Vapor-Liquid Equilibria

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Vapor-liquid equilibrium data are reported for the carbon tetrachloride, cyclohexane, propanol-2 system and for the ethanol, cyclohexane system at atmospheric pressure; and for the *n*-hexane, ethanol, benzene system at 55° F. The modified Gillespie still was used.

Part 1. System Carbon Tetrachloride-Cyclohexane-Propanol-2 at Atmospheric Pressure

BINARY AND TERNARY vapor-liquid equilibrium data at atmospheric pressure were determined for the mixtures of carbon tetrachloride, cyclohexane and propanol-2 using a modified Gillespie type of still.

Azeotropes were discovered for the binary systems: cyclohexane-propanol-2 and propanol-2-carbon tetrachloride and the ternary system.

The thermodynamic consistency of the binary systems was checked based on the Gibbs-Duhem equation. The three-constant for the binary systems and the thirteen-constant for the ternary system of the Redlich-Kister (*16*) equations were found to represent the systems.

MATERIALS

Carbon tetrachloride, cyclohexane and propanol-2 of the spectroquality of Matheson Coleman and Bell were used. The refractive indices and normal boiling points of these liquids were determined, and the comparisons of these values with the accepted ones (*5, 18*) are listed in Table I.

APPARATUS

A modified Gillespie still (Figure 1) was used in the equilibrium determination. In addition to the modifications suggested by Fowler and Norris (*6*), the following improvements were made in this investigation:

1. A vacuum-sealed double jacket glass thermowell was used for the thermocouple junction to obtain better temperature measurement.
2. A double-jacket tube was used in the receiver to give better mixing.
3. The internal heater in the boiler was placed through the bottom instead of on the top to avoid formation of air bubbles around the opening.

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The still was made of Pyrex glass. The boiler was heated both externally and internally with electric heating elements controlled separately. The Cottrell tube and the equilibrium chamber were insulated with asbestos and raw silk.

The equilibrium temperature was measured by means of a Leeds and Northrup K-3 potentiometer with a Tinsley SRI galvanometer, using a copper-constantan thermocouple. The cold junction of the thermocouple was immersed in an ice-water bath in a Dewar flask. In the thermowell a few drops of Silicone 704 of Dow Corning Silicones Ltd. was added to provide a good contact for the lead of the thermocouple. The accuracy of the temperature measurement was $\pm 0.02°$ C.

PROCEDURE

The still was dried with filtered air and rinsed with one of the pure components of the mixture to be used. It was then filled with the mixture. Approximately 450 ml. mixture was charged to the still. The distillation was continued for 4–5 hours for each run. Ethanol-water system was used to test the performance of the still and the accuracy of temperature measurement. Equilibrium data measured at atmospheric pressure agreed very well with the results of Otsuki and Williams (*13*). Analyses of the binary mixtures were made with a Bausch and Lomb Abbe-3L precision refractometer at 25° C. The scale can be estimated to 0.0001 which gives an accuracy of analysis of compositions of ± 0.002 mole fraction.

Density and refractive index were used to analyze the ternary compositions. Density was measured in a pycnometer with a Gram-atic balance which could be read to 0.1 mg. Refractive index was taken at 25° C. and density was determined at the temperature of the cooled samples. For calibration purpose, charts of log d *vs.* temperature using composition as parameter was prepared. It was found that log d varies linearly with temperature in the tempera-

Table I. Physical Properties of the Chemicals

	Normal Boiling Point ° C.		Refractive Index, 25° C.	
	Exptl.	Lit.	Exptl.	Lit.
Carbon tetrachloride	76.61	76.75(*18*)	1.4570	1.45704(*5*)
Cyclohexane	80.70	80.74(*5*)	1.4235	1.42354(*5*)
Propanol-2	82.01	82.19(*5*)	1.3750	1.3749(*5*)

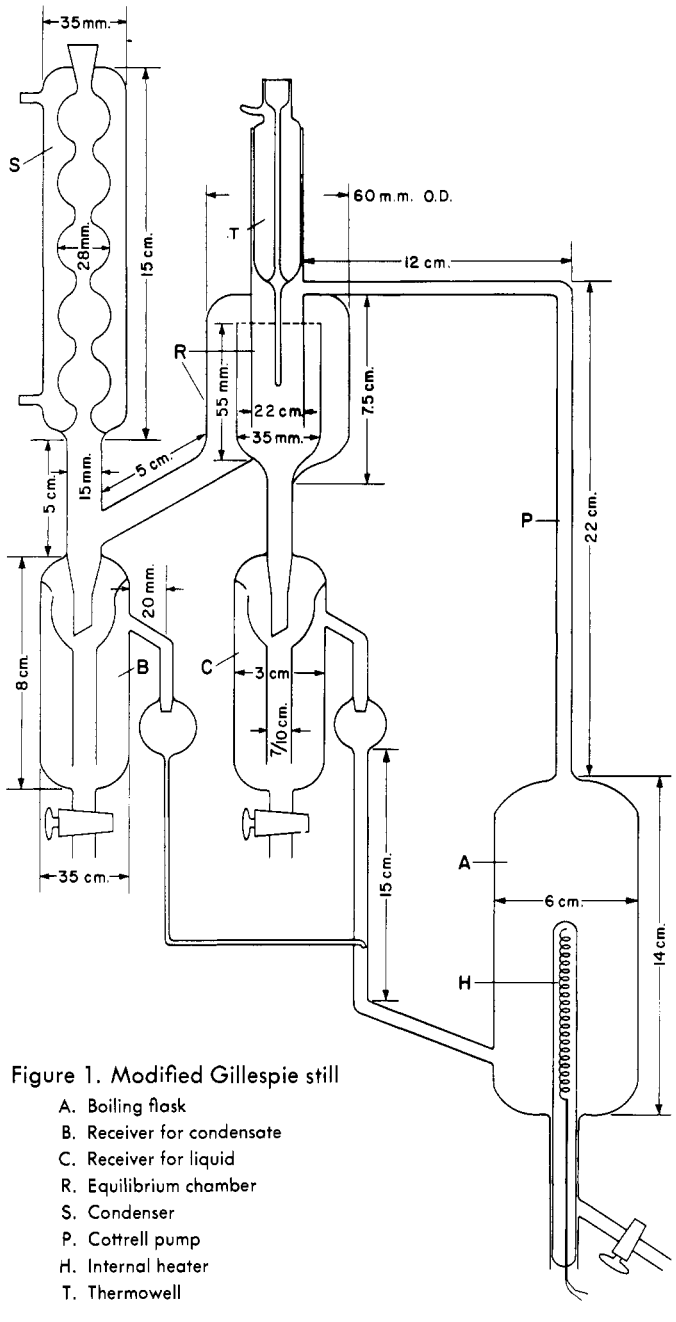

Figure 1. Modified Gillespie still

A. Boiling flask
B. Receiver for condensate
C. Receiver for liquid
R. Equilibrium chamber
S. Condenser
P. Cottrell pump
H. Internal heater
T. Thermowell

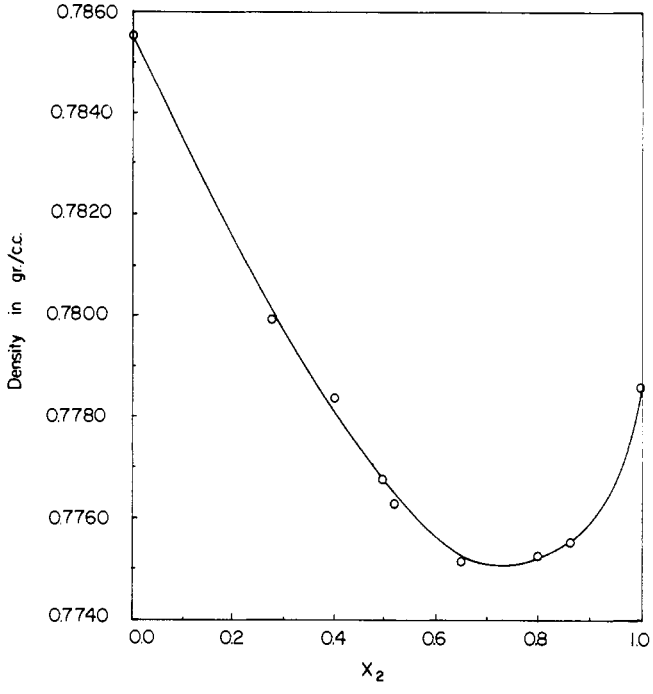

Figure 2. Density diagram of the mixture: cyclohexane(2)-propanol-2(3)

ture range at which densities were determined. This linear relationship makes analyses simpler and easier.

Although densities for binary systems were not used for calibration purposes, it is of interest to note that a minimum exists for the system cyclohexane-propanol-2 as shown in Figure 2.

