

LIQUID-VAPOUR EQUILIBRIUM. XLVIII.*

THE SYSTEMS ACETONE-BENZENE,
ACETONE-TOLUENE, BENZENE-METHYL ETHYL KETONE,
METHYL ETHYL KETONE-TOLUENE AND
METHYL ETHYL KETONE-ETHYLBENZENE

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Vapour-liquid equilibrium has been measured in systems acetone-benzene (at 30, 40 and 50°C), acetone-toluene (at 35, 45 and 55°C), benzene-methyl ethyl ketone (at 40, 50 and 60°C), methyl ethyl ketone-toluene (at 55, 65 and 75°C), and methyl ethyl ketone-ethylbenzene (at 55, 65 and 75°C). The modified circulation still of Gillespie's type has been used for the measurement. The measured data have been correlated by several equations expressing the dependence of activity coefficients on the composition of the liquid phase.

As a part of a systematic study of thermodynamic properties of binary mixtures belonging to various groups of Ewell's classification of liquids¹, the isothermal vapour-liquid equilibria have been measured for binary systems of aromatic hydrocarbons with ketones.

EXPERIMENTAL

Preparation of Pure Substances and Criteria of Purity

Acetone. Analytical grade reagent was purified as the sodium iodide addition compound² and the product obtained was then rectified on a fifty-plate laboratory distillation column.

Methyl ethyl ketone. Analytical grade reagent was refluxed with KMnO_4 and CaO for removing aldehydes² and then rectified on a forty-plate column.

Benzene (Standard from Urxovny závody, Valašské Meziříčí) was used without any further purification.

Toluene. Technical grade reagent was freed from sulphur-containing impurities by treating with H_2SO_4 , washed with water, dried with Na and three times rectified on a forty-plate column².

Ethylbenzene. Technical grade reagent was twice rectified on a forty-plate column.

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TABLE I
Physical Constants of Pure Compounds

Compound	Constant	Measured	Published
Acetone	d_4^{20} , g/cm ³	0.7900	0.78989 ¹³
	n_D^{20}	1.3588	1.3588 ¹⁴
	B. p., °C	56.06	56.1 — 56.3 ¹⁴
Methyl ethyl ketone	d_4^{20} , g/cm ³	0.8048	0.80473 ⁷
	n_D^{20}	1.3785	1.3786 ¹⁴
	B. p., °C	79.50	79.57 — 79.89 ¹⁴
Benzene	d_4^{20} , g/cm ³	0.8790	0.8789—0.8791 ¹⁴
	n_D^{20}	1.5011	1.5009— 1.50115 ¹⁴
	B. p., °C	80.05	80.07 — 80.11 ¹⁴
Toluene	d_4^{20} , g/cm ³	0.8669	0.8669— 0.8672 ¹⁴
	n_D^{20}	1.4967	1.4966— 1.49693 ¹⁴
	B. p., °C	110.625	110.606 — 110.75 ¹⁴
Ethylbenzene	d_4^{20} , g/cm ³	0.8670	0.86696— 0.8672 ¹⁴
	n_D^{20}	1.4959	1.4958— 1.49593 ¹⁴
	B. p. °C	136.26	136.1 — 136.4 ¹⁴

TABLE II

Refractive Indices of the Acetone (1)–Benzene (2) Mixture at 20°C

n_{D1} 1.35880, n_{D2} 1.50110. Constants of the equation (1) A_1 0.01936, A_2 0.01768, A_3 —0.01915.

x_1	n_D (exp)	n_D (calc)	Dev.	Dev., %
0.1091	1.48750	1.48749	—0.00001	—0.00
0.2430	1.47050	1.47050	0.00000	0.00
0.3461	1.45700	1.45696	—0.00004	—0.03
0.4590	1.44150	1.44154	0.00004	0.03
0.5096	1.43430	1.43441	0.00011	0.07
0.6355	1.41600	1.41604	0.00004	0.02
0.7287	1.40200	1.40189	—0.00011	—0.08
0.8365	1.38510	1.38503	—0.00007	—0.05
0.9210	1.37150	1.37154	0.00004	0.03
<i>Mean</i>			± 0.00005	± 0.04

TABLE III

Refractive Indices of the Acetone(1)-Toluene(2) Mixture at 20°C

 n_{D1} 1.35880, n_{D2} 1.49670. Constants of the equation (1) A_1 0.05645, A_2 0.04037, A_3 -0.00580.

x_1	n_D (exp)	n_D (calc)	Dev.	Dev., %
0.1191	1.48470	1.48468	-0.00002	-0.01
0.2446	1.47130	1.47128	-0.00002	-0.02
0.3744	1.45610	1.45619	0.00009	0.06
0.4757	1.44340	1.44338	-0.00002	-0.01
0.5478	1.43350	1.43364	0.00014	0.10
0.6541	1.41830	1.41827	-0.00003	-0.02
0.7643	1.40100	1.40095	-0.00005	-0.04
0.8531	1.38610	1.38591	-0.00019	-0.14
0.9228	1.37330	1.37339	0.00009	0.07
<i>Mean</i>			± 0.00007	± 0.05

TABLE IV

Refractive Indices of the Benzene(1)-Methyl Ethyl Ketone(2) Mixture at 20°C

 n_{D1} 1.50110, n_{D2} 1.37850. Constants of the equation (1) A_1 -0.00787, A_2 -0.00360, A_3 -0.00077.

x_1	n_D (exp)	n_D (calc)	Dev.	Dev., %
0.0306	1.38220	1.38214	-0.00006	-0.05
0.0996	1.39020	1.39035	0.00015	0.13
0.2004	1.40230	1.40238	0.00008	0.06
0.2954	1.41360	1.41374	0.00014	0.11
0.3920	1.42530	1.42535	0.00005	0.04
0.4996	1.43830	1.43837	0.00007	0.05
0.5853	1.44900	1.44883	-0.00017	-0.14
0.6990	1.46300	1.46285	-0.00015	-0.12
0.7561	1.47010	1.46996	-0.00014	-0.11
0.8835	1.48610	1.48607	-0.00003	-0.03
0.9396	1.49320	1.49327	0.00007	0.06
<i>Mean</i>			± 0.00010	± 0.08

