Vapor-Liquid Equilibria for 23 Carbon Tetrachloride–Hydrocarbon Systems

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Binary vapor-liquid equilibrium data at 760 mm. of Hg pressure and density-composition data at 20° C. were determined for a series of 23 systems, each consisting of a hydrocarbon with carbon tetrachloride. The hydrocarbons employed were: *n*-hexane, *n*-heptane, *n*-octane, 1-hexene, 1-octene, 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane, 2,3-dimethylbutane, 2,4-dimethylpentane, 2,2,4-trimethylpentane, 2,2,5-trimethylhexane, cyclopentane, cyclohexane, cyclohexene, methylcyclopentane, methylcyclohexane, benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene, and *p*-xylene. Thermodynamic consistency tests were carried out, and all systems yielded smooth curves of $(y - x)$ plotted against x.

AS PART of an attempt to find a correlation-prediction method for the determination of vapor-liquid equilibrium data, isobaric equilibrium data at 1-atm. pressure were measured experimentally, using a modified Othmer still (*6*). Twenty-three systems are reported, each system being a binary comprised of a hydrocarbon and carbon tetrachloride. Density-composition data at 20° C. also were determined for each system and have been deposited with the ASIS.

MATERIALS

The carbon tetrachloride used was Matheson, Coleman, and Bell, ACS Analyzed Reagent Grade. All hydrocarbons used were Phillips Petroleum Co., Pure Grade. Table I lists the measured values of refractive index and density of the pure compounds, as well as comparisons of these values with data in the literature (*3, 4, 8*).

EXPERIMENTAL

Apparatus. Density-composition data for each system were determined by measuring the loss in weight of a plummet when immersed in a series of solutions of known compositions, all at a fixed temperature of 20° C. Each density was measured three times and the arithmetic average value recorded. Analysis of the possible sources of error—e.g., equilibrium between the liquid in the cylinder and vapor space above, and dissolving of water vapor in the solution—resulted in an estimated mean error in density of ±0.0002 gram per ml. In no case did densities vary by more than ±0.0004 gram per ml. from the average value reported.

The apparatus used for equilibrium determinations was a modified Othmer still (Figure 1). The following alterations were made to Othmer's design (*6*) for purposes of improvement specific to the present study. The droplet counter was removed, since it caused considerable hold-up at high recirculation rates, owing to excessive pressure drop across the counter. The small hole in the top of the vapor condensate chamber, which allowed air to escape while the chamber was filling, was sealed and an external air escape line was provided to prevent condensed vapor from passing through this hole directly into the condensate return line, hence effectively bypassing the chamber.

Heat was applied externally by means of a Bunsen burner, which allowed immediate and precise control of recirculation rates. The walls of the boiling chamber above the level of the liquid were traced with heating wire and lagged with a thick layer of asbestos. Pressure was maintained at 760 ± 0.2 mm. of Hg by means of a Cartesian manostat and barometer. The equilibrium boiling temperature was measured with an immersion thermometer which had been calibrated previously in situ with liquids of known boiling point, which boiled in the temperature region bracketing that of the systems of the present investigation.

Procedure. A number of tests was carried out on the apparatus to determine operating conditions. These included entrainment tests to determine whether any liquid was being carried from the boiling chamber into the vapor condensate chamber, recirculation rate and superheat tests to examine the effect of these variables on the steady state vapor composition, rate of approach to steady state tests, material balance tests to check for losses from the system, and liquid concentration gradient tests to determine whether a concentration gradient existed in the liquid at steady

Table I. Physical Properties of the Chemicals

	Density, G./Ml., 20° C.		Refractive Index, 25° C.	
	Exptl.	Lit.	Exptl.	Lit.
Carbon tetrachloride	1.5932	1.5937	1.4573	1.4573
Benzene	0.8782	0.8790	1.4978	1.4979
Cyclohexane	0.7776	0.7786	1.4237	1.4235
2-Methylpentane	0.6530	0.6532	1.3689	1.3687
n-Hexane	0.6597	0.6594	1.3726	1.3723
Toluene	0.8663	0.8669	1.4940	1.4941
2,3-Dimethylbutane	0.6611	0.6616	1.3724	1.3723
Cyclohexene	0.8101	0.8110	1.4438	1.4438
Hexene-1	0.6729	0.6732	1.3851	1.3850
Octene-1	0.7147	0.7149	1.4062	1.4062
n-Heptane	0.6836	0.6838	1.3855	1.3851
n-Octane	0.7023	0.7025	1.3952	1.3950
3-Methylpentane	0.6639	0.6643	1.3740	1.3739
2,2-Dimethylbutane	0.6490	0.6492	1.3660	1.3660
2,4-Dimethylpentane	0.6726	0.6727	1.3792	1.3788
2,2,4-Trimethylpentane	0.6914	0.6919	1.3891	1.3890
Ethylbenzene	0.8664	0.8670	1.4933	1.4932
2,2,5-Trimethylhexane	0.7071	0.7072	1.3974	1.3973
Cyclopentane	0.7449	0.7454	1.4036	1.4036
Methylcyclopentane	0.7481	0.7486	1.4070	1.4070
Methylcyclohexane	0.7691	0.7694	1.4209	1.4206
o-Xylene	0.8795	0.8802	1.5029	1.5030
m-Xylene	0.8632	0.8642	1.4943	1.4946
p-Xylene	0.8605	0.8610	1.4934	1.4932

