Prediction of Ternary Vapor-Liquid Equilibria from Binary Data

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Wilson equation used to predict vapor compositions

An essential ingredient in the industrial design of distillation equipment is a knowledge of the vapor-liquid equilibria of the system to be separated. Many articles containing experimental equilibrium data for binary systems have appeared in the literature in recent years. However, the vast majority of industrial separations involves several components, and experimental data for systems containing four or more components are almost nonexistent.

Because the cost and time involved in obtaining experimental equilibrium data increase rapidly with the number of components, the distillation practitioner has turned to thermodynamics in search of effective predictive methods.

Our knowledge of liquid mixtures is still far from complete. Ultimately, the design engineer would like to predict multicomponent data from pure component properties. However, the present methods involve reduction of binary data to a small number of parameters with various solution models. These models are then used with the binary parameters to predict multicomponent behavior.

Solution Models

Many solution models which relate activity coefficients to liquid composition and satisfy the well-known Gibbs-Duhem equation

$$\sum_{i}^{N} x_i (d \ln \gamma_i)_{T,P} = 0 \qquad (1)$$

have been proposed. A common procedure in model development is first to relate the molar excess free energy to the liquid composition. For example, Wohl (*69*, *70*) has shown that the Margules, van Laar, and Scatchard-Hamer equations can all be developed as variations of one mathematical scheme. In the derivation the molar excess free energy of the mixture is equated to a sum of empirical interaction terms

$$\frac{g^E}{2.303\, RT \sum_i q_i x_i} = \sum_{ij} z_i z_j a_{ij} + \sum_{ijk} z_i z_j z_k a_{ijk} + \sum_{ijkl} z_i z_j z_k z_l a_{ijkl} + \ldots \qquad (2)$$

where q_i is called the effective molar volume of the ith component and z_i is the effective volumetric fraction

$$z_i \equiv \frac{q_i x_i}{\sum_j q_j x_j} \qquad (3)$$

with the molar excess free energy expressed in terms of the liquid composition, the various models relating activity coefficients to composition can be obtained by the exact relation

$$RT \ln \gamma_i = \left(\frac{\partial n_T g^E}{\partial n_i}\right)_{T,P,n_{j\neq i}} \qquad (4)$$

Four solution models for liquid phase activity coefficients have been compared in this study: the Margules, Bonham, van Laar, and Wilson equations.

Margules equation. One of the most commonly used solution models is that of Margules (*30*). The third-order Margules equations for a binary system are:

$$\log_{10} \gamma_1 = x_2^2[A_{12} + 2\, x_1(A_{21} - A_{12})] \qquad (5)$$

$$\log_{10} \gamma_2 = x_1^2[A_{21} + 2\, x_2(A_{12} - A_{21})] \qquad (6)$$

The third-order Margules equations for a ternary system involve the parameters for the three constituent binary systems and a single ternary parameter:

$$\log_{10} \gamma_1 = x_2^2[A_{12} + 2\, x_1(A_{21} - A_{12})] + x_3^2[A_{13} + 2\, x_1 (A_{31} - A_{13})] + x_2 x_3[(A_{21} + A_{12} + A_{31} + A_{13} - A_{23} - A_{32})/2 + x_1(A_{21} - A_{12} + A_{31} - A_{13}) + (x_2 - x_3)(A_{23} - A_{32}) - (1 - 2\, x_1)C^*] \qquad (7)$$

The expressions for the activity coefficients of the other two components can be obtained by the rotation principle

$$\begin{array}{c} 3 \\ \swarrow\ \nwarrow \\ 1 \rightarrow 2 \end{array}$$

As stated by Wohl (*69*) in a supplement to his earlier work (*70*), the ternary constant C^* can be set equal to zero for systems in which the ternary interactions are negligible. In this case, only binary data are needed for the representation of the ternary system.

Van Laar equation. Van Laar (*63*) attempted to employ a more theoretical approach than Margules by examining the thermodynamic changes occurring during mixing of the pure liquids. The resulting equations are

$$T \ln \gamma_1 = \frac{B_{12}}{[1 + A_{12}(x_1/x_2)]^2} \tag{8}$$

$$T \ln \gamma_2 = \frac{A_{12}B_{12}}{[A_{12} + (x_2/x_1)]^2} \tag{9}$$

Based on van Laar's assumptions, the binary parameters A_{12} and B_{12} can be expressed in terms of van der Waals constants

$$A_{12} = \frac{b_1}{b_2} \tag{10}$$

$$B_{12} = \frac{b_1}{R}\left[\frac{a_1^{0.5}}{b_1} - \frac{a_2^{0.5}}{b_2}\right]^2 \tag{11}$$

However, in practice the van der Waals constants do not yield satisfactory estimates of the binary parameters.

Carlson and Colburn (*9*) modified the original van Laar equations by defining new parameters

$$\bar{A}_{12} \equiv \frac{B_{12}}{2.303\ T} \tag{12}$$

$$\bar{A}_{21} \equiv \frac{B_{12}}{2.303\ A_{12}T} \tag{13}$$

The resulting equations are

$$\log_{10} \gamma_1 \equiv \frac{\bar{A}_{12}}{\left(1 + \frac{x_1}{x_2}\frac{\bar{A}_{12}}{\bar{A}_{12}}\right)^2} \tag{14}$$

$$\log_{10} \gamma_2 = \frac{\bar{A}_{21}}{\left(1 + \frac{x_2}{x_1}\frac{\bar{A}_{21}}{\bar{A}_{12}}\right)^2} \tag{15}$$

It is apparent from Equations 12 and 13 that the equations above are equivalent to the original van Laar equations only under isothermal conditions. In spite of this, the equations presented by Carlson and Colburn are much more widely used today than the original van Laar relations and are generally referred to simply as the "van Laar equations."

These equations have been extended to ternary systems by Wohl (*70*). The second-order equation for the first component is

$$\log_{10} \gamma_1 = \left[x_2^2\bar{A}_{12}\left(\frac{\bar{A}_{21}}{\bar{A}_{12}}\right)^2 + x_3^2\bar{A}_{13}\left(\frac{\bar{A}_{31}}{\bar{A}_{13}}\right)^2 + x_2x_3\frac{\bar{A}_{21}\bar{A}_{31}}{\bar{A}_{12}\bar{A}_{13}}\left(\bar{A}_{12} + \bar{A}_{13} - \bar{A}_{32}\frac{\bar{A}_{13}}{\bar{A}_{31}}\right)\right] \Big/ \left[x_1 + x_2\frac{\bar{A}_{21}}{\bar{A}_{12}} + x_3\frac{\bar{A}_{31}}{\bar{A}_{13}}\right]^2 \tag{16}$$

The corresponding expressions for the other components can be obtained by the rotation principle.

The equation above involves no ternary parameters. However, it was developed with the following restriction

$$\frac{\bar{A}_{12}}{\bar{A}_{21}} \times \frac{\bar{A}_{23}}{\bar{A}_{32}} \times \frac{\bar{A}_{31}}{\bar{A}_{13}} = 1 \tag{17}$$

Often the parameters obtained by a least-squares fit of the binary data do not satisfy Equation 17.

Bonham equation. Bonham (*5*) extended the original van Laar Equations 8 and 9 to multicomponent systems resulting in

$$T \ln \gamma_1 = \frac{(x_2B_{12}^{0.5} + x_3A_{32}B_{13}^{0.5})^2}{(x_1A_{12} + x_2 + x_3A_{32})^2} \tag{18}$$

$$T \ln \gamma_2 = \frac{(x_1A_{12}B_{21}^{0.5} + x_3A_{32}B_{23}^{0.5})^2}{(x_1A_{12} + x_2 + x_3A_{32})^2} \tag{19}$$

$$T \ln \gamma_3 = \frac{(x_1A_{12}B_{31}^{0.5} + x_2B_{32}^{0.5})^2}{(x_1A_{12} + x_2 + x_3A_{32})^2} \tag{20}$$

for a ternary system. The parameters are related by the equations below.

$$A_{ji} = \frac{1}{A_{ij}} \tag{21}$$

$$B_{ji} = \frac{B_{ij}}{A_{ij}} \tag{22}$$

Several difficulties arise when applying the Bonham equations to the prediction of vapor-liquid equilibria. According to the assumptions of van Laar, the parameters in the original van Laar equations can assume only positive values (see Equations 10 and 11). This restriction on B_{ij} prevents adequate representation of a binary system which shows negative deviations from ideality. The van Laar assumptions were used in the development of the Bonham multicomponent equations, and, thus, the model is not satisfactory for multicomponent systems in which some of the B_{ij} are negative. This is apparent from inspection of Equations 18, 19, and 20 where the square root of B_{ij} appears.

A second difficulty with the Bonham equation concerns the sign of $B_{ij}^{0.5}$. According to Robinson and Gilliland (*52*), the sign is determined by the relative polarity of the components in the binary system. For example, if component 1 is more polar than component 2, $B_{12}^{0.5}$ is positive and $B_{21}^{0.5}$ is negative.

