Evaluation of Binary *PTxy* Vapor–Liquid Equilibrium Data for C_6 Hydrocarbons. Benzene + Hexane

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The binary *PTxy* vapor–liquid equilibrium data for the benzene + hexane system are evaluated. The needs for new experimental data are defined.

Key words: activity coefficients; benzene; excess Gibbs function; hexane; vapor–liquid equilibrium.

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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 their 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 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 *PTxy* VLE data for the benzene + hexane system. The "*PTxy*" denotes that all four variables were measured experimentally. Parallel papers for the benzene + hexane system cover the V^E, H^E, and *PTx* VLE (total pressure) VLE data. The V^E, H^E, and *PTxy* VLE data for the benzene + cyclohexane system have been covered in three preceding papers[1–3] which also presented a detailed description of the evaluation procedures used for those three individual properties. The cyclohexane + hexane system will be covered in subsequent papers.

In this paper an attempt is made to establish the "best curves" on the G^E/T versus $1/T$ plots at constant compositions of $x_1 = 0.25, 0.50,$ and 0.75. Thus "best" G^E values are obtained at each data set temperature at each of the three compositions. The availability of selected G^E 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 available data sets are identified.

Finally, based on the evaluation results, the needs for

0047-2689/83/020381-07/$05.00

new experimental measurements are defined.

The procedures used to evaluate *PTxy* VLE data are not repeated in this and subsequent papers. The reader must obtain that information from the benzene + cyclohexane paper on *PTxy* VLE data.[3]

2. Equations

The experimental *PTxy* VLE data were reduced to liquid-phase activity coefficients with the equation

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

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

$$G^{\mathrm{E}} = RT \sum_i x_i \ln \gamma_i. \qquad (2)$$

The Poynting term,

$$\frac{1}{RT} \int_{P'_i}^{P} V_i^{\mathrm{L}} dP, \qquad (3)$$

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

$$\gamma'_I = \frac{y_i P \hat{\phi}_{i,P}}{x_i P'_i \phi_{i,P'_i}}. \qquad (4)$$

The gas-phase nonideality is represented by the two fugacity coefficients. It is always assumed that those fugacity coefficients can be predicted with sufficient accuracy by an assumed equation of state. The equations of state available to the data reduction program, and the logic used to select the best possible equation of state for a given mixture, are described in a previous paper.[4]

3. Summary of Evaluation Results

The evaluation results for the 20 sets of *PTxy* VLE 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 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 each data set tabulation at the end of citation.

The isothermal and isobaric data sets are segregated in Table 1 with the isothermal sets listed first. The temperature is always in Kelvin and the pressure unit is always kilopascal.

Complete information on the evaluation tests and the significance of each test result are given in the paper for the *PTxy* VLE data for benzene + cyclohexane.[3] A brief description is given here to make the Table 1 material meaningful.

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.

Seven scatter ratings are used: E = excellent, G = good, F = fair, U = unacceptable, M = marginal, S = smoothed, and N = none.

The percent P' errors show how much the reported experimental pressures at $x_1 = 0.0$ and $x_1 = 1.0$ differ from the selected pure compound vapor pressures stored in our pure compound data bank CDATA1.

The Gibbs–Duhem area ratio can vary from 0.0 to 1.0 with the 1.0 denoting complete consistency with the Gibbs–Duhem equation. The number in parentheses is the value which includes the V^{E} (for isothermal data) or H^{E} (for isobaric data) correction integral. If a number appears before the parenthetical number, it is the value of the area ratio without the V^{E} or H^{E} correction term.

