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

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Buford D. Smith, Ol Muthu, and Ashok Dewan

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Buford D. Smith, Oi Muthu, and Ashok Dewan

Thermodynamics Research Laboratory, Box 1144, Washington University, St. Louis, Missouri 63130

The excess enthalpy data for the benzene + hexane system are evaluated. The needs for new experimental data are defined.

Key words: benzene; excess enthalpy; heat of mixing; hexane.

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1. Introduction

Of the C_6 hydrocarbon + C_6 hydrocarbon binary systems, three systems—benzene + cyclohexane, benzene + n-hexane, cyclohexane + n-hexane—have special significance for correlators and experimentalists. Together they represent the molecular interactions between three important hydrocarbon types—aromatics, cycloalkanes, and alkanes. Also, because of their moderate volatilities, and the availability at high purities, they have been popular components for experimentalists measuring vapor–liquid equilibrium (VLE), heat of mixing (H^E), or volume change of mixing (V^E) data. All three are used as test systems for new experimental devices. The benzene + cyclohexane has been widely used as a test system for V^E and H^E devices, and the cyclohexane + hexane system has been very heavily used for H^E devices. The benzene + hexane system has been less widely used but has found some use as a test system for VLE devices.

This paper presents the evaluation results for the H^E data for the benzene + hexane system. Parallel papers cover the VLE and V^E data. The benzene + cyclohexane system has been covered in three preceding papers[1–3] which also presented detailed descriptions of the evaluation procedures used for the three individual properties. The cyclohexane + hexane system will be covered in three subsequent papers.

In each of these evaluation papers, an attempt is made to establish selected values of the property at mole fractions of 0.25, 0.50, and 0.75 over the temperature range covered by the literature data. The availability of selected values at three mole fractions will hopefully reduce the practice of comparing data sets only at the midpoint.

Whenever possible, recommended data sets are identified. If no data set can be recommended, the best data sets are identified.

Finally, based on the evaluation results, the needs for new experimental measurements are defined.

The procedures used to evaluate H^E data are not repeated in this and subsequent papers. The reader must obtain that information from the benzene + cyclohexane H^E data paper.[2]

2. Summary of Evaluation Results

The evaluation results for the 13 sets of benzene + hexane data are summarized in Table 1. Each set of data is represented by a single line. The literature reference numbers 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 for each set of data. Note that the sets are listed in the order of increasing temperature. For those sets where an experimental pressure was not reported, the pressure has been assumed to be one atmosphere (101.325 kPa).

Complete information on the evaluation tests and results are given in the benzene + cyclohexane paper on H^E data.[2] There are five quality ratings ranging from A for very good data to E for very bad data. The quality rating assigned to a set of data depends upon the evaluation test results and can be considered to be a "summary" of those test results.

Only two kinds of tests are used for H^E data. The first is a scatter rating which not only reflects scatter in the experimental data points but also reflects how well the shapes of the experimental data plots agree with the basic characteristic shapes for the particular system. Seven scatter ratings are used: E = excellent, G = good, F = fair, U = unacceptable, M = marginal, S = smoothed, N = none.

The % deviation values show how far the individual data set points deviate from the "best" H^E versus $1/T$ curves at $x_1 = 0.25$, 0.50, and 0.75 established by the evaluator. The test compares the data sets at the same temperature and also compares data sets at different temperatures.

The use of data sets for correlation or design purposes should be restricted to those with a quality rating of A, B, or C with a C set being used only if no A or B set is available.

3. Selected Point Values at 298.15 K

The six sets of data at 298.15 K are listed in Tables 2, 3, and 4 in the order of increasing magnitude of the $x_1 = 0.25$, 0.50, and 0.75 values. Five of those sets are plotted in Figs. 1–3. The literature source for each data set is identified by the MRL number (on the abscissa in the figures). The scatter rating letter for each set appears over the point symbol in the figures and in the S (for scatter) column in the tables. The type of equipment used to measure each set of data is indicated by the point symbol used in the figures and by the equipment type code number in the ET column in the tables. A complete glossary of equipment type codes and symbols is given in the H^E paper for benzene + cyclohexane.[2] The 03