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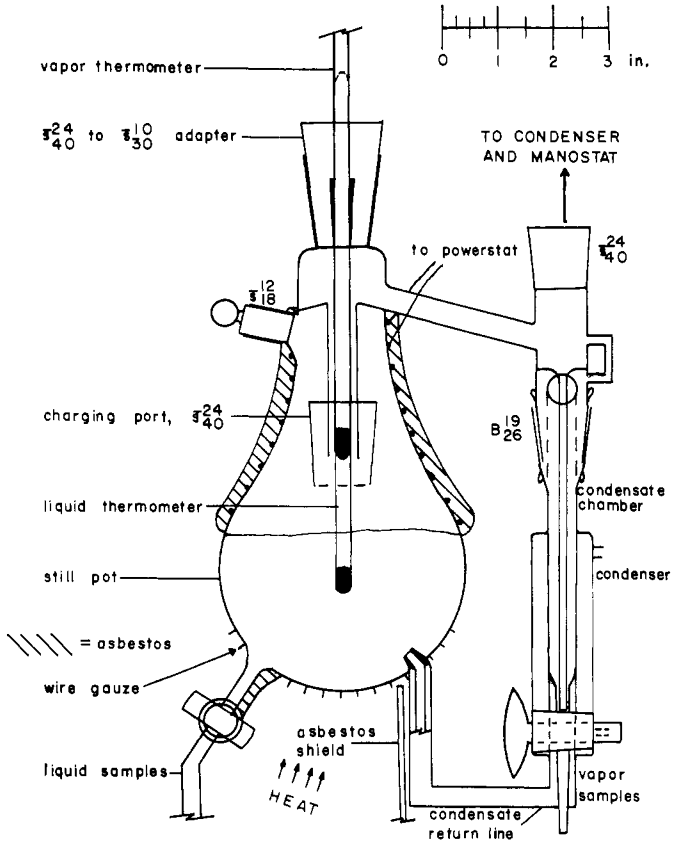

Figure 1. Modified Othmer still

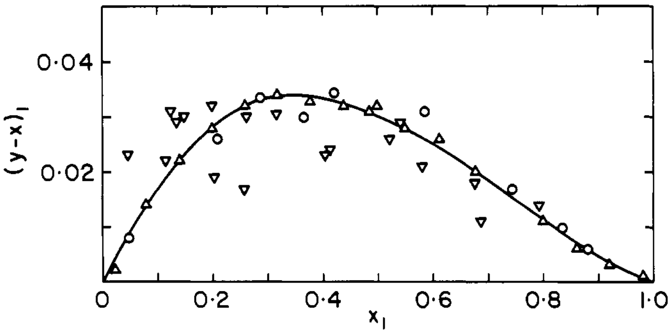

Figure 2. $(y - x)$ vs. x for the system: carbon tetrachloride–cyclohexane at 760 mm. of Hg

△ This work
▽ (*11*)
○ (*5*)

state. The performance of the still was established by equilibrium determinations of three systems for which literature data were available: carbon tetrachloride–benzene, carbon tetrachloride–toluene, and carbon tetrachloride–cyclohexane. Average absolute deviations in vapor composition between experimental data and literature values for these systems were 0.001, 0.004, and 0.003 mole fraction, respectively. A typical example of the agreement with literature values is shown in Figure 2, which is a plot of $(y - x)$ *vs.* x for the system carbon tetrachloride–cyclohexane.

The charge to the modified Othmer equilibrium still was 450 ml. for all runs. The recirculation rate was set at between 10 and 15 ml. per minute, with recirculation allowed to continue for 30 minutes before sampling. These values were arrived at after the performance tests described previously had been performed and the time to steady state was known. The data were measured for each system by performing two series of runs, one sequence beginning with pure hydrocarbon and the other with pure carbon tetrachloride. When starting from pure hydrocarbon, for example, pure carbon tetrachloride was added to increase the value of x. The sequence of runs for each system involved 18 liquid-phase compositions. Boiling points of the pure components had been determined for each system in the course of thermometer calibration, using boiling points for calibration correction purposes from the API tables (*8*).