The experiment was conducted under atmospheric pressure at approximately 760 mm. of Hg. The correction to be made for the equilibrium temperature at a pressure of 760 mm. of Hg was calculated according to the Craft's Rule.

$$\Delta T = 0.0001\ (760 - P)\ T \qquad (1)$$

EQUILIBRIUM DATA

The experimental t–x–y data for the three binary systems are presented in Table II and in Figures 3, 4 and 5. For the system cyclohexane-propanol-2, an azeotrope containing 59.2 mole % of cyclohexane with a boiling point of 68.80° C. was found. The reported literature values (2) are 59.25 mole % cyclohexane and 68.6° C., respectively. For the system propanol-2-carbon tetrachloride, an azeotrope containing 64.0 mole % of carbon tetrachloride with a boiling point of 68.65° C. was found. The reported literature values are 64.02 mole % carbon tetrachloride and 68.95° C., respectively.

Data for the ternary system are presented in Table III. It is believed that a ridge of the t–x and t–y surfaces exists as indicated by the dotted line in Figure 6 connecting the two minimum binary azeotropes. Along this line and within the experimental error, the equilibrium vapor compositions are identical with the liquid compositions. Further investigation is being carried out to study the behavior of the ridge at different conditions.

Calculation of log γ. The following equation was used to evaluate the liquid activity coefficient, γ

$$\log \gamma_i = \log \frac{y_i P}{x_i p_i} + \frac{(P - p_i)(\beta_i - v_i)}{2.303\ RT} \qquad (2)$$

The values of vapor pressures of the pure components used in the calculation were taken from charts prepared using literature values (15, 17).

The second virial coefficient of carbon tetrachloride was calculated according to the equation given by Black (3). Those for cyclohexane and propanol-2 were taken from literature (3, 7).

The liquid molal volume was calculated by Lindersen Greenkorn and Hougen's method (11).

The experimental γ values for the binary systems are listed in Table II and for the ternary system, in Table III.

Correlation of Data. Redlich and Kister (16) developed an expression for the function Q as a power series of $(x_1 - x_2)$ for the binary system

$$Q = x_1 \log \gamma_1 + x_2 \log \gamma_2$$

$$Q = x_1 x_2[B_{12} + C_{12}\ (x_1 - x_2) + D_{12}\ (x_1 - x_2)^2 + \ldots .] \qquad (3)$$

Table II. Experimental Data for the Binary Systems at 760 mm. of Hg Pressures

Carbon tetrachloride(*1*)-cyclohexane(2)

t °C.	x_1	y_1	γ_1	γ_2
80.34	0.045	0.068	1.430	0.9886
79.60	0.124	0.155	1.161	0.9986
79.66	0.134	0.163	1.128	0.9993
79.17	0.201	0.230	1.073	1.012
78.88	0.256	0.273	1.033	1.031
79.10	0.201	0.220	1.107	1.028
76.74	0.791	0.805	1.015	1.053
77.06	0.675	0.693	1.019	1.052
77.07	0.685	0.696	1.007	1.074
77.40	0.579	0.600	1.015	1.048
77.53	0.540	0.569	1.030	1.028
77.63	0.519	0.545	1.024	1.035
78.06	0.412	0.436	1.021	1.039
78.46	0.314	0.345	1.050	1.022
78.80	0.260	0.285	1.039	1.024
79.25	0.198	0.230	1.087	1.005
79.54	0.146	0.171	1.088	1.009
79.73	0.113	0.135	1.106	1.006
78.07	0.404	0.427	1.019	1.041

Cyclohexane(2)-propanol-2(*3*)

t °C.	x_2	y_2	γ_2	γ_3
69.35	0.473	0.555	1.652	1.420
69.37	0.442	0.550	1.751	1.355
69.01	0.538	0.582	1.539	1.542
69.10	0.708	0.627	1.257	2.169
69.45	0.784	0.660	1.181	2.639
69.20	0.516	0.570	1.562	1.503
68.80	0.528	0.583	1.581	1.520
69.21	0.631	0.605	1.355	1.809
69.42	0.742	0.649	1.229	2.287
69.66	0.807	0.673	1.163	2.840
70.11	0.862	0.697	1.112	3.669
71.50	0.921	0.773	1.105	4.436
74.01	0.990	0.838	1.033	22.56
76.73	0.995	0.893	1.009	13.89
74.96	0.116	0.283	2.892	1.086
74.80	0.120	0.276	2.730	1.111
72.28	0.191	0.271	2.498	1.160
70.19	0.306	0.489	2.192	1.198
69.11	0.518	0.568	1.558	1.511
69.14	0.516	0.572	1.571	1.499
69.02	0.485	0.548	1.607	1.495
69.08	0.571	0.582	1.447	1.654
69.06	0.640	0.595	1.321	1.911
74.74	0.978	0.850	1.037	9.208
70.31	0.873	0.709	1.110	3.704
78.71	0.027	0.112	4.399	1.055
76.91	0.070	0.218	3.483	1.040

Propanol-2(*3*)-carbon tetrachloride(*1*)

t °C.	x_3	y_3	γ_3	γ_1
79.15	0.942	0.862	1.038	2.227
75.71	0.896	0.717	1.039	2.810
74.90	0.862	0.690	1.074	2.367
71.62	0.764	0.562	1.144	2.157
69.28	0.153	0.258	2.842	1.094
69.00	0.211	0.292	2.362	1.130
68.75	0.307	0.371	1.609	1.323
69.15	0.578	0.416	1.222	1.744
71.78	0.775	0.567	1.114	2.226
70.12	0.683	0.503	1.201	1.908
70.63	0.711	0.527	1.182	2.109
70.51	0.706	0.517	1.175	1.978
72.54	0.810	0.601	1.083	2.374
74.27	0.860	0.604	1.111	2.350
69.54	0.657	0.500	1.269	1.813
71.40	0.054	0.158	4.526	1.039
74.79	0.011	0.060	7.347	1.004
78.85	0.056	0.854	0.888	3.131
77.96	0.041	0.817	1.035	2.976
74.48	0.868	0.604	1.091	2.474
73.71	0.842	0.655	1.095	2.393
70.87	0.720	0.537	1.179	1.969
69.70	0.623	0.469	1.224	1.722
68.86	0.488	0.411	1.444	1.455
68.46	0.506	0.412	1.421	1.523
68.31	0.413	0.381	1.622	1.355
68.56	0.339	0.359	1.887	1.238
68.76	0.319	0.351	1.897	1.208
68.91	0.259	0.330	2.184	1.141
68.88	0.242	0.325	2.303	1.125
69.08	0.211	0.305	2.447	1.107
69.28	0.176	0.289	2.757	1.068
69.59	0.146	0.265	3.014	1.065
69.43	0.538	0.442	1.373	1.504
68.90	0.258	0.332	2.202	1.138

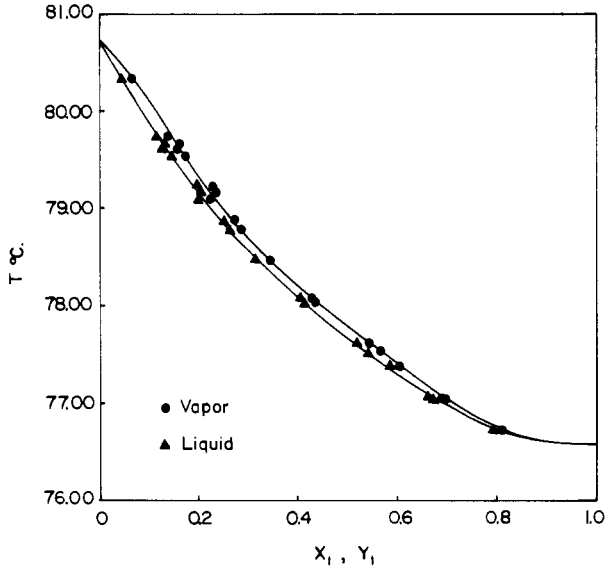

Figure 3. Temperature-composition diagram for the system: carbon tetrachloride (*1*)-cyclohexane(2) at 760 mm. of Hg

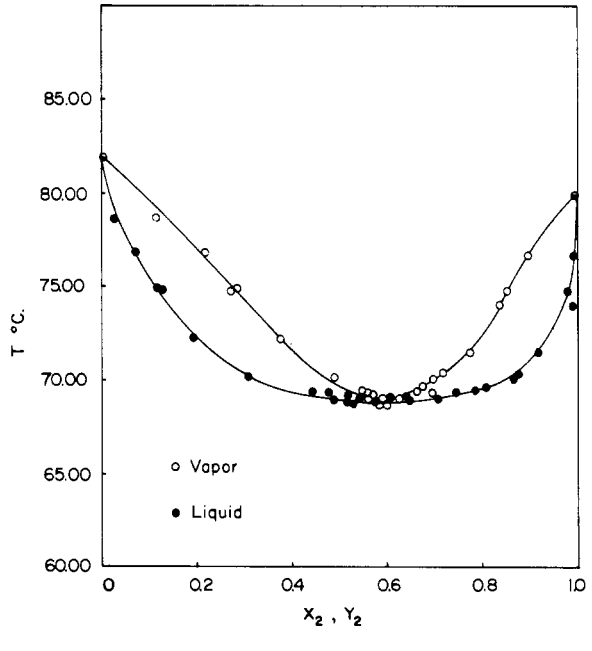

Figure 4. Temperature-composition diagram for the system: cyclohexane(2)-propanol-2(3) at 760 mm. of Hg