TABLE V

Refractive Indices of the Methyl Ethyl Ketone(1)-Toluene(2) Mixture at 20°C

 n_{D1} 1.37850, n_{D2} 1.49670. Constants of the equation (1) A_1 0.02325, A_2 0.01821, A_3 0.00122.

x_1	n_D (exp)	n_D (calc)	Dev.	Dev., %
0.1353	1.48280	1.48281	0.00001	0.01
0.2219	1.47370	1.47370	0.00000	0.00
0.3654	1.45810	1.45803	-0.00007	-0.06
0.4552	1.44780	1.44785	0.00005	0.04
0.5474	1.43710	1.43708	-0.00002	-0.02
0.6299	1.42720	1.42713	-0.00007	-0.06
0.7196	1.41580	1.41597	0.00017	0.14
0.8200	1.40310	1.40303	-0.00007	-0.06
0.9084	1.39120	1.39120	0.00000	0.00
<i>Mean</i>			± 0.00005	± 0.04

TABLE VI

Refractive Indices of the Methyl Ethyl Ketone(1)-Ethylbenzene(2) Mixture at 20°C

 n_{D1} 1.37850, n_{D2} 1.49590. Constants of the equation (1) A_1 0.04834, A_2 0.03689, A_3 0.02776.

x_1	n_D (exp)	n_D (calc)	Dev.	Dev., %
0.2425	1.47380	1.47378	-0.00002	-0.01
0.2974	1.46810	1.46820	0.00010	0.08
0.3798	1.45950	1.45949	-0.00001	-0.01
0.4931	1.44700	1.44690	-0.00010	-0.08
0.5787	1.43700	1.43692	-0.00008	-0.06
0.6490	1.42850	1.42836	-0.00014	-0.12
0.7536	1.41480	1.41492	0.00012	0.10
0.8452	1.40210	1.40230	0.00020	0.17
0.9285	1.39000	1.38992	-0.00008	-0.07
<i>Mean</i>			± 0.00009	± 0.08

TABLE VII

Vapour Pressure of Acetone

Antoine vapour pressure constants *A* 7·083940, *B* 1191·632, *C* 227·448.

<i>t</i> °C	<i>P</i> _{exp} Torr	<i>P</i> _{calc} Torr	Dev. Torr	%
15·394	150·47	150·28	-0·19	-0·12
19·972	185·09	185·23	0·14	0·07
21·609	199·16	199·23	0·07	0·04
23·985	220·76	221·09	0·33	0·15
26·231	243·60	243·52	-0·08	-0·03
28·677	270·52	270·02	-0·50	-0·18
30·539	292·00	291·73	-0·27	-0·09
33·569	328·94	330·06	1·12	0·34
35·649	359·08	358·66	-0·42	-0·12
39·505	417·17	416·97	-0·20	-0·05
43·133	478·92	478·59	-0·33	-0·07
47·518	562·03	562·59	0·56	0·10
52·523	672·66	672·46	-0·20	-0·03
55·202	737·98	737·92	-0·06	-0·01
<i>Mean</i>			±0·32	±0·10

TABLE VIII

Vapour Pressure of Methyl Ethyl Ketone

Antoine vapour pressure constants *A* 7·122316, *B* 1294·530, *C* 225·708.

<i>t</i> °C	<i>P</i> _{exp} Torr	<i>P</i> _{calc} Torr	Dev. Torr	%
31·690	123·88	123·89	0·01	0·01
36·472	153·12	153·02	-0·10	-0·06
40·422	181·30	181·15	-0·15	-0·08
42·250	195·51	195·54	0·03	0·01
44·417	213·97	213·79	-0·18	-0·09
47·142	238·24	238·69	0·45	0·19
49·049	257·08	257·50	0·42	0·16
51·877	287·66	287·59	-0·07	-0·02
54·042	312·70	312·51	-0·19	-0·06
61·515	412·35	412·35	0·00	0·00
65·856	481·16	481·24	0·08	0·02
69·982	555·61	555·03	-0·58	-0·10
75·229	662·26	661·69	-0·57	-0·09
78·761	741·41	742·26	0·85	0·11
<i>Mean</i>			±0·26	±0·07

TABLE IX
 Vapour Pressure of Toluene
 Antoine vapour pressure constants *A* 6.970241, *B* 1356.139, *C* 220.981.

<i>t</i> °C	<i>P</i> _{exp} Torr	<i>P</i> _{calc} Torr	Dev. Torr	%
55.741	117.36	117.36	0.00	0.00
59.979	139.09	139.13	0.04	0.03
64.674	167.11	167.02	-0.09	-0.05
68.745	194.85	194.75	-0.10	-0.05
71.684	217.15	217.01	-0.14	-0.06
73.846	234.74	234.67	-0.07	-0.03
76.249	255.63	255.65	0.02	0.01
78.666	277.71	278.26	0.55	0.20
81.506	306.38	306.86	0.48	0.16
86.055	357.89	357.57	-0.32	-0.09
90.049	407.85	407.46	-0.39	-0.10
94.684	472.36	472.18	-0.18	-0.04
99.996	556.03	556.17	0.14	0.02
105.960	664.41	664.17	-0.24	-0.04
109.790	741.53	741.83	0.30	0.04
<i>Mean</i>			±0.20	±0.06

TABLE X
 Vapour Pressure of Ethylbenzene
 Antoine vapour pressure constants *A* 6.883838, *B* 1379.331, *C* 208.306.

<i>t</i> °C	<i>P</i> _{exp} Torr	<i>P</i> _{calc} Torr	Dev. Torr	%
76.633	110.58	110.42	-0.16	-0.14
81.810	134.74	134.72	-0.02	-0.01
86.212	158.60	158.67	0.07	0.04
90.188	183.10	183.18	0.08	0.04
93.825	208.02	208.21	0.19	0.09
96.968	231.91	232.01	0.10	0.04
99.106	249.42	249.42	0.00	0.00
101.880	273.74	273.56	-0.18	-0.06
105.480	307.18	307.66	0.48	0.16
110.340	359.47	359.02	-0.45	-0.12
119.530	474.64	474.75	0.11	0.02
124.750	553.31	552.60	-0.71	-0.13
131.110	661.34	660.71	-0.63	-0.10
135.410	741.66	742.76	1.10	0.15
<i>Mean</i>			±0.31	±0.08