Analysis of the steady-state liquid and condensed vapor samples from the still was made by density determination,

Table II. Density-Composition Data

Hydrocarbon	Coefficients of $d = A + Bx + Cx^2 + Dx^3 + Ex^4$				
	A	B	C	D	E
Benzene	0.8782	0.7820	−0.0890	0.0343	−0.0122
Cyclohexane	0.7776	0.7272	0.0600	0.0389	−0.0104
2-Methylpentane	0.6530	0.6899	0.1891	0.0319	0.0294
n-Hexane	0.6597	0.6870	0.1884	0.0265	0.0316
Toluene	0.8663	0.6614	0.0526	0.0194	−0.0065
2,3-Dimethylbutane	0.6611	0.6932	0.1805	0.0381	0.0202
Cyclohexene	0.8101	0.7547	0.0280	0.0072	−0.0067
Hexene-1	0.6729	0.7165	0.1627	0.0335	0.0076
Octene-1	0.7149	0.5330	0.2425	0.0015	0.1015
n-Heptane	0.6836	0.5932	0.2192	0.0228	0.0745
n-Octane	0.7023	0.5168	0.2646	−0.0364	0.1459
3-Methylpentane	0.6639	0.6908	0.1761	0.0413	0.0211
2,2-Dimethylbutane	0.6490	0.6887	0.1969	0.0312	0.0273
2,4-Dimethylpentane	0.6726	0.5898	0.2429	0.0009	0.0870
2,2,4-Trimethylpentane	0.6912	0.5010	0.3442	−0.1377	0.1945
Ethylbenzene	0.8664	0.5275	0.1218	0.0269	0.0057
2,2,5-Trimethylhexane	0.7071	0.4572	0.2942	−0.0889	0.2235
Cyclopentane	0.7449	0.8639	0.0049	−0.0440	0.0234
Methylcyclopentane	0.7481	0.7170	0.1308	−0.0280	0.0253
Methylcyclohexane	0.7691	0.6144	0.1856	−0.0194	0.0435
o-Xylene	0.8795	0.5724	0.0962	0.0593	−0.0142
m-Xylene	0.8632	0.5681	0.1230	0.0320	0.0068
p-Xylene	0.8605	0.5723	0.1268	0.0200	0.0135