Table III. Experimental Data of the System Carbon Tetrachloride (1) Cyclohexane(2) and Propanol -2(3)

Equilibrium Temperature in ° C.	Liquid Composition Mole Fraction		Vapor Composition Mole Fraction						
	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3	$Q_{exptl.}$	$Q_{calcd.}$
70.17	0.118	0.224	0.155	0.376	1.597	2.274	1.160	0.1462	0.1442
69.28	0.202	0.219	0.273	0.294	1.687	1.892	1.258	0.1642	0.1629
68.82	0.326	0.154	0.389	0.198	1.510	1.841	1.366	0.1695	0.1673
68.55	0.473	0.135	0.502	0.139	1.352	1.485	1.591	0.1641	0.1654
68.45	0.567	0.118	0.563	0.111	1.271	1.361	1.802	0.1552	0.1521
68.80	0.730	0.055	0.672	0.013	1.165	3.384	2.525	0.1641	0.1147
70.10	0.875	0.032	0.763	0.037	1.061	1.592	3.512	0.0796	0.0586
69.10	0.119	0.367	0.147	0.428	1.552	1.655	1.404	0.1786	0.1702
68.40	0.387	0.223	0.413	0.233	1.367	1.515	1.587	0.1709	0.1757
68.44	0.406	0.163	0.338	0.337	1.065	2.992	1.316	0.1401	0.1711
68.45	0.483	0.172	0.480	0.172	1.273	1.447	1.869	0.1664	0.1648
68.60	0.622	0.145	0.577	0.132	1.182	1.312	2.165	0.1403	0.1346
69.00	0.757	0.103	0.661	0.086	1.016	1.190	3.081	0.0816	0.0913
72.90	0.952	0.022	0.893	0.021	1.115	1.203	4.923	0.0401	0.0184
68.80	0.117	0.447	0.133	0.485	1.439	1.553	1.514	0.1824	0.1734
68.60	0.222	0.379	0.229	0.403	1.314	1.533	1.598	0.1778	0.1797
68.50	0.351	0.320	0.344	0.309	1.252	1.395	1.836	0.1673	0.1741
68.62	0.489	0.240	0.451	0.215	1.175	1.289	2.773	0.1504	0.1568
68.84	0.617	0.192	0.551	0.165	1.130	1.230	2.551	0.1277	0.1247
71.50	0.884	0.058	0.801	0.063	1.058	1.431	3.607	0.0629	0.0415
68.60	0.253	0.473	0.231	0.441	1.158	1.343	2.062	0.1627	0.1635
68.60	0.380	0.394	0.343	0.346	1.150	1.265	2.385	0.1486	0.1514
68.40	0.481	0.179	0.477	0.195	1.271	1.579	1.687	0.1627	0.1649
68.30	0.630	0.241	0.560	0.201	1.143	1.213	3.255	0.1229	0.0993
69.00	0.725	0.090	0.586	0.252	1.017	3.986	1.493	0.0916	0.1093
72.30	0.893	0.068	0.827	0.066	1.054	1.246	4.084	0.0509	0.0303
69.10	0.133	0.667	0.126	0.557	1.190	1.185	2.690	0.1450	0.1302
69.10	0.356	0.399	0.224	0.486	0.790	1.728	2.005	0.0630	0.1575
69.40	0.397	0.472	0.345	0.388	1.081	1.155	3.416	0.1129	0.1099
69.60	0.524	0.379	0.457	0.292	1.079	1.076	4.305	0.0907	0.0872
71.60	0.770	0.179	0.699	0.163	1.055	1.189	4.155	0.0030	0.0045
72.16	0.889	0.077	0.848	0.078	1.096	1.306	3.267	0.0618	0.0276
72.69	0.100	0.055	0.183	0.240	2.058	5.535	1.004	0.0745	0.0774
70.19	0.088	0.322	0.240	0.336	3.314	1.431	1.191	0.1408	0.1575
69.31	0.330	0.100	0.520	0.000	1.970	0.987	1.418	0.1831	0.1560
68.73	0.463	0.075	0.540	0.090	1.482	1.722	1.373	0.1604	0.1592
68.43	0.585	0.075	0.601	0.063	1.316	1.214	1.731	0.1571	0.1493
70.69	0.242	0.721	0.201	0.630	1.005	1.181	7.275	0.0845	0.0425
70.87	0.393	0.557	0.340	0.510	1.029	1.227	4.739	0.0883	0.0554
71.64	0.514	0.452	0.480	0.353	1.085	1.023	7.506	0.2178	0.0417
72.40	0.645	0.326	0.600	0.267	1.056	1.048	6.908	0.1058	0.0350
69.49	0.250	0.057	0.313	0.234	1.554	5.754	1.091	0.1173	0.1277
69.11	0.335	0.116	0.431	0.190	1.616	2.324	1.173	0.1503	0.1604
68.59	0.465	0.118	0.525	0.124	1.441	1.514	1.464	0.1639	0.1647
69.21	0.196	0.294	0.274	0.320	1.751	1.539	1.347	0.1686	0.1742
68.67	0.351	0.215	0.396	0.230	1.435	1.538	1.494	0.1709	0.1761
68.25	0.448	0.027	0.488	0.171	1.372	0.108	1.148	0.0919	0.1489
68.65	0.224	0.371	0.257	0.381	1.460	1.478	1.550	0.1769	0.1799
68.54	0.361	0.284	0.367	0.288	1.298	1.464	1.694	0.1691	0.1760
68.45	0.493	0.230	0.470	0.220	1.222	1.386	1.958	0.1562	0.1575
69.02	0.251	0.429	0.248	0.397	1.245	1.315	1.622	0.1421	0.1731
68.66	0.381	0.365	0.352	0.327	1.178	1.289	2.193	0.1539	0.1594
68.78	0.503	0.291	0.482	0.196	1.216	9.649	2.696	0.4179	0.1395
69.03	0.235	0.575	0.245	0.437	1.311	1.080	2.854	0.1335	0.1348
69.16	0.383	0.436	0.350	0.363	1.146	1.179	2.686	0.1315	0.1345
69.29	0.514	0.350	0.458	0.281	1.111	1.131	3.236	0.1116	0.1097
69.97	0.201	0.738	0.210	0.550	1.277	1.029	6.439	0.0798	0.0590
70.28	0.410	0.540	0.358	0.426	1.042	1.079	6.992	0.0674	0.0554
70.79	0.530	0.458	0.465	0.340	1.047	1.000	2.577	0.0155	0.0224
71.18	0.080	0.220	0.164	0.316	2.415	1.872	1.160	0.1356	0.1314
74.45	0.130	0.000	0.251	0.055	2.062	66.00	1.090	0.0733	...
71.85	0.100	0.259	0.334	0.169	3.858	8.482	3.831	0.0658	0.1478

Using Equation 3 and the Gibbs-Duhem equation, they proposed the useful relationship

$$\int_{x_1=0}^{x_1=1} \log \frac{\gamma_1}{\gamma_2}\, dx_1 = 0 \qquad (4)$$

which is valid for the conditions of constant temperature and pressure. At constant pressure, the exact expression for testing data consistency is as follows (9)

$$\int_{x_1=0}^{x_1=1} \log \frac{\gamma_1}{\gamma_2}\, dx_1 = -\int_{T_0 \text{ at } x_1=0}^{T_1 \text{ at } x_1=1} \frac{\Delta H^M}{RT^2}\, dT \qquad (5)$$

where ΔH^M is the heat of mixing of the two components at the temperature, pressure and compositions of the mixture.

The term of the left hand side of Equation 5 is evaluated by measuring the area under the curve log $[(\gamma_1)/(\gamma_2)]$ *vs.* x_1 from $x_1 = 0$ to $x_1 = 1$ using experimental values. For all the three binary systems, the measured net area under the curve was found to be less than 0.0004. The term of the right hand side may be evaluated graphically, provided ΔH^M is available as a function of composition and at the temperature and pressure in question. In this investigation, the right hand term was estimated approximately by

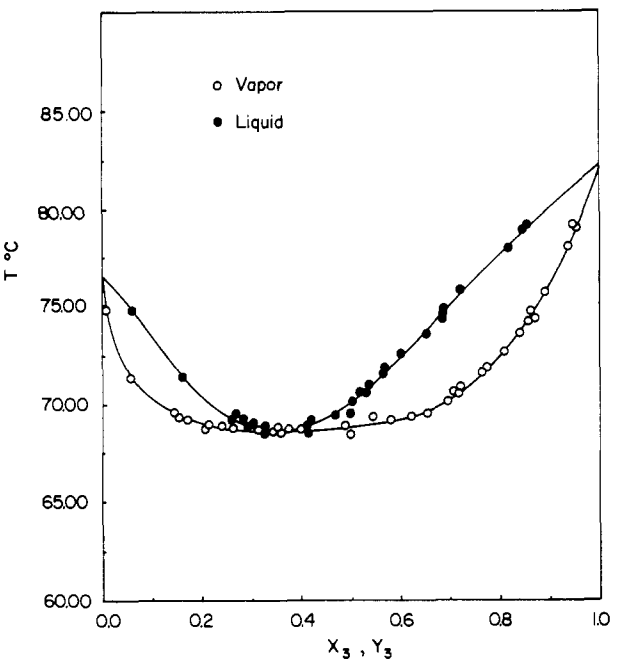

Figure 5. Temperature composition diagram for the system: propanol-2(3)-carbon tetrachloride(1) at 760 mm. of Hg

assuming ΔH^M independent of temperature and using ΔH^M values available in the literature (*8, 10*) at 40° C. It was found that the numerical value of the term was less than 0.0013 for all the three binary systems. This suggests the applicability of the Redlich-Kister equation for the systems of the present investigation.