The percent deviation values in the last three columns show where the data set points at $x_1 = 0.25$, 0.50, and 0.75 fall relative to the best G^{E}/T versus $1/T$ curves drawn by the evaluator through all the data sets. The H's following the deviation values indicate that H^{E} values were available to establish the slopes of the G^{E}/T versus $1/T$ curves, and

Table 1. Summary list for PTxy VLE sets

LITERATURE REFERENCES	SYSTEM T OR P	QUALITY RATING	SCATTER RATING	P' ERROR, %		GIBBS-DUHEM AREA RATIO	% DEVIATION FROM GE/T VS. 1/T CURVE		
				X1=0	X1=1		X1=0.25	X1=0.50	X1=0.75
BENZENE(1) + HEXANE(2)									
05099	328.24 K	B	G	--	--	(0.97)	5.7 H	3.2 H	1.5 H
00914	333.14 K	E	S	0.1	0.0	(0.51)	-3.1 H	-5.6 H	-14.6 H
00028	343.14 K	D	S	--	--	(0.75)	0.4 H	-12.0 H	-17.5 H
00254	26.66 KPA	D	F	1.9	--	0.77(0.74)	-2.5 H	-1.9 H	-4.4 H
00254	40.00 KPA	E	F	1.0	--	0.86(0.83)	3.6 H	-3.3 H	-19.4 H
00254	53.33 KPA	E	F	1.8	--	0.69(0.67)	8.0 H	10.9 H	-1.5 H
00216	97.99 KPA	E	M	1.4	1.4	0.70(0.67)	6.5 H	-3.2 H	-3.1 H
00043	101.32 KPA	C	F	--	0.4	0.98(0.97)	-0.8 H	-4.8 H	-8.6 H
00175	101.32 KPA	D	F	1.3	-0.2	0.96(0.92)	-6.3 H	-4.1 H	-7.6 H
00253	101.32 KPA	-	N	-0.4	--		-	-	-
00286	101.32 KPA	C	G	0.1	0.6	0.77(0.81)	-9.1 H	-2.9 H	-6.7 H
08971	101.32 KPA	C	G	0.7	0.9	0.98(0.93)	0.0 H	0.0 H	0.0 H
15861	101.32 KPA	-	-	--	--		-	-	-
16231	101.32 KPA	E	G	-0.1	-0.0	0.53(0.51)	-14.9 H	-11.3 H	-14.7 H
22484	101.32 KPA	E	F	-1.2	-1.4	0.83(0.87)	-19.6 H	-11.0 H	-9.5 H
00271	405.41 KPA	E	M	2.3	1.1	0.38(0.36)	8.8 H	-4.2 H	-24.5 H
00271	610.88 KPA	E	M	0.2	-0.9	0.45(0.43)	-19.1 H	-31.6 H	- H
00271	810.82 KPA	E	M	-1.6	-0.5	0.39(0.41)	-44.1 H	-41.3 H	- H
00271	1013.53 KPA	E	M	-1.9	-2.3	0.49(0.46)	- H	- H	- H
00271	1013.53 KPA	E	M	-1.9	-2.3	0.57(0.54)	-61.3 H	- H	- H

therefore the deviation values represent the results of the Gibbs–Helmholtz consistency test.

Criteria which relate the individual evaluation test results to the assigned quality rating must be established for each class of mixtures. Those established for the $C_6 + C_6$ hydrocarbons are presented in the preceding benzene + cyclohexane paper on *PTxy* VLE data.[3]

4. Selected G^E/T Values

Before the best G^E/T versus $1/T$ curve can be drawn, it is necessary to identify those sets which are probably the most reliable and which should be given the most weight when drawing the G^E/T versus $1/T$ curves at $x_1 = 0.25$, 0.50, and 0.75. At this point in the evaluation, all the tests have been performed except the Gibbs–Helmholtz test which requires the G^E/T versus $1/T$ curves.

The only pressure at which multiple *PTxy* VLE measurements are available for the benzene + hexane system is 101.325 kPa. The six available sets are listed in Tables 2, 3, and 4 in the order of increasing G^E/T values. The S and AR column headings denote scatter rating and Gibbs–Duhem area ratios, respectively. The MRL 8971 set (Hanson and Van Winkle, 1967) is probably the best set at 101.325 kPa. The MRL 43 set (Butler and Ridgway, 1967) has a higher area ratio but its $\ln \gamma_1'/\gamma_2'$ versus x_1 curve has more scatter and other, equally valid, locations of that curve would give lower area ratios. Also, the G^E/x_1x_2 points for the MRL 43 set fall off badly at high x_1 values and that resulted in only a fair scatter rating. The MRL 175 set (Myers, 1955) has about the same area ratio as the MRL 8971 set but the scatter rating is only fair based on the G^E/x_1x_2 plot. The MRL 22484 set (Saito, 1969) has a fairly good area ratio but both P' errors are large.