Table III. Experimental Vapor-Liquid

t	x_1	y_1	t	x_1	y_1	t	x_1	y_1	t	x_1	y_1
Carbon tetrachloride–benzene			Carbon tetrachloride–*n*-hexane			Carbon tetrachloride–cyclohexene			Carbon tetrachloride–*n*-heptane		
79.9	0.021	0.025	68.8	0.026	0.023	82.9	0.020	0.022	97.8	0.021	0.037
79.7	0.061	0.072	68.9	0.081	0.071	82.7	0.080	0.090	95.9	0.082	0.142
79.2	0.124	0.144	69.0	0.140	0.125	82.5	0.140	0.156	94.1	0.142	0.236
78.8	0.188	0.213	69.2	0.203	0.179	82.2	0.196	0.220	92.2	0.209	0.328
78.5	0.251	0.281	69.4	0.264	0.233	81.9	0.257	0.288	90.8	0.261	0.396
78.1	0.313	0.344	69.6	0.325	0.286	81.5	0.316	0.352	89.3	0.322	0.468
77.8	0.376	0.407	69.9	0.385	0.338	81.1	0.376	0.417	87.9	0.378	0.531
77.6	0.439	0.467	70.3	0.448	0.394	80.7	0.435	0.480	86.5	0.438	0.591
77.3	0.495	0.520	70.7	0.509	0.448	80.4	0.482	0.530	85.2	0.497	0.645
77.3	0.501	0.525	70.7	0.516	0.455	80.3	0.491	0.540	85.1	0.501	0.650
77.1	0.559	0.582	71.1	0.570	0.505	79.9	0.545	0.594	83.8	0.564	0.706
77.0	0.622	0.641	71.6	0.631	0.562	79.4	0.608	0.657	82.5	0.631	0.758
76.8	0.686	0.701	72.2	0.691	0.622	79.0	0.669	0.714	81.3	0.696	0.806
76.7	0.751	0.760	72.9	0.748	0.681	78.5	0.731	0.773	80.2	0.760	0.849
76.7	0.815	0.820	73.6	0.807	0.745	78.1	0.792	0.827	79.2	0.821	0.889
76.7	0.878	0.881	74.4	0.865	0.812	77.6	0.856	0.883	78.3	0.881	0.926
76.7	0.939	0.941	75.4	0.925	0.888	77.2	0.918	0.935	77.5	0.940	0.963
76.7	0.978	0.979	76.4	0.982	0.972	76.8	0.982	0.986	77.0	0.976	0.987
Carbon tetrachloride–cyclohexane			Carbon tetrachloride–toluene			Carbon tetrachloride–hexene-1			Carbon tetrachloride–*n*-octane		
80.6	0.022	0.024	109.8	0.016	0.036	63.6	0.020	0.014	123.6	0.024	0.067
80.1	0.077	0.091	107.6	0.060	0.132	64.1	0.080	0.057	118.5	0.088	0.234
79.7	0.140	0.162	105.3	0.109	0.228	64.5	0.141	0.103	113.8	0.151	0.380
79.3	0.199	0.227	103.1	0.159	0.313	65.1	0.206	0.151	109.6	0.213	0.489
78.9	0.258	0.290	101.0	0.207	0.387	65.7	0.269	0.201	106.1	0.268	0.571
78.6	0.316	0.350	98.9	0.258	0.458	66.4	0.342	0.260	102.6	0.327	0.647
78.2	0.376	0.409	97.0	0.308	0.521	67.0	0.397	0.308	99.6	0.382	0.705
77.9	0.438	0.470	95.0	0.361	0.583	67.7	0.460	0.364	96.7	0.439	0.753
77.7	0.482	0.513	93.5	0.401	0.626	68.4	0.511	0.411	93.9	0.497	0.796
77.7	0.497	0.529	93.1	0.414	0.640	68.5	0.524	0.422	93.9	0.498	0.798
77.5	0.548	0.576	91.2	0.468	0.688	69.2	0.571	0.468	91.0	0.565	0.839
77.2	0.610	0.636	88.9	0.540	0.749	70.0	0.630	0.528	88.3	0.632	0.874
77.0	0.676	0.696	86.8	0.610	0.801	70.9	0.690	0.590	85.9	0.697	0.904
76.9	0.737	0.753	84.7	0.683	0.849	71.9	0.750	0.658	83.8	0.759	0.928
76.8	0.799	0.810	82.7	0.757	0.890	72.9	0.808	0.726	81.9	0.820	0.950
76.8	0.860	0.866	80.9	0.828	0.927	74.0	0.866	0.803	80.2	0.877	0.967
76.7	0.919	0.922	79.0	0.905	0.961	75.1	0.924	0.881	78.6	0.932	0.982
76.7	0.980	0.981	77.3	0.978	0.991	76.3	0.981	0.970	77.2	0.982	0.996
Carbon tetrachloride–2-methylpentane			Carbon tetrachloride–2,3-dimethylbutane			Carbon tetrachloride–octene-1			Carbon tetrachloride–3-methylpentane		
60.4	0.021	0.015	58.2	0.022	0.014	120.0	0.021	0.058	63.5	0.021	0.016
60.8	0.079	0.056	58.7	0.087	0.057	115.8	0.084	0.202	64.0	0.081	0.063
61.3	0.138	0.100	59.2	0.147	0.098	112.0	0.145	0.329	64.5	0.145	0.115
61.9	0.202	0.145	59.8	0.211	0.143	108.3	0.206	0.435	65.0	0.209	0.165
62.4	0.263	0.190	60.5	0.276	0.187	105.1	0.262	0.527	65.5	0.268	0.213
63.0	0.328	0.239	61.4	0.347	0.241	101.9	0.324	0.602	66.1	0.333	0.265
63.7	0.388	0.288	62.2	0.404	0.286	99.1	0.379	0.665	66.7	0.398	0.319
64.5	0.454	0.340	63.2	0.469	0.338	96.3	0.438	0.726	67.4	0.462	0.375
65.3	0.518	0.394	64.2	0.526	0.389	94.2	0.482	0.763	68.0	0.511	0.418
65.4	0.520	0.396	64.3	0.532	0.390	93.6	0.497	0.774	68.1	0.526	0.432
66.3	0.583	0.452	65.3	0.586	0.441	91.3	0.552	0.812	68.7	0.570	0.472
67.4	0.642	0.509	66.5	0.646	0.501	88.6	0.619	0.855	69.5	0.632	0.531
68.4	0.698	0.566	67.8	0.702	0.557	86.3	0.685	0.889	70.4	0.690	0.590
69.7	0.754	0.629	69.2	0.759	0.622	84.1	0.750	0.917	71.4	0.749	0.653
71.1	0.814	0.699	70.7	0.814	0.688	82.1	0.811	0.942	72.4	0.806	0.720
72.6	0.871	0.774	72.5	0.874	0.771	80.4	0.870	0.962	73.6	0.864	0.792
74.3	0.926	0.860	74.2	0.927	0.854	78.7	0.928	0.980	74.8	0.922	0.873
76.1	0.982	0.963	76.1	0.982	0.961	77.3	0.980	0.995	76.2	0.978	0.963

employing the density-composition data obtained as described previously. The density of each sample was measured three times to determine whether directive loss of components affected the experimental value. No density trend was observed, indicating that this source of error was negligible.