A final difficulty with the Bonham equation is the restrictions given by Equations 23 and 24

TABLE I. ANTOINE CONSTANTS

Component	A	B	C	Temperature range, °C	Data reference
Acetone	7.02447	1161.0	224.	...	(26)
Acetonitrile	7.07354	1279.2	224.	5 to 119	(11)
Benzene	6.90565	1211.033	220.790	0 to 160	(11)
1-Butanol	8.27488	1873.9	230.	...	(66)
Butyl cellosolve	7.16462	1538.7	188.0	...	(47)
Carbon tetrachloride	6.93390	1242.43	230.0	−15 to 138	(11)
Cellosolve	8.416	2135.0	253.0	...	(60)
Chloroform	6.90328	1163.03	227.4	−30 to 150	(26)
Cyclohexane	6.84498	1203.526	222.863	−20 to 142	(11)
Cyclopentane	6.88676	1124.162	231.361	−25 to 110	(11)
2,3-Dimethylbutane	6.80983	1127.187	228.900	−20 to 100	(11)
1,4-Dioxane	7.8642	1866.7	273.0	...	(60)
Ethanol	8.04494	1554.3	222.65	...	(26)
Ethyl acetate	7.09808	1238.71	217.0	−20 to 150	(26)
Ethylbenzene	6.95719	1424.255	213.206	45 to 190	(11)
Ethylcyclohexane	6.87041	1384.036	215.128	40 to 170	(11)
n-Heptane	6.90240	1268.115	216.900	15 to 130	(11)
n-Hexane	6.87776	1171.530	224.366	−10 to 110	(11)
Hexene-1	6.8657	1152.97	225.85	...	(60)
Hexylene glycol	7.8876	1890.38	180.46	...	(50)
Methanol	7.87863	1473.11	230.0	−20 to 140	(26)
Methyl acetate	7.20211	1232.83	228.0	...	(26)
Methylcyclohexane	6.82689	1276.864	221.630	10 to 155	(11)
Methylcyclopentane	6.86283	1186.059	226.042	−5 to 125	(11)
Methyl-ethyl-ketone	6.97421	1209.6	216.	...	(26)
n-Octane	6.92377	1355.126	209.517	40 to 155	(11)
n-Pentane	6.85221	1064.63	232.000	−35 to 80	(11)
1-Propanol	7.99733	1569.70	209.5	...	(26)
2-Propanol	6.66040	813.055	132.93	0 to 113	(26)
Toluene	6.95334	1343.943	219.377	20 to 200	(11)
1,2,3-Trichloropropane	6.98716	1502.3	209.	64 to 204	(11)
2,2,4-Trimethylpentane	6.81189	1257.840	220.735	15 to 135	(11)
Water	7.96681	1668.21	228.0	60 to 150	(11)

$$A_{jk} = A_{ji}A_{ik} \tag{23}$$

$$\left(\frac{B_{12}}{A_{12}}\right)^{0.5} + \left(\frac{B_{23}}{A_{22}}\right)^{0.5} + \left(\frac{B_{34}}{A_{32}}\right)^{0.5} + \ldots + \left(\frac{B_{N1}}{A_{N2}}\right)^{0.5} = 0 \tag{24}$$

Thus, for a ternary system, data on only two binaries are needed for use with the Bonham equations; the parameters for the third binary can be calculated by the relations above. This is useful if experimental data for one of the binaries are not available. However, if data for all the binaries are available, the parameters obtained by a least-squares fit often do not satisfy Equations 23 and 24.

Wilson equation. Recently, Wilson (*68*) proposed an expression for the molar-excess free-energy which differs from the usual Wohl expansion. Instead of the polynomial expansion given by Equation 2, Wilson proposed the following logarithmic function

$$\frac{g^E}{RT} = -\sum_{i=1}^{N} x_i \ln\left[\sum_{j=1}^{N} \wedge_{ij} x_j\right] \tag{25}$$

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TABLE II. MOLAR VOLUME DATA

Component	T_1, °K	v_1^L, cc/g mol	T_2, °K	v_2^L, cc/g mol	T_3, °K	v_3^L, cc/g mol	Data reference[a]
Acetone	228.15	67.380	273.15	71.483	323.15	76.826	(49)
Acetonitrile	273.15	51.092	303.15	53.214	355.15	57.4	(49)
Benzene	273.15	86.783	323.15	92.263	373.15	98.537	(49)
1-Butanol	273.15	89.873	343.15	97.8	413.15	108.7	(49, C)
Butyl cellosolve	293.15	130.86	373.15	143.1	453.15	161.1	(26, C)
Carbon tetrachloride	293.15	96.518	353.15	104.192	413.15	114.379	(49)
Cellosolve	293.15	96.80	353.15	104.1	413.15	114.0	(26, C)
Chloroform	273.15	78.218	303.15	81.185	333.15	84.5	(49, C)
Cyclohexane	288.15	107.470	306.30	109.841	352.35	116.630	(49)
Cyclopentane	273.15	91.9	333.15	99.4	373.15	105.2	(18)
2,3-Dimethylbutane	273.15	126.80	303.15	132.06	333.15	138.03	(53)
1,4-Dioxane	293.15	85.24	333.15	89.3	373.15	93.9	(61, C)
Ethanol	273.15	57.141	323.15	60.356	373.15	64.371	(49)
Ethyl acetate	273.15	95.3	323.15	102.1	373.15	110.5	(13)
Ethylbenzene	273.15	120.02	343.15	129.09	413.15	140.29	(53)
Ethylcyclohexane	293.15	142.48	353.15	152.1	413.15	163.9	(62, C)
n-Heptane	273.15	143.045	323.15	152.303	373.15	163.619	(49)
n-Hexane	273.15	127.301	323.15	136.388	373.15	148.211	(49)
Hexene-1	273.15	121.62	303.15	126.80	333.15	132.45	(53)
Hexylene glycol	273.15	122.20	373.15	135.0	473.15	154.1	(26, C)
Methanol	273.15	39.556	373.15	44.874	473.15	57.939	(49)
Methyl acetate	273.15	77.221	373.15	90.111	473.15	121.443	(49)
Methylcyclohexane	303.15	129.116	333.85	133.833	372.65	140.609	(49)
Methylcyclopentane	273.15	109.670	303.15	113.810	373.15	126.2	(49, C)
Methyl-ethyl-ketone	273.15	87.3	333.15	94.5	373.15	100.0	(18)
n-Octane	273.15	158.970	333.15	170.630	393.15	185.182	(49)
n-Pentane	273.15	111.8	333.15	122.9	373.15	131.4	(18)
1-Propanol	293.15	74.785	343.15	78.962	393.15	84.515	(49)
2-Propanol	298.15	77.0	333.15	80.5	373.15	86.1	(18, C)
Toluene	303.15	107.415	353.15	113.717	400.00	120.879	(49)
1,2,3-Trichloropropane	293.15	106.22	353.15	112.6	433.15	124.1	(62, C)
2,2,4-Trimethylpentane	273.15	161.26	323.15	171.24	373.15	183.66	(53)
Water	277.13	18.060	323.15	18.278	373.15	18.844	(49)

[a] "C" indicates that one or two of the molar volumes were calculated from a molar volume at another temperature by an appropriate method in reference (*51*).

where

$$\wedge_{ij} \equiv \frac{v_j^L}{v_i^L} \exp\left[-\frac{(\lambda_{ij} - \lambda_{ii})}{RT}\right] \tag{26}$$

When we apply Equation 4 to the expression above, the Wilson equation for a multicomponent system becomes

$$\ln \gamma_i = 1 - \ln\left[\sum_{j=1}^{N} x_j \wedge_{ij} - \sum_{k=1}^{N} \frac{x_k \wedge_{ki}}{\sum_{j=1}^{N} x_j \wedge_{kj}}\right] \tag{27}$$

For a binary system, the equations reduce to

$$\ln \gamma_1 = -\ln(x_1 + \wedge_{12} x_2) + x_2\left[\frac{\wedge_{12}}{x_1 + \wedge_{12} x_2} - \frac{\wedge_{21}}{\wedge_{21} x_1 + x_2}\right] \tag{28}$$

$$\ln \gamma_2 = -\ln(x_2 + \wedge_{21} x_1) - x_1\left[\frac{\wedge_{12}}{x_1 + \wedge_{12} x_2} - \frac{\wedge_{21}}{\wedge_{21} x_1 + x_2}\right] \tag{29}$$

An advantage of the Wilson equation is that it involves only two parameters per binary, $(\lambda_{ij} - \lambda_{ii})$ and

(*Continued on page 28*)