TABLE XI
Vapour-Liquid Equilibrium in the Acetone(1)-Benzene(2) System at 30°C

Experimental values			Deviation in vapour phase composition				
<i>x</i>	<i>y</i>	<i>P</i> , Torr	Laar 3	Marg. 3	Marg. 4	Wils. 2	Alpha 2
0.0610	0.1702	139.27	0.0222	0.0192	0.0130	0.0223	-0.0026
0.1035	0.2761	151.86	0.0074	0.0057	0.0012	0.0074	-0.0168
0.1608	0.3697	166.00	0.0076	0.0077	0.0066	0.0075	-0.0095
0.2607	0.4949	185.38	0.0031	0.0041	0.0065	0.0030	-0.0009
0.3233	0.5604	197.03	-0.0020	-0.0015	0.0010	-0.0021	-0.0008
0.3734	0.6021	205.13	-0.0004	-0.0006	0.0011	-0.0005	0.0028
0.4629	0.6690	219.18	0.0023	0.0009	0.0005	0.0023	0.0054
0.5334	0.7156	229.13	0.0058	0.0038	0.0019	0.0058	0.0061
0.5885	0.7513	237.80	0.0071	0.0050	0.0023	0.0071	0.0041
0.7661	0.8588	259.56	0.0099	0.0097	0.0086	0.0099	-0.0045
0.8795	0.9294	273.39	0.0045	0.0057	0.0072	0.0045	-0.0112
0.9474	0.9678	279.18	0.0037	0.0047	0.0063	0.0037	-0.0065
<i>Mean</i>			0.0063	0.0057	0.0047	0.0063	0.0060

Equation	Order	A_{12}	A_{21}	D_{12}
Van Laar	3	0.2243	0.1174	—
Margules	3	0.2050	0.0938	—
Margules	4	0.1716	0.0501	-0.1263
Wilson	2	0.4058	1.3830	—
Alpha	2	2.1956	-0.2017	—

The comparison of the measured and published values of physical constants of the used substances is given in Table I.

Procedure

Vapour pressures of the pure compounds were measured by the Swientoslawski standard ebulliometer connected to a vacuum station³. Temperature was measured by platinum resistance thermometers calibrated by means of a Mueller bridge with platinum resistance thermometer Leeds and Northrup. The accuracy of the temperature measurements was $\pm 0.01^\circ\text{C}$. The pressure was measured indirectly by measuring the boiling point of water in an ebulliometer connected in parallel.

For measuring the vapour-liquid equilibria, the Gillespie-type circulation apparatus¹ was used. The samples of the equilibrium phases were analysed refractometrically. Refractive indices were measured by an Abbe-type refractometer with an accuracy of ± 0.0001 . Refractive indices of

TABLE XII
Vapour-Liquid Equilibrium in the Acetone(1)-Benzene(2) System at 40°C

Experimental values			Deviation in vapour phase composition				
<i>x</i>	<i>y</i>	<i>P</i> , Torr	Laar 3	Marg. 3	Marg. 4	Wils. 2	Alpha 2
0.0570	0.1758	211.04	0.0113	0.0065	0.0055	0.0115	-0.0183
0.1027	0.2769	229.73	0.0089	0.0060	0.0052	0.0090	-0.0204
0.1608	0.3689	234.90	0.0097	0.0096	0.0093	0.0097	-0.0107
0.2615	0.4921	280.65	0.0038	0.0056	0.0059	0.0037	-0.0005
0.3240	0.5535	296.95	0.0006	0.0020	0.0024	0.0006	0.0028
0.3734	0.5946	309.35	0.0009	0.0017	0.0019	0.0009	0.0059
0.4636	0.6631	328.86	0.0012	0.0005	0.0004	0.0012	0.0069
0.5300	0.7085	344.83	0.0025	0.0011	0.0008	0.0026	0.0058
0.5892	0.7481	356.72	0.0027	0.0010	0.0006	0.0028	0.0024
0.7325	0.8355	381.56	0.0065	0.0059	0.0056	0.0065	-0.0044
0.8051	0.8782	393.34	0.0080	0.0084	0.0084	0.0079	-0.0070
0.8807	0.9238	406.38	0.0073	0.0085	0.0087	0.0072	-0.0083
<i>Mean</i>			<i>0.0053</i>	<i>0.0047</i>	<i>0.0046</i>	<i>0.0053</i>	<i>0.0078</i>

Equation	Order	<i>A</i> ₁₂	<i>A</i> ₂₁	<i>D</i> ₁₂
Van Laar	3	0.2577	0.1313	—
Margules	3	0.2297	0.1072	—
Margules	4	0.2244	0.1003	-0.0195
Wilson	2	0.3776	1.3760	—
Alpha	2	2.1892	-0.1603	—

calibration mixtures were expressed by the equation

$$n_D = x_1 n_{D1} + x_2 n_{D2} + x_1 x_2 (A_1 x_1 + A_2 x_2 - A_3 x_1 x_2), \quad (I)$$

where x_1, x_2 are mole fractions and n_{D1}, n_{D2} refractive indices of the pure compounds 1 and 2, resp., n_D is refractive index of the mixture and A_1, A_2, A_3 are empirical constants determined from the experimental data by the least square method. The measured and calculated values of refractive indices together with the constants of the equation (I) are presented in Tables II—VI.

TABLE XIII
Vapour-Liquid Equilibrium in the Acetone(1)-Benzene(2) System at 50°C

Experimental values			Deviation in vapour phase composition				
<i>x</i>	<i>y</i>	<i>P</i> , Torr	Laar 3	Marg. 3	Marg. 4	Wils. 2	Alpha 2
0.0417	0.1282	299.42	0.0127	0.0077	0.0081	0.0129	-0.0126
0.1011	0.2661	335.56	0.0088	0.0057	0.0059	0.0089	-0.0197
0.1639	0.3585	363.75	0.0158	0.0156	0.0157	0.0158	-0.0040
0.2700	0.4921	411.55	0.0041	0.0060	0.0059	0.0041	-0.0000
0.3248	0.5487	432.92	-0.0014	0.0002	0.0001	-0.0014	-0.0005
0.3734	0.5878	449.12	0.0009	0.0018	0.0017	0.0009	0.0043
0.4629	0.6564	477.91	0.0017	0.0013	0.0013	0.0017	0.0055
0.5300	0.7039	500.32	0.0024	0.0012	0.0013	0.0024	0.0036
0.5885	0.7410	517.09	0.0054	0.0039	0.0040	0.0054	0.0031
0.7319	0.8305	551.16	0.0089	0.0083	0.0084	0.0088	-0.0037
0.8437	0.9001	578.05	0.0079	0.0088	0.0088	0.0079	-0.0090
0.9300	0.9492	596.00	0.0101	0.0113	0.0112	0.0101	-0.0027
<i>Mean</i>			0.0067	0.0060	0.0060	0.0067	0.0057