RESULTS

Density-Composition Data. Density-composition data were determined at 20° C. for each of the 23 carbon tetrachloride–hydrocarbon binary systems, and have been deposited with the ASIS. The data were fitted by a power series, and

Equilibrium Data at 760 mm. of Hg Pressure

t	x_1	y_1	t	x_1	y_1	t	x_1	y_1	t	x_1	y_1
Carbon tetrachloride–2,2-dimethylbutane			Carbon tetrachloride–ethylbenzene			Carbon tetrachloride–methylcyclopentane			Carbon tetrachloride–*m*-xylene		
50.1	0.022	0.012	134.1	0.018	0.060	71.9	0.021	0.019	137.0	0.018	0.058
51.2	0.082	0.046	129.2	0.065	0.215	72.0	0.076	0.069	131.9	0.065	0.219
52.5	0.156	0.089	124.4	0.114	0.352	72.2	0.129	0.120	126.8	0.114	0.356
53.6	0.225	0.130	119.9	0.164	0.456	72.4	0.185	0.171	122.0	0.164	0.465
54.7	0.290	0.170	116.1	0.208	0.539	72.5	0.240	0.223	118.1	0.208	0.552
55.9	0.359	0.215	112.1	0.258	0.616	72.7	0.299	0.278	113.9	0.258	0.626
57.2	0.425	0.260	108.5	0.308	0.676	72.9	0.358	0.331	110.2	0.306	0.687
58.6	0.495	0.309	105.3	0.356	0.729	73.1	0.416	0.388	106.4	0.357	0.739
59.6	0.537	0.344	101.8	0.412	0.777	73.3	0.468	0.436	102.8	0.412	0.788
60.2	0.563	0.365	101.5	0.417	0.782	73.3	0.477	0.445	102.3	0.419	0.796
61.1	0.598	0.396	97.7	0.486	0.829	73.5	0.529	0.494	98.1	0.488	0.843
62.7	0.656	0.451	94.1	0.556	0.869	73.8	0.590	0.555	94.1	0.562	0.880
64.3	0.711	0.514	90.8	0.629	0.901	74.1	0.654	0.616	90.6	0.635	0.911
66.2	0.766	0.578	87.8	0.701	0.928	74.5	0.718	0.682	87.5	0.704	0.935
68.2	0.819	0.647	85.0	0.771	0.950	74.9	0.781	0.747	84.6	0.775	0.955
70.5	0.874	0.732	82.4	0.842	0.967	75.4	0.846	0.818	82.1	0.843	0.971
73.0	0.927	0.833	79.9	0.910	0.983	75.9	0.910	0.890	79.7	0.911	0.984
75.6	0.980	0.949	77.6	0.977	0.996	76.5	0.976	0.970	77.5	0.977	0.996
Carbon tetrachloride–2,4-dimethylpentane			Carbon tetrachloride–2,2,5-trimethylhexane			Carbon tetrachloride–methylcyclohexane			Carbon tetrachloride–*p*-xylene		
80.3	0.023	0.026	122.0	0.025	0.063	100.2	0.020	0.038	136.4	0.017	0.059
79.7	0.087	0.106	116.6	0.094	0.236	98.2	0.077	0.138	131.1	0.063	0.216
79.1	0.155	0.185	111.8	0.160	0.378	96.4	0.133	0.228	126.2	0.111	0.349
78.6	0.227	0.263	107.5	0.225	0.493	94.7	0.188	0.311	121.8	0.157	0.453
78.2	0.286	0.326	103.5	0.290	0.582	92.9	0.248	0.393	117.6	0.203	0.539
77.7	0.352	0.391	100.1	0.351	0.653	91.3	0.306	0.465	113.5	0.252	0.616
77.4	0.413	0.449	97.2	0.408	0.711	89.9	0.357	0.521	109.8	0.301	0.679
77.1	0.473	0.506	94.3	0.469	0.759	88.5	0.413	0.580	106.2	0.351	0.731
76.9	0.518	0.548	91.7	0.526	0.803	87.4	0.458	0.624	102.7	0.405	0.779
76.8	0.535	0.564	91.6	0.529	0.804	87.1	0.469	0.634	102.2	0.413	0.787
76.7	0.582	0.605	88.9	0.596	0.845	85.9	0.520	0.681	98.1	0.485	0.836
76.5	0.642	0.658	86.5	0.662	0.879	84.5	0.586	0.734	94.4	0.558	0.876
76.4	0.701	0.712	84.4	0.725	0.908	83.1	0.654	0.786	91.1	0.629	0.908
76.3	0.760	0.763	82.4	0.788	0.932	81.7	0.721	0.832	88.0	0.701	0.934
76.3	0.816	0.815	80.9	0.841	0.951	80.5	0.787	0.875	85.2	0.772	0.954
76.4	0.872	0.867	79.4	0.893	0.968	79.3	0.850	0.914	82.6	0.840	0.969
76.5	0.926	0.921	78.2	0.941	0.983	78.2	0.915	0.952	80.0	0.911	0.984
76.7	0.979	0.977	77.1	0.986	0.996	77.2	0.976	0.986	77.6	0.977	0.997
Carbon tetrachloride–2,2,4-trimethylpentane			Carbon tetrachloride–cyclopentane			Carbon tetrachloride–*o*-xylene					
98.2	0.028	0.051	49.6	0.015	0.006	142.0	0.018	0.065			
95.7	0.104	0.175	50.5	0.061	0.028	136.0	0.064	0.229			
93.7	0.163	0.264	51.6	0.117	0.055	130.4	0.112	0.369			
91.6	0.232	0.362	52.6	0.166	0.082	125.0	0.161	0.494			
89.9	0.294	0.441	53.7	0.220	0.112	120.7	0.204	0.573			
88.2	0.357	0.515	55.0	0.281	0.147	116.1	0.253	0.646			
86.6	0.419	0.578	56.2	0.339	0.185	111.8	0.302	0.709			
85.2	0.478	0.632	57.6	0.400	0.228	107.9	0.352	0.759			
84.2	0.525	0.677	58.9	0.452	0.270	104.2	0.404	0.803			
83.9	0.537	0.684	59.2	0.464	0.277	104.1	0.405	0.805			
82.8	0.591	0.729	60.4	0.512	0.318	99.4	0.478	0.852			
81.6	0.654	0.774	62.0	0.572	0.372	95.1	0.554	0.889			
80.6	0.713	0.815	63.7	0.634	0.436	91.6	0.624	0.916			
79.6	0.771	0.855	65.7	0.699	0.508	88.2	0.700	0.940			
78.8	0.826	0.890	67.7	0.761	0.587	85.3	0.771	0.958			
78.1	0.881	0.924	70.0	0.829	0.683	82.6	0.841	0.972			
77.5	0.934	0.957	72.8	0.902	0.801	80.0	0.910	0.985			
76.9	0.982	0.989	75.7	0.974	0.944	77.7	0.976	0.996			