The only high-quality set at pressures other than 101.325 kPa is the isothermal MRL 5099 set (Ho and Lu, 1963). It has a good scatter rating and an excellent area ratio of 0.97. However, its G^E/x_1x_2 plot is not as good as that for the MRL 8971 set and, whereas the 8971 set has supporting sets in MRL 43 and MRL 175 which tend to confirm its accuracy, the MRL 5099 set is all alone at 328.24 K. Hence, the MRL 8971 set was chosen as the anchor point for the G^E/T curve. Its choice puts the G^E/T curves closer to the MRL 5099 points than would have been the case if some other 101.325 kPa set had been chosen.

Table 2. Magnitude listing of G^E/T values at $x_1 = 0.25$ and 101.325 kPa

MRL	S	AR	P' Error, % x_1=0	 x_1=1.0	Authors	T,K	G^E	G^E/T
22484	F	0.87	-1.2	-1.4	Saito	342.65	180.0	0.5253
16231	G	0.51	-0.1	-0.0	Brzostowski	343.16	190.0	0.5537
286	G	0.81	0.1	0.6	Prabhu, Van Winkle	342.34	203.5	0.5945
175	F	0.92	1.2	-0.2	Myers	342.07	210.0	0.6139
43	F	0.97		0.4	Butler, Ridgway	342.28	222.0	0.6486
8971	G	0.93	0.7	0.9	Hanson, Van Winkle	342.15	224.0	0.6548

Table 3. Magnitude listing of G^E/T values at x_1=0.50 and 101.325 kPa

MRL	S	AR	P' Error, % x_1=0	 x_1=1.0	Authors	T,K	G^E	G^E/T
16231	G	0.51	-0.1	-0.0	Brzostowski	344.45	282.0	0.8187
22484	F	0.87	-1.2	-1.4	Saito	343.97	283.0	0.8227
43	F	0.97		0.4	Butler, Ridgway	343.63	303.0	0.8818
175	F	0.92	1.2	-0.2	Myers	343.72	305.0	0.8874
286	G	0.81	0.1	0.6	Prabhu, Van Winkle	343.75	308.8	0.8985
8971	G	0.93	0.7	0.9	Hanson, Van Winkle	343.54	318.0	0.9257

Table 4. Magnitude listing of G^E/T values at x_1 = 0.75 and 101.325 kPa

MRL	S	AR	P' Error, % x_1=0	 x_1=1.0	Authors	T,K	G^E	G^E/T
16231	G	0.51	-0.1	-0.0	Brzostowski	346.42	222.0	0.6408
22484	F	0.87	-1.2	-1.4	Saito	346.84	235.0	0.6775
43	F	0.97		0.4	Butler, Ridgway	346.87	237.5	0.6847
175	F	0.92	1.2	-0.2	Myers	346.87	240.0	0.6919
286	G	0.81	0.1	0.6	Prabhu, Van Winkle	346.83	242.5	0.6991
8971	G	0.93	0.7	0.9	Hanson, Van Winkle	346.45	260.0	0.7505

Table 5. Selected H^E values

$1/T, K^{-1}$	H^E 0.25	 0.50	 0.75
0.0022	329.82	525.16	366.17
0.0023	355.35	557.08	399.86
0.0024	380.89	588.99	433.54
0.0025	406.43	620.90	467.22
0.0026	431.96	652.81	500.91
0.0027	457.50	684.72	534.59
0.0028	483.04	716.63	568.27
0.0029	508.57	748.54	601.96
0.0030	534.11	780.45	635.64
0.0031	559.65	812.37	669.32
0.0032	585.18	844.28	703.01
0.0033	610.72	876.19	736.69
0.003354	624.51	893.42	754.88
0.0034	636.26	908.10	770.37

