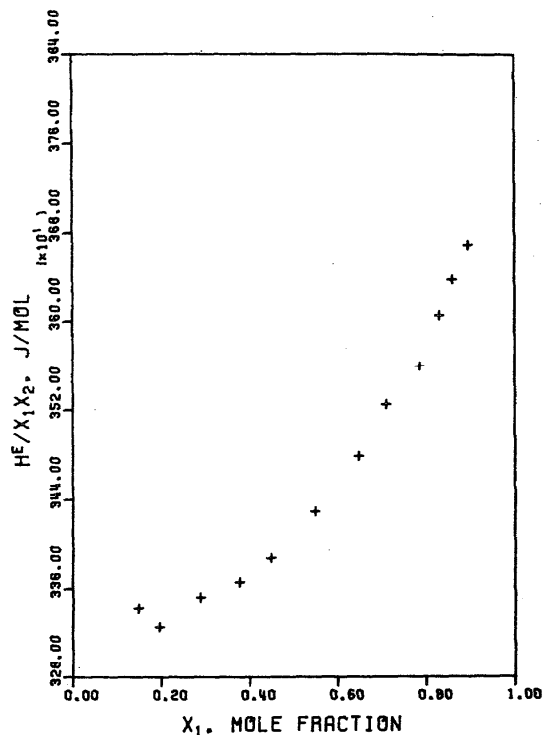| x(1) mole fraction	EXCESS ENTHALPY J/mol	x(1) mole fraction	EXCESS ENTHALPY J/mol
0.1480	280.8	0.6472	526.0
0.1958	352.4	0.7083	482.7
0.2335	403.8	0.7856	400.8
0.2877	460.3	0.8302	338.6
0.3782	527.4	0.8593	287.9
0.5493	566.4	0.8975	216.8

FIGURE 19. Recommended data set at 280.15 K. Elliot and Wormald, 1976. MRL 40319. Ordinate values run from 3280 to 3840.
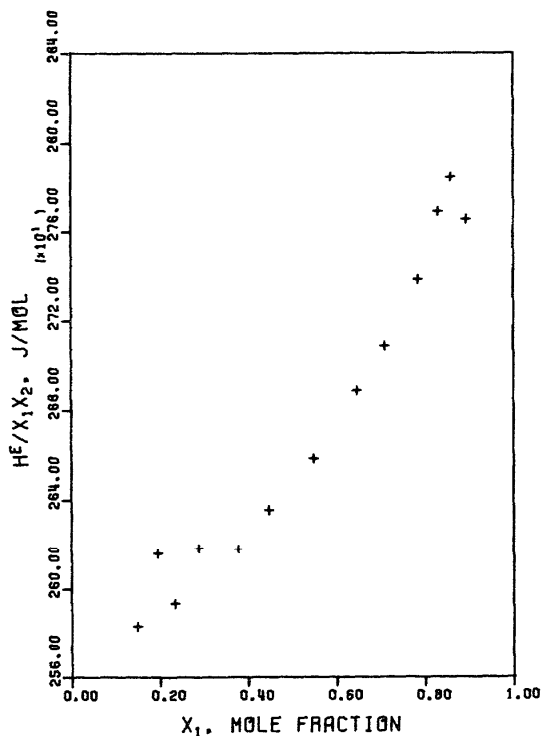

FIGURE 20. Recommended data set at 348.15 K. Elliot and Wormald, 1976. MRL 40319. Ordinate values run from 2560 to 2840.