Table 1. Summary list for excess enthalpy data

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) + HEXANE(2)							
00089	290.650	0.1013	D	M	-	-	-5.6
00165	293.150	0.1013	E	F	-8.4	-6.3	-7.2
17480	293.150	0.1013	D	F	0.5	-0.3	-5.7
00067	298.150	0.1013	B	G	-0.6	-0.4	-0.6
00917	298.150	0.1013	E	S	-6.3	-3.7	-2.6
01028	298.150	0.1013	A	E	0.0	0.0	-0.0
15983	298.150	0.1013	D	F	-0.8	-0.2	-4.2
17480	298.150	0.1013	E	F	-1.2	-3.0	-9.7
18802	298.150	0.1013	E	M	-24.3	-31.6	-43.3
17480	313.950	0.1013	E	F	-5.4	-10.3	-14.4
10272	323.150	0.1013	B	G	-0.0	-0.0	0.0
17480	323.150	0.1013	E	M	-8.5	-14.6	-22.0
18802	323.150	0.1013	E	M	4.3	-3.8	-6.4

Table 2. Magnitude listing of excess enthalpy values at 298.15 K and x(1) = 0.25. The S and ET codes refer to the scatter rating and equipment type respectively.

MRL number	Codes S	Codes ET	Authors	Year	Excess enthalpy J/mol
18802	M	03	Baluja Santos	1970	472.6
917	S	06	Ridgway, Butler	1967	585.0
17480	F	03	Paz Andrade, Regueiro, Baluja	1970	617.2
15983	F	03	Romani, Paz Andrade	1974	619.8
67	G	04	Jones, Lu	1956	621.0
1028	E	06	Schnaible	1955	624.5

Table 3. Magnitude listing of excess enthalpy values at 298.15 K and x(1) = 0.50. The S and ET codes refer to the scatter rating and equipment type respectively.

MRL number	Codes S	Codes ET	Authors	Year	Excess enthalpy J/mol
18802	M	03	Baluja Santos	1970	610.7
917	S	06	Ridgway, Butler	1967	860.0
17480	F	03	Paz Andrade, Regueiro, Baluja	1970	866.4
67	G	04	Jones, Lu	1956	890.0
15983	F	03	Romani, Paz Andrade	1974	892.0
1028	E	06	Schnaible	1955	893.4

Table 4. Magnitude listing of excess enthalpy values at 298.15 K and x(1) = 0.75. The S and ET codes refer to the scatter rating and equipment type respectively.

MRL number	Codes S	Codes ET	Authors	Year	Excess enthalpy J/mol
18802	M	03	Baluja Santos	1970	428.2
17480	F	03	Paz Andrade, Regueiro, Baluja	1970	681.4
15983	F	03	Romani, Paz Andrade	1974	723.3
917	S	06	Ridgway, Butler	1967	735.0
67	G	04	Jones, Lu	1956	750.0
1028	E	06	Schnaible	1955	754.9

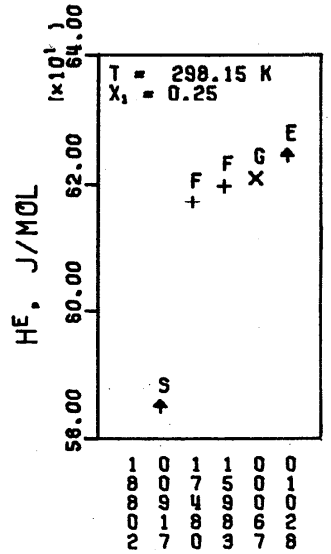

FIGURE 1. Magnitude comparison plot for H^E values at $x_1 = 0.25$ and 298.15 K.

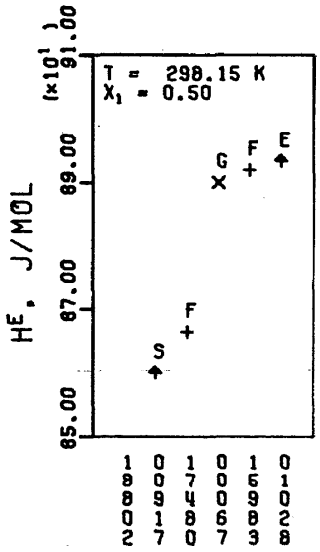

FIGURE 2. Magnitude comparison plot for H^E values at $x_1 = 0.50$ and 298.15 K.

code represents the CRMT (Tian–Calvet) calorimeter type while the 04 and 06 codes represent "miscellaneous batch vessels" and "miscellaneous semi-batch vessels," respectively.

Even though they lie above all the other data sets, the MRL 1028 set values were chosen as the selected values for the benzene(1) + hexane(2) system at 298.15 K.

x_1	Selected value J mol^{-1}
0.25	624.5
0.50	893.4
0.75	754.9

The device used by Schnaible was a forerunner of the reliable Van Ness vessel. Also, the Schnaible set was the only one receiving an excellent scatter rating, and does not differ much from the MRL 67 set which was the only one receiving a good scatter rating.

