NOTE ADDED IN PROOF: The Ni-Cd data of R. A. Schaefer and F. Hovorka [*Trans. Electrochem. Soc.*, **87,** 479 (1945)], should have been mentioned. These data do not agree with the present work, but several problems seem evident: (a) Most serious, Schaefer and Hovorka made no analysis of, or corrections for, differences in the $CdCl_2$ concentration in the Li-KCl-$CdCl_2$ electrolyte in the two H-cell legs. (b) The reported solubility of nickel in cadmium at their lowest temperature was exceeded. (c) The stabilities of NiO and CdO are close enough so that oxidative side reactions were perhaps possible.

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Vapor-Liquid Equilibrium at Atmospheric Pressure

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Vapor-liquid equilibrium of the three binary systems cyclohexane–cyclohexene, cyclohexane–1,2-dichloroethane, and cyclohexene–1,2-dichloroethane and the ternary system cyclohexane–cyclohexene–1,2-dichloroethane were measured at atmospheric pressure using an Ellis recirculation still. Experimental data were tested for thermodynamic consistency, and Wilson's equation provided a good correlation.

Published data (*1, 3*) show the two binary systems cyclohexane–cyclohexene and cyclohexane–1,2-dichloroethane inadequate in thermodynamic consistency tests. This work is an investigation of these systems plus the binary system cyclohexene-1,2-dichloroethane and the ternary system cyclohexane–cyclohexene-1,2-dichloroethane.

EXPERIMENTAL

Materials and Physical Constants. Cyclohexane, cyclohexene, and 1,2-dichloroethane were supplied as chromatography grade and used without further purification. The four-parameter equation, $\ln P_i^s = C_1 + C_2/T + C_4T + C_6 \ln T$, was used to correlate vapor pressure and temperature. The parameters C_1–C_4 were found by the method of least squares, and the best value of C_6 was obtained by trial and error. The agreement between published and calculated vapor pressure data is good. The mean absolute percentage deviation, defined as

$$D = \sum_{j=1}^{N} \left| \frac{P_j^s\ (\text{exp}) - P_j^s\ (\text{calcd})}{P_j^s\ (\text{exp})} \times 100 \right|$$

gave values ranging from 0.008 for cyclohexane to 0.043 for 1,2-dichloroethane.

The necessary physical constants were found in the literature and are reported in Table I.

Apparatus. Experimental vapor-liquid equilibrium data were determined by using a conventional glass Ellis recirculation still fully described in the literature (*2*). Pressure was regulated by a damping reservoir followed by a Cartesian monostat (*2*). Variation of pressure in the system was estimated to be, at the most, 1 mm of mercury.

Temperatures were measured by a calibrated ASTM thermometer. The probable error in the temperature is 0.05°C. The whole system was kept in a heated box, and a total load

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Table I. Physical Constants of Pure Component

		Cyclohexane C_6H_{12}	Cyclohexene C_6H_{10}	1,2-Dichloroethane CH_2Cl-CH_2Cl
Boiling point (7), °C		80.70	82.98	83.47
Molecular weight (7), grams		84.16	82.14	98.97
Critical properties (7)	P_c, atm	40.57	41.82	64.52
	T_c, °K	554.15	559.15	579.15
	V_c, ml	307.3	301.3	200.5
	D_c, g/ml	0.272	0.288	0.517
Dipole moment (4)		0.0	0.28	2.98
Acentric factor (6)		0.2103	0.2046	0.2351
Parameters for Equation (7)	C_1	65.95	143.77	96.38
$P = f(T)$	C_2	−6011.1	−8201.5	−7014.2
	C_3	0.0	0.0	0.0
	C_4	0.0067	0.028	0.015
	C_5	0	0	0
	C_i	−8.75	−22.24	−13.98

of 250 cc was used for each experiment. After about 2 hr of gentle boiling, the steady state was established, and liquid and vapor samples were taken simultaneously and directly analyzed.

Analytical Method. The equilibrium samples were analyzed by gas chromatography with a flame detector. The marker method, used for the calibration, consists in adding a known amount of a compound in the sample. This compound acts as a reference whose chromatographic peak must be near the peak of the marked compound but must not overlap. A calibration curve must be made for each compound of the ternary system; toluene and acetone are the two selected markers.

The chromatographic column was recalibrated regularly to account for possible column degradation. The statistical error in the chromatographic analysis of the sample was at the most 2%.