Table 21. MRL numbers and scatter rating 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

$x_1 = 0.25$	$x_1 = 0.50$	$x_1 = 0.75$
53 (F)	53 (F)	53 (F)
--	66 (F)	66 (F)
69 (F)	69 (F)	--
917 (M)	--	--
942 (E)	942 (E)	942 (E)
1065 (E)	1065 (E)	1065 (E)
--	--	1558 (F)
1616 (S)	1616 (S)	1616 (S)
1616 (S)	1616 (S)	1616 (S)
--	3647 (M)	--
3990 (E)	3990 (E)	3990 (E)
4882 (F)	4882 (F)	4882 (F)
5308 (E)	5308 (E)	5308 (E)
5308 (E)	5308 (E)	5308 (E)
--	5936 (M)	--
--	8388 (M)	--
10317 (G)	10317 (G)	10317 (G)
10643 (G)	--	10643 (G)
--	18301 (G)	--
18302 (F)	18302 (F)	18302 (F)
19177 (S)	19177 (S)	19177 (S)
--	40307 (F)	40307 (F)
40319 (G)	40319 (G)	40319 (G)
40319 (E)	40319 (E)	40319 (E)
40365 (E)	40365 (E)	40365 (E)
--	40439 (F)	--
--	40451 (G)	--
40920 (G)	40920 (G)	40920 (G)
--	40966 (E)	--

6.2. Data Sets at 298.15 K

Table 21 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. Because of the wealth of data, the choice of the recommended data set at 298.15 can be restricted to a set with an excellent (E) or smoothed (S) scatter rating and which falls within the $\pm 0.5\%$ band at all three mole fractions. Those sets of data which satisfy those criteria are listed in table 22.

The data sets in table 22 were compared in two more

Table 22. Data sets which fall within the $\pm 0.05\%$ band at all three mole fractions and which have either an excellent (E) or smoothed (S) scatter rating. The S and ET codes refer to the scatter rating and the equipment type respectively.

	Codes		Percent Deviation		
MRL	S	ET	0.25	0.50	0.75
942	E	05	0.0	0.1	0.1
1065	E	05	-0.2	-0.1	0.0
1616[a]	S	05	-0.3	-0.1	0.1
3990	E	05	-0.5	0.0	0.4
5308[b]	E	05	0.2	0.3	0.5
19177	S	07	0.0	0.1	0.2
40319[c]	E	09	-0.1	-0.1	0.0
40365	E	05	-0.1	-0.1	0.1

[a] Set taken with the Model 3 vessel.

[b] Set which had a pressure fluctuation of 20 inches of Hg.

[c] Set from the second series.

Table 23. Fitting results for some selected data sets at 298.15 K. The S and ET codes refer to the scatter rating and equipment type codes respectively.

Source	Codes[a]		Root Mean Squared Deviation				
	S	ET	D=1[b]	D=2	D=3	D=4	D=5
942	E	05	4.93	1.39	1.09[c]	1.07	1.07
1065	E	05	5.67	0.99	0.35[c]	0.31	0.31
1616	S	05	6.63	0.70	0.04[c]	0.04	0.02
3990	E	05	6.03	1.29	0.66[c]	0.59	0.52
5308	E	05	5.49	1.89	1.88	1.85	1.84
19177	S	07	5.49	0.92	0.38[c]	0.39	0.29
40319	E	09	5.24	0.57	0.22[c]	0.17	0.17
40365	E	05	5.22	1.45	0.69[c]	0.25	0.23

[a] The scatter and equipment type codes are defined in tables 1 and 8.

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

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

ways in order to identify the recommended data set. First, each of those eight sets was fitted with the Redlich-Kister equation (equation (4a)) using D values of 1, 2, 3, 4, and 5. The results are shown in table 23. The root mean squared deviation (RMSD) used is defined by

$$RMSD = \left[\frac{\sum_{i=1}^{N} (H^E_{exp} - H^E_{calc})^2_i}{N} \right] \qquad (5)$$

where N is the number of experimental points. The RMSD provides a measure of the relative amount of scatter in the various data sets. All but one of the data sets in table 23 show a sizeable decrease in RMSD up to $D = 3$. One set showed a further sizeable decrease when $D = 4$ was used. Based on these results D values of 2, 3, and 4 were used for the final comparison.