the coefficients for each system are included as Table II. Sample sizes were 10 ml. in all cases, and a plummet having a displacement volume of approximately 2 ml. was used. Weighing was carried out with a Mettler single-pan balance, type H-15, capacity 160 grams. During the make-up of solutions of known composition, the weight of each component added was measured to within ±0.0001 gram, resulting in composition data believed accurate to the fourth decimal place.

Data were available in the literature for four of the systems used in this investigation: carbon tetrachloride with each of benzene, toluene, cyclohexane, and 2,2,4-trimethylpentane (*9*). In each case, agreement between experiment and the literature was very close.

Equilibrium Data. Isobaric vapor-liquid equilibrium data at 760 mm. of Hg pressure were measured for each of the 23 hydrocarbon-carbon tetrachloride binary systems and are included as Table III. The only azeotrope discovered in all 23 systems occurred in the carbon tetrachloride–2,4-dimethylpentane system at 0.802 mole fraction of carbon tetrachloride and a temperature of 76.3° C.

The reported temperature data are experimental data smoothed by graphical methods. The accuracy of the temperature data was estimated by error analysis to be ±0.1° C. Although the maximum difference between experimental and smoothed temperatures was 0.3° C., by far the vast majority of the smoothed temperatures agreed with the experimental data to within 0.1° C.

Compositions were determined by measuring the densities of samples of the liquid and condensed vapor phases and interpolation of the density-composition data determined previously for this purpose. Linear interpolation was used; second- and third-order interpolation was tried, but made no difference in the composition because of the small change in slope of the density-composition curve between consecutive sets of data points. The compositions listed are those determined experimentally, smoothing being considered unnecessary (Figure 2). An over-all average accuracy of the composition data estimated by error analysis is ±0.002 mole fraction.