The three-constant Redlich-Kister equation was used to represent the data of the binary systems. The constants were determined with the characteristic points on the log $[(\gamma_i)/(\gamma_j)]$ *vs.* x_i curve as suggested by Redlich and Kister (*16*). The values of the constants obtained are listed in Table IV. The calculated log $[(\gamma_1)/(\gamma_j)]$ curves as a function of x_i for the three binary systems, using the obtained constants, are compared with the experimental values as shown in Figures 7, 8 and 9.

By analogy to the binary system, Redlich-Kister (*16*) proposed the following equation for the ternary system.

$$Q_{123} = Q_{12} + Q_{23} + Q_{31} + x_1x_2x_3 [C + D_1 (x_2 - x_3) + D_2 (x_3 - x_1) + D_3 (x_1 - x_2) + \dots .]$$

where

$$Q_{12} = x_1 x_2 [B_{12} + C_{12} (x_1 - x_2) + D_{12} (x_1 - x_2)^2 + \dots .]$$

$$Q_{23} = x_2 x_3 [B_{23} + C_{23} (x_2 - x_3) + D_{23} (x_2 - x_3)^2 + \dots .]$$

$$Q_{31} = x_3 x_1 [B_{31} + C_{31} (x_3 - x_1) + D_{31} (x_3 - x_1)^2 + \dots .] \quad (6)$$

Table IV. Constants of Redlich-Kister Equation for the System Carbon Tetrachloride(1)-Cyclohexane(2)-Propanol-2(3) at 1 Atm.

Binary constants

$B_{12} = 0.0460$	$C_{12} = -0.0120$	$D_{12} = 0.0203$
$B_{23} = 0.6200$	$C_{23} = 0.0780$	$D_{23} = 0.0440$
$B_{31} = 0.5780$	$C_{31} = -0.0480$	$D_{31} = 0.0440$

Ternary constants

$C = 0.9980$
$D_1 = 1.3636$
$D_2 = 0.6561$
$D_3 = 0.9362$

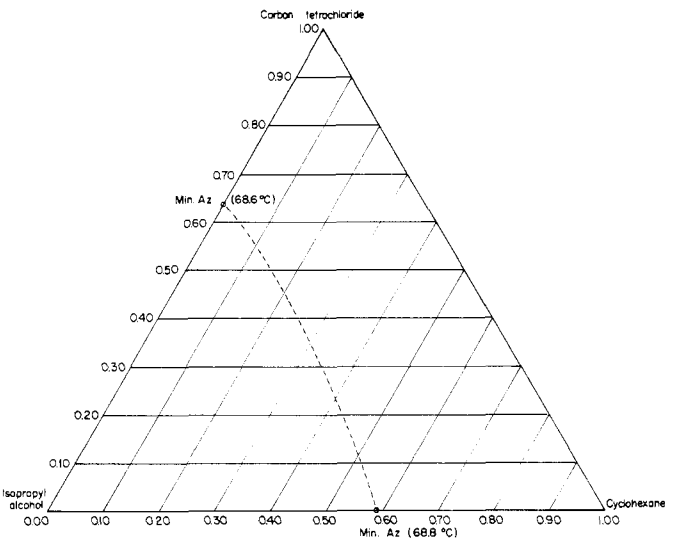

Figure 6. Ridge of the *t–x* and *t–y* surfaces, as indicated by the dotted line of the ternary system carbon tetrachloride-cyclohexane-propanol-2 at 1 atm.

In this investigation, four ternary constants were used in addition to the nine binary constants. The ternary constants were calculated with IBM least square programming. The constants thus determined are listed in Table IV. The calculated Q values for the ternary systems are compared with experimental values in Table III. Good agreement is obtained.

Vapor-liquid equilibrium data for the binary systems carbon tetrachloride-cyclohexane and propanol-2-carbon tetrachloride are available in the literature.

For the system carbon tetrachloride-cyclohexane, Scatchard, Wood and Mochel (*17*) measured the equilibrium data at 40° and 70° C., and Brown and Ewald (*4*), at 70° C. Good agreement was obtained by these authors. The data of Scatchard *et al.* were extrapolated to isobaric condition at atmospheric pressure by assuming linear relationships for log P *vs.* $1/T$ plot at constant compositions. The extrapolated values were compared with the experimental values obtained in this investigation and reasonable agreement was found. Norrish and Twigg (*12*) determined the equilibrium compositions, but not the temperature, for this system at atmospheric pressure. Their data agree well with the results of the present investigation.

Papousĕk, Papoŭskovã and Pãgo (*14*) measured the equilibrium data for the system propanol-2-carbon tetrachloride at 70° C. The total pressure range covered in their investigation was from 579.6 mm. of Hg to 675.1 mm. of Hg. Their data taken at 760 mm. of Hg are compared with the results obtained in this study at 70° C. and 760 mm. of Hg as follows.

	x_1	y_1	x_1	y_1
Papousĕk's	0.360	0.547	0.898	0.800
Present investigation	0.330	0.500	0.885	0.785

Some discrepancies are observed.

Part II. System *n*-Hexane-Ethanol-Benzene at 55° C.

Binary and ternary vapor-liquid equilibrium data at 55° C. were determined for the mixtures of *n*-hexane,

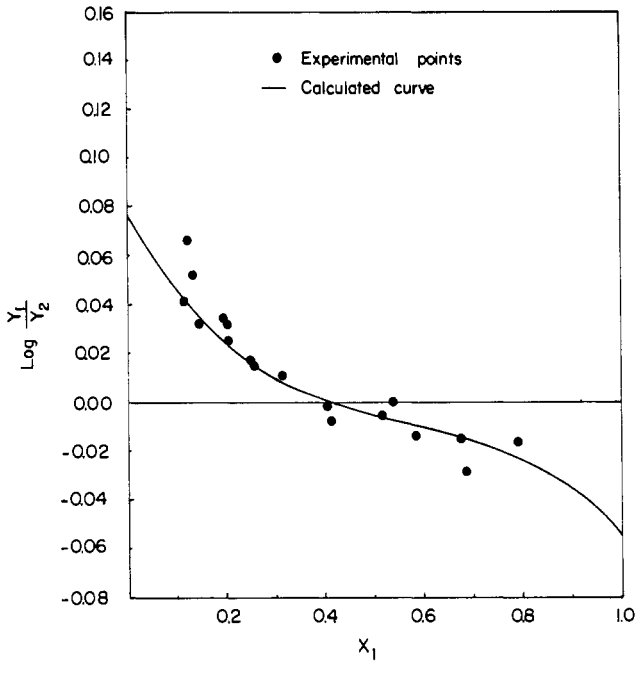

Figure 7. Log $[(\gamma_1)/(\gamma_2)]$ vs. composition diagram for the system: carbon tetrachloride(1)-cyclohexane(2) at 760 mm. of Hg

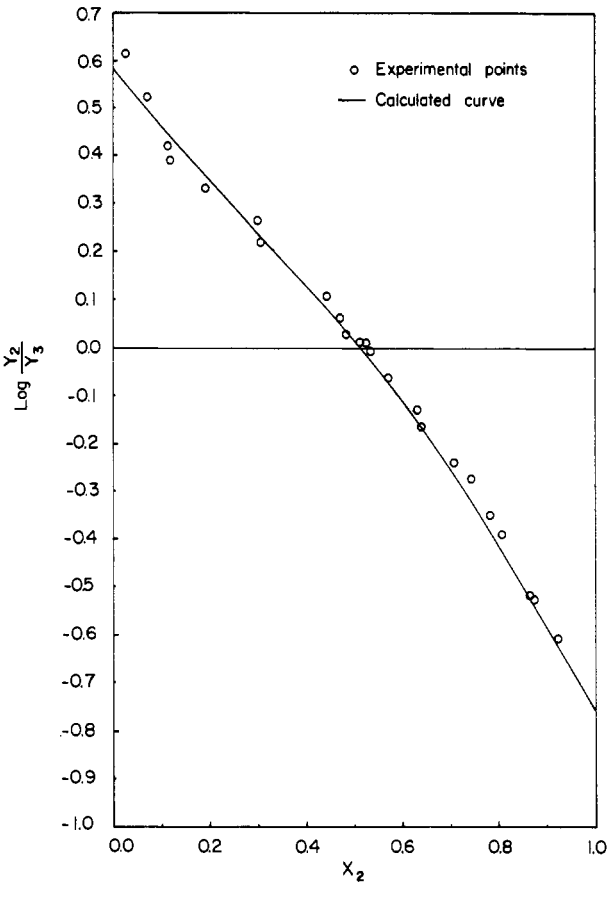

Figure 8. Log $[(\gamma_2)/(\gamma_3)]$ vs. composition diagram for the system: cyclohexane(2)-propanol-2(3) at 760 mm. of Hg

ethanol and benzene, using a modified Gillespie still. Azeotropes were found for the binary systems *n*-hexane-ethanol and ethanol-benzene. Although the ternary system departs considerably from ideal liquid phase behavior, no ternary azeotrope was detected. The thermodynamic consistency of the data was checked by fitting the data with the Redlich-Kister equations (*16*).