Activity Coefficients from Experimental Data (x_i, y_i, P, T). Activity coefficients were calculated for each component using equation

$$\gamma_i = \frac{y_i \phi_i P}{x_i f_i^{OL}} \qquad (1)$$

With a general thermodynamic function for the fugacity coefficient (5),

$$\ln \phi_i = \frac{1}{RT} \int_v^\infty \left[\left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_j} - \frac{RT}{v^V} \right] dv - \ln z \qquad (2)$$

and the virial equation of state truncated after the second term

$$z = \frac{P v^V}{RT} = 1 + \frac{B \text{ mix}}{v^V} \qquad (3)$$

where B mix = mixture virial coefficient and is given by

$$B \text{ mix} = \sum_{i=1}^{N} \sum_{j=1}^{N} y_i y_j B_{ij} \qquad (4)$$

The fugacity coefficient for any component i in a mixture of components is obtained by substitution of Equations 3 and 4 in Equation 2. After differentiating and integrating, one obtained

$$\ln \phi_i = \frac{2}{v^V} \sum_j^N y_j B_{ij} - \ln z \qquad (5)$$

The fugacity coefficient ϕ_i was calculated with the help of Equation 5 and the standard state fugacity by

$$f_i^{OL} = \phi_i^s P_i^s \exp \left(- \frac{v_i^L P_i^s}{RT} \right) \qquad (6)$$

The calculation of the virial coefficients B_{ij} is explained in the literature (6).

Correlation of Results. The Wilson equation

$$\ln \gamma_i = 1 - \ln \left[\sum_{j=1}^{N} x_j \Lambda_{ij} \right] - \sum_{k=1}^{N} \left[\frac{x_k \Lambda_{ki}}{\sum_{j=1}^{N} x_j \Lambda_{kj}} \right] \qquad (7)$$

was selected for correlating the data. The Λ_{ij} is defined by

$$\Lambda_{ij} = \frac{v_j^L}{v_i^L} \exp \left[- \frac{(\lambda_{ij} - \lambda_{ii})}{RT} \right] \qquad (8)$$

and $(\lambda_{ij} - \lambda_{ii})$ are Wilson's energy parameters, determined by successive approximation from isobaric or isothermal experimental data. Even for multicomponent systems, only binary parameters are needed for Wilson's equation.

The Wilson parameters are calculated as follows:

$$\Sigma\, y_i = 1.0 \qquad (9)$$

$P = (\Sigma\, y_i)P$ and for a binary system, $P = y_1 P + y_2 P$ (10)

but

$$P = \frac{f_1^L}{\phi_1} + \frac{f_2^L}{\phi_2} = \frac{\gamma_1 x_1 f_1^{OL}}{\phi_1} + \frac{\gamma_2 x_2 f_2^{OL}}{\phi_2} \qquad (11)$$

For a given $(\lambda_{ij} - \lambda_{ii})$, activity coefficients are calculated at the reference pressure of the standard state fugacity and the total pressure P of the system is evaluated by Equation 11. A comparison is made between calculated and experimental P:

$$SQ = \Sigma \left[\frac{(P_{\text{exp}} - P_{\text{calcd}})}{P_{\text{calcd}}} \times 100 \right]^2 \qquad (12)$$

Then, the minimum SQ is searched for. The vapor phase y_i is calculated by Equation 1. These computations were carried out using an IBM 360/40 computer.

Van Laar and Margules models were used for binary systems:

Van Laar (3rd order)

$$\log \gamma_1 = A_{12}/(1 + A_{12}x_1/A_{21}x_2)^2 \qquad (13)$$

$$\log \gamma_2 = A_{21}/(1 + A_{21}x_2/A_{12}x_1)^2 \qquad (14)$$

Margules (3rd order)

$$\log \gamma_1 = x_2^2(2\,A_{21} - A_{12}) + 2\,x_2^3(A_{12} - A_{21}) \qquad (15)$$

$$\log \gamma_2 = x_1^2(2\,A_{12} - A_{21}) + 2\,x_1^3(A_{21} - A_{12}) \qquad (16)$$

Ternary systems using Van Laar and Margules models were:

Van Laar (3rd order)

$$\log \gamma_i = Z_j^2 A_{ij} + Z_k^2 A_{ik} + Z_j Z_k \left(A_{ij} + A_{ik} - \frac{A_{kj} A_{ik}}{A_{ki}} - C(1 - 2\,Z_i) \frac{A_{i1}}{A_{1i}} \right) \qquad (17)$$

with

$$Z_i = \frac{x_i A_{i1}/A_{1i}}{x_1 + x_2 A_{21}/A_{12} + x_3 A_{31}/A_{13}} \tag{18}$$

$$ijk = 123,\ 231,\ 312$$

Margules (3rd order)

$$\begin{aligned}\log \gamma_i = {} & x_j^2[A_{ij} + 2\,x_i(A_{ji} - A_{ij})] + \\ & x_k^2[A_{ik} + 2\,x_i(A_{ki} - A_{ik})] + \\ & x_j x_k[A_{ji} + A_{ik} - A_{kj} + 2\,x_i(A_{ki} - A_{ik}) + \\ & 2\,x_k(A_{kj} - A_{jk}) - C(1 - 2\,x_i)]\end{aligned} \tag{19}$$

with

$$C = {}^1/_2(A_{21} - A_{12} + A_{31} - A_{13} + A_{32} - A_{23}) \tag{20}$$

$$A_{ij} = \lim_{x_i \to 0} \log \gamma_i \tag{21}$$

RESULTS FOR BINARY SYSTEMS

Thermodynamic Consistency of Experimental Data. The three binary systems have been tested thermodynamically by the method of Herington (*2*) who proposed an equation for isobaric conditions derived from the Gibbs-Duhem equation:

$$\int_0^{1.0} \log \frac{\gamma_1}{\gamma_2}\, dx_1 = \int_0^{1.0} \frac{H^E}{2.30\, RT^2} \frac{dT}{dx_1}\, dx_1 \tag{22}$$

where H^E = molar heat of mixing.

For isobaric conditions this right-hand term is not negligible. From the graph $\log(\gamma_1/\gamma_2) = f(x_1)$, the area under the curve is measured and compared with values given by Herington to take in account this second term of the integral. This entire method is reported by Hala et al. (*2*). For each system the plot of $\log(\gamma_i/\gamma_j) = f(x_i)$ is presented in Figures 1–3.

The two systems cyclohexane–1,2-dichloroethane and cyclohexene–1,2-dichloroethane were consistent. The system cyclohexane–cyclohexene is not consistent although the positive and negative areas are nearly equal (positive area = 0.00199, negative area = 0.00158), but these numerical values are so small that actual experimental errors are sufficient to destroy the internal consistency of the data.