Equation	Order	A_{12}	A_{21}	D_{12}
Van Laar	3	0.2500	0.1252	—
Margules	3	0.2205	0.1018	—
Margules	4	0.2223	0.1041	0.0065
Wilson	2	0.3766	1.3972	—
Alpha	2	2.0722	-0.1507	—

RESULTS

The temperature dependence of vapour pressures of the pure compounds was correlated by means of the Antoine equation⁴

$$\log P^0 = A - B/(t + C), \quad (2)$$

where P^0 is the vapour pressure (in Torr), t is temperature (°C) and A , B , C are constants determined by the least square method using the statistical weights⁵. The comparison of the measured and calculated vapour pressures of acetone, methyl ethyl ketone, toluene and ethylbenzene is listed in Tables VII-X. The constants of the Antoine equation (2) for benzene of the given purity were taken from the literature³.

TABLE XIV
Vapour-Liquid Equilibrium in the Acetone(1)-Toluene(2) System at 35°C

Experimental values			Deviation in vapour phase composition				
<i>x</i>	<i>y</i>	<i>P</i> , Torr	Laar 3	Marg. 3	Marg. 4	Wils. 2	Alpha 2
0.1469	0.6356	116.64	0.0160	0.0149	0.0078	0.0162	-0.0071
0.1988	0.7164	135.77	-0.0039	-0.0039	-0.0045	-0.0039	-0.0140
0.2126	0.7201	141.00	0.0053	0.0054	0.0058	0.0052	-0.0021
0.2757	0.7775	161.79	-0.0045	-0.0041	-0.0012	-0.0046	-0.0030
0.3761	0.8273	190.85	-0.0006	-0.0008	0.0015	-0.0007	0.0066
0.4541	0.8573	212.13	0.0010	0.0005	0.0008	0.0010	0.0082
0.5234	0.8788	228.92	0.0035	0.0027	0.0014	0.0035	0.0085
0.5821	0.8988	242.83	0.0016	0.0009	-0.0012	0.0016	0.0038
0.6450	0.9132	258.76	0.0050	0.0044	0.0022	0.0050	0.0036
0.7043	0.9306	271.76	0.0032	0.0029	0.0013	0.0032	-0.0019
0.7519	0.9441	283.05	0.0016	0.0015	0.0007	0.0015	-0.0065
0.8026	0.9548	295.14	0.0029	0.0031	0.0033	0.0028	-0.0080
0.8578	0.9670	308.72	0.0032	0.0036	0.0048	0.0031	-0.0098
0.9257	0.9823	325.54	0.0025	0.0029	0.0045	0.0025	-0.0101
<i>Mean</i>			<i>0.0039</i>	<i>0.0037</i>	<i>0.0029</i>	<i>0.0039</i>	<i>0.0067</i>

Equation	Order	A_{12}	A_{21}	D_{12}
Van Laar	3	0.2898	0.1708	—
Margules	3	0.2699	0.1478	—
Margules	4	0.1873	0.0525	-0.2704
Wilson	2	0.4103	1.2119	—
Alpha	2	9.6339	-0.4204	—

The mutual dependence of the equilibrium compositions of the liquid and vapour phases in a binary system is given by

$$y_1 = [\alpha_{12}(x_1/x_2)]/[1 + \alpha_{12}(x_1/x_2)], \quad (3a)$$

$$y_2 = 1/[1 + \alpha_{12}(x_1/x_2)], \quad (3b)$$

where x_1, x_2 are the mole fractions of the components 1, 2 in the liquid phase and y_1, y_2 their mole fractions in the vapour phase. The relative volatility α_{12} is defined by the relation

$$\alpha_{12} = (y_1/y_2)/(x_1/x_2), \quad (4)$$

TABLE XV
Vapour-Liquid Equilibrium in the Acetone(1)-Toluene(2) System at 45°C

Experimental values			Deviation in vapour phase composition				
<i>x</i>	<i>y</i>	<i>P</i> , Torr	Laar 3	Marg. 3	Marg. 4	Wils. 2	Alpha 2
0.0367	0.2915	101.20	0.0225	0.0217	0.0123	0.0231	-0.0133
0.0688	0.4518	126.15	0.0062	0.0057	-0.0016	0.0066	-0.0284
0.1421	0.6261	172.93	0.0040	0.0039	0.0024	0.0039	-0.0142
0.2145	0.7201	211.70	-0.0023	-0.0022	-0.0012	-0.0024	-0.0076
0.2757	0.7684	240.74	-0.0022	-0.0022	-0.0007	-0.0023	-0.0007
0.3752	0.8197	281.79	0.0013	0.0010	0.0017	0.0013	0.0079
0.4518	0.8498	311.60	0.0026	0.0022	0.0019	0.0027	0.0096
0.5226	0.8760	338.25	0.0008	0.0004	-0.0007	0.0009	0.0063
0.5821	0.8927	357.29	0.0024	0.0020	0.0006	0.0025	0.0055
0.6450	0.9115	382.07	0.0014	0.0011	-0.0003	0.0015	0.0013
0.7056	0.9285	400.69	0.0005	0.0003	-0.0008	0.0005	-0.0032
0.7525	0.9403	416.94	0.0006	0.0005	-0.0001	0.0006	-0.0059
0.8026	0.9516	434.40	0.0017	0.0017	0.0017	0.0017	-0.0077
0.8573	0.9649	453.99	0.0016	0.0017	0.0022	0.0016	-0.0102
0.9252	0.9813	479.03	0.0013	0.0014	0.0022	0.0012	0.0108
<i>Mean</i>			0.0034	0.0032	0.0020	0.0035	0.0088