DISCUSSION OF RESULTS

The composition error seemed to be largest at low concentrations of the more volatile component for the higher-boiling systems—e.g., at the higher temperatures, where the slope of the y *vs.* x curve is greatest. Such possible sources of error as that due to proportionally greater loss of the more volatile component through evaporation while sampling, and inadequate mixing of the returning condensate with the bulk of the liquid in the still, would also tend to be more prevalent in this area. In addition, the question of whether the vapor leaving the surface of a boiling liquid is truly in equilibrium with the bulk of the liquid itself would tend to be most dubious where the enrichment of the vapor is greatest. Calculations indicated that the maximum error in composition in this area is ±0.010 mole fraction, and that the experimental vapor composition would tend to be lower than the true value. This error tends to diminish rapidly, both at higher carbon tetrachloride concentrations and at lower temperatures.

Self-consistency of the data for each system was examined by plotting $(y - x)$ against x. In each case the curves were very smooth, indicating that little or no random error in the data appeared to exist (Figure 2). Systematic errors in vapor-liquid equilibrium data can be checked by comparison with the requirements of some thermodynamically exact relation, such as the Redlich-Kister test (*7*), the most common of these relations. At constant pressure, Redlich and Kister's exact expression for testing data consistency is

$$\int_0^1 \ln(\gamma_1/\gamma_2)\, dx_1 = -\int_0^1 \frac{\Delta H^m}{RT^2}\frac{dT}{dx_1}\, dx_1 \qquad (1)$$

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

The term on the left hand side requires the evaluation of γ, the activity coefficient of each component

$$\ln \gamma_i = \ln(y_i P/x_i p_i) - (P - p_i)(\beta_i - v_i)/RT \qquad (2)$$

which requires knowledge of vapor pressures and second virial coefficients, β. Vapor pressures were calculated by means of the Antoine equation

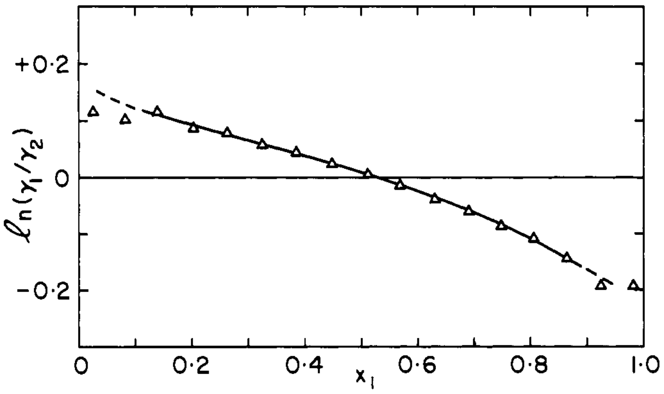

Figure 3. Ln (γ_1/γ_2) *vs.* composition for the system: carbon tetrachloride–*n*-hexane at 760 mm. of Hg

$$\log p_i = A - B/(t + C) \qquad (3)$$

The Antoine equation constants for the hydrocarbons were taken from API tables (*8*). For carbon tetrachloride, data were taken from two sources (*2, 10*), with average values of the Antoine constants being determined for the temperature range involved.

At normal pressures, the second term on the right hand side of Equation 2 is usually negligible. This term accounts for nonidealities in the vapor phase. The term on the right hand side of Equation 1 requires heat of mixing and temperature-composition data. Heat of mixing data were not available for these systems. However, for systems having differences in the pure-component boiling points of less than 10° C., the term on the right hand side of Equation 1 usually is negligible.

Neglecting these terms, the Redlich-Kister test reduces to

$$\int_0^1 [\ln(y_1x_2/y_2x_1) - \ln(p_1/p_2)]\, dx_1 = 0 \qquad (4)$$

which is limited to systems having small differences in pure-component boiling points and nearly-ideal vapor phases. This test was applied successfully to those systems of the present investigation whose pure-component boiling points were close, by plotting $\ln(\gamma_1/\gamma_2)$ against x_1 over the entire composition range of x, from 0 to 1, and measuring the area under the curve, taking sign into account (Figure 3). For systems with differences in pure-component boiling points greater than 10° C. and a maximum boiling temperature less than 85° C., the Herington criterion (*1*) was used successfully. Above 85° C., difficulty was encountered in calculating the activity coefficient of carbon tetrachloride, since the only vapor pressure data available above atmospheric pressure are 78 years old (*10*), and were established using an apparatus for which a description could not be located.