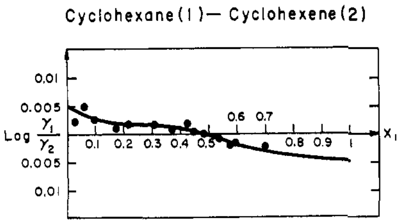

Figure 1. Herington consistency test

Positive area, 0.0020. Negative area, 0.0016. Test inconclusive

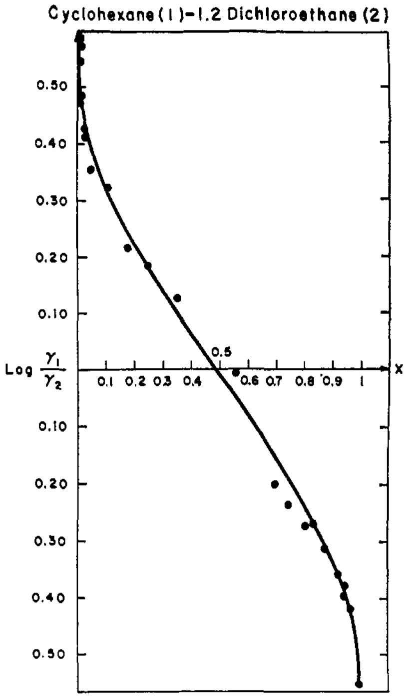

Figure 2. Herington consistency test

Positive area, 0.097. Negative area, 0.112. Results consistent

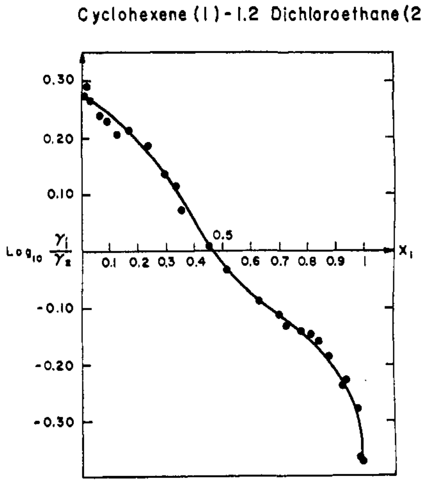

Figure 3. Herington consistency test

Positive area, 0.073. Negative area, 0.069. Results consistent

Correlation. Consistent experimental data were used to determine the various binary parameters used in conjunction with Wilson, Van Laar, and Margules equations. These parameters are reported in Table II. Following this determination, correlation was attempted for the cyclohexane (1)–cyclohexene (2) system. Experimental results are reported in Table III, and Figure 4 indicates nearly ideal behavior.

Table II. Parameters Used in Three Equations of Prediction

	Cyclohexane (1)–cyclohexene (2) system		Cyclohexane (1)–1,2-dichloroethane (2) system		Cyclohexene (1)–1,2-dichloroethane (2) system	
	A_{12}	A_{21}	A_{12}	A_{21}	A_{12}	A_{21}
Wilson energy parameters $(\lambda_{ij} - \lambda_{ii}) = A_{ij}$	967.85	−487.15	426.27	352.14	238.01	186.35
Van Laar	0.035	0.040	0.65	0.55	0.30	0.36

Table III. Experimental Data for Cyclohexane(1)–Cyclohexene (2) System

$P = 1$ atm

T, °K	x_1	y_1	γ_1	γ_2
356.07	0.0281	0.0321	1.0729	1.0245
356.00	0.0276	0.0312	1.0638	1.0271
355.79	0.0627	0.0758	1.1453	1.0227
355.96	0.0997	0.1139	1.0777	1.0157
355.73	0.1742	0.1902	1.0379	1.0186
355.60	0.2211	0.2428	1.0485	1.0134
355.30	0.2939	0.3128	1.0258	1.0232
355.32	0.3149	0.3438	1.0521	1.0062
355.15	0.3770	0.4020	1.0332	1.0130
355.08	0.4291	0.4610	1.0437	1.0000
355.01	0.4538	0.4798	1.0193	1.0170
354.95	0.4886	0.5085	1.0153	1.0194
354.82	0.5395	0.5546	1.0070	1.0294
354.67	0.5776	0.5868	1.0000	1.0454
354.61	0.5998	0.6100	1.0027	1.0430
354.50	0.6547	0.6677	1.0090	1.0326
354.27	0.7070	0.7140	1.0061	1.0539

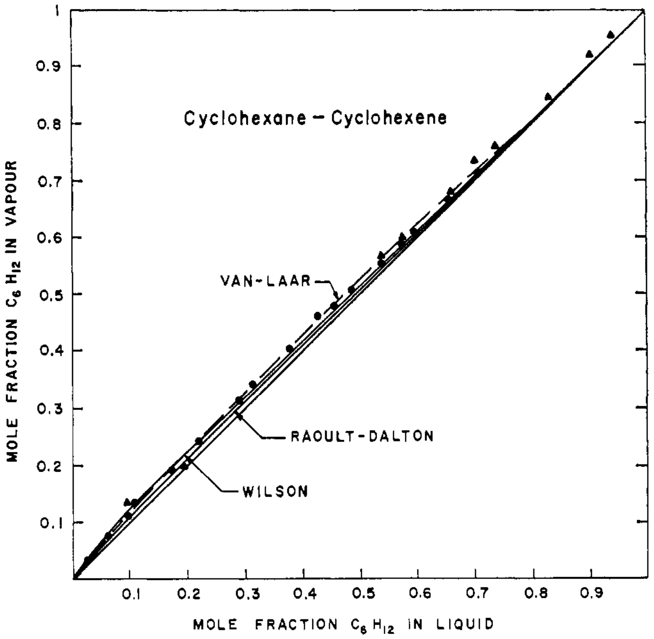

Figure 4. Equilibrium curve

— Experimental results ● Wilson
▲ Published results --- Van Laar

A trial has been made with the Dalton-Raoult law, and the vapor phase composition is evaluated by:

$$y_i = \frac{x_i P_i^s}{P}$$

Goodness of fit of the Raoult, Wilson, and Van Laar models are compared in Table IV. A mean error on the calculated vapor phase composition and on the calculated activity coefficients is evaluated in regard to experimental data. The assumption that this system is ideal is justified: The vapor phase compositions predicted by the Raoult-Dalton law differ slightly from the experimental values. In fact, the three methods are rather equivalent for this system.