Table 6. Selected G^E/T and G^E values

T,K	x_1=0.25 G^E/T	 G^E	x_1=0.50 G^E/T	 G^E	x_1=0.75 G^E/T	 G^E
303.15	0.872	264.3	1.222	370.4	1.019	308.9
313.15	0.809	253.3	1.145	358.6	0.944	295.6
323.15	0.751	242.7	1.069	345.4	0.880	284.4
333.15	0.698	232.5	0.999	332.8	0.822	273.8
343.15	0.652	223.7	0.930	319.1	0.768	263.5
353.15	0.611	215.8	0.869	306.9	0.720	254.3
363.15	0.576	209.2	0.813	295.2	0.676	245.5
373.15	0.542	202.2	0.761	284.0	0.635	237.0
383.15	0.504	193.1	0.716	274.3	0.597	228.7
393.15	0.485	190.7	0.672	264.2	0.567	222.9
403.15	0.459	185.0	0.632	254.8	0.538	216.9
413.15	0.436	180.1	0.597	246.7		
423.15	0.416	176.0	0.564	238.7		
433.15	0.397	172.0	0.534	231.3		
443.15	0.379	168.0				
453.15	0.353	160.0				

In the parallel paper on the evaluation of the H^E data for the benzene(1) + hexane(2) system, the best H^E versus $1/T$ curve was established as a straight line through points at 298.15 and 323.15 K. That straight line was extrapolated in both directions to give the H^E values in Table 5. Starting at the MRL 8971 G^E/T value at each of the three mole fractions, the G^E/T curves were constructed using the relation

$$\left[\frac{d(G^E/T)}{d(1/T)}\right]_{x_1} \cong [H^E]_x, \qquad (1)$$

and the H^E values in Table 5. The G^E/T values read from those curves, and the corresponding G^E values, at temperatures over the range of the literature data are shown in Table 6.

The values given in Table 6 must be considered to be tentative. New reliable experimental measurements will undoubtedly shift the curve.

5. Best Data Sets

None of the data sets received an A quality rating. As can be seen from Table 1, the isothermal MRL 5099 set received a B rating while three of the isobaric sets at 101.325 kPa received C ratings. Of the three C rating sets, the MRL

Table 7. Best-rated set of data

SYSTEM. Benzene(1) + Hexane(2) C(6)H(6) + C(6)H(14) PTXY

RATING. B AREA RATIO. (0.97 with VE) P' ERRORS. -- % and -- % at x(1) = 0 and 1 SCATTER. Good

DEVIATION FROM GE/T VS. 1/T CURVE AT x(1) = 0.25. 5.7%
DEVIATION FROM GE/T VS. 1/T CURVE AT x(1) = 0.50. 3.2%
DEVIATION FROM GE/T VS. 1/T CURVE AT x(1) = 0.75. 1.5%

INFINITE DILUTION ACTIVITY COEFFICIENTS. 1 = 1.42
2 = 1.84

EQUATIONS OF STATE. 1 = Virial, C zero, B from Tsonopoulos.
2 = Virial, C zero, B from Tsonopoulos.

REFERENCE. Ho, J. C. K., Lu, B. C.-Y., Journal of Chemical and Engineering Data, 8(4), 553 (1963). (MRL 5099)