EXPERIMENTAL

Purity of Compounds. The spectro grade *n*-hexane and benzene used in this study were supplied by the Matheson, Coleman and Bell Co. The absolute ethanol was supplied by the Canadian Industrial Alcohols and Chemicals Ltd. All the chemicals were used without further purification, and their physical properties are listed in Table V.

Table V. Physical Properties of the Chemicals

	Normal Boiling Point ° C.		Refractive Index 25° C.	
	Exptl.	Lit.	Exptl.	Lit
n-Hexane	68.71	68.74(*1*)	1.3722	1.37226(*1*)
Ethanol	78.34	78.33(*5*)	1.3591	1.35914(*5*)
Benzene	80.05	80.103(*5*)	1.4977	1.49790(*5*)

Procedure. The modified Gillespie still used in this study has been described above. The experimental technique outlined was followed. The temperature was controlled at 55 ± 0.2° C. by adjusting the total pressure of the still. A vacuum system connected to the vapor condenser line was employed to regulate the total pressure. Temperatures were measured by a copper-constantan thermocouple used with a micro-step potentiometer of the Cambridge Instrument Co. Ltd. The thermocouple was calibrated in a stirred bath by comparing with a standard resistance thermometer. The reference junction was held at 0° C. The uncertainty of the calibration was 0.02° C. The error in the temperature measurements is believed to be accurate within ±0.05° C. Analyses of the binary samples for the systems ethanol-benzene and *n*-hexane-benzene were made with a Bausch and Lomb Abbe–3L precision refractometer at 25° C. The scale could be estimated to 0.0001. Therefore, the error in the reported composition is estimated to be ±0.2 mole %. Analyses of the samples for the binary mixture *n*-hexane-ethanol and the ternary system were made with a Perkin-Elmer Model 154-C Vapor Fractometer. Calibrations and determination of unknowns were carried out using two 2-meter "R" columns with helium as the carrier gas. The Vapor Fractometer was operated at 100° C., 25 p.s.i.g. column pressure and a bridge voltage of 8 volts. Under these conditions and a helium flow rate of 152 cc. per minute, an analysis of a ternary sample could be completed in 15 minutes. The peaks were well spaced and completely separated. The retention times for the three components in the column were in the following order: *n*-hexane, ethanol and benzene. Numerous known samples were used for the calibration purpose. The calibration method was similar to that of Wagner and Weber (*19*). The average deviation obtained was less than ±0.5 mole %, and the error in the reported composition is of the same order of magnitude.

VAPOR-LIQUID EQUILIBRIUM DATA

Binary Systems. The experimental total pressure-composition data for the three binary systems are presented in Tables VI, VII and VIII and in Figures 10, 11 and 12.

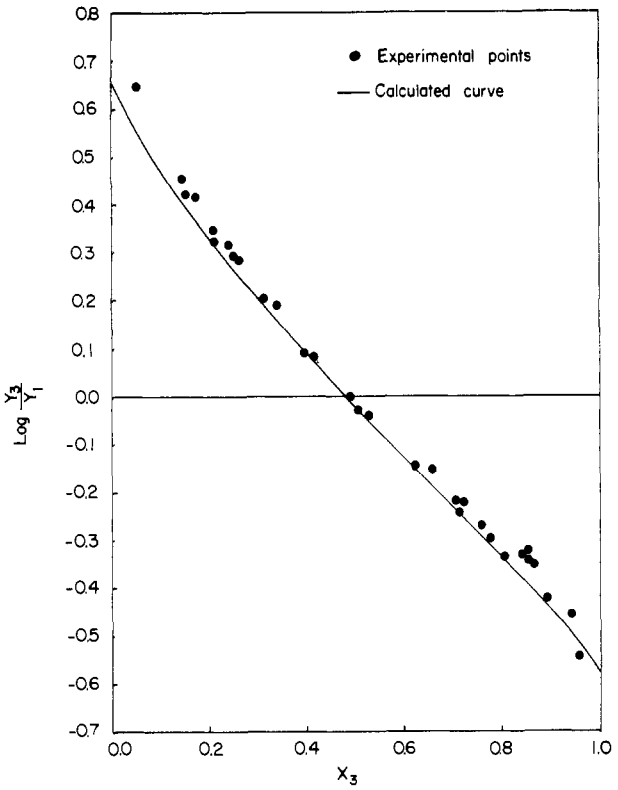

Figure 9. Log $[(\gamma_3)/(\gamma_1)]$ *vs.* composition diagram for the system: propanol-2(3)-carbon tetrachloride(1) at 760 mm. of Hg

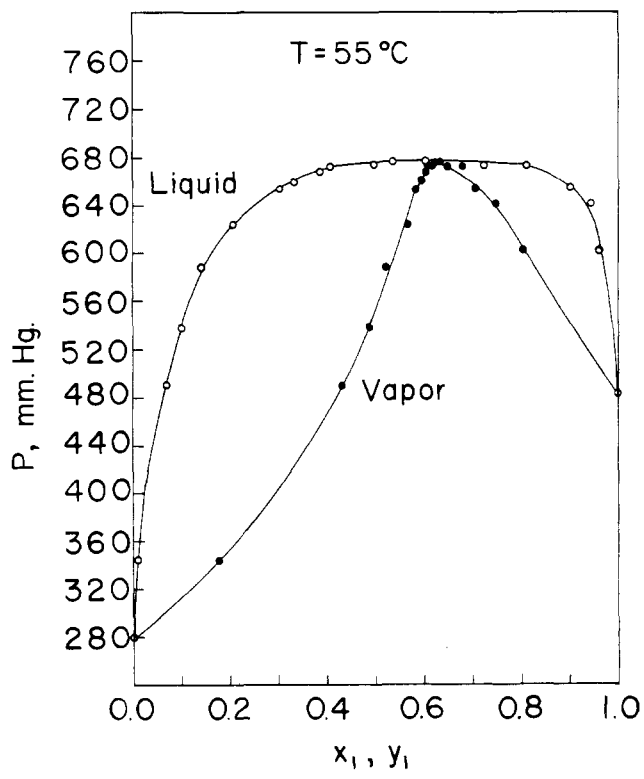

Figure 10. Total pressure-composition diagram for the system *n*-hexane(1)-ethanol(2) at 55° C.

Table VI. Equilibrium Data for the System *n*-Hexane(1)-Ethanol(2)

Temp., ° C.	Total Pressure mm. of Hg	x_1	y_1	γ_1	γ_2
55.26	345.3	0.011	0.178	11.55	1.01
55.20	491.2	0.070	0.431	6.19	1.05
55.14	538.5	0.100	0.487	5.38	1.07
55.14	588.4	0.141	0.520	4.40	1.13
55.15	624.0	0.206	0.568	3.50	1.17
55.05	654.4	0.303	0.583	2.57	1.35
55.07	660.3	0.332	0.595	2.41	1.38
55.10	668.4	0.387	0.606	2.13	1.48
55.22	673.2	0.409	0.609	2.03	1.52
55.10	674.5	0.498	0.621	1.71	1.75
55.10	676.5	0.537	0.622	1.59	1.90
55.14	676.7	0.603	0.635	1.45	2.13
55.14	674.6	0.724	0.650	1.23	2.93
55.22	673.5	0.810	0.682	1.15	3.85
54.90	654.9	0.900	0.704	1.05	6.78
55.10	640.5	0.943	0.746	1.03	9.55
55.25	602.0	0.961	0.802	1.02	10.48

Table VII. Equilibrium Data for the System Benzene(3)-*n*-Hexane(1)

Temp., ° C.	Total Pressure mm. of Hg	x_3	y_3	γ_1	γ_3
55.08	486.0	0.123	0.117	1.01	1.40
55.02	485.1	0.230	0.214	1.02	1.37
55.10	480.0	0.294	0.265	1.03	1.31
55.02	470.5	0.400	0.341	1.07	1.22
55.03	468.0	0.427	0.364	1.07	1.21
54.92	458.0	0.505	0.419	1.12	1.16
55.26	445.2	0.625	0.511	1.20	1.10
54.98	425.0	0.727	0.595	1.31	1.06
55.12	409.7	0.794	0.656	1.42	1.03
55.22	402.5	0.824	0.694	1.45	1.02
55.20	401.4	0.829	0.700	1.46	1.03
55.14	383.9	0.882	0.773	1.53	1.02
55.25	371.9	0.915	0.822	1.61	1.01
55.07	371.6	0.914	0.816	1.65	1.01

Equation 2 was used to evaluate the liquid activity coefficient, γ. The calculated log γ values were fitted by means of the 3-constant Redlich-Kister equation (Equation 3). The constants obtained for the three binaries are listed in Table IX. The calculated log γ values agree with the experimental values as shown in Figures 13, 14 and 15, and the data are therefore considered thermodynamically consistent.