Cyclohexane (1)–1,2-dichloroethane (2) and cyclohexene (1)–1,2-dichloroethane (2) systems present an azeotropic point (Figures 5 and 6). The comparison of experimental azeotropic compositions with those obtained by Wilson and Van Laar equations is tabulated (Table V). Experimental values are

Table IV. Comparison between Raoult, Wilson, and Van Laar Models for Cyclohexane (1)–Cyclohexene (2) System

Equation	95% Confidence limits of errors	
	y	γ
Raoult-Dalton	$\Delta y_1 = 0.0052 \pm 0.0031$	
Wilson	$\Delta y_1 = -0.0045 \pm 0.0043$	$\Delta\gamma_1 = 0.0146 \pm 0.0712$
	$\Delta y_2 = \Delta y_1$	$\Delta\gamma_2 = 0.0071 \pm 0.0797$
Van Laar	$\Delta y_1 = 0.0019 \pm 0.0022$	$\Delta\gamma_1 = 0.0017 \pm 0.0109$
	$\Delta y_2 = -0.0071 \pm 0.0049$	$\Delta\gamma_2 = -0.0094 \pm 0.0058$

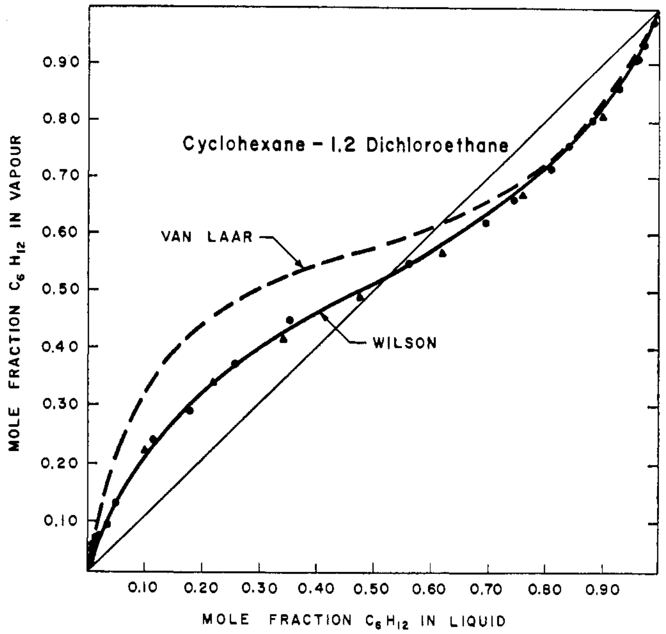

Figure 5. Equilibrium curve

— Experimental results ● Wilson
▲ Published results ---Van Laar

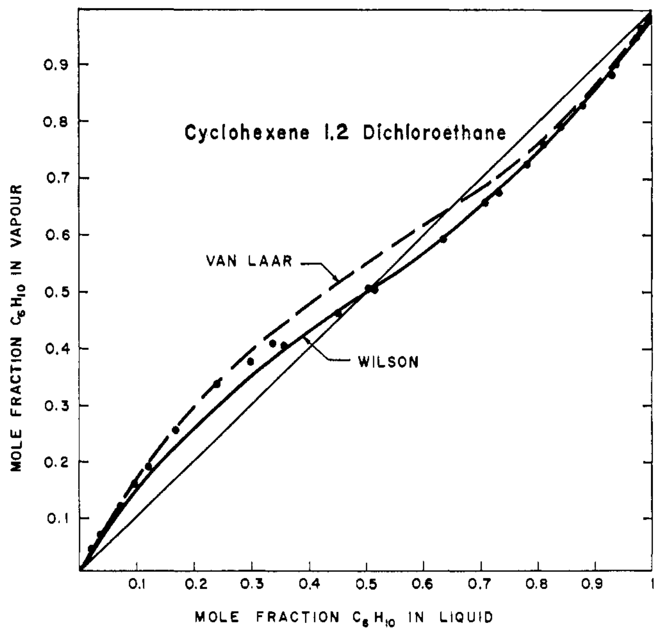

Figure 6. Equilibrium curve

— Experimental results. ● Wilson. --- Van Laar tabulated (Tables VI and VII), and vapor-liquid equilibria data are plotted in Figures 5 and 6.