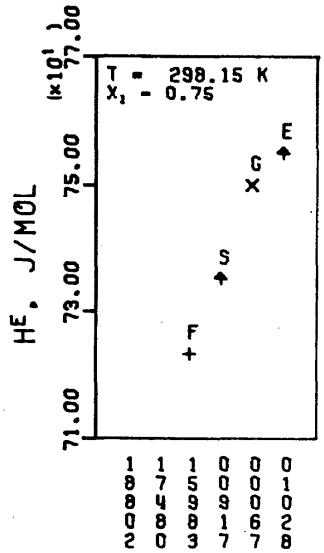

FIGURE 3. Magnitude comparison plot for H^E values at $x_1 = 0.75$ and 298.15 K.

Table 5. Best curve H^E values for benzene(1) + hexane(2) system

T,K	Values from best curves x_1=0.25	x_1=0.50	x_1=0.75
298.65	646.8	920.8	784.0
293.15	639.2	911.5	773.9
298.15	624.5	893.4	754.9
313.95	581.5	839.8	698.3
323.15	558.4	810.8	667.6

4. Selected Point Values at Other Temperatures

As shown in Table 1, the H^E data sets range from 290.65 to 323.15 K. Besides the six sets at 298.15, multiple measurements have been reported at two other temperatures—two at 293.15 and three at 323.15 K.

Of the three sets at 323.15, the MRL 10272 set is by far the superior one; it received a good scatter rating whereas the other two sets were so scattered on the H^E/x_1x_2 versus x_1 plot that only an approximate idea of the magnitude and directon of the deviation is provided (marginal scatter rating).

Both the 293.15 sets received fair scatter ratings with the MRL 17480 having a slightly better H^E/x_1x_2 plot. However, the deciding factor between the two 293.15 K sets is the alignment with the Schnaible set at 298.15 (MRL 1028) and the Diaz Pena and Menduina set at 323.15 (MRL 10272). The MRL 17480 set at 293.15 falls very close to a straight line through those two sets on the H^E versus $1/T$ plot at both

Table 6. Recommended data set at 298.15 K

SYSTEM. Benzene(1) + Hexane(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. 0.0 %

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. -0.0 %

REFERENCE. Schnaible, H. W., Ph.D. Dissertation, Purdue University, West Lafayette, Ind., 1955. (MRL 1028)

x(1) mole fraction	EXCESS ENTHALPY joule/mole	x(1) mole fraction	EXCESS ENTHALPY joule/mole
0.0810	239.6	0.4690	874.6
0.0810	244.2	0.4690	888.5
0.1280	360.5	0.5400	902.5
0.1280	365.2	0.5400	907.1
0.2270	572.2	0.5950	897.8
0.2270	581.5	0.6480	869.9
0.3060	716.4	0.6480	872.3
0.3700	793.2	0.7100	809.4
0.3700	802.5	0.7100	814.1
0.4240	853.6	0.7460	760.6
0.7860	688.5	0.8800	462.9
0.7860	693.1	0.9360	269.8
0.8300	593.1	0.9360	274.5
0.8300	595.5	0.9610	174.4
0.8800	458.2	0.9610	176.8

$x_1 = 0.25$ and 0.50 and is also better located than the MRL 165 set at $x_1 = 0.75$.

Based on the above observations the "best" curves on the H^E versus $1/T$ plots were drawn as straight lines through the MRL 1028 (298.15 K) and MRL 10272 (323.15 K) points at all three mole fractions. The values read from those best curves at the various data set temperatures are shown in Table 5.