The final comparison is shown in figure 21, 22, and 23. Those plots used $D = 2$, 3, and 4, respectively, for the Redlich-Kister equation used to represent each of the eight sets of data. The percent deviation plotted is relative to a second degree (three-constant) Redlich-Kister equation fitted to the selected point H^E values at $x_1 = 0.25$, 0.50, and 0.75. The percent deviation is defined by

$$\frac{H^E_{set} - H^E_{ref}}{H^E_{ref}} (100) \qquad (6)$$

where H^E_{ref} was calculated from the following fit of the three selected values.

$$H^E/x_1 x_2$$
$$= 3200.0000 + 168.0005(x_1 - x_2)$$
$$+ 122.6660(x_1 - x_2)^2. \qquad (7)$$

Figures 21, 22, and 23 show that the impression created by this type of plot is a function of the equation used to represent the individual data sets. Obviously, the same degree should be used for all the sets compared and that degree must be chosen carefully after trying all the reasonable possibilities. For the system being considered here, $D = 2$ is obvi-
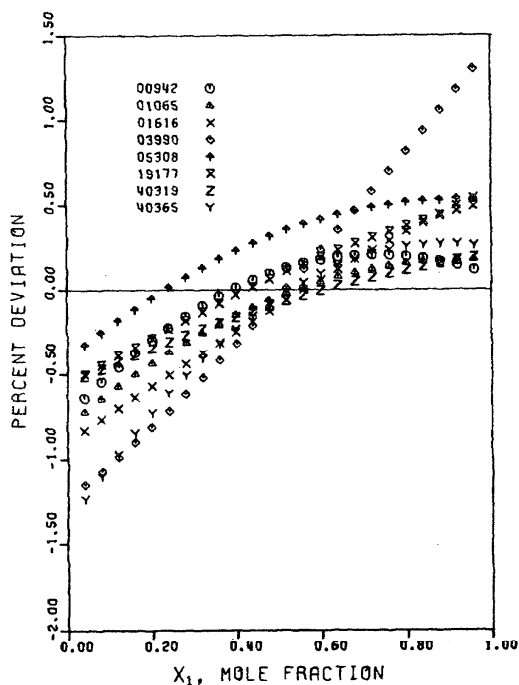
FIGURE 21. Comparison of the better sets of data at 298.15 K to a three-constant $(D = 2)$ fit of the selected values at $x_1 = 0.25$, 0.50, and 0.75. The eight literature sets are represented by three-constant $(D = 2)$ equations.

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 eight literature sets are represented by five-constant $(D = 4)$ equations.
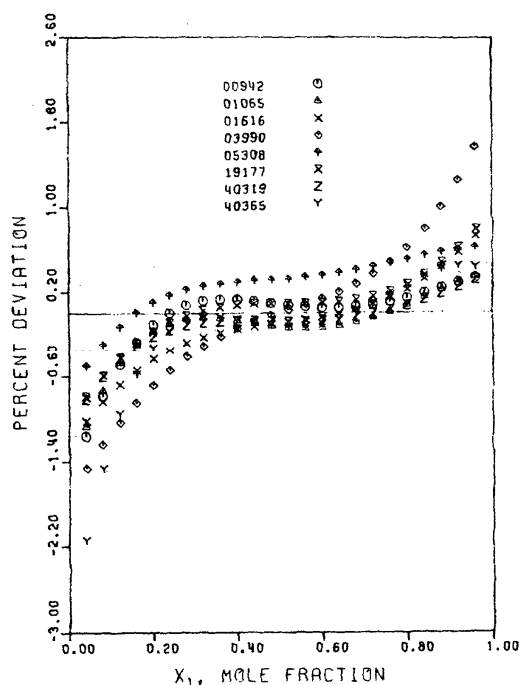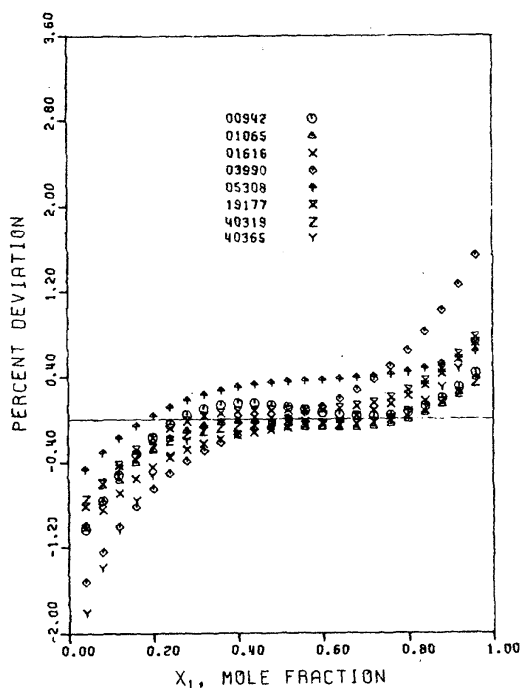