The predicted values of vapor phase composition and activity coefficients are again compared with experimental data, and the mean error on y and γ is tabulated in Tables VIII and IX. These results provide evidence that the Wilson equation gives a better correlation than the Van Laar model.

RESULTS FOR TERNARY SYSTEMS

All the results are tabulated in Table X. Three prediction methods have been tried. The Wilson method is again the best for this ternary system (Table XI).

Table V. Azeotropic Composition for Cyclohexane–1,2-Dichloroethane and Cyclohexene–1,2-Dichloroethane Systems

	Experimental composition	Wilson composition	Van Laar composition
Cyclohexane (1)–1,2-dichloroethane (2)	$x_1 = y_1 = 0.53$	0.53	0.62
Cyclohexene (1)–1,2-dichloroethane (2)	0.505	0.500	0.655

Table VI. Experimental Data for Cyclohexane (1)–1,2-Dichloroethane (2) System

$P = 1$ atm

T, °K	x_1	y_1	γ_1	γ_2
356.39	0.0065	0.0209	2.9823	1.0130
355.95	0.0113	0.0426	3.5422	1.0088
356.01	0.0123	0.0498	3.7984	1.0004
355.57	0.0165	0.0646	3.7203	1.0024
355.40	0.0206	0.0661	3.0639	1.0103
354.84	0.0321	0.0891	2.6944	1.0144
354.70	0.0326	0.0878	2.6247	1.0208
354.10	0.0537	0.1249	2.3078	1.0198
352.05	0.1165	0.2357	2.1349	1.0167
350.65	0.1804	0.2869	1.7501	1.0685
349.62	0.2582	0.3712	1.6334	1.0750
348.85	0.3533	0.4478	1.4752	1.1091
348.23	0.5631	0.5489	1.1574	1.3664
348.57	0.6979	0.6170	1.0398	1.6576
348.85	0.7473	0.6560	1.0242	1.7628
349.53	0.8103	0.7158	1.0105	1.8960
349.90	0.8395	0.7579	1.0128	1.8850
350.75	0.8826	0.8015	1.0025	2.0547
351.85	0.9280	0.8598	1.0000	2.2826
352.47	0.9521	0.9007	1.0000	2.3810
353.45	0.9545	0.9024	1.0000	2.4651
353.95	0.9731	0.9369	1.0000	2.6517
353.15	0.9754	0.9424	1.0000	2.6301
353.65	0.9930	0.9771	1.0000	3.6148

Table VII. Experimental Data for Cyclohexene (1)–1,2-Dichloroethane (2) System

$P = 1$ atm

T, °K	x_1	y_1	γ_1	γ_2
356.05	0.9935	0.9852	1.0029	2.3363
355.87	0.9854	0.9672	1.0000	2.3189
355.65	0.9735	0.9514	1.0000	1.9065
355.25	0.9385	0.9010	1.0000	1.6961
354.75	0.9276	0.8835	1.0002	1.7224
354.35	0.8775	0.8270	1.0012	1.5324
353.95	0.8428	0.7918	1.0097	1.4561
353.63	0.8124	0.7598	1.0144	1.4226
353.37	0.7808	0.7251	1.0148	1.4057
353.05	0.7318	0.6743	1.0161	1.3761
352.90	0.7047	0.6547	1.0289	1.3317
352.60	0.6349	0.5944	1.0454	1.2784
352.25	0.5144	0.5040	1.1044	1.1899
352.33	0.5056	0.5059	1.1252	1.1613
352.53	0.4512	0.4629	1.1462	1.1307
352.70	0.3564	0.4042	1.2596	1.0645
352.70	0.3387	0.4079	1.3376	1.0296
352.87	0.2978	0.3752	1.3917	1.0180
353.35	0.2401	0.3382	1.5331	1.0000
353.97	0.1671	0.2560	1.6349	1.0000
354.65	0.1215	0.1886	1.6218	1.0011
354.95	0.0969	0.1590	1.6984	1.0002
355.35	0.0719	0.1214	1.7261	1.0044
355.95	0.0367	0.0673	1.8402	1.0087
356.43	0.0200	0.0398	1.9682	1.0058
356.80	0.0040	0.0078	1.9068	1.0112
356.80	0.0038	0.0069	1.7756	1.0119