Binary azeotropes were found for two systems. At 55.0° C., an azeotrope containing 64.0 mole % of *n*-hexane was obtained for the system *n*-hexane-ethanol at a total pressure of 674 mm. of Hg, and for the system ethanol-benzene, an azeotrope containing 40.8 mole % ethanol was obtained at a total pressure of 468 mm. of Hg.

Ternary System. The experimental equilibrium data for the ternary system are presented in Table X. They were correlated by the Redlich-Kister equation (Equation 6).

The ternary constants C, D_1, D_2 and D_3 of Equation 6 were obtained by the least square method using an IBM 650 computer. The evaluated constants are listed in Table IX. The calculated Q_{123} values are compared with the experimental values in Table X. Good agreement is obtained.

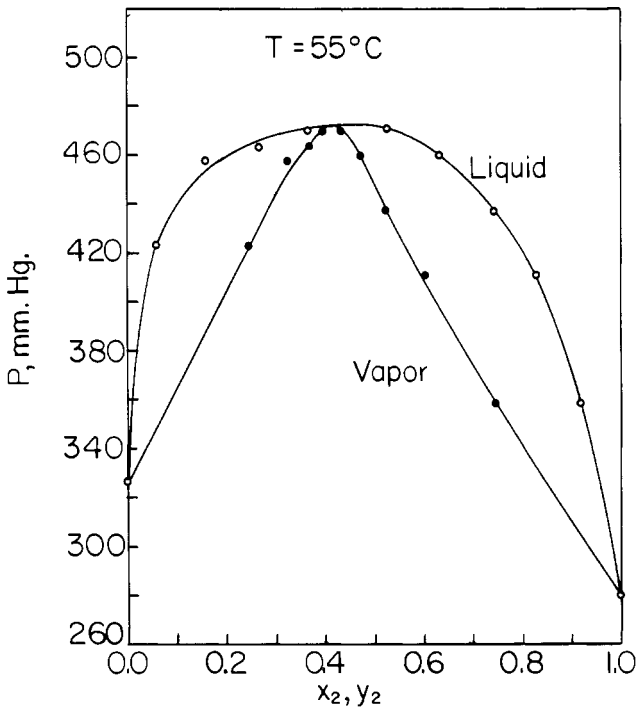

Figure 11. Total pressure-composition diagram for the system ethanol(2)-benzene(3) at 55° C.

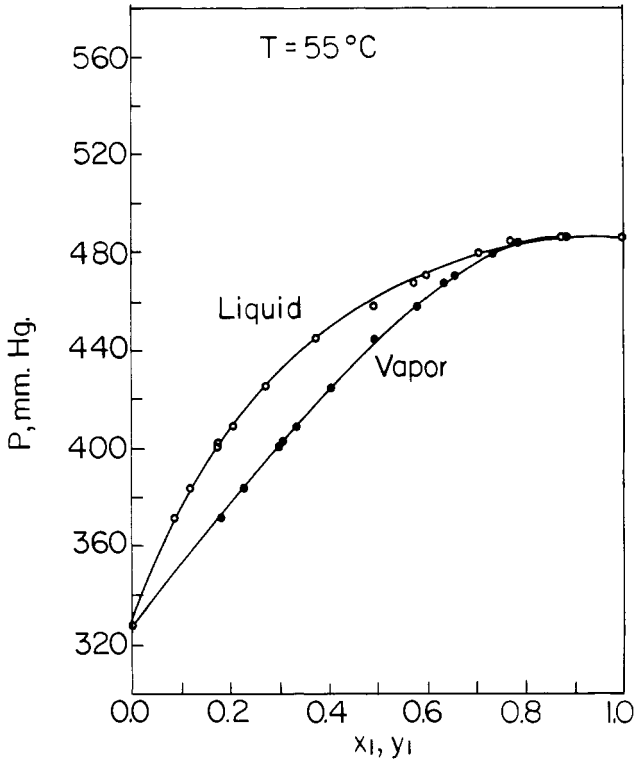

Figure 12. Total pressure-composition diagram for the system benzene(3)-*n*-hexane(1) at 55° C.

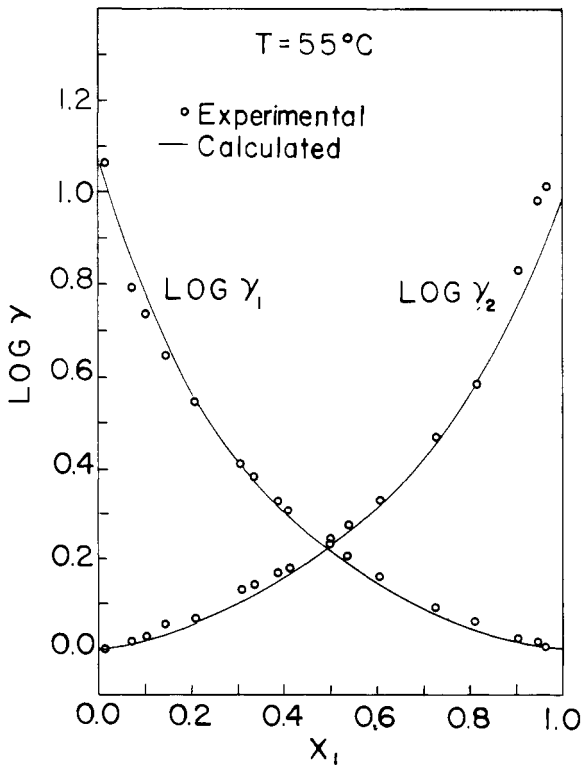

Figure 13. Activity coefficient-composition curves for the system *n*-hexane(1)-ethanol(2) at 55° C.

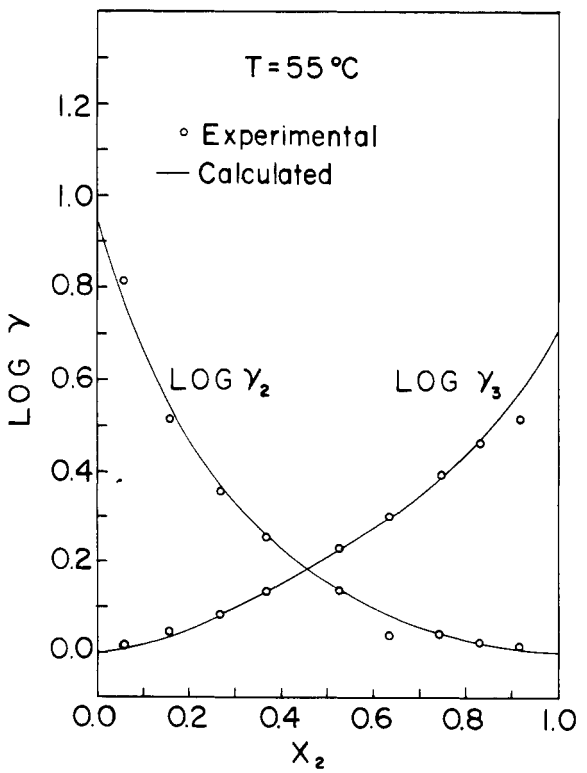

Figure 14. Activity coefficient-composition curves for the system ethanol(2)-benzene(3) at 55° C.

Table VIII. Equilibrium Data for the System Ethanol(2)-Benzene(3)

Temp., °C.	Total Pressure mm. of Hg	x_2	y_2	γ_2	γ_3
54.95	422.8	0.057	0.246	6.44	1.03
55.18	457.9	0.159	0.326	3.27	1.11
55.00	463.9	0.266	0.369	2.26	1.21
55.10	470.0	0.367	0.398	1.78	1.35
55.18	471.0	0.526	0.434	1.35	1.69
55.10	460.0	0.632	0.472	1.08	2.00
54.88	437.4	0.743	0.523	1.09	2.48
55.08	411.6	0.830	0.602	1.05	2.92
55.15	358.8	0.916	0.747	1.03	3.29

Table IX. Constants of Redlich-Kister Equation for the System *n*-Hexane(1)-Ethanol(2)-Benzene(3) at 55° C.