Mole Fraction				Vapor Pressure, kPa		Liquid Molar Volume, ml/mol		Φ(mix,P)/Φ(pure,P') exp(V(P-P')/RT)		ln Gamma Ratio	Activity Coefficient		E G J/mol
x(1)	y(1)	T, K	P, kPa	1	2	1	2	1	2		1	2	
0.1230	0.1170	328.219	64.79	43.73	64.56	92.86	137.48	0.9894	0.9999	0.3230	1.3945	1.0103	136.2
0.2300	0.2140	328.160	64.67	43.63	64.43	92.85	137.47	0.9895	0.9998	0.2874	1.3646	1.0245	245.9
0.2940	0.2650	328.239	63.99	43.76	64.61	92.86	137.48	0.9899	1.0004	0.2357	1.3048	1.0316	273.4
0.4000	0.3410	328.160	62.72	43.63	64.43	92.85	137.47	0.9905	1.0010	0.1265	1.2139	1.0704	322.9
0.4270	0.3640	328.170	62.39	43.65	64.45	92.85	137.47	0.9907	1.0012	0.1159	1.2072	1.0758	333.6
0.5050	0.4190	328.060	61.06	43.47	64.21	92.84	137.44	0.9912	1.0019	0.0332	1.1552	1.1183	349.7
0.6250	0.5110	328.400	59.35	44.02	64.97	92.88	137.52	0.9924	1.0033	-0.0877	1.0941	1.1954	336.2
0.7270	0.5950	328.119	56.66	43.57	64.34	92.85	137.46	0.9935	1.0046	-0.2152	1.0575	1.3125	313.3
0.7940	0.6560	328.259	54.62	43.79	64.65	92.86	137.49	0.9946	1.0060	-0.3246	1.0250	1.4193	250.3
0.8240	0.6940	328.359	53.66	43.95	64.88	92.88	137.51	0.9952	1.0067	-0.3461	1.0233	1.4478	229.7
0.8290	0.7000	328.340	53.51	43.92	64.83	92.87	137.50	0.9953	1.0068	-0.3525	1.0239	1.4580	229.6
0.8820	0.7730	328.279	51.18	43.82	64.70	92.87	137.49	0.9964	1.0081	-0.4074	1.0198	1.5342	185.1
0.9140	0.8160	328.209	49.54	43.71	64.54	92.86	137.48	0.9971	1.0090	-0.4952	1.0089	1.6571	140.7
0.9150	0.8220	328.389	49.58	44.00	64.94	92.88	137.51	0.9973	1.0092	-0.4680	1.0095	1.6135	134.7

Table 8. The best set of data at 101.325 kPa

SYSTEM. Benzene(1) + Hexane(2) C(6)H(6) + C(6)H(14) PTXY

RATING. C AREA RATIO. 0.98 (0.93 with HE) P' ERRORS. 0.7% and 0.9% at x(1) = 0 and 1 SCATTER. Good

DEVIATION FROM GE/T VS. 1/T CURVE AT x(1) = 0.25. 0.0%
DEVIATION FROM GE/T VS. 1/T CURVE AT x(1) = 0.50. 0.0%
DEVIATION FROM GE/T VS. 1/T CURVE AT x(1) = 0.75. 0.0%

INFINITE DILUTION ACTIVITY COEFFICIENTS. 1 = 1.39
2 = 1.71

EQUATIONS OF STATE. 1 = Virial, C zero, B from Tsonopoulos.
2 = Virial, C zero, B from Tsonopoulos.

REFERENCE. Hanson, D. O., Van Winkle, M., Journal of Chemical and Engineering Data, 12(3), 319 (1967). (MRL 8971)