Equation	Order	<i>A</i> ₁₂	<i>A</i> ₁₂	<i>D</i> ₁₂
Van Laar	3	0.2661	0.2041	—
Margules	3	0.2635	0.1960	—
Margules	4	0.2359	0.1550	-0.1137
Wilson	2	0.5561	0.9693	—
Alpha	2	9.3112	-0.3917	—

and for the low pressure region the equation holds

$$\alpha_{12} = (\gamma_1/\gamma_2)/(P_1^0/P_2^0) (*, g), \quad (5)$$

where P_1^0 , P_2^0 denote the vapour pressures of the pure components 1, 2 at a given temperature, γ_1 , γ_2 their activity coefficients and the symbol (*, g) indicates the ideal behaviour of vapour phase. The concentration dependence of the activity coefficients was expressed by the relations

TABLE XVI
Vapour-Liquid Equilibrium in the Acetone(1)-Toluene(2) System at 55°C

Experimental values			Deviation in vapour phase composition				
x	y	P, Torr	Laar 3	Marg. 3	Marg. 4	Wils. 2	Alpha 2
0.0356	0.2774	149.49	0.0179	0.0159	0.0145	0.0186	-0.0199
0.0708	0.4479	187.40	0.0016	0.0002	-0.0009	0.0021	-0.0354
0.1431	0.6139	252.35	0.0018	0.0015	0.0013	0.0018	-0.0180
0.2108	0.6979	303.09	0.0015	0.0017	0.0019	0.0014	-0.0049
0.2739	0.7513	346.29	0.0000	0.0003	0.0005	-0.0001	0.0015
0.3678	0.8062	403.87	-0.0003	-0.0002	-0.0001	-0.0003	0.0069
0.4533	0.8418	450.67	0.0014	0.0012	0.0011	0.0015	0.0092
0.5212	0.8675	486.20	0.0005	0.0002	0.0000	0.0006	0.0067
0.5821	0.8855	514.28	0.0025	0.0021	0.0019	0.0026	0.0061
0.6463	0.9066	549.94	0.0008	0.0005	0.0003	0.0009	0.0008
0.7037	0.9203	575.73	0.0034	0.0032	0.0030	0.0035	-0.0002
0.7537	0.9414	601.28	-0.0040	-0.0041	-0.0042	-0.0040	-0.0108
0.8032	0.9484	625.65	0.0021	0.0021	0.0021	0.0020	-0.0077
0.8567	0.9623	652.75	0.0020	0.0021	0.0022	0.0019	-0.0102
0.9257	0.9766	688.43	0.0050	0.0052	0.0053	0.0050	-0.0072
<i>Mean</i>			<i>0.0030</i>	<i>0.0027</i>	<i>0.0026</i>	<i>0.0031</i>	<i>0.0097</i>

Equation	Order	A_{12}	A_{21}	D_{12}
Van Laar	3	0.2725	0.1981	--
Margules	3	0.2664	0.1894	--
Margules	4	0.2623	0.1835	-0.0166
Wilson	2	0.5219	1.0171	--
Alpha	2	8.5720	-0.3842	--

van Laar 3rd order^{6,8}

$$\log \gamma_1 = A_{12}x_2^2/[x_1(A_{12}/A_{21}) + x_2]^2, \quad (6a)$$

$$\log \gamma_2 = A_{21}x_1^2/[x_2(A_{21}/A_{12}) + x_1]^2, \quad (6b)$$

Margules 3rd order^{8,9}

$$\log(\gamma_1/\gamma_2) = x_2^2A_{12} - x_1^2A_{21} - 2x_1x_2(A_{12} - A_{21}), \quad (7)$$

Margules 4th order^{8,9}

$$\log(\gamma_1/\gamma_2) = x_2^2A_{12} - x_1^2A_{21} - 2x_1x_2[(A_{12} - A_{21}) + (x_2 - x_1)D_{12}], \quad (8)$$

TABLE XVII
Vapour-Liquid Equilibrium in the Benzene(1)-Methyl Ethyl Ketone(2) System at 40°C

Experimental values			Deviation in vapour phase composition				
<i>x</i>	<i>y</i>	<i>P</i> , Torr	Laar 3	Marg. 3	Marg. 4	Wils. 2	Alpha 2
0.0597	0.0723	179.33	-0.0055	-0.0084	-0.0061	-0.0060	-0.0011
0.1201	0.1386	180.78	-0.0058	-0.0091	-0.0070	-0.0065	0.0007
0.1830	0.2023	182.68	-0.0023	-0.0044	-0.0037	-0.0029	0.0044
0.2391	0.2583	183.80	0.0003	-0.0004	-0.0010	-0.0001	0.0059
0.2959	0.3201	184.91	-0.0034	-0.0028	-0.0043	-0.0035	0.0005
0.3659	0.3891	187.12	-0.0025	-0.0011	-0.0027	-0.0024	-0.0012
0.4289	0.4504	187.57	-0.0025	-0.0012	-0.0023	-0.0022	-0.0033
0.4752	0.4917	188.01	0.0004	0.0011	0.0007	0.0006	-0.0017
0.5483	0.5606	188.78	-0.0002	-0.0012	-0.0004	-0.0003	-0.0034
0.6047	0.6120	188.89	-0.0000	-0.0024	-0.0009	-0.0004	-0.0031
0.6615	0.6623	189.11	0.0008	-0.0028	-0.0011	-0.0001	-0.0009
0.7171	0.7131	189.22	-0.0006	-0.0046	-0.0033	-0.0018	0.0002
0.7843	0.7747	191.31	-0.0026	-0.0056	-0.0055	-0.0039	0.0026
0.8516	0.8382	188.01	-0.0054	-0.0051	-0.0067	-0.0060	0.0053
0.9197	0.9080	185.35	-0.0089	-0.0043	-0.0070	-0.0080	0.0052
<i>Mean</i>			0.0027	0.0036	0.0035	0.0030	0.0026

Equation	Order	A_{12}	A_{21}	D_{12}
Van Laar	3	0.0519	0.2092	—
Margules	3	0.0208	0.1221	—
Margules	4	0.0494	0.1511	0.0865
Wilson	2	1.8235	0.2912	—
Alpha	2	0.2304	0.1188	—

Wilson¹⁰

$$\ln(\gamma_1/\gamma_2) = \ln(x_2 + A_{21}x_1)/(x_1 + A_{12}x_2) + A_{12}/(x_1 + x_2A_{12}) - A_{21}/(x_1A_{21} + x_2), \quad (9)$$

and expansion of relative volatility 2nd order^{1,11}

$$\alpha_{12} = (1 + A_{12}x_2)/(1 + A_{21}x_1), \quad (10)$$

where A_{12} , A_{21} , D_{12} are constants characteristic for the given binary mixture and