Table VIII. Comparison between Wilson and Van Laar Models for Cyclohexane (1)–1,2-Dichloroethane (2) System

	95% Confidence limits of errors	
Equations	y	γ
Wilson	$\Delta y_1 = 0.0047 \pm 0.0046$	$\Delta\gamma_1 = -0.0996 \pm 0.2959$
	$\Delta y_2 = \Delta y_1$	$\Delta\gamma_2 = -0.1581 \pm 0.3057$
Van Laar	$\Delta y_1 = 0.0357 \pm 0.0160$	$\Delta\gamma_1 = 0.4619 \pm 0.2218$
	$\Delta y_2 = 0.0249 \pm 0.0148$	$\Delta\gamma_2 = 0.2735 \pm 0.1422$

Table IX. Comparison between Wilson and Van Laar Models for Cyclohexene (1)–1,2-Dichloroethane (2) System

	95% Confidence limits of errors	
Equations	y	γ
Wilson	$\Delta y_1 = -0.0023 \pm 0.0053$	$\Delta\gamma_1 = -0.0406 \pm 0.0678$
	$\Delta y_2 = \Delta y_1$	$\Delta\gamma_2 = -0.0851 \pm 0.2045$
Van Laar	$\Delta y_1 = 0.0165 \pm 0.0067$	$\Delta\gamma_1 = 0.0577 \pm 0.0214$
	$\Delta y_2 = 0.0145 \pm 0.0063$	$\Delta\gamma_2 = 0.0820 \pm 0.0485$

Table X. Experimental Data for Cyclohexane (1)–Cyclohexene (2)–1,2-Dichloroethane (3) System

$P = 1$ atm

T, °K	x_1	y_1	x_2	y_2	γ_1	γ_2	γ_3
353.39	0.0761	0.0845	0.7450	0.6690	1.1263	0.9996	1.5516
353.20	0.1614	0.1705	0.6852	0.6025	1.0790	0.9848	1.6757
353.52	0.2025	0.2144	0.6105	0.5333	1.1036	0.9977	1.5605
351.88	0.2326	0.2438	0.5394	0.4592	1.1134	0.9910	1.5373
351.54	0.2611	0.2681	0.4887	0.4076	1.1019	0.9808	1.5462
351.05	0.2931	0.3090	0.4136	0.3426	1.1483	0.9884	1.4389
351.15	0.2963	0.3124	0.4211	0.3573	1.4452	1.0094	1.4112
350.34	0.2774	0.3166	0.2884	0.2365	1.2692	0.9996	1.2755
350.49	0.2610	0.2471	0.2313	0.1939	1.0468	1.0173	1.3590
350.63	0.2038	0.2763	0.1863	0.1731	1.4935	1.1226	1.1091
350.93	0.1796	0.2543	0.1756	0.1588	1.5454	1.0828	1.1079

(*Continued on next page*)