Mole Fraction				Vapor Pressure, kPa		Liquid Molar Volume, ml/mol		Φ(mix,P)/Φ(pure,P') exp(V(P-P')/RT)		ln Gamma Ratio	Activity Coefficient		E G J/mol
x(1)	y(1)	T, K	P, kPa	1	2	1	2	1	2		1	2	
0.0600	0.0580	341.741	101.32	70.13	100.86	94.52	140.42	0.9864	0.9998	0.3150	1.3776	1.0064	71.8
0.0630	0.0610	341.741	101.32	70.13	100.86	94.52	140.42	0.9864	0.9998	0.3166	1.3799	1.0065	74.8
0.1020	0.0980	341.841	101.32	70.36	101.18	94.54	140.44	0.9865	0.9999	0.3063	1.3649	1.0058	104.9
0.1030	0.0980	341.841	101.32	70.36	101.18	94.54	140.44	0.9865	0.9999	0.2955	1.3516	1.0069	105.7
0.2020	0.1860	341.941	101.32	70.60	101.50	94.55	140.46	0.9867	1.0001	0.2483	1.3039	1.0183	193.6
0.2070	0.1910	342.041	101.32	70.83	101.82	94.56	140.48	0.9868	1.0003	0.2500	1.3025	1.0154	190.1
0.2800	0.2510	342.241	101.32	71.30	102.47	94.59	140.53	0.9870	1.0006	0.2012	1.2573	1.0293	241.6
0.2830	0.2540	342.241	101.32	71.30	102.47	94.59	140.53	0.9870	1.0006	0.2022	1.2589	1.0295	244.6
0.3940	0.3410	342.842	101.32	72.74	104.42	94.66	140.67	0.9878	1.0016	0.1204	1.1909	1.0570	291.9
0.3970	0.3430	342.842	101.32	72.74	104.42	94.66	140.67	0.9878	1.0016	0.1168	1.1888	1.0590	294.3
0.4970	0.4210	343.541	101.32	74.43	106.72	94.75	140.83	0.9886	1.0028	0.0406	1.1400	1.0959	317.5
0.5010	0.4230	343.541	101.32	74.43	106.72	94.75	140.83	0.9886	1.0028	0.0328	1.1362	1.1009	319.7
0.6130	0.5130	344.642	101.32	77.16	110.44	94.89	141.08	0.9899	1.0046	-0.0630	1.0878	1.1599	312.3
0.6190	0.5170	344.642	101.32	77.16	110.44	94.89	141.08	0.9899	1.0046	-0.0723	1.0856	1.1685	315.8
0.6770	0.5680	345.342	101.32	78.94	112.85	94.98	141.24	0.9907	1.0058	-0.1228	1.0668	1.2079	300.9
0.6800	0.5700	345.442	101.32	79.20	113.20	94.99	141.26	0.9908	1.0060	-0.1287	1.0625	1.2100	293.7
0.6880	0.5780	345.542	101.32	79.46	113.55	95.01	141.28	0.9909	1.0062	-0.1332	1.0616	1.2144	292.3
0.6880	0.5760	345.542	101.32	79.46	113.55	95.01	141.28	0.9909	1.0062	-0.1414	1.0579	1.2202	289.7
0.6890	0.5780	345.542	101.32	79.46	113.55	95.01	141.28	0.9909	1.0062	-0.1378	1.0601	1.2183	291.9
0.7660	0.6530	346.742	101.32	82.60	117.81	95.16	141.56	0.9923	1.0083	-0.2130	1.0377	1.2860	251.4

8971 set was chosen as the best one for the reasons given in the last section.

None of the sets is firm enough to be a reliable test set for new experimental VLE devices. For correlation work, the isothermal MRL 5099 set at 328.14 K (Ho and Lu, 1963) and the isobaric MRL 8971 set at 101.325 kPa (Hanson and Van Winkel, 1967) can be used but with caution. The tabulations for the two sets are shown in Tables 7 and 8 and the G^E/x_1x_2 plots are given in Figs. 1 and 2.

6. Equipment Types

All authors reporting benzene + hexane data used a circulating equilibrium still. The type of still used in each case is shown in Table 9 along with the quality ratings assigned to the data sets. If a document did not designate the apparatus as being of a certain type (e.g., a Colburn still) the name of the senior author of the document has been used for the name of the still.

The set of data receiving the highest quality rating—the MRL 5099 set with a B rating—was taken with a Gillespie still, which supports the impression gained from the evaluation of the benzene + cyclohexane data that the Gillespie still is one of the more reliable equilibrium stills.

It should be pointed out that bad data can be measured in a good still. An impure component, poor phase analysis, improper operating technique, etc., can all cause a poor quality rating. Hence, the quality ratings listed in Table 9 must be related to the data set itself and not considered to be necessarily typical of the still used.