FIGURE 22. Comparison of the better sets of data at 298.15 K to a three-constant $(D = 2)$ fit of the selected values at $x_1 = 0.25$, 0.50, and 0.75. The eight literature sets are represented by four-constant $(D = 3)$ equations.

ously not sufficient; all the eight sets fall within the $\pm 0.5\%$ band at $x_1 = 0.25$, 0.50, and 0.75 but, as shown in figure 21, the $D = 2$ representations fall outside the band for two sets at $x_1 = 0.25$ and for one set at 0.75. The $D = 3$ representations in figure 22 all fall within the $\pm 0.5\%$ band at all three mole fractions but, as can be seen from figure 23, one set falls outside the band at $x_1 = 0.25$ when $D = 4$ is used.

The large deviations shown at high and low x_1 values are unfortunate but not important insofar as the comparisons of the eight selected sets are concerned. Those deviations simply reflect the fact that a three-constant equation constrained to the $x_1 = 0.25$, 0.50, and 0.75 points is not likely to have the correct shape in the 0.0 to 0.25, and 0.75 to 1.0 mole fraction ranges. The primary consideration in figures 21, 22, and 23 is not how well the individual sets agree with eq (7) but how well they agree with each other; eq (7) simply provides a common reference for all the sets being compared.

It can be seen from figure 22 that sets 3990, 5308, and 40365 deviate significantly from the other five sets. Further deletions are difficult and may be incorrect. However, the 1616 set lies below the remaining sets in the $x_1 = 0.0$ to 0.5 range, and the 942 set is first low and then high in that range.

The remaining sets—1065, 19177, and 40319—are tabulated in tables 24, 25, and 26 and plotted in figures 24, 25, and 1, respectively. The H^E/x_1x_2 plots indicate that the 19177 and 40319 sets are somewhat better behaved at low x_1 values. Figure 22 shows that the 19177 and 40319 sets agree within about 0.1% at low x_1 values but differ by almost 0.5%

Table 24. One of the three best sets at 298.15 K

SYSTEM. Benzene(1) + Cyclohexane(2)

TEMPERATURE. 298.15 K   PRESSURE. 0.1013 MPa

QUALITY RATING. A   SCATTER. Excellent

DEVIATION FROM HE VS. 1/T CURVE AT x(1) = 0.25.   -0.2 %

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

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

REFERENCE. Stokes, R. H., Marsh, K. N., Tomlins, R. P.,
            Journal of Chemical Thermodynamics, 1, 211
            (1969). (MRL 1065)

x(1) mole fraction	EXCESS ENTHALPY J/mol	x(1) mole fraction	EXCESS ENTHALPY J/mol
0.0206	62.7	0.3752	741.8
0.0485	143.9	0.4196	773.2
0.1006	283.3	0.4580	790.7
0.1477	394.0	0.4916	798.7
0.1897	481.9	0.5186	800.1
0.2279	552.6	0.5789	786.0
0.2626	608.7	0.6047	773.4
0.2944	654.2	0.6365	752.0
0.3236	690.2	0.6718	720.5
0.3504	719.0	0.7113	675.6
0.7559	612.0	0.8957	319.4
0.7803	571.4	0.9305	223.4
0.8063	523.3	0.9674	109.5
0.8340	466.7	0.9872	44.1
0.8638	399.3		