TABLE III. WILSON PARAMETERS

Components 1	2	$\lambda_{12}-\lambda_{11}$, cal/g mol	$\lambda_{12}-\lambda_{22}$, cal/g mol	Press., mm Hg	Temp., °C	Data ref.
Acetone	Benzene	494.92	−167.91	760	..	(14)
	Carbon tetrachloride	651.76	−12.67	760	..	(2)
	Chloroform	−72.20	−332.23	760	..	(21)
	2,3-Dimethylbutane	948.29	234.96	760	..	(67)
	Ethanol	38.17	418.96	760	..	(1)
	Methanol	−214.95	664.08	760	..	(1)
		−203.03	666.99	...	55	(15)
	n-Pentane	996.75	262.74	760	..	(27)
	2-Propanol	127.43	284.99	760	..	(15)
		429.17	53.40	...	55	(15)
	Water	439.64	1405.49	760	..	(45)
Acetonitrile	Water	694.08	1610.07	760	..	(46)
Benzene	Acetone	−167.91	494.93	760	..	(14)
	1-Butanol	160.12	817.67	760	..	(29)
	Carbon tetrachloride	−103.41	204.82	760	..	(12)
	Chloroform	141.62	−204.22	760	..	(37)
	Cyclohexane	187.23	80.02	760	..	(39)
	Cyclopentane	266.56	−24.18	760	..	(34)
	Ethanol	131.47	1297.90	760	..	(25)
	n-Heptane	99.35	292.94	760	..	(55)
		73.63	364.63	...	75	(16)
	n-Hexane	173.93	169.92	760	..	(48)
	Methanol	153.86	1620.36	760	..	(41)
	Methyl acetate	229.25	−23.84	760	..	(19)
	Methylcyclohexane	−4.15	360.92	760	..	(34)
	Methylcyclopentane	161.44	97.33	760	..	(34)
	1-Propanol	−73.91	1370.32	760	..	(48)
		67.14	1222.07	...	75	(16)
	2-Propanol	160.53	1007.94	760	..	(36)
		272.35	1066.93	500	..	(40)
1-Butanol	Benzene	817.67	160.12	760	..	(29)
	Toluene	887.80	104.68	760	..	(28)
Butyl cellosolve	Ethylcyclohexane	643.51	636.11	400	..	(47)
	n-Octane	1070.54	298.62	400	..	(47)
Carbon tetrachloride	Acetone	−12.67	651.76	760	..	(2)
	Benzene	204.82	−103.41	760	..	(12)
	2-Propanol	111.11	1232.94	760	..	(40)
Cellosolve	Ethylbenzene	755.77	121.89	760	..	(32)
	n-Hexane	834.86	656.23	760	..	(59)
	Hexene-1	370.05	705.47	760	..	(59)
	n-Octane	989.04	622.77	760	..	(32)
Chloroform	Acetone	−332.23	−72.20	760	..	(21)
	Benzene	−204.22	141.62	760	..	(37)
	2,3-Dimethylbutane	213.88	223.69	760	..	(31)
	Ethyl acetate	−367.50	−92.50	760	..	(38)
	Methanol	−373.30	1703.68	760	..	(38)
	Methyl acetate	−451.09	113.24	760	..	(37)
	Methyl-ethyl-ketone	−231.61	−235.12	760	..	(24)
Cyclohexane	Benzene	80.02	187.23	760	..	(39)
	Ethanol	303.42	2151.01	760	..	(72)
	Methyl acetate	345.11	691.65	760	..	(39)
	2-Propanol	69.02	1734.12	760	..	(72)
		223.13	1590.51	500	..	(40)
	Toluene	−414.68	909.36	760	..	(34)
Cyclopentane	Benzene	−24.18	266.56	760	..	(34)
2,3-Dimethylbutane	Acetone	234.96	948.29	760	..	(67)
	Chloroform	223.69	213.88	760	..	(31)
	Methanol	449.08	2771.85	760	..	(23)
1,4-Dioxane	*n*-Hexane	806.80	164.58	760	..	(59)
	Hexene-1	495.19	176.39	760	..	(59)
Ethanol	Acetone	418.96	38.17	760	..	(1)
	Benzene	1297.90	131.47	760	..	(25)
	Cyclohexane	2151.01	303.42	760	..	(72)
	Ethyl acetate	844.69	−178.81	760	..	(33)
		822.03	−62.43	...	40	(33)
		744.81	−52.14	...	60	(33)
	n-Heptane	2096.50	617.57	760	..	(22)
	n-Hexane	2281.99	283.63	760	..	(56)
	Methanol	−511.39	598.44	760	..	(10)
	Methylcyclopentane	2221.47	161.53	760	..	(56)
	Toluene	1238.70	251.93	756	..	(25)
	Water	382.30	955.45	760	..	(8)
Ethyl acetate	Chloroform	−92.50	−367.50	760	..	(38)
	Ethanol	−178.81	844.69	760	..	(33)
		−62.43	822.03	...	40	(33)
		−52.14	744.81	...	60	(33)
	Methanol	−200.36	985.69	760	60	(38)
		−316.92	1203.57	...	40	(33)
		20.32	866.15	...	50	(33)
		−173.45	1030.15	...	60	(33)
	1-Propanol	−198.72	661.24	760	..	(33)
		42.39	558.40	...	40	(33)
		−25.10	519.67	...	60	(33)
	2-Propanol	60.99	289.68	760	..	(33)
		39.77	664.42	...	40	(33)
		45.72	488.11	...	60	(33)
Ethylbenzene	Cellosolve	121.89	755.77	760	..	(32)
	Ethylcyclohexane	396.01	−240.92	400	..	(50)
	Hexylene glycol	52.43	1601.04	400	..	(50)
	n-Octane	304.31	−134.87	760	..	(71)
Ethylcyclohexane	Butyl cellosolve	636.11	643.51	400	..	(47)
Ethylcyclohexane (*Contd.*)	Ethylbenzene	−240.92	396.01	400	..	(50)
	Hexylene glycol	76.95	3592.40	400	..	(50)
n-Heptane	Benzene	292.94	99.35	760	..	(55)
		364.63	73.63	...	75	(16)
	Ethanol	617.57	2096.50	760	..	(22)
	1-Propanol	316.22	1353.98	...	75	(16)
n-Hexane	Benzene	169.92	173.93	760	..	(48)
	Cellosolve	656.23	834.86	760	..	(59)
	1,4-Dioxane	164.58	806.80	760	..	(59)
	Ethanol	283.63	2281.99	760	..	(56)
	Hexene-1	415.18	−279.86	760	..	(59)
	Methylcyclopentane	272.09	−175.70	760	..	(35)
	1-Propanol	834.85	812.66	760	..	(48)
	1,2,3-Trichloropropane	116.39	1106.54	760	..	(59)
Hexene-1	Cellosolve	705.47	370.05	760	..	(59)
	1,4-Dioxane	176.39	495.19	760	..	(59)
	n-Hexane	−279.86	415.18	760	..	(59)
	1,2,3-Trichloropropane	156.93	570.31	760	..	(59)
Hexylene glycol	Ethylbenzene	1601.04	52.43	400	..	(50)
	Ethylcyclohexane	3592.40	76.95	400	..	(50)
Methanol	Acetone	664.08	−214.95	760	..	(1)
		666.99	−203.03	...	55	(15)
	Benzene	1620.36	153.86	760	..	(41)
	Chloroform	1703.68	−373.30	760	..	(38)
	2,3-Dimethylbutane	2771.85	449.08	760	..	(23)
	Ethanol	598.44	−511.39	760	..	(10)
	Ethyl acetate	985.69	−200.36	760	..	(38)
		1203.57	−316.92	...	40	(33)
		866.15	20.32	...	50	(33)
		1030.15	−173.45	...	60	(33)
	Methyl acetate	834.06	−78.81	760	..	(7)
	2-Propanol	88.02	−30.19	760	..	(3)
	Water	205.30	482.16	760	..	(44)
Methyl acetate	Benzene	−23.84	229.25	760	..	(19)
	Chloroform	113.24	−451.09	760	..	(37)
	Cyclohexane	691.65	345.11	760	..	(39)
	Methanol	−78.81	834.06	760	..	(7)
Methylcyclohexane	Benzene	360.92	−4.15	760	..	(34)
	2-Propanol	209.75	1831.76	500	..	(40)
Methylcyclopentane	Benzene	97.33	161.44	760	..	(34)
	Ethanol	161.53	2221.47	760	..	(56)
	n-Hexane	−175.70	272.09	760	..	(35)
	Toluene	−451.92	957.61	760	..	(34)
Methyl-ethyl-ketone	Chloroform	−235.12	−231.61	760	..	(24)
n-Octane	Butyl cellosolve	298.62	1070.54	400	..	(47)
	Cellosolve	622.77	989.04	760	..	(32)
	Ethylbenzene	−134.87	304.31	760	..	(71)
	2-Propanol	422.41	1391.09	400	..	(47)
n-Pentane	Acetone	262.74	996.75	760	..	(27)
1-Propanol	Benzene	1370.32	−73.91	760	..	(48)
		1222.07	67.14	...	75	(16)
	Ethyl acetate	661.24	−198.72	760	..	(33)
		558.40	42.39	...	40	(33)
		519.67	−25.10	...	60	(33)
	n-Heptane	1353.98	316.22	...	75	(16)
	n-Hexane	812.66	834.85	760	..	(48)
	Water	1015.80	1284.61	760	..	(33)
		1942.36	1144.00	...	40	(33)
		1051.44	1188.52	...	60	(33)
2-Propanol	Acetone	284.99	127.43	760	..	(15)
		53.40	429.17	...	55	(15)
	Benzene	1007.94	160.53	760	..	(36)
		1066.93	272.35	500	..	(40)
	Carbon tetrachloride	1232.94	111.11	760	..	(40)
	Cyclohexane	1734.12	69.02	760	..	(72)
		1590.51	223.13	500	..	(40)
	Ethyl acetate	289.68	60.99	760	..	(33)
		664.42	39.77	...	40	(33)
		418.11	45.72	...	60	(33)
	Methanol	−30.19	88.02	760	..	(3)
	Methylcyclohexane	1831.76	209.75	500	..	(40)
	n-Octane	1391.09	422.41	400	..	(47)
	2,2,4-Trimethylpentane	1231.69	183.12	760	..	(6)
Toluene	1-Butanol	104.68	887.80	760	..	(28)
	Cyclohexane	909.36	−414.68	760	..	(34)
	Ethanol	251.93	1238.70	756	..	(25)
	Methylcyclopentane	957.61	−452.92	760	..	(34)
1,2,3-Trichloropropane	*n*-Hexane	1106.54	116.93	760	..	(59)
	Hexene-1	570.31	156.39	760	..	(59)
2,2,4-Trimethylpentane water	2-Propanol	183.12	1231.69	760	..	(6)
	Acetone	1405.49	439.64	760	..	(45)
	Acetonitrile	1610.07	694.08	760	..	(46)
	Ethanol	955.45	382.30	760	..	(8)
	Methanol	482.61	205.30	760	..	(44)
	1-Propanol	1284.61	1015.80	760	..	(33)
		1144.00	1942.36	...	40	(33)
		1188.52	1051.44	...	60	(33)