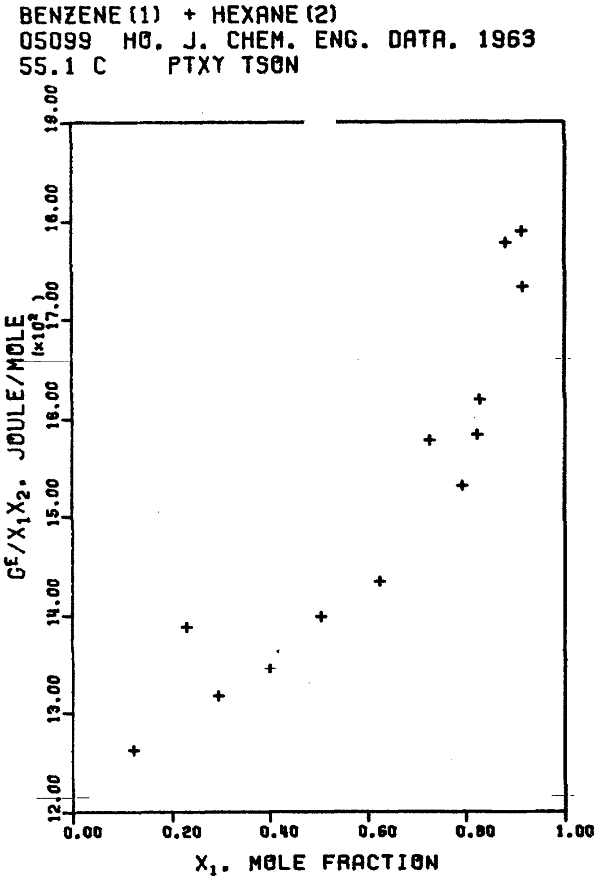

FIGURE 1. Best-rated set of data. Ho and Lu, 1963. MRL 5099.

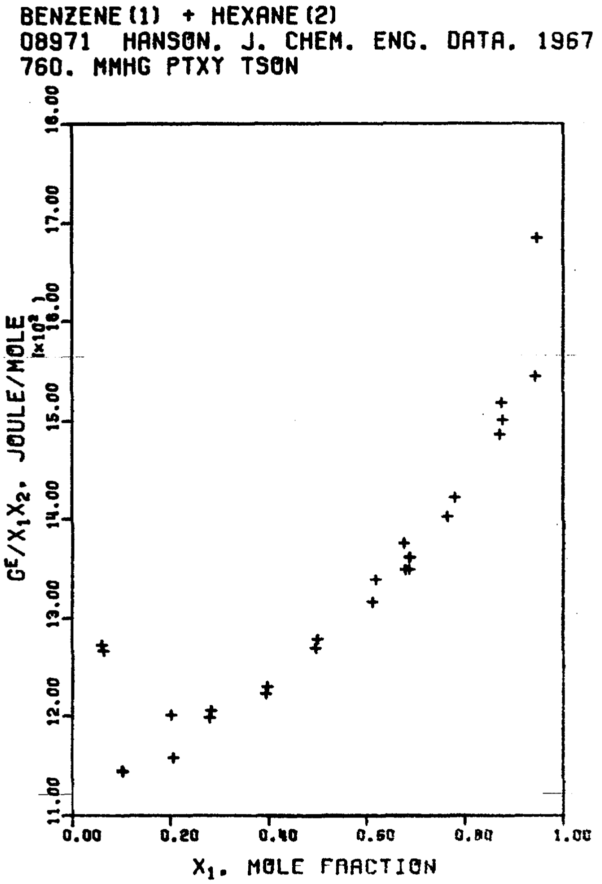

FIGURE 2. Best set of data at 101.325 kPa. Hanson and Van Winkle, 1967. MRL 8971.

7. Experimental Measurements Needed

Data are needed at any temperature from 298.15 up to 400 or 425 K. New measurements should be isothermal rather than isobaric because isothermal data sets are ultimately more valuable to the user. If reliable new measurements confirm the MRL 5099 set at 328.14 K, it will be necessary to relocate the best G^E/T versus $1/T$ curve through that point rather than through the MRL 8971 set.

8. Pure Compound Values

The pure compound vapor pressure and liquid density values used by program PTXY2 to reduce the experimental P,T,x,y values to activity coefficients and excess Gibbs function values always come from the pure compound data bank CDATA1 regardless of whether or not the authors reported pure compound values. The reasons for this are explained in the preceding evaluation report on the *PTxy* VLE data for the benzene + cyclohexane system.[3]

The *PTxy* VLE data for the benzene + hexane system fall in the 300 to 455 K temperature range. The vapor pressure data for benzene have been presented in the benzene + cyclohexane paper.[3] The vapor pressure data over that nge for hexane were represented in CDATA1 by the

Table 9. Apparatus types used

Equilibrium still	Document number	Set quality ratings
Colburn	286	C
Gillespie	5099	B
Griswold	271	E
Gotthard	253,254	D,E
Kireyev	28	D
Myers	175	D
Othmer	216	E
Saito	22484	E
Schuberth	914	E
Swietoslawski	16231	E
Van Winkle	8971	C
Multi-stage Ellis stills	43	C