Table 26. One of the three best sets at 298.15 K

SYSTEM. Benzene(1) + Cyclohexane(2)

OTHER DATA SET INFORMATION. Second series

TEMPERATURE. 298.15 K   PRESSURE. 0.1013 MPa

QUALITY RATING. A   SCATTER. Excellent

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

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

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

REFERENCE. Elliott, K., Wormald, C. J., Journal of Chemical
            Thermodynamics, 8, 881 (1976). (MRL 40319)

x(1) mole fraction	EXCESS ENTHALPY J/mol	x(1) mole fraction	EXCESS ENTHALPY J/mol
0.0576	169.6	0.5487	796.2
0.1086	302.8	0.5747	788.1
0.1951	492.4	0.6033	774.8
0.2674	615.9	0.6349	754.1
0.3272	694.5	0.6697	723.0
0.3779	743.8	0.7089	679.4
0.4220	774.1	0.7529	616.8
0.4597	791.1	0.8019	532.0
0.4929	798.8	0.8589	410.9
0.5224	799.5	0.9240	241.4
0.9604	132.0		

at high x_1 values. The 1065 set agrees closely with the 40319 set at high x_1 values and differs from the 19177 and 40319 sets by about 0.2 and 0.3%, respectively, at low x_1 values.

Based on the above observations, the MRL 40319 set (Elliot and Wormald, 1976) is a reasonable choice for the recommended data set at 298.15 K. However, the strongest

argument for that choice is the fact that Elliot and Wormald have also measured one of the two data sets recommended at 323.15 plus four other reliable sets at 280.15, 348.15, 373.15, and 393.15.

Table 25. One of the three best sets at 298.15 K

SYSTEM. Benzene(1) + Cyclohexane(2)

TEMPERATURE. 298.15 K   PRESSURE. 0.1013 MPa

QUALITY RATING. A   SCATTER. Smoothed

DEVIATION FROM HE VS. 1/T CURVE AT x(1) = 0.25.   0.0 %

DEVIATION FROM HE VS. 1/T CURVE AT x(1) = 0.50.   0.1 %

DEVIATION FROM HE VS. 1/T CURVE AT x(1) = 0.75.   0.2 %

REFERENCE. Tanaka, R., D'Arcy, P. J., Benson, G. C.,
            Thermochimica Acta, 11, 163 (1975).
            (MRL 19177)

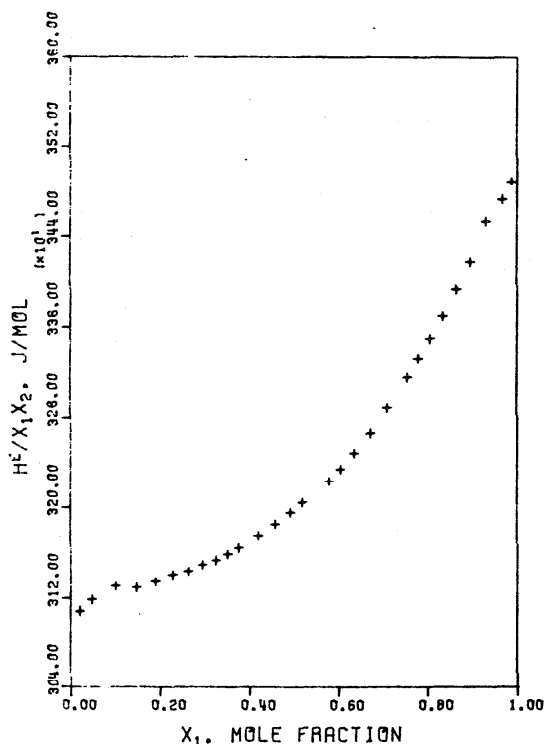| x(1) mole fraction	EXCESS ENTHALPY J/mol	x(1) mole fraction	EXCESS ENTHALPY J/mol
0.0500	148.5	0.5500	796.7
0.1000	281.5	0.6000	777.7
0.1500	399.1	0.6500	742.0
0.2000	501.5	0.7000	691.5
0.2500	590.3	0.7500	622.6
0.3000	661.9	0.8000	536.9
0.3500	719.8	0.8500	432.5
0.4000	762.3	0.9000	308.7
0.4500	789.1	0.9500	165.1
0.5000	800.6		