TABLE IV. MARGULES PARAMETERS

Components 1	Components 2	A_{12}	A_{21}	Press., mm Hg	Temp., °C	Data ref.
Acetone	Benzene	0.2012	0.1533	760	..	(14)
	Carbon tetrachloride	0.3874	0.3282	760	..	(2)
	Chloroform	−0.3051	−0.2676	760	..	(21)
	2,3-Dimethylbutane	0.6345	0.6358	760	..	(67)
	Ethanol	0.2569	0.2870	760	..	(1)
	Methanol	0.2634	0.2798	760	..	(1)
		0.2762	0.2877	...	55	(15)
	n-Pentane	0.7386	0.6329	760	..	(27)
	2-Propanol	0.2152	0.2688	760	..	(15)
		0.3154	0.2428	...	55	(15)
	Water	0.9709	0.5576	760	..	(45)
Acetonitrile	Water	1.0489	0.8231	760	..	(46)
Benzene	Acetone	0.1533	0.2012	760	..	(14)
	1-Butanol	0.3449	0.5651	760	..	(29)
	Carbon tetrachloride	0.0359	0.0488	760	..	(12)
	Chloroform	−0.0824	−0.0532	760	..	(37)
	Cyclohexane	0.1462	0.1640	760	..	(39)
	Cyclopentane	0.1634	0.1290	760	..	(34)
	Ethanol	0.5718	0.7883	760	..	(25)
	n-Heptane	0.0842	0.1899	760	..	(55)
		0.0953	0.2088	...	75	(16)
	n-Hexane	0.1430	0.2010	760	..	(48)
	Methanol	0.7494	0.8923	760	..	(41)
	Methyl acetate	0.1219	0.0939	760	..	(19)
	Methylcyclohexane	0.0760	0.1760	760	..	(34)
	Methylcyclopentane	0.1342	0.1606	760	..	(34)
	1-Propanol	0.3251	0.7332	760	..	(48)
		0.4303	0.7286	...	75	(16)
	2-Propanol	0.4523	0.6551	760	..	(39)
		0.5392	0.7527	500	..	(40)
1-Butanol	Benzene	0.5651	0.3449	760	..	(29)
	Toluene	0.5340	0.3699	760	..	(28)
Butyl cellosolve	Ethylcyclohexane	0.5814	0.5784	400	..	(47)
	n-Octane	0.6903	0.5227	400	..	(47)
Carbon tetrachloride	Acetone	0.3282	0.3874	760	..	(2)
	Benzene	0.0488	0.0359	760	..	(12)
	2-Propanol	0.4763	0.7656	760	..	(40)
Cellosolve	Ethylbenzene	0.4379	0.3750	760	..	(32)
	n-Hexane	0.6633	0.7183	760	..	(59)
	Hexene-1	0.4228	0.5818	760	..	(59)
	n-Octane	0.6117	0.7467	760	..	(32)
Chloroform	Acetone	−0.2676	−0.3051	760	..	(21)
	Benzene	−0.0532	−0.0824	760	..	(37)
	2,3-Dimethylbutane	0.1637	0.2677	760	..	(31)
	Ethyl acetate	−0.2726	−0.4275	760	..	(38)
	Methanol	0.3702	0.7767	760	..	(38)
	Methyl acetate	−0.2112	−0.3270	760	..	(37)
	Methyl-ethyl-ketone	−0.2938	−0.3507	760	..	(24)
Cyclohexane	Benzene	0.1640	0.1462	760	..	(39)
	Ethanol	0.7743	1.0699	760	..	(72)
	Methyl acetate	0.5789	0.5313	760	..	(39)
	2-Propanol	0.5006	0.9539	760	..	(72)
		0.5883	0.9795	500	..	(40)
	Toluene	0.0689	0.1563	760	..	(34)
Cyclopentane	Benzene	0.1290	0.1634	760	..	(34)
2,3-Dimethylbutane	Acetone	0.6358	0.6345	760	..	(67)
	Chloroform	0.2677	0.1637	760	..	(31)
	Methanol	1.1265	1.5255	760	..	(23)
1,4-Dioxane	*n*-Hexane	0.5230	0.4857	760	..	(59)
	Hexene-1	0.3577	0.3755	760	..	(59)
Ethanol	Acetone	0.2870	0.2569	760	..	(1)
	Benzene	0.7883	0.5718	760	..	(25)
	Cyclohexane	1.0699	0.7743	760	..	(72)
	Ethyl acetate	0.3925	0.3313	760	..	(33)
		0.4816	0.4130	...	40	(33)
		0.4080	0.3849	...	60	(33)
	n-Heptane	1.0806	1.0226	760	..	(22)
	n-Hexane	1.1738	0.8337	760	..	(56)
	Methanol	0.0081	0.0189	760	..	(10)
	Methylcyclopentane	1.1965	0.7065	760	..	(56)
	Toluene	0.7066	0.6933	756	..	(25)
	Water	0.6848	0.3781	760	..	(8)
Ethyl acetate	Chloroform	−0.4275	−0.2726	760	..	(38)
	Ethanol	0.3313	0.3925	760	..	(33)
		0.4130	0.4816	...	40	(33)
		0.3849	0.4080	...	60	(33)
	Methanol	0.4463	0.4229	760	..	(38)
		0.4213	0.5626	...	40	(33)
		0.5324	0.4482	...	50	(33)
		0.4737	0.4767	...	60	(33)
	1-Propanol	0.1982	0.2849	760	..	(33)
		0.3412	0.3923	...	40	(33)
		0.2749	0.3094	...	60	(33)
	2-Propanol	0.2112	0.1961	760	..	(33)
		0.3717	0.4573	...	40	(33)
		0.3037	0.3256	...	60	(33)
Ethylbenzene	Cellosolve	0.3750	0.4379	760	..	(32)
	Ethylcyclohexane	0.0800	0.0626	400	..	(50)
	Hexylene glycol	0.3105	0.7358	400	..	(50)
	n-Octane	0.0889	0.0903	760	..	(71)
Ethylcyclohexane	Butyl cellosolve	0.5784	0.5814	400	..	(47)
	Ethylbenzene	0.0626	0.0800	400	..	(50)
Ethylcyclohexane (*Contd.*)	Hexylene glycol	0.4293	0.9448	400	..	(50)
n-Heptane	Benzene	0.1899	0.0842	760	..	(55)
		0.2088	0.0953	...	75	(16)
	Ethanol	1.0226	1.0806	760	..	(22)
	1-Propanol	0.7719	0.7548	...	75	(16)
n-Hexane	Benzene	0.2010	0.1430	760	..	(48)
	Cellosolve	0.7183	0.6633	760	..	(59)
	1,4-Dioxane	0.4857	0.5238	760	..	(59)
	Ethanol	0.8337	1.1738	760	..	(56)
	Hexene-1	0.0283	0.0078	760	..	(59)
	Methylcyclopentane	0.0188	0.0014	760	..	(35)
	1-Propanol	0.8511	0.5763	760	..	(48)
	1,2,3-Trichloropropane	0.4298	0.6916	760	..	(59)
Hexene-1	Cellosolve	0.5818	0.4228	760	..	(59)
	1,4-Dioxane	0.3755	0.3577	760	..	(59)
	n-Hexane	0.0078	0.0283	760	..	(59)
	1,2,3-Trichloropropane	0.3382	0.4307	760	..	(59)
Hexylene glycol	Ethylbenzene	0.7358	0.3105	400	..	(50)
	Ethylcyclohexane	0.9448	0.4293	400	..	(50)
Methanol	Acetone	0.2798	0.2634	760	..	(1)
		0.2877	0.2762	...	55	(15)
	Benzene	0.8923	0.7494	760	..	(41)
	Chloroform	0.7767	0.3702	760	..	(38)
	2,3-Dimethylbutane	1.5255	1.1265	760	..	(23)
	Ethanol	0.0189	0.0081	760	..	(10)
	Ethyl acetate	0.4229	0.4463	760	..	(38)
		0.5626	0.4213	...	40	(33)
		0.4482	0.5324	...	50	(33)
		0.4767	0.4737	...	60	(33)
	Methyl acetate	0.4393	0.4261	760	..	(7)
	2-Propanol	−0.0326	−0.0329	760	..	(3)
	Water	0.3794	0.2211	760	..	(44)
Methyl acetate	Benzene	0.0939	0.1219	760	..	(19)
	Chloroform	−0.3270	−0.2112	760	..	(37)
	Cyclohexane	0.5313	0.5789	760	..	(39)
	Methanol	0.4261	0.4393	760	..	(7)
Methylcyclohexane	Benzene	0.1760	0.0760	760	..	(34)
	2-Propanol	0.6785	1.0343	500	..	(40)
Methylcyclopentane	Benzene	0.1606	0.1342	760	..	(34)
	Ethanol	0.7065	1.1965	760	..	(56)
	n-Hexane	0.0014	0.0188	760	..	(35)
	Toluene	0.0694	0.1627	760	..	(34)
Methyl-ethyl-ketone	Chloroform	−0.3507	−0.2938	760	..	(24)
n-Octane	Butyl cellosolve	0.5227	0.6903	400	..	(47)
	Cellosolve	0.7467	0.6117	760	..	(32)
	Ethylbenzene	0.0903	0.0889	760	..	(71)
	2-Propanol	0.8524	0.8044	400	..	(47)
n-Pentane	Acetone	0.6329	0.7386	760	..	(27)
1-Propanol	Benzene	0.7332	0.3251	760	..	(48)
		0.7286	0.4303	...	75	(16)
	Ethyl acetate	0.2849	0.1982	760	..	(33)
		0.3923	0.3412	...	40	(33)
		0.3094	0.2749	...	60	(33)
	n-Heptane	0.7548	0.7719	...	75	(16)
	n-Hexane	0.5763	0.8511	760	..	(48)
	Water	1.0536	0.4393	760	..	(33)
		1.0748	0.4507	...	40	(33)
		1.0825	0.4653	...	60	(33)
2-Propanol	Acetone	0.2688	0.2152	760	..	(15)
		0.2428	0.3154	...	55	(15)
	Benzene	0.6551	0.4523	760	..	(36)
		0.7527	0.5392	500	..	(40)
	Carbon tetrachloride	0.7656	0.4763	760	..	(40)
	Cyclohexane	0.9539	0.5006	760	..	(72)
		0.9795	0.5883	500	..	(40)
	Ethyl acetate	0.1961	0.2112	760	..	(33)
		0.4573	0.3717	...	40	(33)
		0.3256	0.3037	...	60	(33)
	Methanol	−0.0329	−0.0326	760	..	(3)
	Methylcyclohexane	1.0343	0.6785	500	..	(40)
	n-Octane	0.8044	0.8524	400	..	(47)
	2,2,4-Trimethylpentane	0.6601	0.6924	760	..	(6)
Toluene	1-Butanol	0.3699	0.5340	760	..	(28)
	Cyclohexane	0.1563	0.0689	760	..	(34)
	Ethanol	0.6933	0.7066	756	..	(25)
	Methylcyclopentane	0.1627	0.0694	760	..	(34)
1,2,3-Trichloropropane	*n*-Hexane	0.6916	0.4298	760	..	(59)
	Hexene-1	0.4307	0.3382	760	..	(59)
2,2,4-Trimethylpentane	2-Propanol	0.6924	0.6601	760	..	(6)
Water	Acetone	0.5576	0.9709	760	..	(45)
	Acetonitrile	0.8231	1.0489	760	..	(46)
	Ethanol	0.3781	0.6848	760	..	(8)
	Methanol	0.2211	0.3794	760	..	(44)
	1-Propanol	0.4393	1.0536	760	..	(33)
		0.4507	1.0748	...	40	(33)
		0.4653	1.0825	...	60	(33)