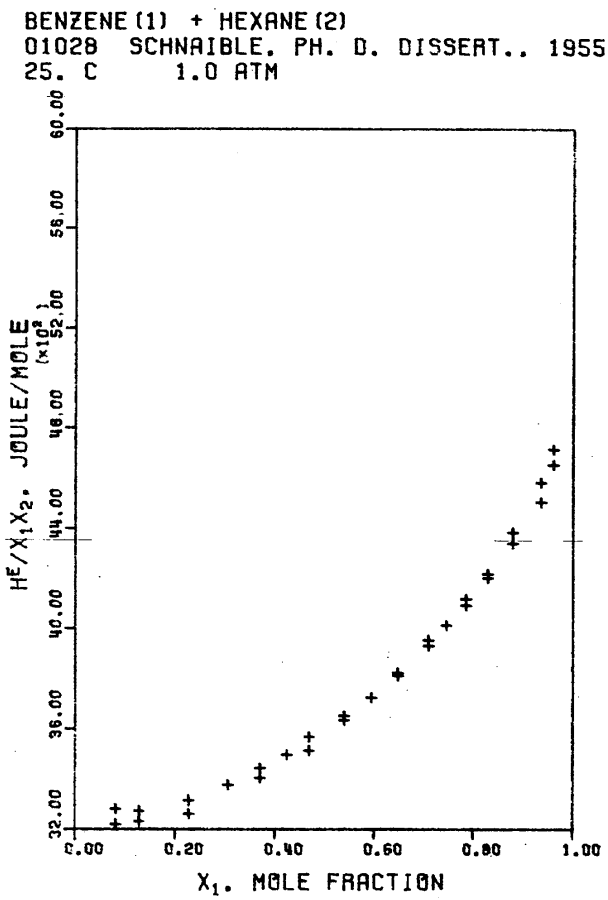

FIGURE 4. Recommended data set at 298.15 K. Schnaible, 1955. MRL 1028.

Table 7. Another high-quality data set at 298.15 K

SYSTEM. Benzene(1) + Hexane(2)

TEMPERATURE. 298.15 K PRESSURE. 0.1013 MPa

QUALITY RATING. B SCATTER. Good

DEVIATION FROM HE VS. 1/T CURVE AT x(1) = 0.25. -0.6 %

DEVIATION FROM HE VS. 1/T CURVE AT x(1) = 0.50. -0.4 %

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

REFERENCE. Jones, H. K. DeQ., Lu, B. C.-Y., Journal of Chemical and Engineering Data, 11(4), 488 (1966). (MRL 67)

x(1) mole fraction	EXCESS ENTHALPY joule/mole	x(1) mole fraction	EXCESS ENTHALPY joule/mole
0.1519	430.5	0.6497	858.6
0.2136	543.1	0.6957	820.5
0.3575	776.1	0.7211	792.0
0.4678	877.4	0.8075	649.8
0.5242	893.3	0.9157	346.4
0.6427	868.2		

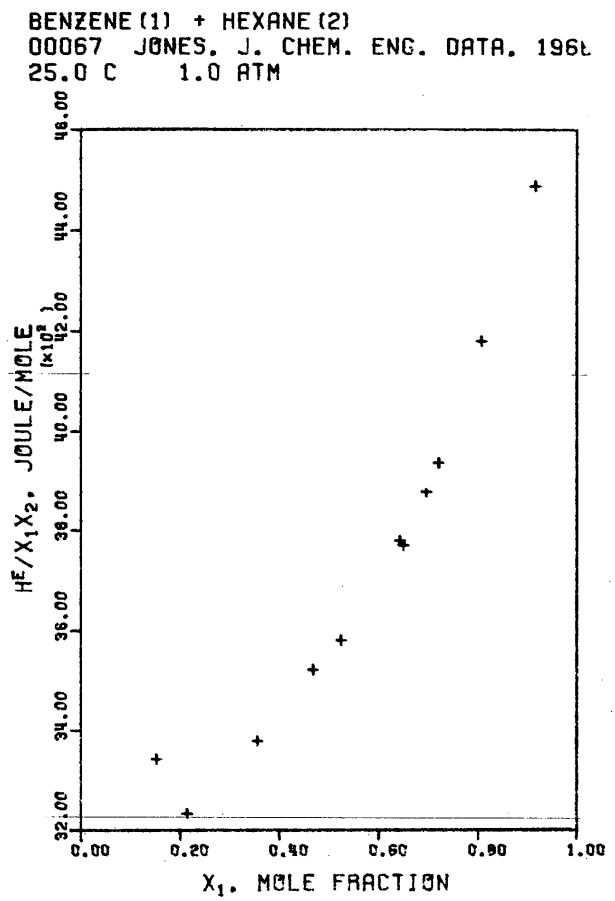

FIGURE 5. Another high-quality data set at 298.15 K. Jones and Lu, 1966. MRL 67.

Table 8. Recommended data set at 323.15 K

SYSTEM. Benzene(1) + Hexane(2)

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. -0.0 %

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. 0.0 %

REFERENCE. Diaz Pena, M., Menduina, C., Journal of Chemical Thermodynamics, 6, 1097 (1974). (MRL 10272)

x(1) mole fraction	EXCESS ENTHALPY joule/mole	x(1) mole fraction	EXCESS ENTHALPY joule/mole
0.0750	194.0	0.5304	817.0
0.1508	369.0	0.5323	821.0
0.2151	499.0	0.5387	817.0
0.2687	590.0	0.5566	816.0
0.3237	668.0	0.5616	816.0
0.3750	727.0	0.5626	816.0
0.4205	767.0	0.5835	809.0
0.4610	794.0	0.5889	810.0
0.4974	809.0	0.5926	810.0
0.5165	815.0	0.6126	798.0
0.6176	799.0	0.7630	653.0
0.6199	799.0	0.7647	641.0
0.6451	777.0	0.8082	571.0
0.6457	785.0	0.8122	553.0
0.6486	781.0	0.8573	451.0
0.6674	768.0	0.8579	459.0
0.6808	749.0	0.9066	316.0
0.6835	752.0	0.9087	319.0
0.7205	706.0	0.9542	168.0
0.7213	714.0	0.9579	159.0