TABLE XVIII

Vapour-Liquid Equilibrium in the Benzene(1)-Methyl Ethyl Ketone(2) System at 50°C

Experimental values			Deviation in vapour phase composition				
x	y	P, Torr	Laar 3	Marg. 3	Marg. 4	Wils. 2	Alpha 2
0.0597	0.0706	269.24	-0.0046	-0.0076	-0.0061	-0.0051	0.0001
0.1210	0.1369	270.86	-0.0045	-0.0079	-0.0065	-0.0052	0.0024
0.1830	0.2023	273.36	-0.0041	-0.0064	-0.0059	-0.0047	0.0030
0.2400	0.2592	275.15	-0.0018	-0.0026	-0.0030	-0.0022	0.0043
0.2959	0.3201	277.34	-0.0058	-0.0052	-0.0062	-0.0059	-0.0013
0.3659	0.3875	278.85	-0.0034	-0.0020	-0.0031	-0.0033	-0.0016
0.4289	0.4463	279.88	-0.0009	0.0003	-0.0003	-0.0007	-0.0013
0.4752	0.4892	280.40	0.0005	0.0010	0.0008	0.0005	-0.0013
0.5483	0.5573	281.44	0.0008	-0.0004	0.0001	0.0006	-0.0022
0.6039	0.6079	281.44	0.0013	-0.0015	-0.0005	0.0006	-0.0017
0.6615	0.6615	281.87	-0.0003	-0.0044	-0.0033	-0.0015	-0.0020
0.7171	0.7115	281.78	-0.0007	-0.0053	-0.0044	-0.0023	0.0001
0.7835	0.7731	280.56	-0.0034	-0.0068	-0.0068	-0.0051	0.0021
0.8500	0.8366	278.64	-0.0069	-0.0069	-0.0080	-0.0078	0.0042
0.9189	0.9072	276.09	-0.0106	-0.0056	-0.0074	-0.0096	0.0045
<i>Mean</i>			<i>0.0033</i>	<i>0.0043</i>	<i>0.0042</i>	<i>0.0037</i>	<i>0.0021</i>

Equation	Order	A_{12}	A_{21}	D_{12}
Van Laar	3	0.0516	0.2224	—
Margules	3	0.0192	0.1237	—
Margules	4	0.0383	0.1430	0.0575
Wilson	2	1.8401	0.2828	—
Alpha	2	0.2207	0.1274	—

evaluated by means of the weighted least square method for the correlation equation

$$\log(\gamma_1/\gamma_2) = F(x_1). \quad (11)$$

The statistical weight was calculated by the relation¹²

$$w = [(1/2 \cdot 303^2)(1/x_1^2 x_2^2 + 1/y_1^2 y_2^2) + (dF(x_1)/dx_1)^2]^{-1}. \quad (12)$$

The comparison of the experimental and calculated vapour-liquid equilibrium data is summarized in Tables XI-XXV.

TABLE XIX

Vapour-Liquid Equilibrium in the Benzene(1)-Methyl Ethyl Ketone(2) System at 60°C

Experimental values			Deviation in vapour phase composition				
<i>x</i>	<i>y</i>	<i>P</i> , Torr	Laar 3	Marg. 3	Marg. 4	Wils. 2	Alpha 2
0.0597	0.0697	395.79	-0.0042	-0.0069	-0.0051	-0.0046	0.0005
0.1201	0.1344	398.45	-0.0039	-0.0069	-0.0054	-0.0045	0.0028
0.1830	0.2014	402.85	-0.0047	-0.0067	-0.0061	-0.0052	0.0022
0.2391	0.2575	404.31	-0.0030	-0.0036	-0.0040	-0.0033	0.0029
0.2968	0.3168	407.50	-0.0039	-0.0033	-0.0044	-0.0040	0.0002
0.3667	0.3842	409.24	-0.0022	-0.0008	-0.0021	-0.0021	-0.0006
0.4289	0.4413	410.11	0.0009	0.0021	0.0012	0.0011	0.0003
0.4752	0.4867	410.68	-0.0005	0.0000	-0.0003	-0.0004	-0.0024
0.5483	0.5557	412.12	-0.0013	-0.0024	-0.0018	-0.0015	-0.0044
0.6039	0.6055	410.83	-0.0002	-0.0027	-0.0016	-0.0008	-0.0031
0.6615	0.6558	411.55	0.0015	-0.0021	-0.0008	0.0005	-0.0000
0.7171	0.7075	411.26	-0.0005	-0.0044	-0.0034	-0.0017	0.0006
0.7843	0.7708	408.96	-0.0036	-0.0064	-0.0063	-0.0049	0.0020
0.8516	0.8358	406.64	-0.0068	-0.0065	-0.0077	-0.0074	0.0041
0.9189	0.9049	402.28	-0.0090	-0.0044	-0.0066	-0.0081	0.0052
<i>Mean</i>			<i>0.0031</i>	<i>0.0039</i>	<i>0.0038</i>	<i>0.0033</i>	<i>0.0021</i>

Equation	Order	A_{12}	A_{21}	D_{12}
Van Laar	3	0.0534	0.2051	—
Margules	3	0.0239	0.1235	—
Margules	4	0.0461	0.1458	0.0666
Wilson	2	1.8008	0.2988	—
Alpha	2	0.2116	0.1502	—

TABLE XX

Vapour-Liquid Equilibrium in the Methyl Ethyl Ketone(1)-Toluene(2) System at 55°C