TABLE V. VAN LAAR PARAMETERS

Components 1	Components 2	$\bar{A}_{12}$	$\bar{A}_{21}$	Press., mm Hg	Temp., °C	Data ref.
Acetone	Benzene	0.2039	0.1563	760	..	(14)
	Carbon tetrachloride	0.3889	0.3301	760	..	(2)
	Chloroform	−0.3045	−0.2709	760	..	(21)
	2,3-Dimethylbutane	0.6345	0.6358	760	..	(67)
	Ethanol	0.2574	0.2879	760	..	(1)
	Methanol	0.2635	0.2801	760	..	(1)
		0.2763	0.2878	...	55	(15)
	n-Pentane	0.7403	0.6364	760	..	(27)
	2-Propanol	0.2186	0.2690	760	..	(15)
		0.3158	0.2495	...	55	(15)
	Water	0.9972	0.6105	760	..	(45)
Acetonitrile	Water	1.0680	0.8207	760	..	(46)
Benzene	Acetone	0.1563	0.2039	760	..	(14)
	1-Butanol	0.3594	0.5865	760	..	(29)
	Carbon tetrachloride	0.0360	0.0509	760	..	(12)
	Chloroform	−0.0858	−0.0556	760	..	(37)
	Cyclohexane	0.1466	0.1646	760	..	(39)
	Cyclopentane	0.1655	0.1302	760	..	(34)
	Ethanol	0.5804	0.7969	760	..	(25)
	n-Heptane	0.0985	0.2135	760	..	(55)
		0.1072	0.2361	...	75	(16)
	n-Hexane	0.1457	0.2063	760	..	(48)
	Methanol	0.7518	0.8975	760	..	(41)
	Methyl acetate	0.1292	0.0919	760	..	(19)
	Methylcyclohexane	0.0910	0.1901	760	..	(34)
	Methylcyclopentane	0.1360	0.1605	760	..	(34)
	1-Propanol	0.3772	0.7703	760	..	(48)
		0.4508	0.7564	...	75	(16)
	2-Propanol	0.4638	0.6723	760	..	(36)
		0.5455	0.7716	500	..	(40)
1-Butanol	Benzene	0.5865	0.3594	760	..	(24)
	Toluene	0.5430	0.3841	760	..	(28)
Butyl cellosolve	Ethylcyclohexane	0.5814	0.5784	400	..	(47)
	n-Octane	0.6967	0.5318	400	..	(47)
Carbon tetrachloride	Acetone	0.3301	0.3889	760	..	(2)
	Benzene	0.0509	0.0360	760	..	(12)
	2-Propanol	0.4918	0.7868	760	..	(40)
Cellosolve	Ethylbenzene	0.4402	0.3762	760	..	(32)
	n-Hexane	0.6629	0.7206	760	..	(59)
	Hexene-1	0.4367	0.5860	760	..	(59)
	n-Octane	0.6158	0.7507	760	..	(32)
Chloroform	Acetone	−0.2709	−0.3045	760	..	(21)
	Benzene	−0.0556	−0.0858	760	..	(37)
	2,3-Dimethylbutane	0.1736	0.2790	760	..	(31)
	Ethyl acetate	−0.2868	−0.4478	760	..	(38)
	Methanol	0.4104	0.8263	760	..	(38)
	Methyl acetate	−0.2249	−0.3343	760	..	(37)
	Methyl-ethyl-ketone	−0.2990	−0.3486	760	..	(24)
Cyclohexane	Benzene	0.1646	0.1466	760	..	(39)
	Ethanol	0.7811	1.1031	760	..	(72)
	Methyl acetate	0.5799	0.5317	760	..	(39)
	2-Propanol	0.5322	1.0162	760	..	(72)
		0.6156	1.0158	500	..	(40)
	Toluene	0.0702	0.2578	760	..	(34)
Cyclopentane	Benzene	0.1302	0.1655	760	..	(34)
2,3-Dimethylbutane	Acetone	0.6358	0.6345	760	..	(67)
	Chloroform	0.2790	0.1736	760	..	(31)
	Methanol	1.1276	1.5408	760	..	(23)
1,4-Dioxane	*n*-Hexane	0.5260	0.4850	760	..	(59)
	Hexene-1	0.3578	0.3757	760	..	(59)
Ethanol	Acetone	0.2879	0.2574	760	..	(1)
	Benzene	0.7969	0.5804	760	..	(25)
	Cyclohexane	1.1031	0.7811	760	..	(72)
	Ethyl acetate	0.3972	0.3311	760	..	(33)
		0.4833	0.4151	...	40	(33)
		0.4093	0.3842	...	60	(33)
	n-Heptane	1.0832	1.0208	760	..	(22)
	n-Hexane	1.2005	0.8422	760	..	(56)
	Methanol	0.0088	0.0254	760	..	(10)
	Methylcyclopentane	1.2330	0.7332	760	..	(56)
	Toluene	0.7067	0.6932	756	..	(25)
	Water	0.7292	0.4104	760	..	(8)
Ethyl acetate	Chloroform	−0.4478	−0.2868	760	..	(38)
	Ethanol	0.3311	0.3972	760	..	(33)
		0.4151	0.4833	...	40	(33)
		0.3842	0.4093	...	60	(33)
	Methanol	0.4470	0.4227	760	..	(38)
		0.4278	0.5741	...	40	(33)
		0.5399	0.4476	...	50	(33)
		0.4736	0.4768	...	60	(33)
	1-Propanol	0.2051	0.2893	760	..	(33)
		0.3444	0.3913	...	40	(33)
		0.2762	0.3092	...	60	(33)
	2-Propanol	0.2113	0.1964	760	..	(33)
		0.3747	0.4604	...	40	(33)
		0.3039	0.3261	...	60	(33)
Ethylbenzene	Cellosolve	0.3762	0.4402	760	..	(32)
	Ethylcyclohexane	0.0821	0.0628	400	..	(50)
	Hexylene glycol	0.3719	0.8383	400	..	(50)
	n-Octane	0.0890	0.0902	760	..	(71)
Ethylcyclohexane	Butyl cellosolve	0.5784	0.5814	400	..	(47)
	Ethylbenzene	0.0628	0.0821	400	..	(50)
	Hexylene glycol	0.4770	1.1219	400	..	(50)
n-Heptane	Benzene	0.2135	0.0985	760	..	(55)
		0.2361	0.1072	...	75	(16)
	Ethanol	1.0208	1.0832	760	..	(22)
	1-Propanol	0.7719	0.7550	...	75	(16)
n-Hexane	Benzene	0.2063	0.1457	760	..	(48)
	Cellosolve	0.7206	0.6629	760	..	(59)
	1,4-Dioxane	0.4850	0.5260	760	..	(59)
	Ethanol	0.8422	1.2005	760	..	(56)
	Hexene-1	0.0393	0.0114	760	..	(59)
	Methylcyclopentane	0.0023	0.0226	760	..	(35)
	1-Propanol	0.8734	0.5952	760	..	(48)
	1,2,3-Trichloropropane	0.4520	0.7257	760	..	(59)
Hexene-1	Cellosolve	0.5860	0.4367	760	..	(59)
	1,4-Dioxane	0.3757	0.3578	760	..	(59)
	n-Hexane	0.0114	0.0393	760	..	(59)
	1,2,3-Trichloropropane	0.3419	0.4372	760	..	(59)
Hexylene glycol	Ethylbenzene	0.8383	0.3719	400	..	(50)
	Ethylcyclohexane	1.1219	0.4770	400	..	(50)
Methanol	Acetone	0.2801	0.2635	760	..	(1)
		0.2878	0.2763	...	55	(15)
	Benzene	0.8975	0.7518	760	..	(41)
	Chloroform	0.8263	0.4104	760	..	(38)
	2,3-Dimethylbutane	1.5408	1.1276	760	..	(23)
	Ethanol	0.0254	0.0088	760	..	(10)
	Ethyl acetate	0.4227	0.4470	760	..	(38)
		0.5741	0.4278	...	40	(33)
		0.4476	0.5399	...	50	(33)
		0.4768	0.4736	...	60	(33)
	Methyl acetate	0.4394	0.4262	760	..	(7)
	2-Propanol	−0.0325	−0.0329	760	..	(3)
	Water	0.3861	0.2439	760	..	(44)
Methyl acetate	Benzene	0.0919	0.1292	760	..	(19)
	Chloroform	−0.3343	−0.2249	760	..	(37)
	Cyclohexane	0.5317	0.5799	760	..	(39)
	Methanol	0.4262	0.4394	760	..	(7)
Methylcyclohexane	Benzene	0.1901	0.0910	760	..	(34)
	2-Propanol	0.6886	1.0659	500	..	(40)
Methylcyclopentane	Benzene	0.1605	0.1360	760	..	(34)
	Ethanol	0.7332	1.2330	760	..	(56)
	n-Hexane	0.0226	0.0023	760	..	(35)
	Toluene	0.0717	0.2475	760	..	(34)
Methyl-ethyl-ketone	Chloroform	−0.3486	−0.2990	760	..	(24)
n-Octane	Butyl cellosolve	0.5318	0.6967	400	..	(47)
	Cellosolve	0.7507	0.6158	760	..	(32)
	Ethylbenzene	0.0902	0.0890	760	..	(71)
	2-Propanol	0.8535	0.8043	400	..	(47)
n-Pentane	Acetone	0.6364	0.7403	760	..	(27)
1-Propanol	Benzene	0.7703	0.3772	760	..	(48)
		0.7564	0.4508	...	75	(16)
	Ethyl acetate	0.2893	0.2051	760	..	(33)
		0.3913	0.3444	...	40	(33)
		0.3092	0.2762	...	60	(33)
	n-Heptane	0.7550	0.7719	...	75	(16)
	n-Hexane	0.5952	0.8734	760	..	(48)
	Water	1.1433	0.5037	760	..	(33)
		1.2315	0.5305	...	40	(33)
		1.1879	0.5224	...	60	(33)
2-Propanol	Acetone	0.2690	0.2186	760	..	(15)
		0.2495	0.3158	...	55	(15)
	Benzene	0.6723	0.4638	760	..	(36)
		0.7716	0.5455	500	..	(40)
	Carbon tetrachloride	0.7868	0.4918	760	..	(40)
	Cyclohexane	1.0162	0.5322	760	..	(72)
		1.0158	0.6156	500	..	(40)
	Ethyl acetate	0.1964	0.2113	760	..	(33)
		0.4604	0.3747	...	40	(33)
		0.3261	0.3039	...	60	(33)
	Methanol	−0.0329	−0.0325	760	..	(3)
	Methylcyclohexane	1.0659	0.6886	500	..	(40)
	n-Octane	0.8043	0.8535	400	..	(47)
	2,2,4-Trimethylpentane	0.6603	0.6927	760	..	(6)
Toluene	1-Butanol	0.3841	0.5430	760	..	(28)
	Cyclohexane	0.2578	0.0702	760	..	(34)
	Ethanol	0.6932	0.7067	756	..	(25)
	Methylcyclopentane	0.2475	0.0717	760	..	(34)
1,2,3-Trichloropropane	*n*-Hexane	0.7257	0.4520	760	..	(59)
	Hexene-1	0.4372	0.3419	760	..	(59)
2,2,4-Trimethylpentane	2-Propanol	0.6927	0.6603	760	..	(6)
Water	Acetone	0.6105	0.9972	760	..	(45)
	Acetonitrile	0.8207	1.0680	760	..	(46)
	Ethanol	0.4104	0.7292	760	..	(8)
	Methanol	0.2439	0.3861	760	..	(44)
	1-Propanol	0.5037	1.1433	760	..	(33)
		0.5305	1.2315	...	40	(33)
		0.5224	1.1879	...	60	(33)