FIGURE 24. One of the three best sets at 298.15 K. Stokes, Marsh, and
            Tomlins, 1969. MRL 1065. Ordinate values run from 3040 to
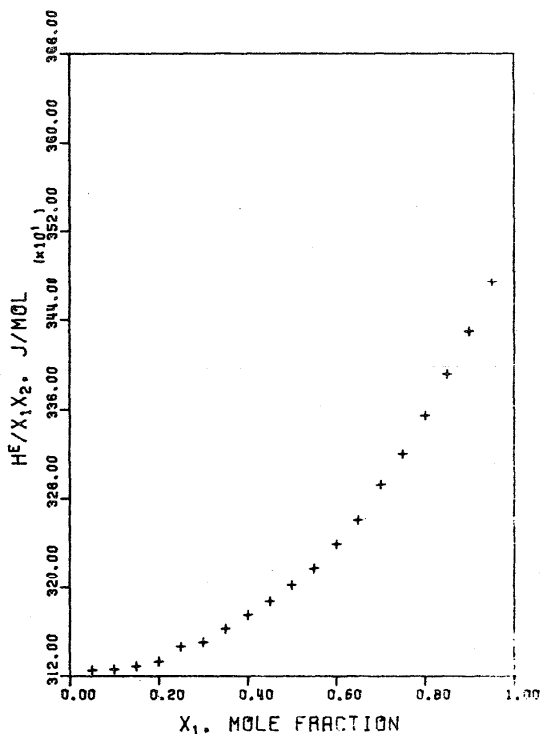   3600.

FIGURE 25. One of the three best sets at 298.15 K. Tanaka, D'Arcy, and Benson, 1975. MRL 19177. Ordinate values run from 3120 to 3680.

7. New Experimental Measurements Needed

Firm selections of recommended data sets can be made at 298.15 and 323.15 K. Reliable measurements are available at 280.15, 348.15, 373.15, and 393.15 K. Obviously, the situation is good for H^E data for the benzene + cyclohexane system.

New measurements to confirm the Elliot and Wormald measurements at temperatures other than 298.15 and 323.15 K would be desirable, particularly at 280.15 K to determine whether or not there is curvature in the H^E versus $1/T$ plot at low temperature. Measurements at temperatures higher than393.15 K would be interesting but probably would not satisfy any pressing practical need. The 280.15 to 393.15 K range already covered will probably by sufficient for any practical correlation or chemical processing purposes for this system.

8. Data Set Tabulations

Tabulations 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 H^E tables with the H^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. The entire set of tables/plots must be ordered; requests for individual sets of data will not be processed. An invoice will be mailed with the tables.

9. Bibliography

Table 27 is the bibliography for excess enthalpy 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 27 to the data set tabulations, and to the various tables and figures used in the main body of this report.

A few of the documents listed in table 27 report H^E data in a form which did 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 H^E literature for the benzene(1) + cyclohexane(2) system.

TABLE 27. Bibliography for excess enthalpy data.