NOMENCLATURE

A, B, C = Antoine equation constants
d = density of mixture, grams per ml. at 20° C.
ΔH^m = heat of mixing of a mixture at a given temperature and pressure, cal. per gram mole ° C.
P = total pressure, mm. of Hg
p = vapor pressure of pure component at equilibrium temperature of the system, mm. of Hg
R = gas constant
T = absolute temperature, ° K.
t = temperature, ° C.
v = liquid molal volume of pure component, cm.^{3} per gram mole
x = mole fraction of component in liquid phase

y = mole fraction of component in vapor phase
β = second virial coefficient of pure component in vapor phase, cm.^{3} per gram mole
γ = liquid phase activity coefficient

Subscripts

1 = carbon tetrachloride
2 = hydrocarbon

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Solubility in the System NH_3-H_3PO_4-$H_4P_2O_7$-$H_5P_3O_{10}$-H_2O at 0° C.

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Measurements were made of the compositions of solutions in the system NH_3-H_3PO_4-$H_4P_2O_7$-$H_5P_3O_{10}$-H_2O at 0° C., in which solid phases of all three phosphate species are in equilibrium over the pH range 5.5 to 7.5. The most concentrated solution contained 12.00% N and 41.00% P_2O_5, and had pH 5.75.

IN THE CONTINUING study of the properties of ammonium polyphosphates (*1*, *2*), measurements were made of the compositions of solutions in the system ammonia–orthophosphoric acid–pyrophosphoric acid–tripolyphosphoric acid–water at 0° C., in which solid phases of all three phosphate species are in equilibrium over the pH range 5.5 to 7.5.

The equilibration mixtures were prepared from reagent mono- and diammonium orthophosphates, and ammonium pyro- and tripolyphosphates that were crystallized from fluid fertilizers produced by ammoniation of electric furnace superphosphoric acid, 80% P_2O_5 (*7*). The composition and phosphate distribution of the ammonium phosphates are given in Table I. Conductivity water (30 ml.) at about 5° C. was saturated with salts of the three phosphate species, and the pH of each solution was adjusted to a predetermined value with anhydrous ammonia or reagent 86% H_3PO_4. Cold water or solid salt was added when necessary to adjust the ratio of solids to liquid. The complexes were equilibrated in 60-ml. plastic-capped bottles at 0.0° ± 0.5° C. with occasional manual agitation.

Table I. Ammonium Phosphates Used to Prepare Equilibration Mixtures

Salt	Composition, %		Distribution, %, of P_2O_5			
	N	P_2O_5	Ortho	Pyro	Tripoly	Other
$NH_4H_2PO_4$	12.1	61.6	100.0	. . .	. . .	. . .
$(NH_4)_2HPO_4$	21.2	53.5	100.0	. . .	. . .	. . .
$(NH_4)_3HP_2O_7 \cdot H_2O$	17.0	57.2	0.8	98.3	. . .	0.9
$(NH_4)_4HP_3O_{10}$	18.5	56.7	4.0	7.4	88.0	0.6

The approach to equilibrium was followed by periodic petrographic examinations of the solid phases (*4*) and by determinations of the composition and pH of the liquid phases. When examination of the wet solids indicated the absence of any of the three phosphate species, a few grams of the missing species was added and equilibration was continued.

Phosphorus was determined gravimetrically as quinolinium molybdophosphate (*6*), and nitrogen was determined

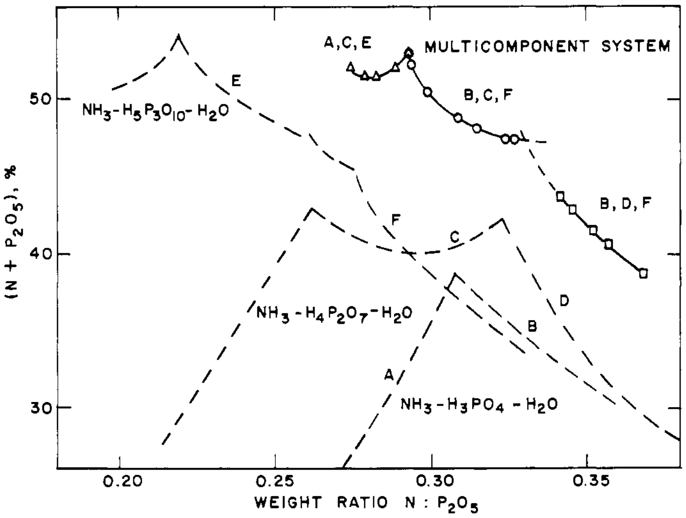

Figure 1. Solubility in the system NH_3-H_3PO_4-$H_4P_2O_7$-$H_5P_3O_{10}$-H_2O at 0° C.

Saturating solids: A = $NH_4H_2PO_4$, B = $(NH_4)_2HPO_4$, C = $(NH_4)_3HP_2O_7 \cdot H_2O$, D = $(NH_4)_4P_2O_7 \cdot H_2O$, E = $(NH_4)_4HP_3O_{10}$, F = $(NH_4)_5P_3O_{10} \cdot 2H_2O$