TABLE VI. BONHAM PARAMETERS

Components 1	Components 1	A_{12}	B_{12}	Press., mm Hg	Temp., °C	Data Ref.
Acetone	Benzene	1.3956	165.00	760	..	(14)
	Carbon tetrachloride	1.2453	309.17	760	..	(2)
	Chloroform	1.1324	−235.66	760	..	(21)
	2,3-Dimethylbutane	1.0136	476.83	760	..	(67)
	Ethanol	0.9567	207.41	760	..	(1)
	Methanol	0.9703	203.96	760	..	(1)
		0.9601	208.77	...	55	(15)
	n-Pentane	1.1152	518.82	760	..	(27)
	2-Propanol	0.8735	176.70	760	..	(15)
		1.2604	238.20	...	55	(15)
	Water	1.7808	809.19	760	..	(45)
Acetonitrile	Water	1.3325	880.60	760	..	(46)
Benzene	Acetone	0.7165	118.23	760	..	(14)
	1-Butanol	0.6749	316.04	760	..	(29)
	Carbon tetrachloride	0.7154	28.76	760	..	(12)
	Chloroform	1.4841	−65.91	760	..	(37)
	Cyclohexane	0.8889	118.61	760	..	(39)
	Cyclopentane	1.1850	122.99	760	..	(34)
	Ethanol	0.7285	463.40	760	..	(25)
	n-Heptane	0.4831	83.24	760	..	(55)
		0.4542	85.97	...	75	(16)
	n-Hexane	0.6919	115.10	760	..	(48)
	Methanol	0.8182	574.98	760	..	(41)
	Methyl acetate	1.3793	99.38	760	..	(19)
	Methylcyclohexane	0.5030	77.46	760	..	(34)
	Methylcyclopentane	0.8308	107.89	760	..	(34)
	1-Propanol	0.5107	315.03	760	..	(48)
		0.5960	361.35	...	75	(16)
	2-Propanol	0.6984	374.64	760	..	(36)
		0.7186	427.16	500	..	(40)
1-Butanol	Benzene	1.4816	468.26	760	..	(29)
	Toluene	1.3975	474.56	760	..	(28)
Butyl cellosolve	Ethylcyclohexane	0.9244	505.49	400	..	(47)
	n-Octane	1.2027	594.72	400	..	(47)
Carbon tetrachloride	Acetone	0.8030	248.26	760	..	(2)
	Benzene	1.3979	40.20	760	..	(12)
	2-Propanol	0.6345	396.69	760	..	(40)
Cellosolve	Ethylbenzene	1.1752	410.97	760	..	(32)
	n-Hexane	0.8347	509.22	760	..	(59)
	Hexene-1	0.6332	328.77	760	..	(59)
	n-Octane	0.8028	556.00	760	..	(32)
Chloroform	Acetone	0.8831	−208.11	760	..	(21)
	Benzene	0.6738	−44.41	760	..	(37)
	2,3-Dimethylbutane	0.6145	131.28	760	..	(31)
	Ethyl acetate	0.6559	−230.60	760	..	(38)
	Methanol	0.5023	314.59	760	..	(38)
	Methyl acetate	0.6665	−172.86	760	..	(37)
	Methyl-ethyl-ketone	0.8859	−242.43	760	..	(24)
Cyclohexane	Benzene	1.1250	133.44	760	..	(39)
	Ethanol	0.7186	616.87	760	..	(72)
	Methyl acetate	1.0249	433.12	760	..	(39)
	2-Propanol	0.5240	424.58	760	..	(72)
		0.6120	477.61	500	..	(40)
	Toluene	0.2964	61.08	760	..	(34)
Cyclopentane	Benzene	0.8439	103.79	760	..	(34)
2,3-Dimethylbutane	Acetone	0.9866	470.43	760	..	(67)
	Chloroform	1.6273	213.64	760	..	(31)
	Methanol	0.7428	847.09	760	..	(23)
1,4-Dioxane	*n*-Hexane	1.0057	407.35	760	..	(59)
	Hexene-1	0.8744	275.80	760	..	(59)
Ethanol	Acetone	1.0453	216.80	760	..	(1)
	Benzene	1.3762	636.07	760	..	(25)
	Cyclohexane	1.3916	858.41	760	..	(72)
	Ethyl acetate	1.1933	317.30	760	..	(33)
		1.1641	348.46	...	40	(33)
		1.0641	313.91	...	60	(33)
	n-Heptane	1.0821	873.68	760	..	(22)
	n-Hexane	1.3937	916.21	760	..	(56)
	Methanol	0.3359	6.90	760	..	(10)
	Methylcyclopentane	1.6462	950.96	760	..	(56)
	Toluene	1.0654	592.14	756	..	(25)
	Water	1.8512	611.20	760	..	(8)
Ethyl acetate	Chloroform	1.5246	−351.57	760	..	(38)
	Ethanol	0.8380	265.90	760	..	(33)
		0.8590	299.34	...	40	(33)
		0.9397	295.00	...	60	(33)
	Methanol	1.0244	343.83	760	..	(38)
		0.7452	308.50	...	40	(33)
		1.2061	401.73	...	50	(33)
		0.9932	363.28	...	60	(33)
	1-Propanol	0.7517	173.49	760	..	(33)
		0.8803	248.36	...	40	(33)
		0.8935	211.89	...	60	(33)
	2-Propanol	1.0853	171.63	760	..	(33)
		0.8139	270.15	...	40	(33)
		0.9319	233.13	...	60	(33)
Ethylbenzene	Cellosolve	0.8509	349.69	760	..	(32)
	Ethylcyclohexane	1.2951	72.15	400	..	(50)
	Hexylene glycol	0.5031	360.97	400	..	(50)
	n-Octane	0.9793	82.01	760	..	(71)
Ethylcyclohexane	Butyl cellosolve	1.0818	546.86	400	..	(47)
	Ethylbenzene	0.7721	55.71	400	..	(50)
	Hexylene glycol	0.4747	448.72	400	..	(50)
n-Heptane	Benzene	2.0702	172.32	760	..	(55)
		2.2015	189.27	...	75	(16)
	Ethanol	0.9241	807.35	760	..	(22)
	1-Propanol	1.0229	618.90	...	75	(16)
n-Hexane	Benzene	1.4453	166.36	760	..	(48)
	Cellosolve	1.1981	610.08	760	..	(59)
	1,4-Dioxane	0.9944	405.05	760	..	(59)
	Ethanol	0.7175	657.40	760	..	(56)
	Hexene-1	6.8583	54.43	760	..	(59)
	Methylcyclopentane	2.2445	12.72	760	..	(35)
	1-Propanol	1.5664	719.18	760	..	(48)
	1,2,3-Trichloropropane	0.7269	401.53	760	..	(59)
Hexane-1	Cellosolve	1.5793	519.23	760	..	(59)
	1,4-Dioxane	1.1436	315.20	760	..	(59)
	n-Hexane	0.1458	7.94	760	..	(59)
	1,2,3-Trichloropropane	0.9258	308.67	760	..	(59)
Hexylene glycol	Ethylbenzene	1.9878	717.54	400	..	(50)
	Ethylcyclohexane	2.1068	945.37	400	..	(50)
Methanol	Acetone	1.0307	210.21	760	..	(1)
		1.0416	217.44	...	55	(15)
	Benzene	1.2222	702.72	760	..	(41)
	Chloroform	1.9909	626.32	760	..	(38)
	2,3-Dimethylbutane	1.3462	1140.38	760	..	(23)
	Ethanol	2.9767	20.53	760	..	(10)
	Ethyl acetate	0.9762	335.65	760	..	(38)
		1.3418	413.96	...	40	(33)
		0.8291	333.09	...	50	(33)
		1.0068	365.76	...	60	(33)
	Methyl acetate	1.0103	330.77	760	..	(7)
	2-Propanol	1.0196	−26.05	760	..	(3)
	Water	1.7376	328.21	760	..	(44)
Methyl acetate	Benzene	0.7250	72.05	760	..	(19)
	Chloroform	1.5004	−259.36	760	..	(37)
	Cyclohexane	0.9759	422.62	760	..	(39)
	Methanol	0.9898	327.41	760	..	(7)
Methylcyclohexane	Benzene	1.9881	154.00	760	..	(34)
	2-Propanol	0.6317	539.24	500	..	(40)
Methylcyclopentane	Benzene	1.2037	129.87	760	..	(34)
	Ethanol	0.6074	577.66	760	..	(56)
	n-Hexane	0.4455	5.67	760	..	(35)
	Toluene	0.3296	62.38	760	..	(34)
Methyl-ethyl-ketone	Chloroform	1.1288	−273.65	760	..	(24)
n-Octane	Butyl cellosolve	0.8314	494.48	400	..	(47)
	Cellosolve	1.2456	692.54	760	..	(32)
	Ethylbenzene	1.0211	83.74	760	..	(71)
	2-Propanol	0.9996	659.05	400	..	(47)
n-Pentane	Acetone	0.8967	465.22	760	..	(27)
1-Propanol	Benzene	1.9583	616.91	760	..	(48)
		1.6779	606.32	...	75	(16)
	Ethyl acetate	1.3303	230.79	760	..	(33)
		1.1359	282.12	...	40	(33)
		1.1192	237.16	...	60	(33)
	n-Heptane	0.9776	605.06	...	75	(16)
	n-Hexane	0.6384	459.11	760	..	(48)
	Water	2.2542	956.85	760	..	(33)
		2.3212	887.98	...	40	(33)
		2.2738	911.26	...	60	(33)
2-Propanol	Acetone	1.1449	202.30	760	..	(15)
		0.7934	188.98	...	55	(15)
	Benzene	1.4317	536.39	760	..	(36)
		1.3917	594.47	500	..	(40)
	Carbon tetrachloride	1.5760	625.18	760	..	(40)
	Cyclohexane	1.9083	810.24	760	..	(72)
		1.6339	780.39	500	..	(40)
	Ethyl acetate	0.9214	158.14	760	..	(33)
		1.2287	331.93	...	40	(33)
		1.0730	250.16	...	60	(33)
	Methanol	0.9808	−25.55	760	..	(3)
	Methylcyclohexane	1.5831	853.67	500	..	(40)
	n-Octane	1.0004	659.33	400	..	(47)
	2,2,4-Trimethylpentane	0.9820	549.24	760	..	(6)
Toluene	1-Butanol	0.7156	339.57	760	..	(28)
	Cyclohexane	3.3744	206.10	760	..	(34)
	Ethanol	0.9386	555.77	756	..	(25)
	Methylcyclopentane	3.0343	189.29	760	..	(34)
1,2,3-Trichloropropane	*n*-Hexane	1.3757	552.37	760	..	(59)
	Hexene-1	1.0802	333.41	760	..	(59)
2,2,4-Trimethylpentane	2-Propanol	1.0183	559.31	760	..	(6)
Water	Acetone	0.5615	454.39	760	..	(45)
	Acetonitrile	0.7505	660.85	760	..	(46)
	Ethanol	0.5402	330.17	760	..	(8)
	Methanol	0.5755	188.89	760	..	(44)
	1-Propanol	0.4436	424.48	760	..	(33)
		0.4308	382.55	...	40	(33)
		0.4398	400.77	...	60	(33)

$(\lambda_{ij} - \lambda_{jj})$, with no restrictions such as those that limit the van Laar and Bonham equations. A second advantage suggested by Orye and Prausnitz (*43*) is that the assumption of temperature independence for the parameters has a least approximate theoretical significance.