Table 10. Pure compound vapor pressure data for hexane

	Vapress-2 equation[a] (177 to 354 K)	Wagner equation[b] (322 to 508 K)
A	-0.22919783D+03	-0.75346817D+01
B	-0.63811025D+03	0.14152605D+01
C	-0.20871521D+00	-0.22906092D+01
D	0.12931528D-03	-0.11694111D+02
E	0.50034351D+02	

[a] $\ln P = A + B/T + CT + DT^2 + E \ln T$

[b] $\ln Pr = (1/Tr)\left[A(1-Tr) + B(1-Tr)^{1.5} + C(1-Tr)^3 + D(1-Tr)^6\right]$ where Pr and Tr are the reduced pressure and temperature.

Vapres-2 and the Wagner equation fits given in Table 10. The P_c and T_c values used were 3.040 MPa and 507.68 K for hexane.

The hexane vapor pressure correlations in CDATA1 are based on data (one or more points) from 66 primary literature documents; the data from another 36 documents were totally excluded from the correlations. The low range (Vapres-2) correlation fitted 214 selected data points with a RMSD of 0.101 kPa. The high-range (Wagner) correlation used 101 experimental data points with a RMSD of 0.77 kPa. In the overlap region, the two correlations agree within 3 in the fourth digit.

The liquid density correlations in CDATA1 which provided values needed by program PTXY2 have been presented in a parallel paper[5] on the evaluation of the excess volume data for the benzene + hexane system.

The actual vapor pressure and liquid density values used for each set of data are shown in columns 5–8 in the VLE tabulations. (See Tables 7 and 8 for examples.)

The individual pure component fugacity coefficients are not given in the VLE tabulations. However, the equation of state used to calculate those coefficients, and those of the individual components in the mixture, is listed. The fugacity coefficients are tabulated in the combined correction term

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

where $\phi(\text{mix},P)=\hat{\phi}_{i,P}=\hat{f}_{i,P}/y_iP$, and $\phi(\text{pure},P')=\phi_{i,P'_i}=f_{i,P'_i}/P'_i$.

9. Data Set Tabulations

Any person who wants a complete set of the tables for the benzene + hexane system should contact the Director, Thermodynamics Research Laboratory, Box 1144, Washington University, St. Louis, Missouri 63130. Copies of the *PTxy* VLE tables will be provided for \$1.00 per table plus \$5.00 for handling charges. An invoice will be mailed with the tables.

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

10. Bibliography

Table 11 is the bibliography for the *PTxy* VLE data for the benzene + hexane system. The identifying number for each citation is the Laboratory's Master Reference List (MRL) number which was assigned to the cited document when its copy was retrieved. The MRL numbers relate the citations in Table 11 to the data set tabulation and to the various tables and figures used in this paper.

Some of the documents listed in Table 11 report VLE 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 *PTxy* VLE literature for the benzene + hexane system.

TABLE 11. Bibliography for *PTxy* VLE data

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11. Nomenclature

f_{i,P'_i}	Vapor-phase fugacity of pure component i at system temperature and the vapor pressure of i.
$\hat{f}_{i,P}$	Fugacity of component i in the vapor-phase mixture at the system T and P.
G^E	Molar excess Gibbs function.
MRL	Acronym for Master Reference List.
P	Pressure.
P'_i	Component i vapor pressure.
R	Gas constant.
RMSD	Root mean square deviation.
T	Absolute temperature.
V_i^L	Liquid molar volume of component i.
x_i	Liquid mole fraction.
y_i	Vapor mole fraction.
γ_i	Liquid-phase activity coefficient of component i referred to the total pressure standard state.
γ'_i	Liquid-phase activity coefficient of component i referred to the vapor-pressure standard state.
ϕ_{i,P'_i}	Vapor-phase fugacity, $f_{i,P'_i}/P'_i$, of pure component i as a gas at its vapor pressure at the system T.
$\hat{\phi}_{i,P}$	Vapor-phase fugacity, $\hat{f}_{i,P}/y_iP$, for component i in a gaseous mixture at the system T and P.

12. Acknowledgments

This work was supported by the Office of Standard Reference Data and by the Industrial Participants in the Thermodynamics Research Laboratory.

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