Binary constants

$B_{12} = 0.900$	$C_{12} = -0.020$	$D_{12} = 0.160$
$B_{23} = 0.720$	$C_{23} = -0.120$	$D_{23} = 0.109$
$B_{31} = 0.228$	$C_{31} = 0.033$	$D_{31} = 0.016$

Ternary constants

$C = 0.760$
$D_1 = 0.176$
$D_2 = -0.133$
$D_3 = -0.053$

Table XI. Vapour-liquid Equilibrium Data for the System Ethanol(1)-Cyclohexane(2) at 760 mm. of Hg

Temperature, °C.	x_1	y_1	γ_1	γ_2
73.99	0.020	0.175	10.36	1.03
69.08	0.030	0.302	14.55	1.03
66.94	0.065	0.358	8.64	1.04
66.08	0.081	0.363	7.27	1.08
66.37	0.086	0.365	6.97	1.07
65.59	0.125	0.388	5.16	1.11
65.23	0.151	0.396	4.41	1.14
65.12	0.206	0.408	3.34	1.20
64.93	0.258	0.415	2.75	1.28
64.87	0.283	0.418	2.53	1.32
64.84	0.315	0.426	2.32	1.35
64.78	0.366	0.430	2.02	1.47
64.77	0.403	0.431	1.84	1.55
64.77	0.431	0.431	1.72	1.63
64.78	0.444	0.438	1.70	1.64
64.81	0.500	0.443	1.52	1.81
64.88	0.557	0.455	1.40	1.99
65.01	0.613	0.460	1.28	2.25
64.99	0.621	0.458	1.25	2.32
65.25	0.678	0.475	1.18	2.61
65.56	0.738	0.505	1.14	2.99
66.03	0.763	0.496	1.06	3.25
65.93	0.776	0.515	1.09	3.20
66.40	0.781	0.498	1.02	3.48
66.90	0.809	0.545	1.06	3.62
67.26	0.833	0.578	1.08	3.79
67.98	0.853	0.595	1.05	4.03
68.86	0.881	0.623	1.03	4.54
69.44	0.898	0.653	1.03	4.75
70.11	0.909	0.678	1.03	4.79
71.42	0.929	0.725	1.02	5.09
72.48	0.951	0.778	1.02	5.84

Table X. Equilibrium Data for the Ternary System *n*-Hexane(1)-Ethanol(2)-Benzene(3)

Temp., °C.	Total Pressure mm. of Hg	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3	$Q_{123(\text{expt.})}$	$Q_{123(\text{calcd.})}$
55.05	601.1	0.895	0.042	0.737	0.219	1.01	10.76	1.28	0.056	0.054
55.10	562.7	0.738	0.026	0.657	0.156	1.03	11.91	1.34	0.066	0.064
55.25	503.2	0.473	0.015	0.523	0.092	1.14	10.42	1.14	0.071	0.071
54.73	657.5	0.758	0.186	0.631	0.324	1.13	4.01	1.61	0.163	0.156
54.92	648.0	0.718	0.145	0.609	0.300	1.13	4.65	1.30	0.149	0.145
55.00	632.9	0.625	0.143	0.532	0.295	1.10	4.51	1.42	0.155	0.159
55.16	621.9	0.587	0.117	0.480	0.280	1.04	5.11	1.50	0.145	0.143
54.95	580.7	0.437	0.079	0.416	0.272	1.14	7.01	1.13	0.116	0.121
55.00	656.5	0.637	0.233	0.594	0.323	1.25	3.15	1.27	0.191	0.192
54.95	640.0	0.561	0.213	0.514	0.325	1.20	3.38	1.38	0.189	0.193
55.05	599.3	0.400	0.138	0.418	0.273	1.28	4.11	1.20	0.165	0.159
55.00	554.1	0.314	0.099	0.323	0.253	1.17	4.91	1.20	0.138	0.131
55.00	438.9	0.118	0.014	0.205	0.143	1.59	15.71	1.00	0.041	0.040
55.13	663.6	0.546	0.338	0.558	0.346	1.40	2.34	1.63	0.225	0.226
55.00	637.6	0.460	0.271	0.476	0.330	1.35	2.68	1.38	0.214	0.219
54.98	609.7	0.381	0.207	0.416	0.303	1.37	3.09	1.25	0.194	0.194
55.05	538.2	0.223	0.104	0.270	0.266	1.34	4.79	1.00	0.099	0.125
55.16	669.9	0.443	0.535	0.594	0.381	1.82	1.64	2.24	0.237	0.229
54.98	661.4	0.396	0.528	0.553	0.367	1.89	1.59	2.07	0.240	0.238
55.22	646.4	0.335	0.487	0.500	0.341	1.95	1.55	1.73	0.232	0.246
55.10	629.9	0.299	0.461	0.437	0.350	1.88	1.65	1.68	0.236	0.246
55.08	608.0	0.272	0.372	0.369	0.349	1.69	1.97	1.44	0.228	0.236
55.20	579.9	0.227	0.281	0.230	0.375	1.20	2.67	1.39	0.209	0.209
54.85	548.5	0.168	0.201	0.237	0.315	1.60	3.02	1.18	0.176	0.174
55.10	506.4	0.105	0.119	0.170	0.306	1.69	4.53	1.03	0.113	0.116
54.95	411.8	0.046	0.038	0.081	0.189	1.52	7.27	1.00	0.044	0.045
54.94	635.7	0.253	0.633	0.465	0.403	2.40	1.40	2.21	0.229	0.222
55.14	612.0	0.224	0.523	0.378	0.373	2.11	1.51	1.80	0.230	0.237
55.16	585.0	0.183	0.434	0.310	0.371	2.03	1.73	1.46	0.222	0.231
55.18	524.5	0.107	0.234	0.164	0.338	1.64	2.62	1.19	0.171	0.173
55.15	618.7	0.196	0.694	0.435	0.429	2.81	1.32	2.29	0.210	0.200
55.05	601.0	0.174	0.630	0.372	0.406	2.64	1.34	2.05	0.214	0.214
55.05	558.5	0.116	0.459	0.238	0.385	2.36	1.63	1.49	0.214	0.218
55.08	530.0	0.089	0.345	0.158	0.367	1.94	1.97	1.34	0.198	0.199
55.10	471.0	0.040	0.141	0.068	0.306	1.67	3.59	1.09	0.116	0.114
55.05	560.1	0.095	0.843	0.371	0.437	4.52	1.01	5.11	0.110	0.123
55.16	548.4	0.087	0.793	0.338	0.477	4.37	1.14	2.54	0.150	0.144
54.73	541.4	0.083	0.726	0.270	0.444	3.64	1.17	2.49	0.171	0.168
55.00	540.9	0.074	0.640	0.201	0.441	3.04	1.30	2.04	0.197	0.188
54.98	517.8	0.059	0.526	0.145	0.399	2.66	1.37	1.72	0.194	0.199
55.10	406.4	0.030	0.928	0.198	0.677	5.57	1.04	3.66	0.063	0.058
54.96	470.5	0.028	0.759	0.124	0.525	4.40	1.14	2.35	0.139	0.138
54.80	483.5	0.023	0.548	0.061	0.447	2.65	1.40	1.69	0.188	0.185

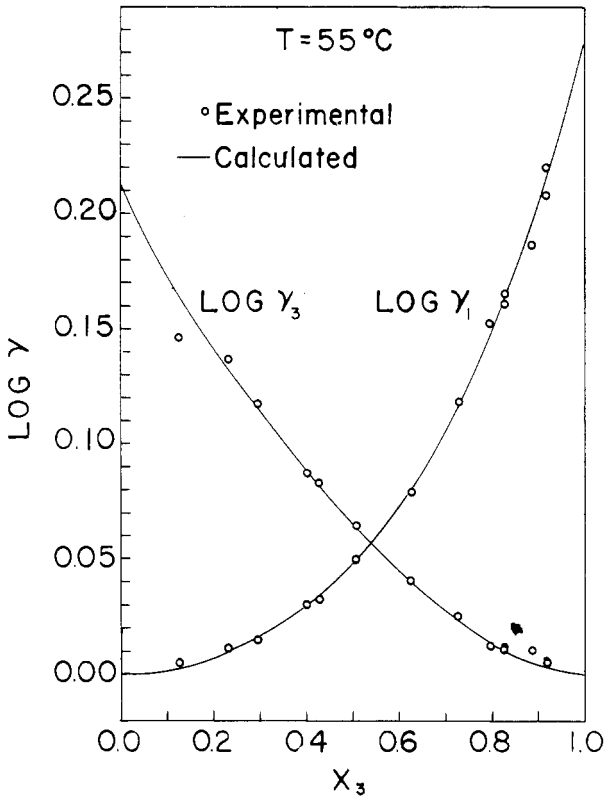

Figure 15. Activity coefficient-composition curves for the system benzene(3)-*n*-hexane(1) at 55° C.

Part III. System Ethanol-Cyclohexane at Atmospheric Pressure

Vapor-liquid equilibrium data for the ethanol-cyclohexane system were determined at atmospheric pressure using a modified Gillespie still. Equilibrium data for this system are only available in the literature at 25° C. (*20*). The boiling temperature range of the system was 16° C. at atmospheric pressure, and the binary azeotrope composition was determined as 0.431 mole fraction ethanol at 64.8° C. The thermodynamic consistency of the data was checked by fitting the data with a three-constant Redlich-Kister equation (*16*).

EXPERIMENTAL

The physical properties of the spectro grade cyclohexane and the absolute ethanol used in this study are listed above in Tables I and V.

The modified Gillespie still and the experimental technique used in this study have been described above. Analyses of the samples were made with a Bausch and Lomb Abbe-3L precision refractometer at 25° C. The error in the reported composition is estimated to be ±0.2 mole % and in the reported temperature, ±0.05° C.