Binary Systems

The parameters for 89 binary systems were calculated by the authors for the four models listed below:

Third-order Margules equation
Bonham equation (original van Laar equation)
Van Laar equation (as modified by Carlson and Colburn)
Wilson equation

Each equation requires the determination of two parameters for a binary system. These parameters have been calculated by using a computer program to minimize the following objective function

$$\phi = \omega_1 \sum_{i=1}^{n} (\gamma_{1\text{exp}} - \gamma_{1\text{calc}})_i^2 + \omega_2 \sum_{i=1}^{n} (\gamma_{2\text{exp}} - \gamma_{2\text{calc}})_i^2 \tag{30}$$

The scale factors ω_1 and ω_2, given by

$$\omega_1 \equiv \left[\sum_{i=1}^{n} (\gamma_{1\text{exp}} - 1.0)_i^2 \right]^{-1} \tag{31}$$

$$\omega_2 \equiv \left[\sum_{i=1}^{n} (\gamma_{2\text{exp}} - 1.0)_i^2 \right]^{-1} \tag{32}$$

serve to scale the objective function if the system is highly unsymmetrical. For systems that are fairly symmetrical

$$\omega_1 \equiv \omega_2 \tag{33}$$

and minimization of ϕ is approximately equivalent to minimization of the unscaled objective function.

The activity coefficients were calculated from experimental binary data by Equation 34

$$\gamma_i = \frac{y_i P}{x_i P_i^*} \tag{34}$$

All of the systems used in the study were at or below atmospheric pressure where this simplified expression is usually adequate. The vapor pressures were calculated using the Antoine equation

$$\log_{10} P^* = A - \frac{B}{C + t} \tag{35}$$

The Antoine constants that were used are tabulated in Table I.

To use the Wilson equation it is also necessary to have the liquid molar volume as a function of temperature for each component. The volumetric data used in this study are listed in Table II. Using the molar volumes at three different temperatures, the constants in the quadratic equation

$$v^L = a' + b'T + c'T^2 \tag{36}$$

were calculated for each component. The molar volume at any temperature could then be calculated when required in the computer program by using Equation 36.

A general minimum seeking method was used to determine the set of binary parameters which minimizes Equation 30. The Wilson parameters for 89 binary systems are listed in Table III. The van Laar, Margules, and Bonham parameters were calculated and are presented in Tables IV, V, and VI deposited with the ASIS.

Multicomponent Systems

The capabilities of the four equations to predict multicomponent vapor-liquid equilibria were determined by the authors by comparing the predictions to the data for 19 ternary systems. Each of the equations requires only binary parameters for the three constituent binaries (it was assumed that $C^* = 0$ in the Margules equation). The ternary systems are listed in Table VII.

A computer program was used for each of the four equations to predict the ternary equilibrium data. In the computer programs the liquid composition and total pressure were fixed by the experimental data and the solution models were used to predict the vapor composition and temperature.

Results

For almost all the ternary systems that were investigated the equations can be ranked in the order given below, with the Wilson equation being the most useful:

Wilson equation
Margules equation
Van Laar equation
Bonham equation

Examples of the results in the prediction of vapor compositions are shown for three of the systems in Figures 1, 2, and 3.

For the ternary systems exhibiting behavior close to ideality (for example, the benzene–methylcyclopentane–*n*-hexane system and the acetone–carbon tetrachloride–benzene system) the differences in the calculated results from the different equations are small. However, for highly nonideal systems (*e.g.*, the 2,3-dimethylbutane–methanol–chloroform system and the 2,3-dimethylbutane–acetone–methanol system), the Wilson equation gives much better predictions than any of the other equations.

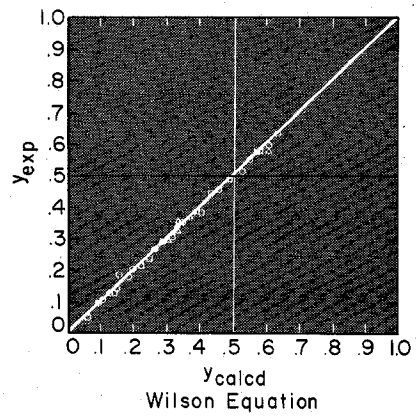
The prediction accuracy of the Wilson equation is shown in Table VIII where

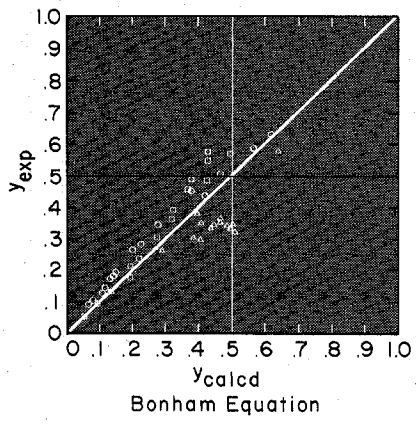
$$\Delta T \equiv |T_{\text{exp}} - T_{\text{calc}}| \tag{37}$$

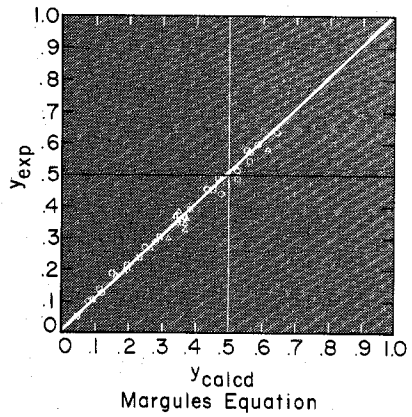
$$\Delta y_i \equiv |y_{i\text{exp}} - y_{i\text{calc}}| \tag{38}$$

For the 262 ternary data points examined, 92% of the predicted vapor mole fractions were within 0.020 mole fraction of the experimental data and 85% of the predicted temperatures were within 1.0°C of the experimental data. For the essentially ideal systems, the predictions were as would be expected, much better.

For a few of the systems, the prediction accuracy is significantly below the average. The poorest predic-







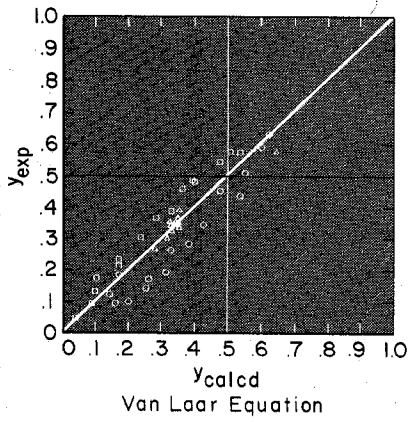
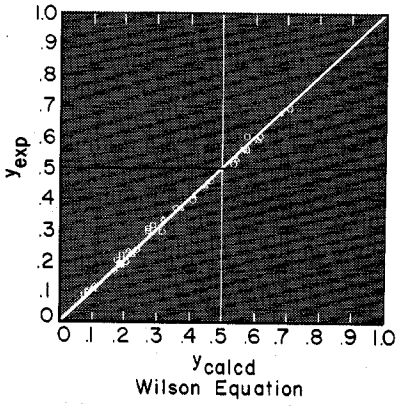
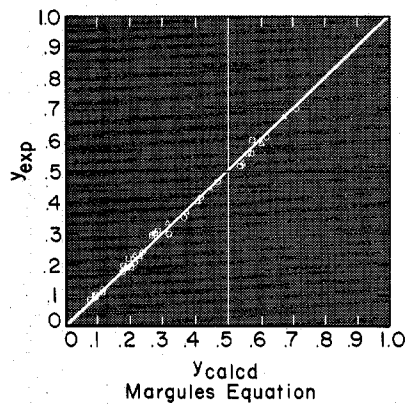
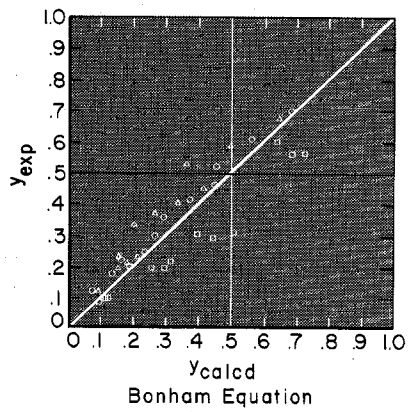


Figure 1. Ethanol–methylcyclopentane–n-hexane system at 760 mm Hg.

△ *Ethanol.* ○ *Methylcyclopentane.* □ *n-Hexane*







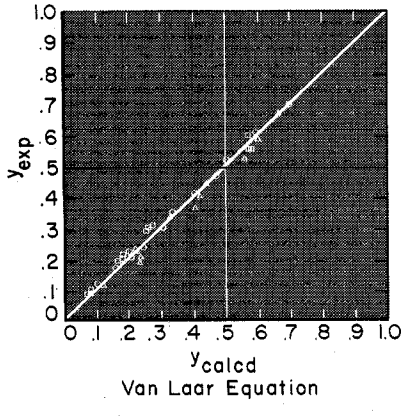


Figure 2. n-Hexane–hexene-1–1,4-dioxane system at 760 mm Hg.