Experimental values			Deviation in vapour phase composition				
<i>x</i>	<i>y</i>	<i>P</i> , Torr	Laar 3	Marg. 3	Marg. 4	Wils. 2	Alpha 2
0.0565	0.1861	129.71	0.0058	0.0035	0.0019	0.0059	-0.0156
0.1421	0.3668	153.46	0.0072	0.0064	0.0056	0.0072	-0.0113
0.2293	0.4948	175.50	0.0022	0.0026	0.0027	0.0022	-0.0057
0.2933	0.5660	190.29	0.0006	0.0011	0.0014	0.0005	-0.0010
0.3488	0.6174	202.24	0.0006	0.0010	0.0013	0.0006	0.0029
0.4059	0.6646	213.31	0.0003	0.0004	0.0006	0.0003	0.0047
0.5017	0.7347	231.24	-0.0008	-0.0012	-0.0014	-0.0008	0.0038
0.5660	0.7744	243.93	0.0009	0.0003	-0.0000	0.0009	0.0039
0.6231	0.8075	253.78	0.0021	0.0015	0.0011	0.0021	0.0028
0.6791	0.8386	263.63	0.0027	0.0023	0.0020	0.0027	0.0008
0.7456	0.8738	275.72	0.0034	0.0033	0.0031	0.0034	-0.0016
0.8060	0.9071	287.21	0.0011	0.0013	0.0013	0.0010	-0.0062
0.8708	0.9370	297.48	0.0030	0.0035	0.0037	0.0030	-0.0052
0.9319	0.9673	308.54	0.0016	0.0021	0.0024	0.0016	-0.0050
<i>Mean</i>			<i>0.0023</i>	<i>0.0022</i>	<i>0.0021</i>	<i>0.0023</i>	<i>0.0050</i>

Equation	Order	A_{12}	A_{21}	D_{12}
Van Laar	3	0.1750	0.1057	—
Margules	3	0.1630	0.0944	—
Margules	4	0.1556	0.0858	-0.0239
Wilson	2	0.4956	1.2978	—
Alpha	2	2.4952	-0.3993	—

TABLE XXI
Vapour-Liquid Equilibrium in the Methyl Ethyl Ketone(1)-Toluene(2) System at 65°C

Experimental values			Deviation in vapour phase composition				
<i>x</i>	<i>y</i>	<i>P</i> , Torr	Laar 3	Marg. 3	Marg. 4	Wils. 2	Alpha 2
0.0575	0.1842	193.60	0.0068	0.0038	0.0034	0.0069	-0.0164
0.1441	0.3641	228.31	0.0063	0.0052	0.0051	0.0063	-0.0136
0.2303	0.4879	259.20	0.0019	0.0024	0.0024	0.0019	-0.0068
0.2933	0.5559	278.24	0.0020	0.0028	0.0029	0.0020	-0.0001
0.3470	0.6075	294.54	0.0005	0.0011	0.0012	0.0005	0.0023
0.4024	0.6541	309.88	0.0001	0.0003	0.0004	0.0001	0.0041
0.4646	0.7015	327.19	-0.0005	-0.0006	-0.0006	-0.0005	0.0043
0.5017	0.7268	336.88	0.0002	-0.0001	-0.0002	0.0002	0.0046
0.5652	0.7682	354.53	0.0006	0.0000	-0.0000	0.0006	0.0033
0.6231	0.8044	369.63	0.0001	-0.0005	-0.0006	0.0001	0.0003
0.6799	0.8341	383.90	0.0035	0.0030	0.0030	0.0035	0.0010
0.7441	0.8694	399.24	0.0037	0.0036	0.0036	0.0037	-0.0018
0.8060	0.9035	414.02	0.0023	0.0026	0.0026	0.0023	-0.0055
0.8708	0.9363	431.77	0.0022	0.0028	0.0028	0.0022	-0.0064
0.9312	0.9658	446.09	0.0020	0.0026	0.0027	0.0020	-0.0049
<i>Mean</i>			<i>0.0022</i>	<i>0.0021</i>	<i>0.0021</i>	<i>0.0022</i>	<i>0.0050</i>

Equation	Order	A_{12}	A_{21}	D_{12}
Van Laar	3	0.1812	0.1024	—
Margules	3	0.1650	0.0890	—
Margules	4	0.1634	0.0872	-0.0051
Wilson	2	0.4637	1.3504	—
Alpha	2	2.3680	-0.3866	—

TABLE XXII

Vapour-Liquid Equilibrium in the Methyl Ethyl Ketone(1)-Toluene(2) System at 75°C

Experimental values			Deviation in vapour phase composition				
<i>x</i>	<i>y</i>	<i>P</i> , Torr	Laar 3	Marg. 3	Marg. 4	Wils. 2	Alpha 2
0.0575	0.1747	438.03	0.0097	0.0068	0.0067	0.0097	-0.0119
0.1450	0.3560	327.75	0.0068	0.0059	0.0058	0.0068	-0.0120
0.2284	0.4759	369.03	0.0029	0.0034	0.0034	0.0029	-0.0059
0.2942	0.5500	399.45	0.0008	0.0016	0.0016	0.0008	-0.0015
0.3479	0.5993	421.30	0.0022	0.0028	0.0028	0.0022	0.0035
0.4024	0.6484	443.67	-0.0008	-0.0005	-0.0005	-0.0008	0.0027
0.4629	0.6935	465.10	0.0006	0.0005	0.0005	0.0006	0.0047
0.5017	0.7221	480.80	-0.0002	-0.0006	-0.0006	-0.0002	0.0035
0.5668	0.7659	504.29	-0.0004	-0.0010	-0.0010	-0.0004	0.0016
0.6215	0.7968	523.80	0.0030	0.0025	0.0024	0.0030	0.0029
0.6799	0.8295	543.11	0.0051	0.0046	0.0046	0.0051	0.0023
0.7441	0.8716	568.98	-0.0008	-0.0009	-0.0009	-0.0008	-0.0064
0.8060	0.9013	588.61	0.0028	0.0030	0.0030	0.0028	-0.0049
0.8716	0.9319	611.12	0.0059	0.0065	0.0065	0.0059	-0.0025
0.9319	0.9651	631.44	0.0025	0.0031	0.0031	0.0025	-0.0042
<i>Mean</i>			0.0030	0.0029	0.0029	0.0030	0.0047

Equation	Order	A_{12}	A_{21}	D_{12}
Van Laar	3	0.1727	0.0977	—
Margules	3	0.1572	0.0850	—
Margules	4	0.1568	0.0845	-0.0015
Wilson	2	0.4700	1.3569	—
Alpha	2	2.2449	-0.3851	—

TABLE XXIII
Vapour-Liquid Equilibrium in the Methyl Ethyl Ketone(1)-Ethylbenzene(2) System at 55°C