48. Nicholson, D. E., J. Chem. Eng. Data 6, 5 (1961).
51. Ratnam, A. V., Rao, C. V., Murti, P. S., Chem. Eng. Sci. 17, 392 (1962).
53. Lundberg, G. W., J. Chem. Eng. Data 9, 193 (1964).
57. Grosse-Wortmann, H., Jost, W., Wagner, H. G., Z. Phys. Chem. (Frankfurt am Main) 49, 74 (1966).
62. Paz Andrade, M. I., Ocon, J., Casanova, J., An. Real Soc. Espan. Fis. Quim., Ser. B 61, 707 (1965).
63. Kokalos, J. J., Ph.D. Dissertation, Purdue University, Lafayette, Indiana, 1963.
66. Sabinin, V. E., Belousov, V. P., Morachevskii, A. G., Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol. 9, 382 (1966).
69. Watson, A. E. P., McLure, I. A., Bennett, J. E., Benson, G. C., J. Phys. Chem. 69, 2753 (1965).
149. Lacher, J. R., Buck, W. B., Parry, W. H., J. Amer. Chem. Soc. 63, 2422 (1941).
165. Mathieson, A. R., Thynne, J. C. J., J. Chem. Soc., London, 3708 (1956).
172. Moore, W. R., Styan, G. E., Trans. Faraday Soc. 52, 1556 (1956).
178. Noordtzij, R. M. A., Helv. Chim. Acta. 39, 637 (1956).
241. Donald, M. B., Ridgway, K., J. Appl. Chem. 8, 403 (1958).
686. Mrazek, R. V., Van Ness, H. C., AIChE J. 7, 190 (1961).
770. Brown, C. P., Mathieson, A. R., Thynne, J. C. J., J. Chem. Soc., London, 4141 (1955).
904. Savini, C. G., Winterhalter, D. R., Kovach, L. H., Van Ness, H. C., J. Chem. Eng. Data 11, 40 (1966).
917. Ridgway, K., Butler, P. A., J. Chem. Eng. Data 12, 509 (1967).
921. Goates, J. R., Sullivan, R. J., Ott, J. B., J. Phys. Chem. 63, 589 (1959).
924. Schnaible, H. W., Van Ness, H. C., Smith, J. M., AIChE J. 3, 147 (1957).
942. Murakami, S., Benson, G. C., J. Chem. Thermodyn. 1, 559 (1969).
977. Mato, F., Coca, J., An. Quim. 65, 1 (1969).
1028. Schnaible, H. W., Ph.D. Dissertation, Purdue University, West Lafayette, Indiana, 1955.
1065. Stokes, R. H., Marsh, K. N., Tomlins, R. P., J. Chem. Thermodyn. 1, 211 (1969).
1325. Scatchard, G., Ticknor, L. B., Goates, J. R., McCartney, E. R., J. Amer. Chem. Soc. 74, 3721 (1952).
1535. Thacker, R., Rowlinson, J. S., Trans. Faraday Soc. 50, 1036 (1954).
1545. Anderson, R., Prausnitz, J. M., Rev. Sci. Instrum. 32, 1224 (1961).
1555. Diaz Pena, M., Fernandex Martin, F., An. Real Soc. Espan. Fis. Quim., Ser. B 59, 323 (1963).
1558. Woycicki, W., Sadowska, K. W., Bull. Acad. Pol. Sci., Ser. Sci. Chim. 16, 147 (1968).
1616. Ewing, M. B., Marsh, K. N., Stokes, R. H., Tuxford, C. W., J. Chem. Thermodyn. 2, 751 (1970).
3633. Vesely, F., Hynek, V., Svoboda, V., Holub, R., Collect. Czech. Chem. Commun. 39(2), 355 (1974).
3647. Grolier, J.-P., Viallard, A., J. Chim. Phys. Physicochim. Biol. 67,

1582 (1970).