△ *n-Hexane.* ○ *Hexene-1.* □ *1,4-Dioxane*

TABLE VII. TERNARY SYSTEMS

	System	Reference
1	Benzene–Methylcyclopentane–*n*-Hexane	(*4*)
2	Ethanol–Methylcyclopentane–*n*-Hexane	(*20*)
3	Methylcyclopentane–Ethanol–Benzene	(*56*)
4	Benzene–Ethanol–*n*-Hexane	(*65*)
5	Acetone–Carbon tetrachloride–Benzene	(*58*)
6	Acetone–Methanol–2-Propanol	(*15*)
7	*n*-Octane–Ethylbenzene–Cellosolve	(*32*)
8	Chloroform–Methanol–Ethyl acetate	(*38*)
9	Ethanol–Benzene–*n*-Heptane	(*64*)
10	Acetone–Chloroform–2,3-Dimethylbutane	(*17*)
11	*n*-Hexane–Hexene-1–1,4-Dioxane	(*60*)
12	*n*-Hexane–Hexene-1-Cellosolve	(*60*)
13	*n*-Hexane–Hexene-1–1,2,3-Trichloropropane	(*60*)
14	2,3-Dimethylbutane–Acetone–Chloroform	(*23*)
15	2,3-Dimethylbutane–Acetone–Methanol	(*67*)
16	Benzene–Cyclohexane–2-Propanol	(*36*)
17	Methyl acetate–Benzene–Cyclohexane	(*39*)
18	Methyl acetate–Chloroform–Benzene	(*37*)
19	Methanol–Ethanol–Water	(*10*)

TABLE VIII. DEVIATIONS OF PREDICTED AND EXPERIMENTAL DATA

(Using Wilson equation binary parameters)

Ternary System[a]	No. of Data Points	ΔT, °C		Δy_1 (× 10^3)		Δy_2 (× 10^3)		Δy^3 (× 10^3)	
		Av.	Max.	Av.	Max.	Av.	Max.	Av.	Max.
1	15	0.3	0.5	3	7	3	9	2	7
2	15	0.2	0.6	9	25	6	31	5	14
3	15	1.2	1.6	10	26	8	21	4	9
4	7	0.5	0.8	8	16	6	10	9	19
5	15	0.4	1.7	10	22	7	17	4	14
6	15	0.5	1.1	7	22	7	20	6	25
7	15	0.8	2.1	20	30	5	27	22	35
8	15	0.4	1.2	6	16	10	23	7	22
9	15	0.4	1.2	8	27	13	25	10	25
10	15	0.4	0.7	7	21	6	22	8	15
11	12	0.9	2.1	7	18	7	23	14	24
12	9	2.5	5.1	13	18	10	23	14	29
13	9	2.2	5.7	19	76	13	35	27	97
14	15	0.1	0.2	6	15	7	23	5	16
15	15	0.9	1.7	6	20	5	14	5	16
16	15	0.6	0.9	3	7	7	19	10	26
17	15	0.5	1.1	13	31	9	30	4	10
18	15	0.2	0.4	5	10	5	20	6	16
19	15	0.2	0.5	20	46	18	54	29	84

The components are considered in the order shown in Table VII. For example, for ternary system 1: y_1 refers to benzene, y_2 refers to methylcyclopentane, and y_3 refers to *n*-hexane.

[a] The system number refers to the corresponding number in Table VII.

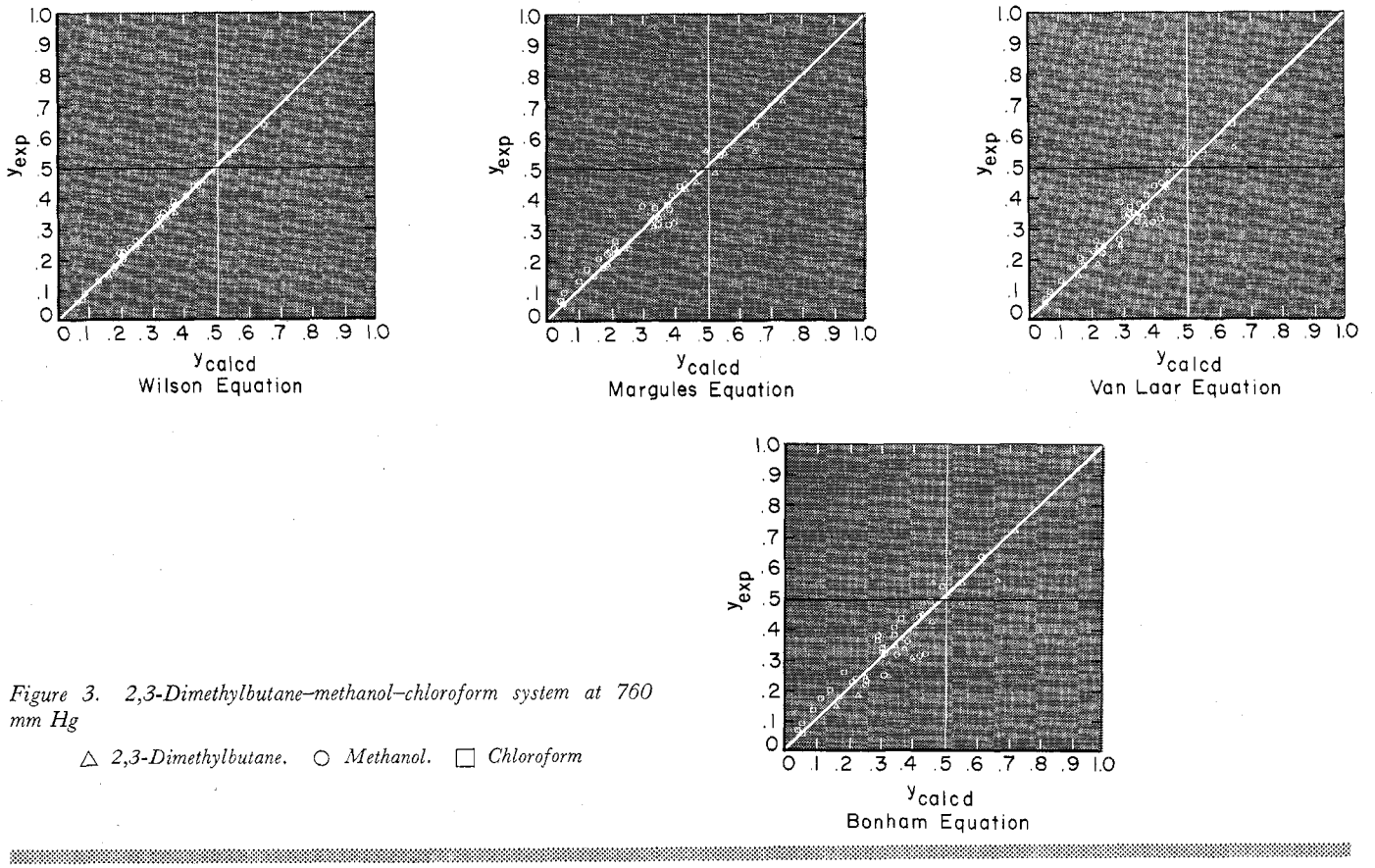


Figure 3. 2,3-Dimethylbutane–methanol–chloroform system at 760 mm Hg

△ *2,3-Dimethylbutane.* ○ *Methanol.* □ *Chloroform*

tions of vapor composition were obtained for the systems listed below:

n-Octane–ethylbenzene–Cellosolve

n-Hexane–hexene-1-1,2,3-trichloropropane

Methanol–ethanol–water

For these systems only 62% of the predicted vapor mole fractions were within 0.020 mole fraction of experimental data.

The temperature predictions for the systems listed below do not fall within the 1°C rule-of-thumb

Methylcyclopentane–ethanol–benzene

n-Hexane–hexene-1-cellosolve

n-Hexane–hexene-1-1,2,3-trichloropropane

For these systems only 12% of the predicted temperatures were within 1.0°C of experimental data. Most of the temperature predictions for the first system differed

from the experimental data by slightly over 1.0°, with the worst error being 1.6°C. However, the predictions for the other two systems were much poorer with some in error by more than 5°C. Of all the temperature predictions made in this study with the Wilson equation for the other sixteen ternary systems, only two points were in error by more than 2°C.

Conclusions

For the systems investigated, the Wilson equation appears to be a much better model of the multicomponent vapor-liquid equilibria. For most of the systems, the equation gives predictions of vapor compositions within 0.020 mole fraction of experimental data and predictions of temperature within 1.0°C of experimental data. In addition, the equation is relatively simple to use and can be easily extended to systems involving more than three components.

Nomenclature

A	= Antoine constant
A_{12}, A_{21}	= parameters in the Margules and Bonham equations
$\bar{A}_{12}$, $\bar{A}_{21}$	= parameters in the van Laar equation (in the Carlson and Colburn modification)
a'	= constant in Equation 36
a_1, a_2	= Van der Waals constants, atm(cm³/g mol)²
a_{ij}, a_{ijk}, etc.	= empirical constants in the Sohl expansion
B	= Antoine constant, °C
B_{12}, B_{21}	= parameters in the Bonham equation
b'	= constant in Equation 36
b_1, b_2	= Van der Waals constants, cm³/g mol
C	= Antoine constant, °C
C^*	= ternary parameter in the third-order Margules equation
c'	= constant in Equation 36
g^E	= molar excess free energy, cal/g mol
N	= number of components
n	= number of experimental points
n_i	= number of moles of the ith component
n_T	= total number of moles
P	= pressure, atm.
P_i^*	= vapor pressure of the ith component, cc/g mol
R	= gas law constant, cal/g mol/°K
T_{exp}	= experimental temperature, °K
T_{calc}	= calculated temperature, °K
T_1, T_2, T_3	= temperatures at which liquid molar volumes are known, °K
t	= temperature, °C
v_i^L	= liquid molar volume of the ith component, c/g mol
x_i	= liquid mole fraction of the ith component
y_i	= vapor mole fraction of the ith component
y_{iexp}	= experimental vapor mole fraction of the ith component
y_{icalc}	= calculated vapor mole fraction of the ith component
z_i	= effective volumetric fraction of the ith component

Greek Letters

γ_i	= activity coefficient of the ith component
γ_{iexp}	= experimental activity coefficient for the ith component
γ_{icalc}	= calculated activity coefficient for the ith component
$\wedge_{ij}$	= variables defined by Equation 26
$(\lambda_{ij} - \lambda_{ii})$, $(\lambda_{ij} - \lambda_{jj})$	= parameters in the Wilson equation, cal/g mol
ϕ	= objective function
ω_1, ω_2	= scale factors in Equation 30

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