EQUILIBRIUM DATA

The experimental temperature-composition data for the system are presented in Table XI and in Figure 16. A binary azeotrope was found at 64.8° C. containing 43.1 mole % ethanol. This is somewhat different from the value (44.6 mole % ethanol at 64.9° C.) compiled by Horsley (*2*). The experimental liquid activity coefficients for the components were calculated using Equation 2. The boiling

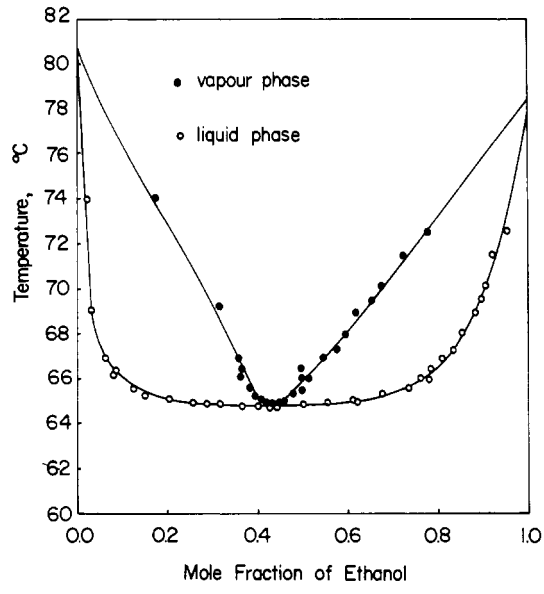

Figure 16. Temperature-composition diagram for the system ethanol(1)-cyclohexane(2) at 760 mm. of Hg

temperature range of this system was about 16° C., and over the concentration range from $x_1 = 0.05$ to $x_1 = 0.95$, 8° C. Therefore, the temperature effect on liquid activity coefficient was neglected and the calculated log γ values were fitted by means of a three-constant Redlich-Kister equation (Equation 3). The constants were determined from a log $[(\gamma_1)/(\gamma_2)]$ *vs.* x_1 plot (Figure 17) and the values obtained are as follows:

$$B_{12} = 0.880$$
$$C_{12} = -0.170$$
$$D_{12} = 0.140$$

The calculated log γ values agree with the experimental values as shown in Figure 18 and the data are considered thermodynamically consistent.

ACKNOWLEDGMENT

The authors are indebted to the National Research Council of Canada for financial support.

NOMENCLATURE

B_{12}, B_{23}, B_{31}		
C_{12}, C_{23}, C_{31}	=	binary constants of the Redlich-Kister equation
D_{12}, D_{23}, D_{31}		
C, D_1, D_2, D_3	=	ternary constants of the Redlich-Kister equation
ΔG^E	=	excess free energy
P	=	total pressure
p	=	vapor pressure of pure component at the equilibrium temperature of the system
$Q = \Delta G^E/2.303\,RT$	=	excess free energy function per mole
R	=	gas constant
T	=	absolute temperature
v	=	liquid molal volume of pure component
x	=	equilibrium mole fraction of component in liquid phase
y	=	equilibrium mole fraction of component in vapor phase
β	=	second virial coefficient of pure component in the vapor phase
γ	=	liquid phase activity coefficient

Subscripts

1, 2, 3, i	=	components

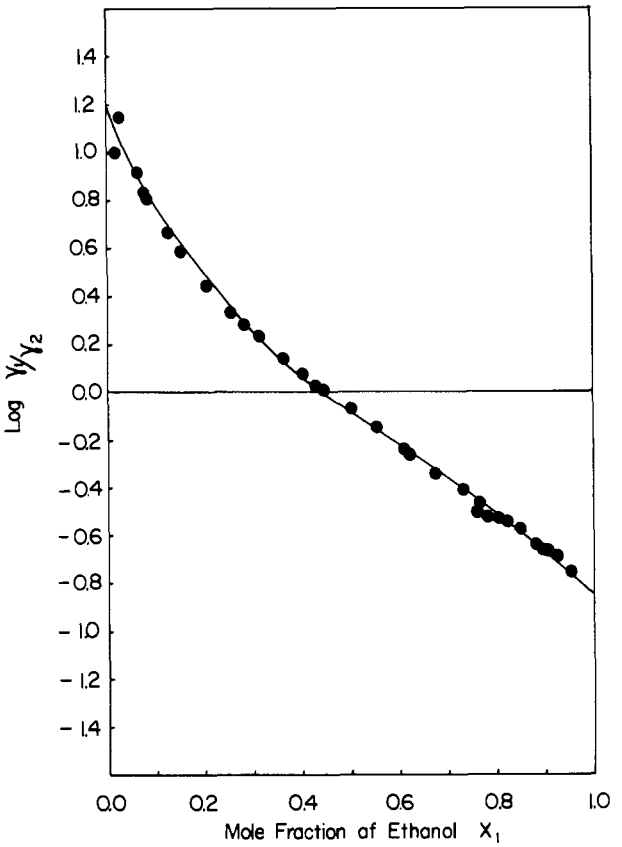

Figure 17. Log $[(\gamma_1)/(\gamma_2)]$ vs. x_1 plot for the system ethanol(1)-cyclohexane(2) at 760 mm. of Hg

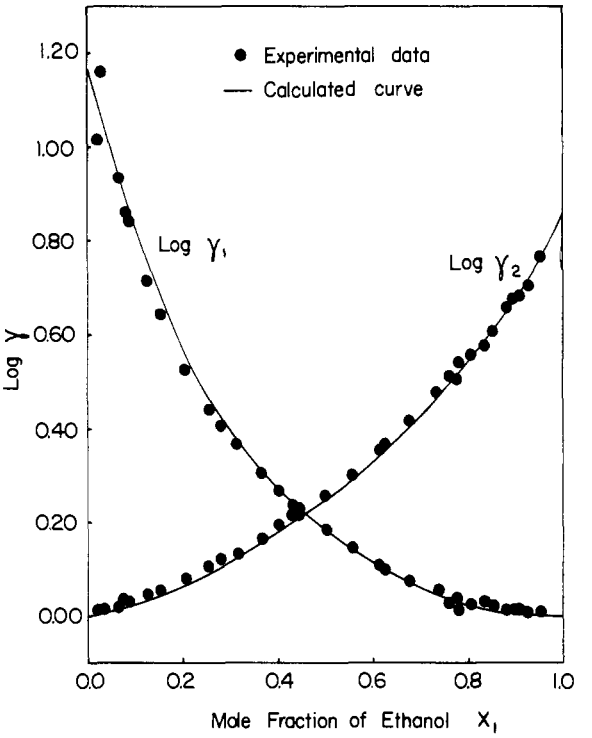

Figure 18. Liquid activity coefficient-composition curves for the system ethanol(1)-cyclohexane(2) at 760 mm. of Hg

LITERATURE CITED

(1) Am. Petrol. Inst. Research Project 44, Carnegie Inst. Technol. Pittsburgh, Pa., 1953.
(2) Azeotropic Data, Compiled by Horsley, L.H., *Advances in Chem. Series* **50**, 391 (1958).
(3) Black, C., *Ind. Eng. Chem.* **50**, 391 (1958).
(4) Brown, L., Eward, A.H., Austral. *J. Sci., Res.* **A 3**, 306 (1950).
(5) Dow Chem. Co., Physical Properties of Chemical Compounds, 1953.
(6) Fowler, R.T., Norris, G.S. *J. Appl. Chem.(London)* **5**, 266 (1955).
(7) Foz, O.R., Morcillo, J., Maria, A.P., Mendez, Y.A., *Anales real soc. expan. fis. y. quim. (Madrid)* **50 B**, 17 (1954).
(8) Goates, J.R., Sullivan, R.J., Ott, J.B., *J. Phys. Chem.* **63**, 589 (1959).
(9) Ibl, M., Dodge, B., *Chem. Eng. Science* **2**, 120 (1953).
(10) Jeun, S.K., Thesis, University of Ottawa, 1960.
(11) Lydersen, A.L., Greekorn, R.A., Hougen, O.A., "Generalized Thermodynamic Properties of Pure Fluids," University Wisconsin Eng. Exp. Station, Report 4, (1955).
(12) Norrish, R.S., Twigg, G.H., *Ind. Eng. Chem.* **46**, 201 (1954).
(13) Otsuki, H., Williams, C.F., *Chem. Eng. Progress Symp. Ser.* **49**, No. 6, 55 (1953).
(14) Papousek, D., Papouskova, Z., Pago, L., *Z. physik Chem.* **211**, 231 (1959).
(15) Parks, G.S., Barton, B., *J. Am. Chem. Soc.* **50**, 24 (1928).
(16) Redlich, O., Kister, A.T., *Ind. Eng. Chem.* **40**, 345 (1948).
(17) Scatchard, G., Wood, S.E., Mochel, J.W., *J. Am. Chem. Soc.* **61**, 3206 (1939).
(18) Timmermanns, J., "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publishing Co., 1950.
(19) Wagner, I.F., Weber, J.H., *Ind. Eng. Chem., Chem. Eng. Data Ser.* **3**, 220 (1958).
(20) Washburn, E.R., Handrof, B.H., *J. Am. Chem. Soc.* **57**, 441 (1935).
(21) Wohl, K., Trans. *A.I.Ch.E.* **42**, 215 (1946).

RECEIVED for review August 24, 1962. Accepted July 8, 1963.