Table X. *(Continued)*

P = 1 atm

T, °K	x_1	y_1	x_2	y_2	γ_1	γ_2	γ_3
351.13	0.1529	0.2297	0.1070	0.1154	1.6291	1.2834	1.0705
350.34	0.2445	0.3172	0.1284	0.1198	1.4422	1.1370	1.1130
349.75	0.3145	0.3528	0.1310	0.1240	1.2698	1.1743	1.1915
349.51	0.3802	0.4083	0.1240	0.1171	1.2253	1.1799	1.2174
349.61	0.4638	0.4465	0.1504	0.1320	1.0958	1.0930	1.3844
350.34	0.4684	0.4549	0.2314	0.1995	1.0821	1.0501	1.4246
349.71	0.3253	0.3461	0.1652	0.1494	1.2057	1.1234	1.2520
350.10	0.2266	0.2916	0.1264	0.1213	1.4401	1.1782	1.1338
350.39	0.1975	0.2771	0.1080	0.1153	1.5563	1.2992	1.0832
350.89	0.1768	0.2781	0.0982	0.1106	1.7193	1.3499	1.0275
351.52	0.1432	0.2295	0.0597	0.0720	1.7178	1.4182	1.0472
350.55	0.4373	0.4253	0.2953	0.2561	1.0767	1.0499	1.4649
350.84	0.3726	0.3678	0.3549	0.2943	1.0827	0.9954	1.5114
350.19	0.2557	0.2794	0.2536	0.2216	1.2197	1.0701	1.2668
352.25	0.7928	0.7509	0.1348	0.1223	1.0005	1.0398	2.0308
353.19	0.7032	0.6773	0.2425	0.2285	0.9896	1.0510	1.9551
353.78	0.6378	0.5999	0.3219	0.3302	0.9496	1.1253	1.9209
352.99	0.5452	0.5085	0.3910	0.3582	0.9626	1.0299	2.3747
352.75	0.4660	0.4254	0.4392	0.4140	0.9479	1.0680	1.9418
353.19	0.3706	0.3580	0.5253	0.4740	0.9896	1.0095	1.8256
353.19	0.3688	0.3582	0.5312	0.4836	0.9950	1.0185	1.7895
352.99	0.4221	0.4621	0.4591	0.3681	1.1293	0.9017	1.6256
353.09	0.3551	0.4108	0.5225	0.4124	1.1892	0.8853	1.6385
353.29	0.3159	0.3432	0.5643	0.4804	1.1095	0.9505	1.6570
353.53	0.2999	0.3218	0.5928	0.5159	1.080	0.9641	1.6934
353.80	0.2931	0.2980	0.6145	0.5587	1.0226	0.9993	1.7219
354.12	0.2524	0.2831	0.6677	0.5930	1.1176	0.9670	1.7047
355.16	0.1848	0.1979	0.7570	1.7143	0.0346	0.9967	1.6064
352.57	0.6413	0.6000	0.2866	0.2723	0.9783	1.0806	2.0375
350.77	0.5494	0.5147	0.2626	0.2192	1.0315	1.0030	1.7262
350.16	0.4864	0.4640	0.2470	0.2155	1.0688	1.0684	1.4960
350.23	0.4470	0.4326	0.2663	0.2408	1.0816	1.1053	1.4149

Table XI. Comparison between Wilson, Van Laar, and Margules Models for Ternary System

	95% Confidence limits of errors	
Equations	y	γ
Wilson	$\Delta y_1 = -0.0036 \pm 0.0056$	$\Delta \gamma_1 = -0.0108 \pm 0.0193$
	$\Delta y_2 = -0.0056 \pm 0.0058$	$\Delta \gamma_2 = 0.0065 \pm 0.0203$
	$\Delta y_3 = 0.0056 \pm 0.0048$	$\Delta \gamma_3 = 0.0671 \pm 0.0347$
Van Laar	$\Delta y_1 = 0.0320 \pm 0.0094$	$\Delta \gamma_1 = 0.1322 \pm 0.0527$
	$\Delta y_2 = 0.0047 \pm 0.0046$	$\Delta \gamma_2 = 0.0464 \pm 0.0160$
	$\Delta y_3 = 0.0526 \pm 0.0067$	$\Delta \gamma_3 = 0.3470 \pm 0.0684$
Margules	$\Delta y_1 = -0.0071 \pm 0.0063$	$\Delta \gamma_1 = -0.0480 \pm 0.0251$
	$\Delta y_2 = -0.0002 \pm 0.0048$	$\Delta \gamma_2 = -0.0364 \pm 0.0188$
	$\Delta y_3 = -0.0334 \pm 0.0051$	$\Delta \gamma_3 = -0.2184 \pm 0.0478$

CONCLUSION

The Van Laar and Margules equations, although easier to use than Wilson's do not yield a good prediction. The method of search for the Wilson parameters is lengthy but the Wilson equation seems more powerful for fitting the binary data featuring azeotropic points. For multicomponent systems the Wilson equation has a real advantage over the others because only binary parameters are needed.

NOMENCLATURE

A = coefficient for Van Laar or Margules equation
B = second virial coefficient, cm^3/g-mol
f = fugacity, atm
n = number of moles, g/mol
P = pressure, atm
R = gas constant, cm^3-atm/g-mol, °K or cal/g-mol, °K
T = temperature, °K
V = total volume of gaseous mixture, cm^3
v = liquid or vapor molar volume, cm^3/g-mol
x = liquid mole fraction
y = vapor mole fraction
z = compressibility factor
γ = activity coefficient
λ = Wilson energy parameters, cal/g-mole
ϕ = fugacity coefficient

Superscripts

L = liquid state
0 = standard state
s = saturation
V = vapor state

Subscripts

i, j = ith, or jth component

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