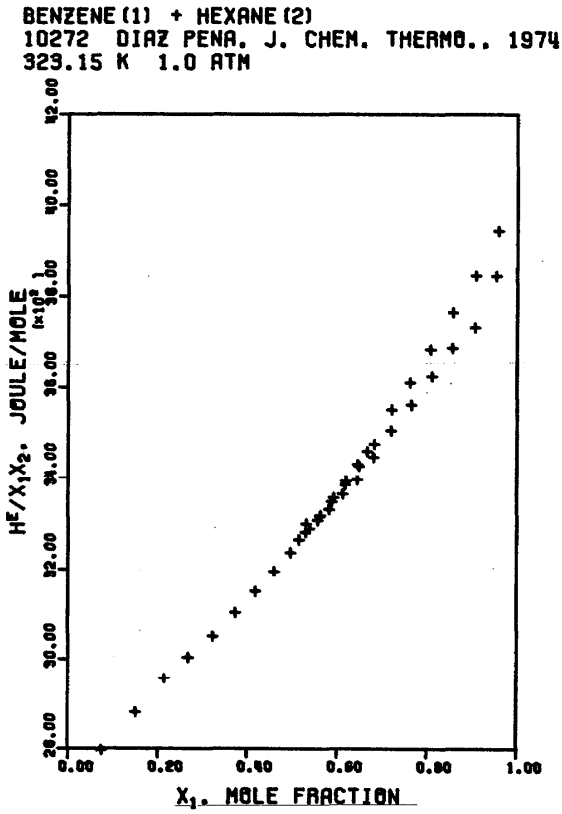

FIGURE 6. Recommended data set at 323.15 K. Diaz Pena and Menduina, 1974. MRL 10272.

5. Recommended Data Sets

The Schnaible data at 298.15 K (MRL 1028), even though it was taken in an early prototype of the Van Ness vessel, was given an A quality rating and is recommended as a reliable set of data. Its tabulation and H^E/x_1x_2 plot appears in Table 6 and Fig. 4. The MRL 67 set at 298.15 (Jones and Lu, 1966) also appears to be a high-quality set (quality rating B) and is shown in Table 7 and Fig. 5.

At 323.15 K, the MRL 10272 set (Diaz Pena and Menduina, 1974) can be recommended. It is tabulated in Table 8 and plotted in Fig. 6. That set was measured in the reliable Van Ness type of semi-batch vessel.

6. Experimental Measurements Needed

The benzene + cyclohexane and the cyclohexane + hexane systems are already well-established as test systems for H^E calorimeters. The benzene + hexane system offers no obvious advantages over those two as a test system, hence multiple high-quality measurements at 298.15 K are not needed. The Schnaible (MRL 1028) and the Jones and Lu (MRL 67) data sets provide adequate support at 298.15 for correlation work. Also, the Diaz Pena and Menduina (MRL 10272) set probably provides adequate support at 323.15. New measurements should be directed initially to temperatures other than 298.15 and 323.15. New measurements at those two temperatures can be deferred until other high-quality sets at other temperatures have extended the best H^E versus $1/T$ curve.

7. Data Set Tabulations

Tabulations of all the data sets covered in this paper can be obtained from 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. 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 will not be processed.

8. Bibliography

Table 9 is the bibliography for excess enthalpy data for the benzene(1) + hexane(2) system. The identifying number for each citation is the Laboratory's Master Reference List (MRL) number. The MRL numbers relate the citations in Table 9 to the various tables and figures used in this paper.

Some of the documents listed in Table 9 may report H^E data in a form which did not permit transcription and processing. In most such cases, the data were presented only in graphical form. Those documents have been included in the bibliography in order to provide a complete coverage of the H^E literature for the benzene + hexane system.

TABLE 9. Bibliography for excess enthalpy data

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9. Acknowledgments

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[3] B. D. Smith, O. Muthu, A. Dewan, and M. Gierlach, J. Phys. Chem. Ref. Data **11**, 1099 (1982).