Experimental values			Deviation in vapour phase composition				
<i>x</i>	<i>y</i>	<i>P</i> , Torr	Laar 3	Marg. 3	Marg. 4	Wils. 2	Alpha 2
0.0691	0.4218	50.80	0.0068	0.0065	0.0030	0.0069	-0.0125
0.0940	0.5097	69.10	-0.0038	-0.0039	-0.0062	-0.0037	-0.0199
0.1183	0.5570	88.19	0.0072	0.0072	0.0060	0.0073	-0.0055
0.1791	0.6655	108.79	0.0006	0.0007	0.0012	0.0006	-0.0044
0.2393	0.7303	128.58	0.0019	0.0020	0.0030	0.0019	0.0021
0.3175	0.7915	150.51	0.0002	0.0001	0.0008	0.0001	0.0040
0.4164	0.8451	178.01	-0.0009	-0.0011	-0.0012	-0.0009	0.0037
0.5115	0.8803	202.40	0.0014	0.0011	0.0003	0.0014	0.0044
0.5881	0.9037	220.79	0.0027	0.0024	0.0014	0.0027	0.0032
0.6759	0.9280	241.87	0.0026	0.0025	0.0016	0.0026	-0.0003
0.7553	0.9467	259.36	0.0033	0.0032	0.0028	0.0033	-0.0028
0.8176	0.9606	274.31	0.0033	0.0033	0.0033	0.0033	-0.0049
0.8917	0.9762	292.93	0.0031	0.0031	0.0035	0.0030	-0.0061
0.9441	0.9885	305.63	0.0010	0.0011	0.0015	0.0010	-0.0066
<i>Mean</i>			0.0028	0.0027	0.0026	0.0028	0.0057

Equation	Order	A_{12}	A_{21}	D_{12}
Van Laar	3	0.1687	0.1291	—
Margules	3	0.1670	0.1241	—
Margules	4	0.1525	0.0974	-0.0715
Wilson	2	0.6268	1.0776	—
Alpha	2	8.5582	-0.5723	—

TABLE XXIV
Vapour-Liquid Equilibrium in the Methyl Ethyl Ketone(1)-Ethylbenzene(2) System at 65°C

Experimental values			Deviation in vapour phase composition				
x	y	P, Torr	Laar 3	Marg. 3	Marg. 4	Wils. 2	Alpha 2
0.0221	0.1697	79.84	0.0106	0.0105	0.0058	0.0107	-0.0042
0.0353	0.2592	87.87	0.0011	0.0010	-0.0043	0.0012	-0.0169
0.0529	0.3404	97.65	0.0053	0.0052	0.0004	0.0054	-0.0138
0.0714	0.4109	107.17	0.0061	0.0061	0.0021	0.0061	-0.0121
0.1172	0.5399	132.17	0.0025	0.0026	0.0013	0.0025	-0.0104
0.1801	0.6479	161.68	0.0023	0.0024	0.0032	0.0023	-0.0032
0.2383	0.7142	187.87	0.0021	0.0021	0.0034	0.0020	0.0014
0.3175	0.7791	221.18	0.0001	-0.0000	0.0009	0.0001	0.0030
0.4127	0.8325	259.08	0.0001	-0.0002	-0.0004	0.0001	0.0040
0.5097	0.8721	294.01	0.0011	0.0008	-0.0004	0.0011	0.0034
0.5881	0.8964	321.38	0.0035	0.0033	0.0018	0.0036	0.0034
0.6751	0.9222	350.63	0.0032	0.0031	0.0018	0.0033	-0.0002
0.7530	0.9416	376.40	0.0041	0.0040	0.0034	0.0041	-0.0025
0.8183	0.9562	398.52	0.0051	0.0051	0.0051	0.0051	-0.0037
0.8924	0.9744	423.72	0.0034	0.0034	0.0040	0.0033	-0.0062
0.9454	0.9879	443.49	0.0010	0.0011	0.0016	0.0010	-0.0067
<i>Mean</i>			<i>0.0032</i>	<i>0.0032</i>	<i>0.0025</i>	<i>0.0032</i>	<i>0.0059</i>

Equation	Order	A_{12}	A_{21}	D_{12}
Van Laar	3	0.1652	0.1312	—
Margules	3	0.1646	0.1266	—
Margules	4	0.1467	0.0912	-0.0932
Wilson	2	0.6533	1.0443	—
Alpha	2	7.8433	-0.5568	—

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TABLE XXV
Vapour-Liquid Equilibrium in the Methyl Ethyl Ketone(1)-Ethylbenzene(2) System at 75°C

Experimental values			Deviation in vapour phase composition				
x	y	P, Torr	Laar 3	Marg. 3	Marg. 4	Wils. 2	Alpha 2
0.0221	0.1591	119.79	0.0141	0.0132	0.0137	0.0143	-0.0044
0.0353	0.2493	134.68	0.0013	0.0003	0.0008	0.0015	-0.0216
0.0552	0.3280	145.46	0.0154	0.0144	0.0149	0.0155	-0.0094
0.0714	0.4018	160.60	0.0018	0.0010	0.0014	0.0019	-0.0223
0.1812	0.6333	234.66	0.0032	0.0033	0.0032	0.0031	-0.0057
0.2383	0.7002	271.80	0.0015	0.0018	0.0017	0.0015	-0.0013
0.3137	0.7605	313.90	0.0031	0.0032	0.0031	0.0031	0.0049
0.4109	0.8190	367.54	0.0017	0.0017	0.0017	0.0018	0.0054
0.5080	0.8625	416.80	0.0012	0.0010	0.0011	0.0013	0.0036
0.5856	0.8904	454.51	0.0016	0.0014	0.0015	0.0016	0.0015
0.6703	0.9156	495.78	0.0031	0.0030	0.0031	0.0032	-0.0004
0.7523	0.9384	532.94	0.0033	0.0032	0.0033	0.0033	-0.0037
0.8176	0.9537	563.67	0.0047	0.0048	0.0048	0.0047	-0.0044
0.8911	0.9693	599.23	0.0067	0.0068	0.0067	0.0067	-0.0033
0.9460	0.9818	626.76	0.0066	0.0066	0.0066	0.0065	-0.0013
<i>Mean</i>			0.0046	0.0044	0.0045	0.0047	0.0062

Equation	Order	A_{12}	A_{21}	D_{12}
Van Laar	3	0.1755	0.1271	—
Margules	3	0.1718	0.1217	—
Margules	4	0.1737	0.1251	0.0091
Wilson	2	0.5885	1.1247	—
Alpha	2	7.1555	-0.5476	—

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