3990. Tanaka, R., Murakami, S., Fujishiro, R., Bull. Chem. Soc. Jap. **45**(7), 2107 (1972).

4882. Vesely, F., Pick, J., Collect. Czech. Chem. Commun. **34**, 1854 (1969).

4983. Sosnkowska-Kehiaian, K., Recko, W., Woycicki, W., Bull. Acad. Pol. Sci., Ser. Sci. Chim. **14**(7), 475 (1966).

5022. Sosnkowska-Kehiaian, K., Woycicki, W., Bull. Acad. Pol. Sci., Cl. Troisieme **13**, 649 (1965).

5308. Savini, C. G., Ph.D. Thesis, Rensselaer Polytechnic Institute, Troy, New York, 1963.

5349. Mrazek, R. V., Ph.D. Thesis, Rensselaer Polytechnic Institute, Troy, New York, 1960.

5936. Cabani, S., Ceccanti, N., J. Chem. Thermodyn. **5**(1), 9 (1973).

5993. Kauer, E., Kirchner, D., Haupt, D., Bittrich, H. J., Z. Phys. Chem. (Leipzig) **250**(3-4), 153 (1972).

8388. Mattingley, B. I., Fenby, D. V., Aust. J. Chem. **28**, 185 (1975).

10317. Hsu, K.-Y., Clever, H. L., J. Chem. Thermodyn. **7**, 435 (1975).

10417. Lenoir, J. M., Hayworth, K. E., Hipkin, H. G., J. Chem. Eng. Data **16**(3), 285 (1971).

10643. Touhara, H., Ikeda, M., Nakanishi, K., Watanabe, N., J. Chem. Thermodyn. **7**, 887 (1975).

16357. Murakami, T., Murakami, S., Fujishiro, R., Bull. Chem. Soc. Jap. **42**(1), 35 (1969).

18301. Abello, L., J. Chim. Phys. Physicochim. Biol. **70**(9), 1355 (1973).

18302. Bares, D., Soulie, M., Metzger, J., J. Chim. Phys. Physicochim. Biol. **70**, 1531 (1973).

19177. Tanaka, R., D'Arcy, P. J., Benson, G. C., Thermochim. Acta **11**, 163 (1975).

40043. Meyer, R., Giusti, G., Vincent, E.-J., Meyer, M., Thermochim. Acta **19**(2), 153 (1977).

40172. Yang, S.-K., Gomez-Ibanez, J. D., J. Chem. Thermodyn. **8**, 209 (1976).

40307. Coomber, B. A., Wormald, C. J., J. Chem. Thermodyn. **8**(8), 793 (1976).

40319. Elliott, K., Wormald, C. J., J. Chem. Thermodyn. **8**, 881 (1976).

40365. Nagata, I., Kazuma, K., J. Chem. Eng. Data **22**(1), 79 (1977).

40439. Grolier, J.-P. E., Thermochim. Acta **16**(1), 27 (1976).

40451. Gracia, M., J. Chem. Thermodyn. **9**(1), 55 (1977).

40920. Nicolaides, G. L., Eckert, C. A., J. Chem. Eng. Data **23**(2), 152 (1978).

40966. Obbink, J. H., van Miltenburg, J. C., van den Berg, G. J. K., J. Chem. Thermodyn. **10**(7), 691 (1978).

10. 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 (5).
H^E	Excess enthalpy.
x	Liquid mole fraction.

11. Acknowledgments

12. Literature Cited

[1] Smith, B. D., Muthu, O., Dewan, A., Gierlach, M., J. Phys. Chem. Ref. Data **11**, 1151 (1982). "Evaluation of Binary Excess Volume Data for C_6 Hydrocarbons. Benzene + Cyclohexane."

[2] Smith, B. D., Muthu, O., Dewan, A., Gierlach, M., J. Phys. Chem. Ref. Data **11**, 1099 (1982). "Evaluation of Binary PTxy Vapor-Liquid Equilibrium Data for C_6 Hydrocarbons. Benzene + Cyclohexane."

[3] Smith, B. D., Muthu, O., Dewan, A., Gierlach, M., J. Phys. Chem. Ref. Data **11**, 941 (1982). "Critical Evaluation of Vapor-Liquid Equilibrium, Heat of Mixing and Volume Change of Mixing Data. General Procedures."